A MINERALOGICAL INVESTIGATION OF CO-EXISTING

IRON-TITANIUM OXIDES FROM VARIOUS IGNEOUS ROCKS

WITH SPECIAL REFERENCE TO SOME SOUTH AFRICAN

TITANIFEROUS IRON ORES.

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PREFACE

The present investigation was undertaken at the instigation of Prof. H. V. Eales. It was originally conceived as a M. Sc. project involving a comparative study of composition, cell dimensions and optical properties of ilmenites from a variety of igneous rocks together with a comprehensive literature review. The writer was fortunate in obtaining a NIM post-graduate bursary and the ilmenite investigation was carried out at Rhodes University between January, 1972 and August, 1973. Following the advice of Prof. Eales the scope of this project was then expanded to include the co-existing titaniferous magnetites. The results of these studies are presented in Part 2 of this thesis.

The writer commenced work as a mineralogist at NIM in September, 1973 and continued these investigations into the iron-titanium oxides during his term of employment at that Institute. A great deal of interest was shown in the possible utilisation of South African titaniferous iron ores at that time and a study of these ores was undertaken with a bias towards information that would be of use in ore dressing and extractive metallurgy. These studies form the basis of Part 3 of this thesis.

The literature on the iron-titanium oxides is very extensive, disseminated and, at times, conflicting. A thorough literature study and synthesis of these data became necessary in order to understand the complex phase relationships and microstructural developments exhibited by this mineral group. This review forms the basis of Part 1 of this thesis.

ABSTRACT.

Part 1 consists of a detailied review of the available literature on the Fe-Ti oxides and their solid solution relationships. Particular attention is given to the microstructures exhibited by these oxides and the hypotheses put forward to explain them. These data are synthesised and models are presented in which the microstructural developments in titaniferous magnetites amd ilmenites are explained in terms of current ideas on the influence of oxygen fugacity, exsolution mechanisms and crystal chemistry. These models have direct application to the microintergrowths observed in the naturally occurring Fe-Ti oxides from a wide range of igneous rocks.

The available data on the minor and trace element chemistry of the Fe-Ti oxides are reviewed with particular reference to their variation in these minerals from different host rocks. The behaviour of the Fe-Ti oxides during secondary oxidation is discussed with particular reference to the oxidation of titaniferous magnetite and the weathering of ilmenite.

The results of a mineralogical investigation into the co-existing Fe-Ti oxides from a range of igneous rocks including kimberlites, gabbros, dolerites, diabases, syenites, granophyres, granites and pegmatites are presented in Part 2 together with data on the ilmenites present in certain Eastern Cape beach sands. The kimberlite ilmenites are chemically distinct and can be readily distinguished on the basis of their relatively high MgO, Fe_2O_3 and Cr_2O_3 contents. They can also be distinguished from ilmenites from other igneous rocks on the basis of unit cell dimensions, d-spacings, reflectivities and micro-indentation hardness.

The ilmenites from a wide range of basic to granitic igneous rocks exhibit a limited compositional range in which the MnO content appears to increase

with increasing SiO_2 content. Relatively insensitive indirectly determined parameters such as unit cell dimensions, reflectivities and micro-indentation hardnesses cannot be used to distinguish between the ilmenites from the different rock types in these classes.

The titaniferous magnetites exhibit progressively decreasing TiO_2 contents from a maximum in the basic igneous rocks to a minimum in the granitic types. The titaniferous magnetite typically exhibits varying degrees of deuteric alteration, while the microstructures developed can be interpreted in terms of the models presented in Part 1.

Part 3 represents an extension of Part 2 and deals with a mineralogical investigation of the titaniferous iron ores in five South African basic intrusions. The Bushveld and Kaffirskraal ores consist of multi-phase titaniferous magnetite grains containing crystallographically oriented ilmenite, ulvospinel and pleonaste microintergrowths. Minor coarser-grained ilmenite is also present. The Usushwana ores are texturally similar but contain abundant lamellar ilmenite in place of the ulvospinel. The primary features are well preserved in the unmetamorphosed Bushveld and Kaffirskraal ores. The Usushwana ores have been slightly metamorphosed resulting in the extensive replacement of the titaniferous magnetites by sphene and chlorite aggregates. The ores from these three complexes cannot be beneficiated by conventional ore-dressing techniques and require direct metallurgical treatment for the recovery of Fe, TiO_2 and V_2O_5.

The metamorphosed Mambula and Rooiwater ores have been recrystallised to a varying degrees and consist of multi-phase titaniferous magnetite grains containing modified ilmenite and pleonaste microintergrowths. These modified microstructures differ from those encountered in titaniferous magnetites from unmetamorphosed basic rocks and their degree of modification can be

related to the degree of metamorphism. Variable amounts of coarse granular ilmenite are also present and their development is related to the metamorphic grade and degree of recrystallisation. These ores can be partially beneficiated to yield ilmenite- and lower-TiO_2 magnetite concentrates in which V_2O_5 contents of the magnetic fractions are higher than those of the original ores.

The Trompsburg ores differ from those of the other complexes in that they are Mg-rich and are characterised by the presence of abundant olivine. The titaniferous magnetites typically exhibit well-defined ulvospinel cloth textures and are often surrounded by small amounts of graphite. They show evidence of a variety of extensive late-stage alteration features.

The ores from the five investigated complexes are compared with similar ores from the Bushveld Complex. The ores from each complex can be readily distinguished on the basis of their chemical compositions and textural relationships. These features can be related to their crystallisation histories and, in some cases, to post-crystallisation processes. The microstructural evolution of the ores from each complex is interpreted in terms of the models developed in Part 1.

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ACKNOWLEDGEMENTS.

PART I

LITERATURE REVIEW

1. INTRODUCTION

Iron-titanium oxides are ubiquitous in the earth's crust. Accessory amounts of these minerals are present in the majority of igneous rocks, while larger concentrations are often developed in certain gabbroic rock types. They are occasionally concentrated in discrete layers in certain stratiform basic intrusions. The iron-titanium oxides are released during weathering of their primary host rocks and become incorporated into a wide variety of sediments as detrital grains. They may also become concentrated in distinct heavy-mineral layers. Subsequent metamorphism of both their primary and secondary host rocks accounts for their presence in a wide range of metamorphic rock types. A portion of these metamorphic iron-titanium oxides may also have formed from the breakdown of other pre-existing iron-rich minerals.

Mineralogical studies of the iron-titanium oxides commenced towards the end of the last century, but were hampered by the lack of suitable microscopes and other analytical apparatus. Considerable progress was nevertheless made in these studies during the first half of this century as microscopes and analytical techniques were improved. These studies resulted in the development of an extensive, but often conflicting, literature as the progressively finer-grained microintergrowths were discovered. The introduction of the electron probe microanalyser and the development of more sophisticated ore microscopes during the

last 15 years, together with more accurate experimental data, have contributed markedly to an increased understanding of the complex relationships exhibited by this group of minerals. These factors have, in part, decreased the amount of confusion that existed in the earlier literature.

Mineralogical investigations of the iron-titanium oxides prior to 1913 were essentially of an academic nature and developed during the petrographic examination of their host rocks. These studies were aimed largely at the characterisation of the iron-titanium oxides. Subsequent levels of investigation have fluctuated over the years with each pulse of renewed interest often being initiated by developments in other branches of geology. These developments can be broadly divided into seven areas of geological interest, each of which has contributed substantially to the understanding of this mineral group as a whole. Research is currently being undertaken in each of these branches of geology and considerable amounts of data on the iron-titanium oxides accumulate annually. The major areas of current interest are as follows:-

1. The economic aspect:

The iron-titanium oxides are important sources of Fe, Ti and V and were first investigated microscopically by Singewald (1913a, b) in order to gain information that would be of use in ore-dressing and extractive metallurgy. Studies of this nature were subsequently carried out world-wide on a large number of deposits and have contributed substantially to our understanding of the mineralogical relationships in this group of oxides. Research in this direction continues and is becoming increasingly important in view of the rapid depletion of the world's rutile reserves and the increased demand for TiO_2 (Roskill, 1971).

2. <u>The academic aspect</u>:

The first detailed mineralogical studies and experimental investigation
of the iron-titanium oxides were carried out by Ramdohr (1926). This
study was followed by that of Edwards (1938) and research in this direc-
tion has continued up to the present time. This category, in part,
overlaps with the other six areas of interest.

3. <u>Palaeomagnetism</u>:

These studies were commenced in the early 1950's and were mainly con-
cerned with detailed mineralogical and crystal-structure determinations
aimed at elucidating the magnetic properties of these minerals and
their behaviour during alteration. Nicholls (1955) has summarised the
earlier literature in this field of research. These studies on the
iron-titanium oxides have contributed to the understanding of their
crystal structures, cation distributions and behaviour during both low
and high temperature oxidation.

4. <u>Petrogenetic indicators</u>:

Buddington and Lindsley (1964) demonstrated that the compositions of
co-existing titaniferous magnetite and ilmenite are dependent largely
on oxygen fugacity and temperature with the result that this informa-
tion can be used to determine the conditions prevailing during certain
stages of magmatic crystallisation. This feature has attracted wide-
spread interest and petrologic studies are now rarely undertaken with-
out analyses of the co-existing iron-titanium oxides being made. The
substitution of foreign ions in these minerals will obviously affect
their phase relationships while re-equilibration during sub-solidus
cooling will also influence the results obtained. These factors are
currently being investigated and evaluated. A number of recent and

current experimental investigations have direct application in this field of research.

5. Kimberlite studies:

The occurrence of magnesium-rich ilmenites has been known for many years, but it is only since the late 1960's that they have been investigated mineralogically as a result of an increased interest in these rocks and their mantle-derived inclusions. The incorporation of large amounts of Mg into the ilmenite crystal structure is problematical and numerous publications on these ilmenites have appeared. Research into the nature and origin of these ilmenites and their associated materials is an important area of petrological interest.

6. Lunar studies:

The investigation of lunar rocks commenced in 1969 and their titanium-rich nature initiated a series of detailed mineralogical studies of their iron-titanium oxides. These investigations are amongst the most sophisticated and detailed yet undertaken on this mineral group and have produced a large amount of data.

7. Microstructure studies:

Transmission electron microscopy was first applied to the study of fine-grained intergrowths in certain of the iron-titanium oxides during the early 1970's. This field of study is well-established in metallurgy, but its application to mineralogy is still in its infancy. It, however, promises to yield a great deal of information on the nature of the sub-microscopic intergrowths, exsolution mechanism and other microstructural features of the iron-titanium oxides. Research in this field is only now commencing and should provide answers to a

number of unsolved problems in this mineral group.

The diverse nature of the fields in which iron-titanium oxides have
been, and are currently being investigated, reflects their importance
in geology. These studies also highlight the need for a thorough
understanding of the mineralogical phase relationships and behaviour
of these minerals under the wide range of physico-chemical conditions
that are encountered in nature. Considerable progress has already
been made in this direction, but accurate determinations of many of
their phase relationships, similar to those carried out in other miner-
al systems, cannot normally be undertaken since the oxides are extrem-
ely sensitive to changes in oxygen fugacity. Suitable buffers are,
unfortunately, not currently available for the control of oxygen
fugacities in many of the hydrothermal temperature and pressure ranges
that require experimental investigations (Lindsley and Lindh, 1974).

The phase relationships exhibited by the various co-existing iron-
titanium oxides are complex and the situation is compounded by the
wide range of ionic substitutions that are possible with other elements
outside the $FeO-Fe_2O_3-TiO_2$ system. The last major literature review
of phase relationships in this system was compiled by Nicholls (1955),
while data on the individual minerals were summarised by Deer, Howie
and Zussman (1962b). Buddington and Lindsley (1964) summarised import-
ant aspects of the additional data that accumulated up to this period,
but since then no detailed synthesis of the available data has been
published apart from a summary by Elsdon (1975a).

Reliable mineral analyses of the iron-titanium oxides were rare prior
to 1966, but since then the electron microprobe has been introduced

as a routine analytical instrument in many laboratories and a large number of analyses have been published. Additional experimental data have also accumulated and numerous detailed microscopic studies have been made with the result there is a need for a new compilation of this data. The aim of this literature survey is thus not only to summarise the historical development of ideas on the phase relationships in the $FeO-Fe_2O_3-TiO_2$ and related systems, but also to present a coherent framework within which the chemical composition and microstructural development of these minerals can be interpreted.

2. THE MINERALS OF THE $FeO-Fe_2O_3-TiO_2$ SYSTEM

2.1 Introduction

The theoretical compositions of the common iron-titanium oxides are illustrated on the $FeO-Fe_2O_3-TiO_2$ ternary diagram in figure 1. The naturally occurring minerals only rarely approximate their theoretical end-member compositions and are commonly members of more complex solid solution series that are discussed further in the following sections.

The minerals magnetite, ulvospinel, titanomagnetite, maghemite, hematite (martite) and ilmenite are of particular interest to this study and their mineralogical data is summarised in this section. The remaining phases (the TiO_2-polymorphs, pseudobrookite, ferropseudobrookite and wüstite) are only of peripheral interest and are not discussed.

2.2 Magnetite

Magnetite is a member of the spinel mineral group and is cubic with an ideal formula of Fe_3O_4 ($FeO.Fe_2O_3$). It is commonly found as octahedra or dodecahedra and the purest, naturally occurring material has cell dimensions of a=8,394 $\pm$ 0,0005 Å (Tombs and Rooksby, 1951; Abrahams and Calhoun, 1953). Basta (1957) obtained a = 8,3963 $\pm$ 0,0005 Å.
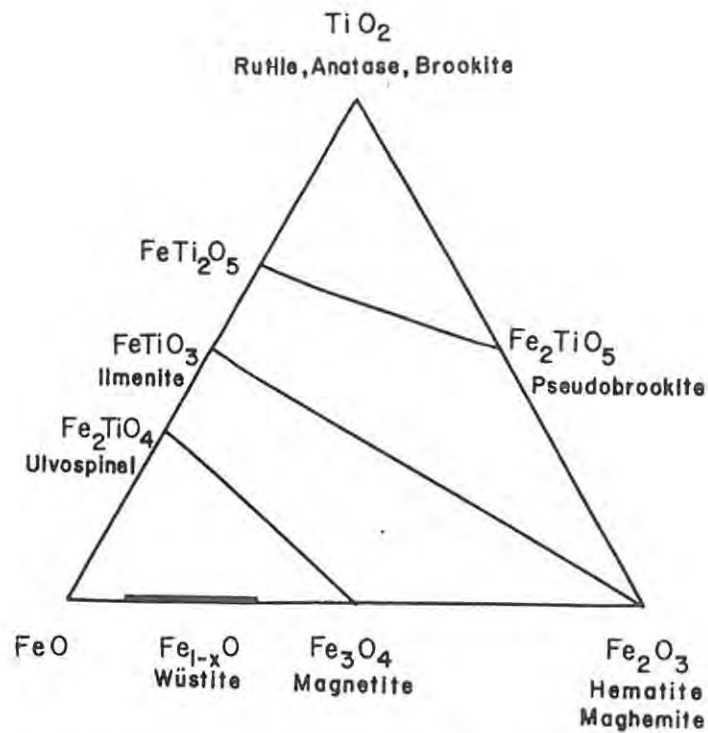
FIGURE 1   Theoretical end-member phases in the system FeO-Fe_2O_3-TiO_2 (from Buddington and Lindsley, 1964).

Bragg (1915) first elucidated the spinel structure and showed that the unit cell contains 32 oxygen ions and 24 cations.   Eight of the cations are tetrahedrally co-ordinated (A-sites) while the remaining 16 are in octahedral co-ordination (B-sites).   Barth and Posnjak (1932) demonstrated the existence of two structural types of spinel, the so-called normal and inverse types, that exhibit differences in their cation distribution between the A and B sites.   Verwey and Heilmann (1947) confirmed that magnetite is an inverse spinel and has a general formula $R_8^{2+} R_{16}^{3+} O_{32}$ in which $8R^{3+}$ occupy the B sites and 8 A sites.   The magnetite crystal structure consists of alternating layers of oxygen ions and cations that are arranged perpendicular to a 3-fold axis.   The cation layers themselves are made up of alternating layers

in which the cations are distributed between the A and B sites in the ratio of 2A:1B.

A wide range of ionic substitutions is possible in the magnetite structure and it forms extensive solid solution series with other spinels at elevated temperatures. In particular, complete high temperature solid solutions exist between magnetite and hercynite (Atlas and Sumida, 1958; Turnock and Eugster, 1962); chromite-magnetite-hercynite and spinel-hercynite (Cremer, 1969; Navrotsky, 1975a); as well as between ulvospinel-chromite-hercynite and spinel-hercynite (Haggerty, 1972a, b). The magnetite formula can consequently be written more generally as:

$$X^{2+} \ Y^{3+} \ O_4$$
$$\text{where } X = Fe^{2+}, \ Mg^{2+}, \ Zn^{2+}, \ Ni^{2+}, \ Co^{2+}, \ Ca^{2+}$$
$$\text{and } Y = Fe^{3+}, \ Cr^{3+}, \ Al^{3+}, \ V^{3+}, \ Si^{4+}$$
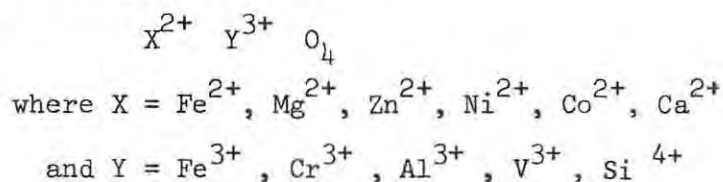
Appreciable amounts of Ti^{4+} may also be present in the magnetite, but the substitutions are more complex and involve coupled substitutions of the type $2Fe^{3+} \longrightarrow Fe^{2+} + Ti^{4+}$ (Annersten et al., 1973). Homogeneous Ti-rich magnetites are essentially intermediate members of the magnetite-ulvospinel solid solution series that exhibits complete miscibility at elevated temperatures (Kawai et al., 1954; Vincent et al., 1957) and are known as titanomagnetites. Minor amounts of Si^{4+} may also substitute in the magnetite structure (Vincent and Phillips, 1954).

Shull et al. (1951) showed that the magnetic moments of the cations in the A and B sites of magnetite are antiparallel with the result that it is a typical ferri-magnetic material. The Curie point of magnetite is at $578^{\circ}C$ and it has a saturation magnetisation of 92-93 e.m.u./g

at room temperature. (Nicholls, 1955).

Magnetite is opaque in transmitted light except when developed as very thin flakes such as those present in micas. It has a moderate reflectivity of 21 per cent in air and is grey, occasionally exhibiting a light brownish tint in air (Ramdohr, 1969). Ramdohr (1969) also noted that a high unexsolved Ti content produces a brownish-pink tint in the grey, while an increased Mn content produces a duller colour that enhances the grey colouration. The colour tints may, however, vary without any obvious relationships to the chemistry. Magnetite is expected to be isotropic on account of its cubic symmetry, but Ramdohr (1969) reported that it is sometimes distinctly anisotropic. The Vickers hardness number varies between 440 and 1100 (Uytenbogaardt and Burke, 1971) and probably reflects slight compositional differences.

The name magnetite is thought to be derived from the locality Magnesia in Thessaly. Pliny, however, suggested that the mineral was named after its discoverer, Magnus, a shepherd who found that the nails of his shoes and the iron ferrule of his staff adhered to the ground at places where this material is present (Palache et al., 1944).

2.3 Ulvospinel

This is also a member of the spinel mineral group and is cubic with an ideal formula of Fe_2TiO_4 ($2FeO.TiO_2$). It was synthesised by Barth and Posnjak (1932) and found to have an inverse spinel structure that is analogous to that of magnetite with two Fe^{3+} ions being replaced by $Fe^{2+} + Ti^{4+}$. It was also subsequently synthesised by Ernst (1943). Forster and Hall (1965) confirmed that the titanium ions preferentially occupy the octahedral sites, but noted that the ordering is incomplete with the result that some titanium ions are also present in the tetra-

hedral sites. The unit cell edge of synthetic ulvospinel is given as
8,535 Å by Taylor et al. (1972) which is slightly greater than the
earlier values of 8,50 Å (Barth and Posnjak, 1932) and 8,49 Å (Ernst,
1943). Vincent et al. (1957) reported values of 8,489 and 8,491 $\pm$
0,005 Å respectively for two natural ulvospinel microintergrowths.

Ulvospinel is only stable under very low oxygen fugacities (Verhoogen,
1962a) and is extremely rare on earth as a discrete mineral. Rice
et al. (1971) reported the occurrence of discrete equant ulvospinel
grains co-existing with skeletal pseudobrookite in a rapidly chilled
dyke, but interpreted this as being due to rapid disequilibrium
crystallisation. Although rare as a discrete mineral, it is commonly
found as an important solid solution component of other spinels,
particularly magnetite and chromite as discussed in sections 2.2 and
2.4. It is characteristically present as micrometre-sized exsolution
lamellae in titaniferous magnetite and was first recognised in nature
by Mogensen (1946) who named it after the locality at Södra Ulvön in
Sweden.

Ulvospinel-rich spinels are present in certain mafic replacement peg-
matites in the eastern Bushveld Complex (Frankel, 1942; Cameron and
Glover, 1973) and in a basaltic lava-lake (Evans and Moore, 1968).
Ulvospinel -rich spinels, particularly chromian types are also widely
developed in lunar basalts (Haggerty, 1972a, b; Smith and Steele, 1976).

Ulvospinel is only stable under low oxygen fugacities (hence its
relative abundance in lunar materials) and decomposes to ilmenite and
magnetite on oxidation (Ramdohr, 1953; Verhoogen, 1962a). The Curie
temperature of ulvospinel is $562^{o}C$ and it has a saturation magnetism of
35 e.m.u./g so that it exhibits no ferro- or ferrimagnetism (Akimoto et

al., 1957a). Ulvospinel is essentially non-magnetic and acts as a diluent on the magnetic properties of magnetite in magnetite-ulvospinel solutions (Vincent, 1960).

Ulvospinel appears darker brown in incident light than its associated magnetite, but this is not a safe criterion for its recognition under the microscope. This is because it is difficult to distinguish between ulvospinel and ilmenite in extremely fine-grained intergrowths when the anisotropy cannot be clearly seen (Ramdohr, 1953). The ulvospinel lamellae are typically oriented parallel to the cubic planes of their magnetite hosts, but may have been pseudomorphously oxidised to ilmenite and retain their original orientation.

2.4 Titanomagnetite

This represents a homogeneous, titanium-bearing, iron-rich spinel that is normally only encountered in rapidly cooled igneous rocks. Titano-magnetites are essentially quenched, high temperature, unexsolved members of the magnetite-ulvospinel solid solution series and consequently exhibit a range in composition between almost pure magnetite and up to approximately 80 mole per cent ulvospinel. The naturally occurring minerals normally also contain minor amounts of Mg^{2+}, Mn^{2+}, Zn^{2+}, Ca^{2+}, Ni^{2+}, Cr^{3+}, Al^{3+} and V^{3+}. Magnetite and ulvospinel (in which Ti^{4+} and Fe^{2+} are in octahedral sites) both exhibit the inverse spinel structure (Barth and Posnjak, 1932), but the cation distribution in the intermediate members has not been fully determined (Annersten et al., 1973 ; Stout and Bayliss, 1975).

Akimoto (1954) noted that there is an increase in the unit cell para-meter as the TiO_2 content of the titanomagnetite increases and suggest-ed that the Fe^{3+} is equally distributed between the tetrahedral and octahedral sites. Neel (1955) and Chevallier et al. (1955)

concluded that more Fe^{3+} was present in the tetrahedral sites than in the octahedral ones in accord with the empirical rule of Verwey and Heilmann (1947) which requires that Fe^{3+} preferentially enters the tetrahedral sites. Akimoto et al. (1957) synthesised intermediate members of this solid solution series and noted an essentially linear variation in cell dimensions between magnetite and ulvospinel.

O'Reilly and Banerjee (1965) prepared synthetic polycrystalline titanomagnetites over the whole range between magnetite and ulvospinel by sintering suitable mixtures of Fe, Fe_2O_3 and TiO_2 pressed into bars. They confirmed, by means of x-ray and magnetic measurements, that the cation distribution followed that of the Neel-Chevallier model and is governed by the preference of Fe^{3+} for the tetrahedral sites. They noted that this tetrahedral preference is, however, partly outweighed by the increase in electrostatic energy obtained by the substitution of Fe^{2+} in the tetrahedral sites in members of intermediate composition.

Banerjee et al. (1967) reported a slight deviation in the linearity of cell dimensions between magnetite and ulvospinel. They concluded that the new Fe^{2+} ion, produced by Ti^{4+} substitution, enters the tetrahedral sites contrary to the known preference of Fe^{3+} for tetrahedral sites with the result that both sublattices are occupied by ions of mixed valency. They suggested the followed three cation distribution patterns for the titanomagnetites based on their compositions:

1). $x = 0 - 0,2$

$$Fe^{3+}_{tet} \left[Fe^{3+}_{1-2x} \quad Fe^{2+}_{1+x} \quad Ti^{4+}_{x} \right]_{oct} O_4$$

2). $x = 0,2 - 0,8$

$$\left[Fe^{3+}_{1,2-x} \quad Fe^{2+}_{x-0,2} \right]_{tet} \left[Fe^{3+}_{0,8-x} \quad Fe^{2+}_{1,2} \quad Ti^{4+}_{x} \right]_{oct} O_4$$

3).   x = 0,8 - 1,0

$$\left[Fe^{3+}_{2-2x} \quad Fe^{2+}_{2x-1} \right]_{tet} \quad \left[Fe^{2+}_{2-x} \quad Ti^{4+}_{x} \right]_{oct} \quad O_4$$
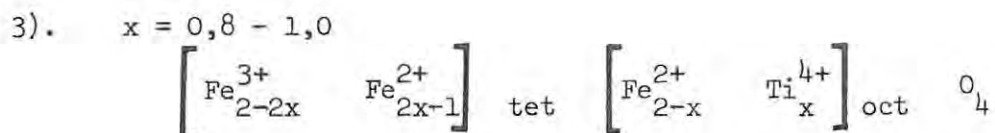
Stephenson (1969) suggested that the cation distribution of iron in titanomagnetite is dependent on the temperature of formation of the spinel. He concluded that random distribution occurs between both octahedral and tetrahedral sites at high temperatures, but that ordering takes place on slow cooling due to the preference of Fe^{3+} for tetrahedral sites. The cation distribution is consequently controlled by the temperature of quenching. These results were confirmed by Bleil (1971) who found that Fe^{3+} statistically occupies more of the tetrahedral sites at lower temperatures, while Ti^{4+} shows a preference for the octahedral positions.

Jensen and Shive (1973) reported a similar cation distribution in titanomagnetite to that reported by Akimoto (1954), but noted that the titanium was present in small titanium-rich clusters surrounded by a magnetite matrix. They suggested that this feature might be due to incipient exsolution, but noted that it is also a known characteristic of sintered samples and might be due to the preparation procedures used. They concluded that it is impossible to preserve a high temperature cation distribution at low temperatures as proposed by Stephenson (1969) and Bleil (1971) because of rapid electron transfer that takes place to produce an averaged oxidation state and an approximately equal ferrous/ferric ratio in both sites, even at low temperatures.

Annersten et al. (1973) also found a non-linear relationship in cell parameters in solid solutions between magnetite and ulvospinel. On the basis of x-ray studies and Mössbauer spectroscopy they concluded that substitution of the type $2Fe^{3+} \longrightarrow Fe^{2+} + Ti^{4+}$ occurred in the octahedral sites for up to 15 mole per cent ulvospinel. They noted

that at between 15 and 20 mole per cent ulvospinel, Fe^{2+} will begin
to enter the tetrahedral sites so that replacements of $Fe^{3+} \rightarrow Fe^{2+}$
will occur in the tetrahedral sites and $Fe^{3+} \rightarrow Ti^{4+}$ will take place
in the octahedral sites. They suggested that this form of substitution
is operative up to between 70 and 80 mole per cent ulvospinel.
Annersten et al. (1973) noted a less rapid increase in cell volumes
above 70 mole per cent ulvospinel and suggested that this might be
due to the substitution of a smaller ion into a tetrahderal site or
substitution entirely within the larger octahedral site.

Stout and Bayliss (1975) investigated the cation distribution in a
natural titanomagnetite containing minor amounts of other elements.
They concluded that the distribution of Fe^{3+} and Fe^{2+} between the
octahedral and tetrahedral sites followed that of a normal spinel in
which Fe^{2+} occurs in both tetrahedral and octahedral sites in the
ratio of 2:1 while Fe^{3+} occupies only the octahedral sites. The
Ti^{4+} is located only in the octahedral sites and is consistent with
the cation distribution in an inverse spinel. Most of the minor elem-
ents (Al^{3+}, Cr^{3+}, Mg^{2+}, V^{3+} and Ca^{2+}) are present in the octahedral
sites while Si^{4+} and Mn^{2+} are located in tetrahedral sites.

The titanomagnetite solid solutions are metastable and exsolve on slow
cooling. The ulvospinel component is also extremely sensitive to
oxidation and is only stable under conditions of low oxygen fugacity
(Verhoogen, 1962a). This oxidation can take place either above or
below the magnetite-ulvospinel solvus (Buddington and Lindsley, 1964;
Duchesne, 1970) and results in the development of a wide variety of
ilmenite and ulvospinel microintergrowths. The nature of the inter-
growths developed is a function of the oxygen fugacity and cooling
histories of the samples concerned and is discussed in sections 4.4

and 4.5.

Titanomagnetite is opaque in transmitted light and appears white with a distinct brownish tint in reflected light in air. Its reflectivity is approximately 17 per cent in air and the mineral is normally isotropic, although it is sometimes slightly anisotropic. The Vickers hardness number ranges between 715 and 734 (Uytenbogaardt and Burke, 1971). Data on the spectral reflectivity of an exsolved and homogenized titaniferous magnetite are given by Halfen (1976).

2.5 Maghemite

This is cubic gamma-Fe_2O_3 that exhibits a defect inverse spinel structure in which one in nine of the iron ions is absent (Hägg, 1935). There are consequently two and two thirds vacant cation sites per unit cell of 32 oxygens and recalculations of various maghemite analyses on this basis have shown that the number of cations present is less than the theoretical 24 for pure Fe_3O_4, being 21,33 for the pure end-member (Deer et al., 1962b).

Verwey (1935) demonstrated that the vacancy ions are probably omitted from the octahedral sites (B positions). Haul and Schoon (1939) suggested that a regular arrangement of the vacancies exists in the lattice and that a portion of the ferric ions must also be tetrahedrally co-ordinated in maghemite in contrast to their occurrence in octahedral sites in alpha-Fe_2O_3. These findings were subsequently substantiated by Henry and Boehm (1956), Sinha and Sinha (1957) and Ferguson and Hass (1958). Katsura and Kushiro (1961) demonstrated that the cell dimensions of naturally occurring titanomagnemite can be related to the number of vacancies present in the crystal structures.

Maghemite is a low-temperature oxidation product of magnetite and this aspect is discussed further in section 6. Basta (1959) report- ed the existence of a series of natural minerals having compositions intermediate between magnetite and maghemite and that reflect succ- essive degrees of oxidation. He termed these intermediate compounds magnetomaghemite (less than 50 per cent magnetite) and maghemomagnetite (more than 50 per cent magnetite). Maghemite is metastable and inverts to the more stable alpha-Fe_2O_3 (hematite) on heating to temperatures above $550^{\circ}C$ (Basta, 1959).

Maghemite proper contains less than 2 per cent TiO_2, but small amounts of Mg^{2+}, Co^{2+}, Ni^{2+}, Al^{3+} and Cr^{3+} may also be present (Basta, 1959). Maghemites containing more than 2 per cent TiO_2 are termed titano- maghemites and are formed by the low temperature oxidation of titano- magnetites. They consequently exhibit the characteristic minor ele- ment contents of these minerals (Basta, 1959).

Maghemite is opaque in transmitted light, except in the thinnest plates. It is isotropic and has a moderate, but variable reflectivity of between 18 and 24 per cent in air in incident light (Ramdohr, 1969). It varies from white to greyish-blue in colour, but Ramdohr (1969) noted that weathered grains exhibit a complete range in colours inter- mediate between that of unaltered magnetite and maghemite. This feature suggests the existence of various intermediate members and that the oxidation process must be of a gradational nature. This is also reflected in the Vickers hardness number that ranges from 357 to 988 (Uytenbogaardt and Burke, 1971).

The term maghemite was introduced by Wagner (1927) in order to distin- guish it from hematite and martite that both have the same bulk

composition, Fe_2O_3.

2.6 Hematite

This is rhombohedral alpha-Fe_2O_3 and represents the stable form of
this oxide. The hematite crystal structure was determined by Pauling
and Hendricks (1925) and is of the corundum-type, consisting of alter-
nating layers of oxygen and iron ions that are arranged perpendicular
to a 3-fold axis. The oxygen ions are arranged in a slightly dis-
ordered hexagonal packing while the cation layers consist of octahed-
rally co-ordinated ferric ions. This structure thus differs from the
spinel structure in which two thirds of the cations in alternate layers
are in tetrahedral co-ordination.

Hematite forms a complete solution series with ilmenite at elevated
temperatures (Ramdohr, 1926; Posnjak and Barth, 1934), but exhibits
only limited miscibility at lower temperatures (Lindsley and Lindh,
1974). Analyses indicate that hematite is essentially pure Fe_2O_3,
but minor amounts of TiO_2, MnO, Al_2O_3 and SiO_2 may also be present
(Deer et al., 1962b).

Hematite is found both as a primary and secondary mineral in nature.
It is an uncommon phase in igneous rocks and is usually present as a
secondary oxidation product of magnetite. It is, however, a common
primary phase in many metamorphic rocks that have formed under condit-
ions of relatively high oxygen fugacity. Hematite that is formed by
the oxidation of magnetite and is pseudomorphous after it is termed
martite.

Hematite exhibits a dark blood-red colour in thin flakes in transmitted

light and may exhibit dichroism from brownish-red (o) to yellowish-
red (e). It also shows very strong dispersion. Hematite is an-
isotropic and has a moderate reflectivity of between 21 and 28 per
cent in incident light in air. It exhibits a weak reflection pleo-
chroism from white (o) to pale grey-blue (e) in air and may show
distinct blood-red internal reflections (Ramdohr, 1969).

The name hematite is derived from the Greek "haema", meaning blood,
from its resemblance to congealed blood (Palache et al., 1944).

2.7 Ilmenite

This is essentially rhombohedral $FeTiO_3$ and has a crystal structure
that is similar to that of hematite, but in which there is some dist-
ortion of the oxygen layers resulting in a decrease in the mean O-O
distances (Barth and Posnjak, 1934; Posnjak and Barth, 1934). Pairs
of Ti ions alternate with pairs of Fe^{2+} ions along the 3-fold axes and
this paired cation distribution results in an uneven distribution of
Fe^{2+} and Ti in successive cation layers perpendicular to the 3-fold
axes. Hamos and Tscherbina, 1933 (reported in Posnjak and Barth,
1934) concluded that the titanium in the ilmenite is in a tetravalent
state on the basis of measurements of the K-absorbtion edge of the Ti
atoms. This implies that the iron in the ilmenite is in the ferrous
state.

Complete solid solution exists between ilmenite and hematite at elev-
ated temperatures (Ramdohr, 1926; Posnjak and Barth, 1934), but this
system exhibits only limited miscibility at lower temperatures
(Lindsley and Lindh, 1974). Posnjak and Barth (1934) reported that
$MgTiO_3$ (geikielite) and $MnTiO_3$ (pyrophanite) are isostructural with

ilmenite. Considerable substitution of Mg^{2+} and Mn^{2+} for Fe^{2+} can consequently occur in natural ilmenites.

Ilmenite is opaque in transmitted light, except in the thinnest flakes and exhibits distinct anisotropism in incident light. The reflectivity is moderate and varies from 18 (e) to 21 per cent (o) in air and the colour is greyish-white with a light brownish tint (Ramdohr, 1969). The grains exhibit a characteristic reflection pleochroism that varies between white and rose brown (o) and a rich brown (e) in oil (Ramdohr, 1969). The Vickers hardness number ranges between 501 and 752 and reflects compositional variations (Uytenbogaardt and Burke, 1971). Cervelle (1967) and Cervelle et al. (1971) have demonstrated that the reflectibity of magnesian ilmenite is dependent on its MgO content, but Morton and Mitchell (1972) have shown that microindentation hardness is dependent on both MgO and Cr_2O_3 contents.

Ilmenite is named after the locality in the Ilmen mountains while geikielite is named after Sir Archibald Geikie (1835-1924), Director of the Geological Survey of Britain. Pyrophanite is derived from the Greek words meaning "fire" and "to appear" which allude to its red colour (Palache et al., 1944).

3. NOMENCLATURE

3.1 Introduction

The names used for the end-member minerals in the $FeO-Fe_2O_3-TiO_2$ system are shown in figure 1 and follow the scheme presented by Buddington and Lindsley (1964). A variety of names has been given to the numerous intermediate solid solution members of this system and their useage has varied with time. The terminology used in this

thesis for the natural minerals and their intergrowths is based on the system of Buddington et al. (1963), while their oxidation products are named according to the scheme of Basta (1959, 1960). In keeping with these authors' useage, hyphenated words refer to a microintergrowth in which the prefix corresponds to the volumetrically smaller intergrowth, while single words refer to homogeneous mineral phases.

3.2 Terminology

1) Titaniferous magnetite: This is a general term for a titanium-bearing magnetite with no implications as to whether the grain is homogeneous or contains titanium-rich microintergrowths (Buddington et al., 1963).

2) Multi-phase titaniferous magnetite (MPTM): The majority of ex-solved titaniferous magnetite grains contain a variety of ilmenite, pleonaste and ulvospinel microintergrowths that cannot be adequately covered by the existing nomenclature. These grains are simply referred to as MPTM (this thesis).

3) Titanomagnetite: This is a homogeneous, single phase, cubic mineral whose analysis can be recalculated essentially in terms of Fe_3O_4 and $2FeO.TiO_2$, or $FeO.TiO_2$ or both, with Fe_3O_4 as the significant component (Buddington et al., 1963).

4) Ilmeno-magnetite: This is magnetite that contains microintergrowths of ilmenite (Buddington et al., 1963)

5) Ferrianilmenite: This is a homogeneous phase consisting essentially of $FeO.TiO_2$ with 6 to 13 per cent Fe_2O_3 and up to 3 or 4 per cent

excess TiO_2 in solid solution (Buddington et al., 1963).

6) <u>Hemo-ilmenite</u>: This is a Fe-rich ilmenite that contains titano-
hematite or ilmeno-hematite microintergrowths (Buddington et al.,
1963).

7) <u>Ilmeno-hematite</u>: This is a Ti-rich hematite that contains micro-
intergrowths of ferrianilmenite or hemo-ilmenite (Buddington et al.,
1963).

8) <u>Titanohematite</u>: This is Fe_2O_3 that contains 5 to 10 per cent TiO_2
in solid solution (usually as $FeO.TiO_2$ with a little excess TiO_2).
Buddington et al. (1963) used the term titanhematite, but Buddington
and Lindsley (1964) introduced the term titanohematite which is more
in keeping with the other names in this system.

9) <u>Magneto-ilmenite</u>: This is an ilmenite containing microintergrowths
of magnetite and the term is used without any genetic implication
(new definition).

10) <u>Martite</u>: This is alpha-Fe_2O_3 (hematite) that has formed from the
oxidation of magnetite (Balsley and Buddington, 1958). This term
is used in order to distinguish magnetite oxidation products from
other forms of hematite.

11) <u>Titaniferous martite</u>: This is a general term for a titanium-
bearing martite and is used without any implication as to whether
the mineral is homogeneous or contains titanium-rich intergrowths
(new definition).

12) <u>Maghemite</u>: This is gamma-Fe_2O_3 containing less than 2 per cent
TiO_2 in solid solution and is an oxidation product of magnetite

(Basta, 1959),

13) <u>Titanomaghemite</u>:   This is a homogeneous, single phase, gamma-Fe_2O_3
containing more than 2 per cent TiO_2 in solid solution and is an
oxidation product of titanomagnetite (Basta, 1959).

14) <u>Titaniferous maghemite</u>:   This is a general term for a titanium-
bearing maghemite and is used without any implications as to whether
the mineral is homogeneous or contains Ti-rich intergrowths.(modif-
ied definition).   The term was introduced by Deer, Howie and Zuss-
mann (1962b) to describe cubic oxidation products of titaniferous
magnetite and is used in an analogous sense.

15) <u>Pseudobrookite</u>:   This is an optically homogeneous, orthorhombic
iron-titanium phase with an oxide stoichiometry near R_3O_5 and
having a mole per cent of Fe_2TiO_5 greater than 50 (Anderson, 1968a).

16) <u>Ferro-pseudobrookite</u>:   This is the same as pseudobrookite, but the
mole per cent of Fe_2TiO_5 is less than 50 (Anderson, 1968a).

4 <u>PHASE RELATIONSHIPS IN THE $FeO-Fe_2O_3-TiO_2$ SYSTEM</u>

4.1 <u>Historical Note</u>

Investigation of the iron-titanium oxide began towards the middle of
the last century, but most of the data obtained were of an indirect
nature and accumulated during mineralogical and petrological studies of
their host rocks.   Many of the early references are, unfortunately,
not available in this country and this historical note has been com-
piled from earlier reviews by Singewald (1913b), Warren (1918) and
Dunn and Dey (1937).   This information, however, provides a useful
introduction to the more detailed studies that followed, and it is
interesting to note that many of the early observations and conclusions
have been substantiated by later investigators using far more sophist-

icated equipment and techniques.

The initial mineralogical studies in this system were of a macroscopic
nature and were initiated by Rammelsberg (1858) who concluded that
the titanium-bearing magnetites consisted of titanium-free octahedral
magnetite and rhombohedral ilmenite.   Knop (1862) reported the pre-
sence of 24,95 per cent TiO_2 in magnetite octahedra from Meiches in
the Vogelsberg.   Seligmann (1877) described regular macroscopic inter-
growths of rutile in magnetite while Cathrein (1884) detected similar,
but microscopic **intergrowths of rutile in magnetite after dissol-**
ving the magnetite in HCL.   Neef (1882) etched a thin section with
hot HCL which dissolved the magnetite and revealed the undecomposed
ilmenite latticeworks.   Kuch (1885) reported similar intergrowths in
a plagioclase-olivine-augite rock while Teall (1884) concluded that
similar intergrowths were developed in the TiO_2-bearing magnetites of
the Whin Sill.

Becke (1886) undertook the first microscopic examination of the ilmenite-
magnetite intergrowths and described the presence of ilmenite tablets
that are intergrown parallel to the octahedral faces of the magnetite.
Cathrein (1887) described similar intergrowths and concluded that the
tabular ilmenite bodies are crystallographically oriented with their
basal planes parallel to the octahedral planes of the magnetite.   He
also presented chemical analyses that demonstrated that the intergrowth-
free magnetite contained no titanium.   Rosenbusch (1892) reported that
the lamellar ilmenite intergrowths in magnetite intersect each other
at 60° in sections parallel to (111) of the magnetite and at 90° in
sections parallel to (100).   Similar intergrowths were described in
titanium-bearing magnetites from other rock types by Adams (1893) and
Rosenbusch (1896).

Kemp (1899) reported that magnetite from the Adirondacks contained up to 18 per cent TiO_2 as well as small amounts of vanadium. Lacroix (1901-1909) concluded that the titanium content of titaniferous magnetite is due to both the presence of ilmenite in magnetite and to the substitution of some Ti_2O_3 for Fe_2O_3 in the magnetite. Intergrowths of ilmenite and rutile in magnetite were also described by Mügge (1903).

The first detailed microscopic investigations of polished sections of titaniferous iron ores were undertaken by Hussak (1904). He etched the polished section surfaces with HCL which attacked the magnetite and produced a dull black surface while the ilmenite remained unaffected and could be easily observed. He reported that the ores consisted of magnetite and ilmenite aggregates and that the magnetite contained both regular and irregular ilmenite intergrowths. He found that the regular lamellar intergrowths varied considerably in size and abundance and published the first photomicrographs of these intergrowths.

The microscopic study of these minerals in polished sections was subsequently taken up by other investigators and Warren (1908) also reported lamellar intergrowths in titaniferous iron ores from Rhode Island. These developments led to a mineralogical investigation of the United States titaniferous iron ore deposits by Singewald (1913a, b) and ultimately to the more detailed mineralogical and phase-relationship studies that are reviewed in the following sections.

4.2 Introduction

The complex phase relationships in the $FeO-Fe_2O_3-TiO_2$ system are reflected in the wide range of microstructures that are developed in the iron-titanium oxides. These relationships have been investigated

in detail and three solid solution series are known to exist in this
system at elevated temperatures (MacChesney and Muan, 1959; Webster
and Bright, 1961; Taylor, 1963, 1964).   The phase relationships at
$1300^{\circ}C$ are illustrated in figure 2 and show the following three solid
solution series:

i)   ferropseudobrookite-pseudobrookite (orthorhombic)

ii) ilmenite-hematite (rhombohedral)

iii) ulvospinel-magnetite (cubic)

FIGURE 2   Isothermal section at $1300^{\circ}C$ in the system $FeO-Fe_2O_3-TiO_2$
showing the three solid solution series ferropseudobrookite-
pseudobrookite; ilmenite-hematite and ulvospinel-magnetite
(from Taylor, 1964)

Restricted solid solution also exists between these three series at
elevated temperatures, but the composition bands between the three
solid solution series become narrower on cooling and exsolution commen-
ces.   These relationships are illustrated in the $1200^{\circ}C$ isothermal

section (figure 3). Only limited solid solution exists in these three series at low temperatures.
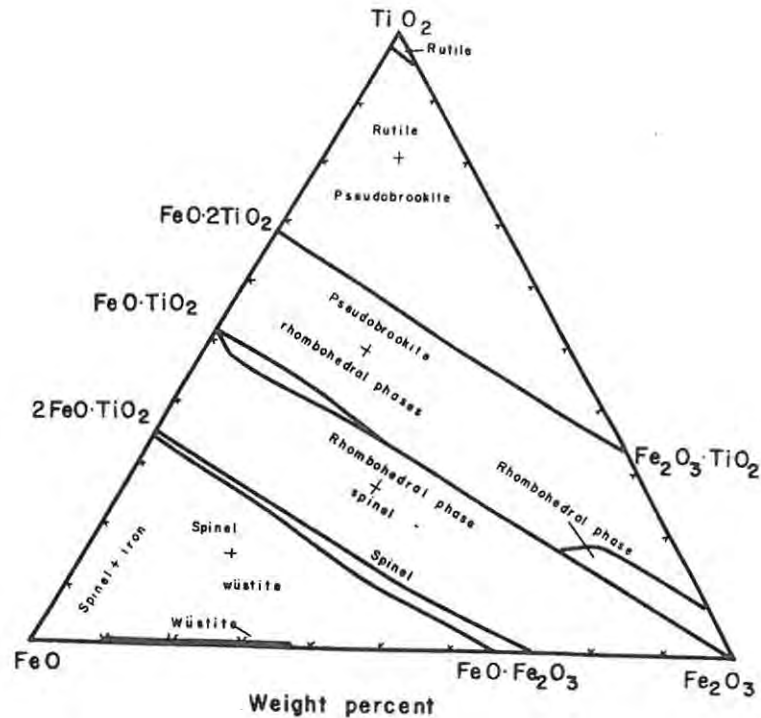
FIGURE 3 Isothermal section at 1200°C in the system $FeO-Fe_2O_3-TiO_2$ showing the phase relationships (from Webster and Bright, 1961).

The oxidation state of the iron in these three solid solution series is sensitive to changes in oxygen fugacity during cooling and this consequently influences the nature of the phases produced (Buddington and Lindsley, 1964). The phases in this system also show varying degrees of solid solution with other related MgO-, Cr_2O_3-, Al_2O_3-, and MnO-bearing systems with the result that the naturally occurring minerals exhibit a wide range of chemical compositions and microintergrowths.

These features combine to produce the extraordinary variety of micro-intergrowths and phase relationships that are reviewed in the follow-

ing sections. The rhombohedral ilmenite-hematite, and the cubic mag-
netite-ulvospinel series are of particular interest in this study since
the bulk of the microstructures exhibited by the investigated iron-
titanium oxides are controlled by phase relationships in and between
these two systems.

4.3 The Rhombohedral Ilmenite-Hematite Series

4.3.1 The ilmenite-hematite microstructures

Naturally occurring ilmenites from a wide range of slowly cooled
igneous rocks commonly contain several per cent of hematite that is
present as fine-grained intergrowths. These lamellae are
invariably oriented parallel to the basal planes of their host and may
be locally abundant in hemo-ilmenites from certain rock types. The
intergrowths generally exhibit distinct elongated, lens-shaped forms
having gently tapering ends when viewed in sections cut parallel to
(0001) of their hosts. The morphology of the intergrowths varies
between these two extremes in randomly oriented sections and they have
the overall appearance of flattened lenses.

Hematite containing essentially similar ilmenite microintergrowths is
also found, but is far less common in igneous rocks, being more abundant
in metamorphic types. A complete gradation between hemo-ilmenite con-
taining only minor ilmenite intergrowths and ilmeno-hematite containing
only minor ilmenite intergrowths is found in nature. Intermediate
members, consisting of approximately equal proportions of ilmenite and
hematite, in which it is difficult to distinguish between the host and
intergrown phases, are developed in some Precambrian anorthosites.

A second series of similar, but very much finer hematite intergrowths
are commonly present in the ilmenite in areas between the larger

hematite bodies. The larger hematite intergrowths themselves also commonly contain a series of similar, very much finer ilmenite inter-growths that are oriented parallel to (0001) of their hosts. the ilmeno-hematite grains exhibit essentially similar relationships with respect to their ilmenite microintergrowths. The composite hemo-ilmenite and ilmeno-hematite grains occasionally exhibit twinning and there is a marked change in orientation of the intergrowths across the twin planes which reflect their crystallographic control .

A series of photomicrographs illustrating many of the ilmenite-hematite microstructure features are given in Ramdohr (1969)·, p. 960-969. Additional photomicrographs are presented in Parts 2 and 3 of this thesis.

4.3.2 Mineralogical investigations of the $FeTiO_3$-Fe_2O_3 system

The first photomicrograph of an ilmenite-hematite microintergrowth was published by Singewald (1913a, fig. VIIb), but he identified the hem-atite as magnetite, even though he reported that it was more resistant to acid etching than is usual for magnetite. Warren (1918) described microintergrowths of both hematite in ilmenite and ilmenite in hematite as well as optically homogeneous ilmenite grains that contained a high proportion of Fe_2O_3. On the basis of the homogeneous grains he con-cluded that a wide range of miscibility existed between $Fe^{2+}TiO_3$ and Fe_2O_3. He noted that ilmenite and hematite are probably miscible at high temperatures, but suggested that their isomorphous mixture would become unstable on cooling and would unmix to form the ilmenite and hematite microintergrowths. He also reported the presence of magnetite intergrowths in ilmenite and noted that some of the hematite intergrow-ths might form via the oxidation of this magnetite.

Ramdohr (1926) investigated the phase relationships in this system microscopically by comparing observations of natural minerals with products obtained by heating ilmenite-hematite intergrowths both in air and nitrogen. He recognised the presence of two distinct size-ranges of intergrown hematite discs in certain ilmenites and stressed the absence of intermediate sized bodies. He regarded these discs as exsolution bodies and referred to the larger-sized series as "generation 1" while the smaller bodies were termed "generation 11".

Ramdohr (1926) succeeded in homogenizing the hematite-ilmenite inter-growths by heating them at $1000^{o}C$ in air for 12 hours and noted that solution of the "generation 1" bodies commenced at approximately $700^{o}C$. No solution of either "generation" of intergrowths was evident after heating at $500^{o}C$ in air for 12 hours, but solution of the "generation 11" bodies commenced at temperatures between 500° and $600^{o}C$.

Ramdohr (1926) prepared a qualitative phase diagram for the $FeTiO_3$-Fe_2O_3 system on the basis of his experimental results (figure 4) which indicates that the ilmenite and hematite are completely miscible at high temperatures. On slow cooling the solvus is intersected and the solid solution unmixes to form the "generation 1" exsolution bodies. Exsolution continues on slow cooling, but a temperature is reached at which Ramdohr (1926) assumed that the ilmenite transformed from its higher symmetry and became tetartohedral. He postulated that the solu-bility of both Fe_2O_3 in $FeTiO_3$ and of $FeTiO_3$ in Fe_2O_3 decreased abrupt-ly at this stage leading to the exsolution of the "generation 11" bodies. He tentatively assigned a temperature of $215^{o}C$ to this trans-formation temperature (based on earlier electrical conductivity studies), but suggested in a footnote (1926, p. 375) that this temperature might be closer to $675^{o}C$.

TEMPERATURE

(T)215°?
or
675°?

FeTiO₃   COMPOSITION   Fe₂O₃
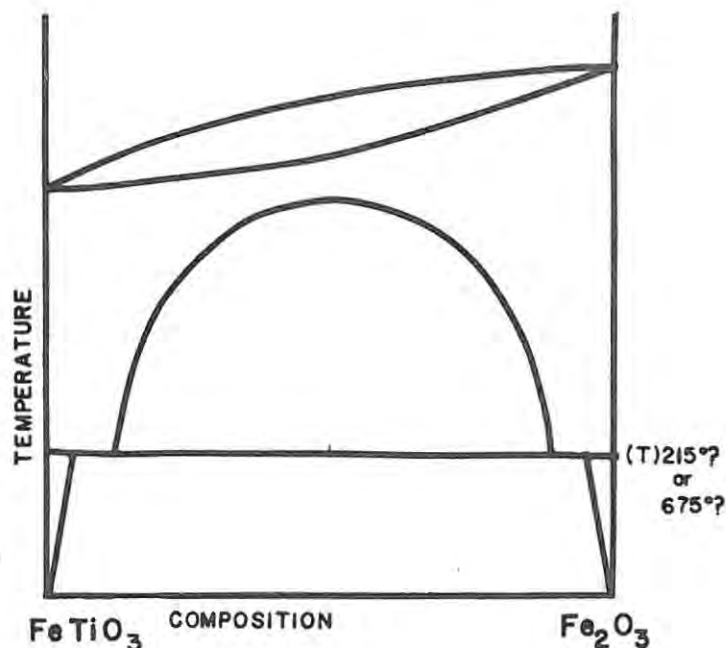
FIGURE 4   The qualitative phase diagram of the ilmenite-hematite

system presented by Ramdohr (1926). Note the absence of

any temperature or other details. He originally placed

the transformation temperature at 215°C, but later changed

it to 675°C (T).

Ramdohr (1926) noted that the presence of foreign ions would also

alter the phase relationships and temperatures in this system.   He

stated that exsolution would not take place under conditions of rapid

cooling thus resulting in the formation of homogeneous ilmenites with

high Fe_2O_3 contents.   Ramdohr (1926) concluded that ilmenite can con-

tain up to 6 per cent Fe_2O_3 in solid solution at normal temperatures.

Osborne (1928) reported the presence of two series of hematite inter-

growths in ilmenite from titaniferous iron ores and also concluded

that there is considerable miscibility in this system.   He also con-

firmed that the hematite bodies are oriented with their basal sections parallel to (0001) of their hosts and noted that twinning in ilmenite is parallel to ($1\bar{1}01$). Knopf and Anderson (1930) applied Ramdohr's results on the $FeTiO_3$-Fe_2O_3 system as a geothermometer to determine the temperature of formation of the Engels copper deposit. They concluded that the presence of two generations of hematite exsolution bodies in exsolved ilmenites indicated a minimum temperature of $675^\circ C$. This led to the publication of an extensive criticism of certain aspects of Ramdohr's work by Greig (1932).

Greig (1932) demonstrated certain technical errors in the construction and operation of Ramdohr's phase diagram (figure 4) and pointed out that his two-stage exsolution mechanism had not been experimentally substantiated. He suggested that the disappearance of the smaller hematite bodies at a lower temperature in Ramdohr's experiment was merely due to their small size which made the changes more obvious and concluded that minor solution of the larger bodies must also have occurred. Greig (1932) concluded that Ramdohr's experiments had only shown that the diffusion rate was dependent on temperature and that these types of intergrowth could consequently not be used as geothermometers.

Posnjak and Barth (1934) synthesized a homogeneous solid solution with a composition midway between ilmenite and hematite by heating suitable mixtures in evacuated silica tubes at $1200^\circ C$ for a few hours. They demonstrated an approximately linear increase in the volume of the unit cell from hematite to ilmenite due to the compensating effects of changes in the unit cell dimensions and the rhombohedral angle.

Edwards (1938) also investigated the ilmenite-hematite intergrowths

microscopically and carried out heating experiments that confirmed
Ramdohr's conclusions about the existence of a continuous solid solu-
tion series at temperatures above 700-800°C. Edwards (1938) reported
that this high temperature solid solution breaks down on slow cooling
into two solid solutions, one rich in $FeTiO_3$ and the other rich in
Fe_2O_3. Each of these solid solutions then continues exsolving as
cooling progresses.

Edwards (1938) recognised the typical crystallographic orientation of
the intergrowths and reported that the earlier-formed exsolution bodies
are distinctly larger than the others and that the spaces between
them contain smaller bodies. He noted that there is a continuous
range in size of the smaller bodies ("generation 11" of Ramdohr, 1926)
and that the largest of these occupy a median position between the
rows of coarser "generation 1" exsolution bodies as far as possible
away from their sphere of influence. The spaces between the "gener-
ation 11" bodies also contain very much smaller exsolution bodies that
range in size down to the limits of optical resolution.

Following the suggestion of Greig (1932) that the exsolution might be
a continuous process over a range of temperatures, Edwards (1938)
postulated that these conditions would allow the titanium-bearing
hematite that precipitated during the early stages of cooling to
segregate and form the larger exsolution bodies. During later stages
of cooling, the diffusion rates would become much slower, resulting
in an increase in the number of centres of precipitation so that prog-
ressively smaller exsolution bodies would be formed. The continuing
decrease in the amount of exsolvable hematite available would also
contribute to their diminishing size.

Edwards (1938) also reported that exsolution of ilmenite had continued in an identical manner within the earlier exsolved hematite bodies that were able to hold less and less TiO_2 in solid solution as the temperature decreased. The largest ilmenite exsolution bodies are formed in the central portions of the earlier hematite bodies and grade into finer bodies towards their margins which are generally free from even the finest intergrowths. Smaller ilmenite exsolution bodies are also developed in the areas between the larger ilmenite bodies. Edwards (1938) ascribed these features to the effects of decreasing solid diffusion and consequent increase in the numbers of centres of nucleation. He concluded that the decrease in size towards the margins is due to the hematite in these areas having exsolved at a lower temperature than their earlier-formed cores and consequently holding less TiO_2 in solid solution.

Edwards (1938) rejected Ramdohr's postulate that the finer exsolution bodies are formed by a sudden decrease in solubility and noted that the size of exsolution bodies in any specimen would depend on both the rate of cooling and the composition of the original solid solution. In particular, he noted that slow cooling of a solid solution containing only minor amounts of solute would produce small exsolution bodies while a similar texture would be produced by the relatively rapid cooling of a solid solution of more intermediate composition. He concluded that the presence of large exsolution bodies is indicative of slow cooling, but that the chemical composition of a fine-grained intergrowth would have to be determined before its rate of cooling could be ascertained.

Edwards (1938) also described similar ilmenite intergrowths in hematite, but noted that there was a continuous gradation in size between the ex-

solution products. He noted that the intergrowths of ilmenite in
hematite and vice versa were always oriented parallel to their (0001)
planes. He concluded that this was due to the (0001) plane having
a wide atomic spacing and being common to both ilmenite and hematite.
He placed the limit of solid solution of TiO_2 in Fe_2O_3 at ordinary
temperatures at between 5,6 and 11,3 per cent and that of Fe_2O_3 in
ilmenite at slightly less than 5,6 per cent.

Edwards (1947) restated his earlier views on ilmenite-hematite inter-
growths and concluded that their capacity to form such an extensive
solid solution was due to their structural similarity. He noted
that both minerals are rhombohedral with the corundum structure and
that it is possible to derive the ilmenite structure from hematite by
replacing half the iron atoms by titanium in a strictly ordered sequ-
ence. On this basis he concluded that the substitution of Ti for
Fe was simplified since "the ionic radii of the two atoms involved
in this substitution - Fe^{3+} 0,67 Å, Ti^{3+} 0,69 Å - are sufficiently
close to cause little distortion of the lattice". (Note that Hamos
and Tscherbina, 1933 (quoted in Barth and Posnjak, 1934) conclude that
the Ti is tetravalent and Fe divalent in ilmenite at normal temperatur-
es).

Pouillard and Michel (1949) synthesised members of the ilmenite-hemat-
ite solid solution series by heating mixtures of TiO_2 and FeO in vacuo
and found that two series were present, one being limited towards the
composition $2Fe_2O_3 \cdot FeTiO_3$ and the other towards $2FeTiO_3 \cdot Fe_2O_3$.
They noted that the Fe_2O_3-rich solid solutions are ferromagnetic while
the $FeTiO_3$-rich solid solutions are paramagnetic. Pouillard (1950)
reported the preparation of members of the ilmenite-hematite solid sol-
ution series at 950°C and concluded that there is a compositional gap

at this temperature that extends from 33 per cent $FeTiO_3$ to 66 per cent $FeTiO_3$. Chevallier et al. (1955) prepared a series of hematite-ilmenite solid solutions by reducing mixtures of Fe_2O_3 and TiO_2 at $1000^{\circ}C$ and confirmed the existence of the miscibility gap between 33 and 66 per cent $FeTiO_3$. They expressed the solid solution in the form $2Fe_2O_3$, $(1-Z)$ $FeTiO_3$ and noted that the range of Z between 0 and 1/3 represents the ferrianilmenites whether they are ferromagnetic or not. The values of Z between 2/3 and 1 represent the ferromagnetic titanohematites while the range between 1/3 and 2/3 represents the miscibility gap.

Akimoto (1955) presented analyses of 12 phenocrysts separated from andesitic and dacitic lavas that are naturally occurring members of the ilmenite-hematite solid solution series. He also noted that there is an almost linear increase in the rhombohedral a-cell edge from hematite (5.42 $\overset{o}{A}$) to ilmenite (5.538 $\overset{o}{A}$). He reported that certain of these solutions are ferromagnetic.

Nicholls (1955) reviewed the available data on the Fe_2O_3-$FeTiO_3$ system and discussed unpublished data of Basta (1953, Ph.D. thesis, Bristol University) who found complete solid solution in this system at temperatures above $1050^{\circ}C$. Basta (1953, quoted in Nicholls, 1955) also reported a steady increase in cell dimensions from hematite (a-hexagonal 5.029 $\overset{o}{A}$) to ilmenite (a-hexagonal 5.083 $\overset{o}{A}$). He concluded that the replacement of $2Fe^{3+}$ by Fe^{2+} + Ti^{4+} must take place continuously since there is no discontinuity in the variation of cell dimensions between the end members.

Nicholls (1955) prepared a phase diagram for this system based on the available data (Figure 5), but noted that insufficient data are avail-

able for the accurate positioning of the solvus curve. He concluded,
however, that the overall shape of the solvus would not deviate from
that shown in this diagram.
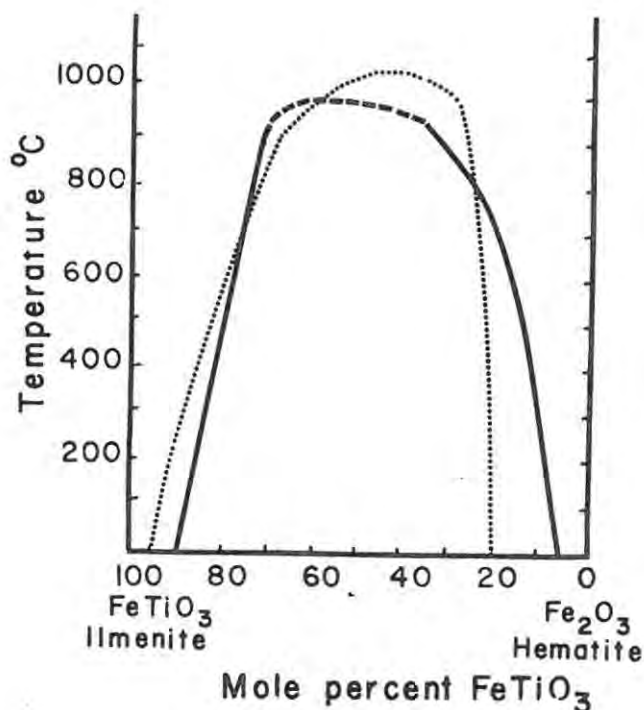
FIGURE 5   Sub-solidus phase diagrams for the ilmenite-hematite system
            from Nicholls, 1955 (dotted line) and Carmichael, 1961
            (solid line).

Ramdohr (1956) denied the existence of a miscibility gap   between
33 and 66 per cent $FeTiO_3$ at high temperatures as shown by Pouillard
(1950) and Chevallier et al. (1955). He also noted that the abrupt
change in solubilities at low temperatures was lower on the Fe_2O_3 side
of the phase diagram than on the $FeTiO_3$ side, but gave no further
details.

Investigations of the magnetic properties of the ilmenite-hematite solid
solution series commenced in the mid-1950's as a result of their recog-
nition as carriers of magnetism in palaeomagnetic studies. These

investigations were mainly undertaken in Japan and provided information on the solid solution relationships and crystal structures of the intermediate members of this series. Only the broader aspects of this work that are relevant to the phase relationships in this system are, however, summarized since this study is not specifically concerned with the magnetic properties of these minerals.

Nagata and Akimoto (1956) and Akimoto (1957) synthesised homogeneous solid solutions over the whole range between ilmenite and hematite at 1200°C. They classified solid solutions of the type $xFeTiO_3 \cdot (1-x)Fe_2O_3$ into the following groups on the basis of their magnetic properties under atmospheric conditions: (i) a feebly ferromagnetic region for values of x between 0 and 0,55 (ii) a ferromagnetic region for values of x between 0,55 and 0,75 and (iii) a paramagnetic region for values of x between 0,75 and 1. They also noted that the ferromagnetism of natural minerals appears more intense than that of their synthetic equivalents and suggested that this might be due to heating effects and the ordering of Fe^{2+} and Ti^{4+} ions in the crystal structure.

Ishikawa and Akimoto (1957a, b) confirmed these observations within a range of solid solutions synthesised at 1100°C and noted that the largest intensity of magnetization corresponds to the most ordered crystal structure. They also reported that the degree of ordering (and hence magnetisation) could be improved by heating at 1200°C for more than 12 hours before quenching. They concluded that the magnetic properties are dependent on the ordering of the Ti^{4+} ions and suggested that they always occupy one of two sublattices in specimens with values of x between 1 and 0,5. They also concluded that Ti and Fe ions are disordered in solid solutions with the range of x between 0 and 0,5.

Ishikawa and Akimoto (1958) investigated other ilmenite-hematite-type solid solutions and drew attention to the substitution problems invoved. In particular, they noted that the unit cell volume increases linearly with composition between hematite and ilmenite in spite of the Fe^{2+} ion being larger (0,75 Å) than those of Ti^{4+} (0,68 Å) and Fe^{3+} (0,60 Å). They also noted that the crystal symmetry changes from $R\bar{3}$ (ilmenite) to $R\bar{3}c$ (hematite) at some intermediate composition and suggested that the $R\bar{3}$ symmetry corresponds to a structure in which the Ti and Fe ions are ordered, while the $R\bar{3}c$ symmetry corresponds to a disordered structure in which the Ti and Fe ions are randomly distributed.

Ishikawa and Akimoto (1958) suggested that complete solid solution in this system was, however, possible since the activation energy required for the migration of the Ti^{4+} ions would be lowered due to the process whereby the Fe^{2+} and Fe^{3+} ions can change their arrangement simply by electron transfer. This process would consequently reduce the repulsive force between Fe and Ti ions during their migration to other lattice points. They concluded that the electrostatic energy due to the re-arrangement of the Ti ions might be reduced by this mechanism and that the order-disorder transformations between the $R\bar{3}$ and $R\bar{3}c$ symmetries might be due to a similar process.

Ishikawa (1958) and Ishikawa and Syono (1963) noted that the cation distribution in ilmenite-hematite solutions might be either ordered or disordered for values of x near 0,5 and concluded that the state of order is a function of the thermal history of the sample concerned. The order-disorder relationships in the ilmenite-hematite solid solution series were subsequently investigated and their existence established by neutron diffraction (Shirane et al., 1959) and by both

neutron diffraction and Mössbauer spectroscopy (Shirane et al., 1962).
Additional data on the magnetic properties of this solid solution
series were also published by Hargraves (1959), Ishikawa (1962) and
Reithler and Bolfa (1963).

Carmichael (1961) examined the magnetic properties of natural exsolved
hemo-ilmenite crystals from Allard Lake and determined their subsolvus
phase relationships by means of a series of heating experiments in
sealed silica tubes containing a little air. He reported that com-
plete resorption of the lamellae, as determined by x-ray diffraction,
Curie point and microscopic observation, was attained by heating at
1250°C for 4 days. He noted that the homogenization times were slow,
particularly at low temperatures, and heated a series of natural ex-
solved crystals at between 300° and 1000°C for 34 days. A second
series was run between 400° and 900°C for 100 days. Two series of
previously homogenized hemo-ilmenite crystals were also heated under
the same sets of conditions in order that the approach to equilibrium
at a given temperature could be observed from both the exsolution and
resolution sides.

Carmichael (1961) analysed the heating products by means of x-ray
diffraction and Curie point determinations and noted that the crystals
heated above 600°C for 100 days were much closer to equilibrium than
those of the 34 day series. He reported that 100 days was insuffic-
ient time for complete resorption of the lamellae at temperatures of
600°C and below. Carmichael (1961) constructed the first quantitat-
ive phase diagram for the solvus of this system on the basis of these
data and it is reproduced in figure 5 for comparison with the earlier
version of the solvus position prepared by Nicholls (1955).

Webster and Bright (1961) investigated the phase relationships in the system Fe-Ti-O at 1200°C over a range of oxygen fugacities (figure 3) and reported the existence of complete solid solution in the alpha-Fe_2O_3-$FeTiO_3$ sub-system which they termed the "alpha-series". They noted that this series exists as a single phase over a range of Fe/ (Fe + Ti) ratios for a given oxygen fugacity (fO_2) in two different regions of figure 6.
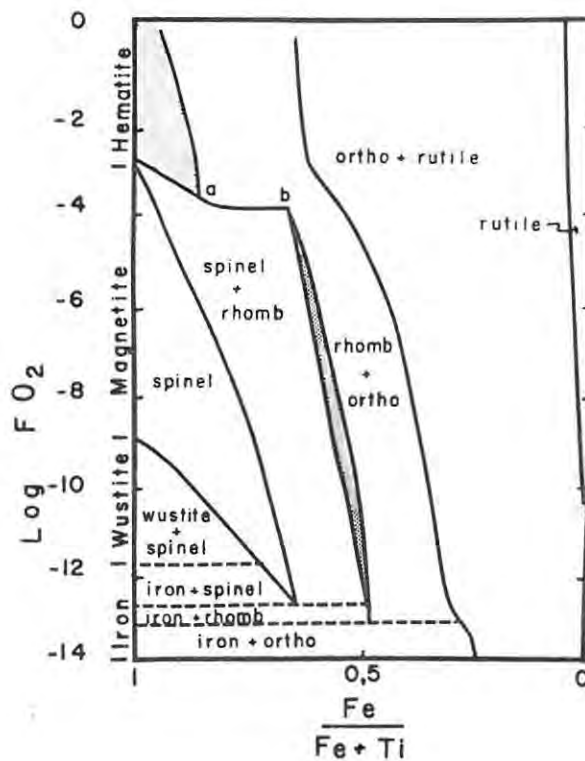
FIGURE 6   Phases present in the system Fe-Ti-O at 1200°C as a

function of the Fe/(Fe + Ti) atom ratio and the oxygen

fugacity.   The shaded areas indicate the ilmenite-

hematite solid solution stability fields and the line

between a and b, has a narrow, but undetermined width

(from Webster and Bright, 1961).

Webster and Bright (1961) also reported that a single phase ilmenite-hematite solid solution is stable over a considerable range of oxygen fugacities for a given Fe/(Fe + Ti) ratio.   In particular, they

noted that a small change in the fO_2 at about $\log fO_2 = -4$ in the region Fe/(Fe + Ti) between 0,65 and 0,85 results in a large change in the Fe/(Fe + Ti) ratio of the ilmenite-hematite solid solution (figure 6). They concluded that this phenomenon would be expected to occur under conditions immediately above the consolute temperature of the miscibility gap in this system and noted that the two solid solutions on either side of the gap would have the same oxygen fugacities.

Lindsley (1962) reported that attempts to determine the ilmenite-hematite solvus hydrothermally (in order to speed up sluggish reaction rates) had been unsuccessful since no buffer was available with an fO_2 at which hematite$_{ss}$ (solid solution) and ilmenite$_{ss}$ could co-exist. He reported that initial compositions of hem$_{50}$ilm$_{50}$ were oxidised to hematite$_{ss}$ + pseudobrookite$_{ss}$ (or hematite$_{ss}$ + rutile) by the magnetite-hematite buffer (MH) while they were reduced to magnetite$_{ss}$ + ilmenite$_{ss}$ by the nickel-nickel oxide buffer (NNO) (figure 7).

Lindsley (1962) concluded that if both ilmenite and hematite solid solutions can co-exist at equilibrium at a given temperature, there must be an overlap of the fO_2 ranges over which each is stable. This zone of overlap must also lie between the oxygen fugacities of the MH and NNO buffers. He also noted that the corresponding fO_2 range of mutual stability would probably decrease on cooling as the compositions of the co-existing hematite and ilmenite solid solutions moved further apart.

Lindsley (1962) noted that many low-grade metamorphic rocks contain the assemblage magnetite + rutile which is chemically equivalent to hematite + ilmenite and can be represented by the reaction:

$$Fe_3O_4 + TiO_2 = Fe_2O_3 + FeTiO_3$$
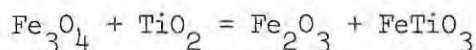
He noted that this reaction has a very small positive free energy of between 1 and 2 kcal over the temperature range of 100° to 1200°C (Verhoogen, 1962a) which accounts for the stability of the magnetite + rutile assemblages. Lindsley (1962) suggested that there is no fO_2 at which hematite and ilmenite solid solutions can exist between approximately 200° and 400°C and that the intergrowths might form, however, since less energy would be required for the migration of Fe and Ti in the inherited oxygen framework of the original phase than for complete reorganisation into new phases such as magnetite + rutile. He suggested that the free energy of mixing of Fe_2O_3 would become large enough to favour the stability of ilmenite-hematite solid solutions over the magnetite + rutile assemblages at higher temperatures.
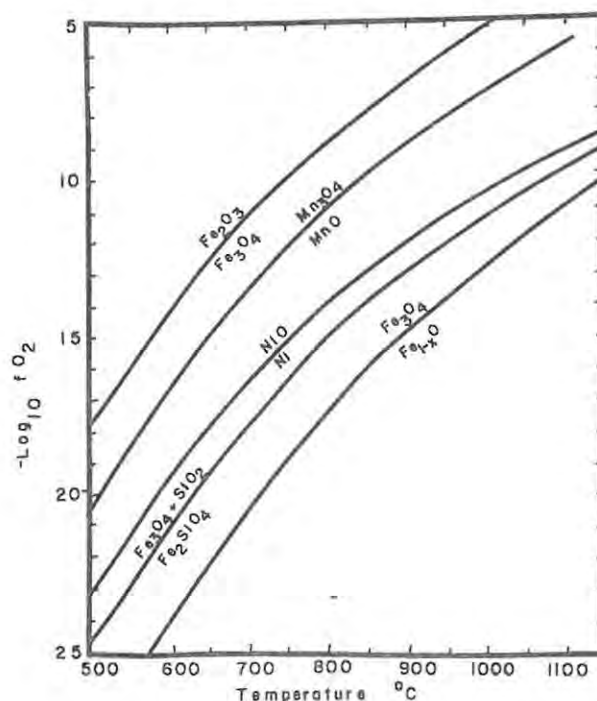
FIGURE 7 Plot of oxygen fugacity versus temperature for the buffer assemblages used during investigations of the $FeO-Fe_2O_3-TiO_2$ system (from Lindsley, 1962).

Lindsley (1963) determined the compositions of hematite-ilmenite solid
solutions in equilibrium with magnetite-ulvospinel solid solutions in
a series of hydrothermal experiments in which the oxygen fugacities
were controlled by the buffers shown in figure 7. He reported that
the phase relationships are not markedly influenced by pressure and
concluded that the compositions of hematite-ilmenite solid solutions
co-existing with magnetite-ulvospinel solid solutions are a function
of temperature and oxygen fugacity as illustrated in figure 8.
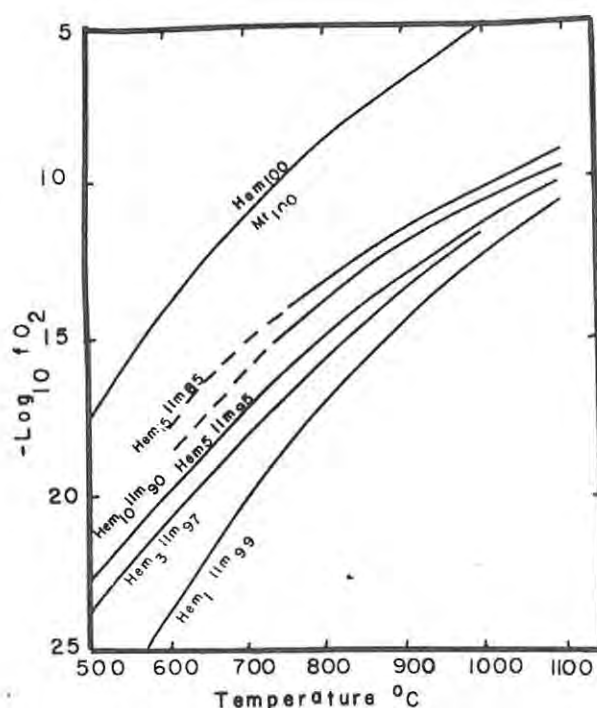
FIGURE 8   Projection parallel to the composition axis of the surface
in fO_2-T-X space of the hematite-ilmenite solid solution
series that co-exists in equilibrium with magnetite-
ulvospinel solid solutions (from Lindsley, 1963).

Taylor (1964) investigated the phase relationships in the $FeO-Fe_2O_3-$
TiO_2 system at $1300^{\circ}C$ (figure 2) and noted the existence of a complete
solid solution series between ilmenite and hematite. He also report-
ed that oxidation of a magnetite-ulvospinel solid solution at temper-

atures above 900°C results in the immediate formation of a hematite-ilmenite solid solution.

Rumble (1971) studied the co-existing Fe-Ti oxides in regionally meta-morphosed rocks and noted that the phase relationships of the natural ilmenite-hematite solid solutions did not correspond well with those determined in the laboratory. In particular, he stressed that the ilmenite-hematite solvus should be redetermined since the solubility of FeTiO$_3$ in hematite believed to have formed at relatively moderate temperatures was greater than that permitted by Carmichael's (1961) data. As an example he noted that hematite with up to 30 per cent FeTiO$_3$ in solution was present in rocks of the sillimanite zone that probably formed at temperatures of less than 600°C. Carmichael's data required a temperature of at least 850°C for this degree of solubility.

Kretchmar and McNutt (1971) investigated hemo-ilmenite grains containing two sizes of exsolution lamellae as discussed in section 4.3.1. On the basis of electron microprobe analyses they concluded that no compositional differences existed between the two sizes of exsolution lamellae and reported that the compositions of the exsolved phases were ilm$_{95}$hem$_5$ and hem$_{72}$ilm$_{28}$.

Kretchmar and McNutt (1971) based their interpretation of the hemo-ilmenite intergrowths largely on the exsolution mechanisms discussed by Brett (1964), Yund and Hall (1970) and Yund and McCallister (1970). They suggested that the elongated, narrow, crystallographically orien-ted hematite lamellae in an ilmenite host are the result of "coherent" exsolution (Brett, 1964) or a discontinuous exsolution mechanism (Yund and McCallister, 1970). The large hematite patches are presumed to

to have formed from a "non-coherent" type of exsolution resulting from a discontinuous exsolution mechanism which led to the breakdown of the lamellae and ultimately caused the recrystallisation of their ilmenite hosts.

Kretchmar and McNutt (1971) deduced the position of the hematite-ilmenite solvus on the basis of their analytical results and on certain other assumptions. The shape and consolute point of their proposed solvus is essentially the same as that of Carmichael (1961), but is shifted more towards the ilmenite-rich side to fit their "end-member" analyses of exsolved lamellae.

Matsuoka (1971) reported the synthesis of intermediate members of the ilmenite-hematite solid solution series under hydrothermal conditions at temperatures of 600° and $700^{\circ}C$ and a water pressure of 2,5 kb. Warner et al. (1972) synthesised a complete range of members of the ilmenite-hematite solid solution series at 5 per cent intervals by heating in vacuo at $1150^{\circ}C$. They studied these samples by Mössbauer spectroscopy and confirmed the existence of order-disorder relationships in certain compositional ranges in this series. In particular, they noted that heat-treated samples with a value of x between 0,55 and 0,60 exhibited a more ordered cation distribution than their quenched equivalents. They also noted that all Fe^{2+} ions participate in electron transfer with an equal number of Fe^{3+} ions and that this process continues up to values of x of 0,6. No electron transfer was noted for values of x between 0,75 and 1 and they concluded that this was due to an ordering of the cations in such a way that electron transfer is inhibited.

Lindh (1972) noted numerous discrepancies in the ilmenite-hematite solvus

and investigated the phase relationships in the $FeO-Fe_2O_3-TiO_2$ system
at temperatures ranging between 300 and $700^\circ C$. The experiments were
carried out under hydrothermal conditions so that the oxygen fugacity
was influenced by the activity of water and he reported that the cond-
itions could be considered isobaric since different applied pressures
caused no significant differences in the equilibrium conditions. The
oxygen fugacities were buffered during experimental runs by using the
NNO, $MnO-Mn_3O_4$ and MH buffers (figure7).

Lindh (1972) reported that hematite and ilmenite co-exist as a stable
assemblage at temperatures below $550^\circ C$ and that the assemblage magnet-
ite + rutile is unstable under these conditions. In contrast, he
noted that the assemblage magnetite + rutile and either ilmenite or
hematite becomes stable above this temperature with the result that
hematite and ilmenite are no longer able to co-exist stably.

On the basis of his experimental work, Lindh (1972) determined that
the consolute point of the hematite-ilmenite solvus curve should be at
about $660^\circ C$. The upper part of this curve would, however, be anomal-
ous since an oversaturated rhombohedral phase would not unmix into
hematite and ilmenite, but would preferentially form one of these oxides
plus magnetite and rutile instead. He prepared a phase diagram indic-
ating the position of the ilmenite-hematite solvus (figure 9), but not-
ed that "it is inaccurate since there are great uncertainties in its
derivation". He indicated that the inflections on the curve corresp-
ond to the change of equilibrium assemblage and stressed the differences
between his diagram and the earlier version of Carmichael (1961), (fig-
ure 5).
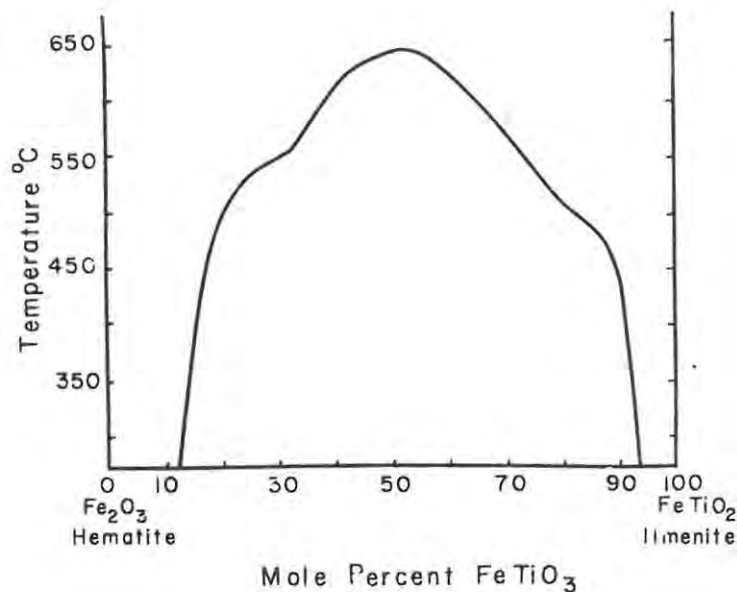
FIGURE 9   Solvus diagram for the ilmenite-hematite system (from Lindh, 1972).

Lindh (1972) noted that the existence of a miscibility gap in the ilmenite-hematite solid solution series represented strong evidence for non-ideality in this system.   He reviewed the available data on the nature of the ilmenite-hematite solid solutions and concluded that the intermediate members are inhomogeneous and consist of small "domains" of hematite and ilmenite that are too small for resolution by x-ray diffraction techniques.   He noted that this theory required the ordering of cations and that this would result in a non-linear variation in unit cell volumes between the end-members in this series in contrast to the results of many earlier investigations.

Lindh (1972) also discussed the exsolution mechanisms proposed for the ilmenite-hematite system and noted that the instability of co-existing hematite and ilmenite at elevated temperatures below the solvus intro-

duced additional complications. The formation of a magnetite + rutile assemblage from a pre-existing intermediate rhombohedral oxide would consequently require the destruction of the original lattice and the formation of new lattices. Lindh (1972) suggested that this did not occur, however, since the required intracrystalline diffusion of Ti^{4+} would be too slow on account of its high charge and the small gain in free energy involved. He concluded that the formation of hematite lamellae in ilmenite and vice versa would be favoured by epitaxial nucleation and noted that his "domain" structure for the solid solution would facilitate the metastable growth of one rhombohedral oxide in the other.

Lindh. (1972) suggested that a large supersaturation would be necessary before nucleation could occur since the exsolving phase is unstable and that this would lead to the formation of only a few nuclei that would in turn grow into a few large lamellae (the "generation 1" of Ramdohr, 1926). He concluded that the required supersaturation would become much less when the temperature fell below the 5-phase point and this would lead to the formation of many nuclei, resulting in the abundant small lamellae of the "second generation". Lindh (1972) noted that the compositions of the larger lamellae ("generation 1") do not correpond to the inflections of the solvus curve with the result that further exsolution must occur during cooling if his model is applicable.

Lindsley (1973) also noted discrepancies between the subsolvus phase relationships in naturally occurring minerals of the ilmenite-hematite system and relationships predicted by Carmichael (1961) (figure 5). He stressed that the miscibility gap should be redetermined, possibly by the use of hydrothermal experiments in order that reaction rates

might be accelerated. He pointed out, however, that the fO_2 of the fluid would have to be maintained within a range over which both rhombohedral phases are stable during the experiments and that no suitable buffers are currently available for this purpose (see discussion of Lindsley, 1962). He concluded that the accurate determination of the miscibility gap would consequently have to await the development of suitable buffers **or** new experimental techniques.

Lindsley (1973) reported that his limited experimental data based on the available buffers cast serious doubt on the validity of Carmichael's (1961) curve. He published these results merely as a shaded area to indicate the possible position of the miscibility gap instead of in the form of solvus (figure 10) and stressed that it does not represent the form of that gap. He also concluded on the grounds of experimental evidence that the consolute temperature must lie at or below $800^{\circ}C$.

Lindsley (1973) discussed Carmichael's (1961) results and suggested that the most likely source of discrepancy between their results lies in the different experimental techniques used. Lindsley (1973) concluded "the published miscibility gap for the hematite-ilmenite system (Carmichael, 1961) should be rejected. I regret that I cannot offer a better one at present".

Lindsley and Lindh (1974) re-examined the phase relationships in the $FeO-Fe_2O_3-TiO_2$ system under hydrothermal conditions and concluded that hematite + ilmenite assemblages could in fact exist at temperatures above $550^{\circ}C$ since a narrow range of fO_2 existed within which they are stable. They concluded that these conditions were not attained during Lindh's (1972) earlier experiments and they discussed the problems involved in obtaining suitable buffers for the control of oxygen fugacities

during experimental runs.
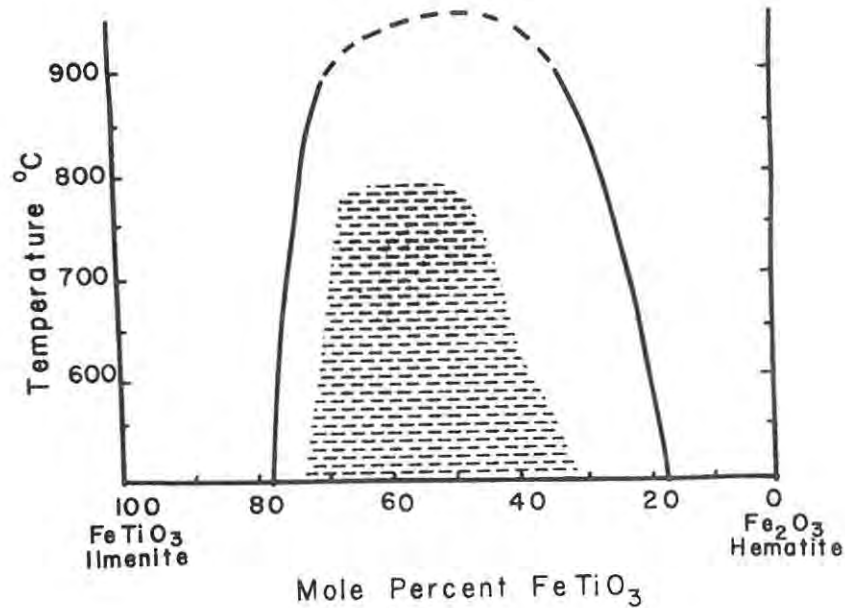
FIGURE 10   Phase relationships in the $FeTiO_3-Fe_2O_3$ system showing

the miscibility gap reported by Carmichael (1961).

The shaded area represents the region within which the

miscibility gap should lie and its irregular shape

emphasises that it merely delimits the possible range

of the miscibility gap and does not represent it (from

Lindsley, 1973).

Lindsley and Lindh (1974) devised a new series of experimental deter-

minations involving the use of the assemblages magnetite$_{ss}$ + hematite$_{ss}$

+ ilmenite$_{ss}$ and hematite$_{ss}$ + ilmenite$_{ss}$ + rutile as oxygen buffers.

They noted that these assemblages are invariant in the 3-component

Fe-Ti-O system so that all intensive variables, including fO_2 are

fixed with the result that they can be used as oxygen buffers having

the required range for the reactions of interest.

Lindsley and Lindh (1974) reported that these buffers would permit the delimitation of the hematite-ilmenite miscibility gap, and that they were proceeding with these studies, although a great deal of work remained to be done. Their preliminary results, however, indicated that the assemblages hematite$_{ss}$ + ilmenite$_{ss}$ or a single homogeneous phase is more stable than magnetite + rutile at 650° and $700^{\circ}C$ contrary to Lindh's (1972) earlier findings. They concluded that the miscibility gap was consequently incorrectly positioned in Lindh's (1972) phase diagram in the range $550-650^{\circ}C$ and that positions at lower temperatures should also be viewed with caution.

Marnier and Bolfa (1974) investigated the crystal structures and magnetic properties of the ilmenite-hematite solid solution series and presented a magnetic model which covers the whole solid solution range. They concluded that the magnetic properties can be correlated with the composition and degree of cationic order in the solid solution. They noted that an excellent agreement exists between the calculated order ratio obtained from the magnetic measurements of Ishikawa (1962) and the neutron diffraction data of Shirane et al. (1962).

The application of transmission electron microscopy techniques to detailed studies of exsolution bodies and structural relationships in the ilmenite-hematite system was initiated by Christie et al. (1971), quoted in Cullen et al. (1973) who noted that the interface between the hematite precipitate and ilmenite matrix is semi-coherent. Cullen et al. (1973) carried out a detailed transmission electron microscopy study on the nature of the misfit dislocation network at the ilmenite-hematite interface. They reported that this network consists of a 3-fold array of half-partial dislocations and that the morphology of this network is such that the stacking fault energy associated with

the extended half-partial dislocations is minimised.

Lally et al. (1976) investigated precipitation in the ilmenite-hematite system by means of transmission electron microscopy and noted that the hematite exsolution bodies have the form of flattened lenses in which the lens axis is parallel to the c-direction of the hexagonal unit cell. They reported that this morphology is consistent with the nature of the lattice mismatch between matrix and precipitate which is greatest in the c-direction and least in the basal plane. They also noted that the interface separating the exsolved hematite part-icle and the ilmenite matrix is composed of 3 sets of misfit disloca-tions arranged in a hexagonal grid pattern that apparently accomodates the differences in lattice parameters between the two phases.

4.3.3 Discussion

The nature and diversity of the investigations carried out on both nat-ural and synthetic members of the ilmenite-hematite system, as well as the variety of results obtained, clearly illustrate the complexities that exist within this subsystem of the larger $FeO-Fe_2O_3-TiO_2$ ternary system. In spite of repeated investigation since 1926, the subsolidus phase relationships are still only vaguely defined, and the only gen-erally accepted feature is that ilmenite and hematite from a continuous solid solution series at elevated temperatures above approximately $1000^{\circ}C$ and that this homogeneous phase exsolves on slow cooling to pro-duce the characteristic microintergrowths.

Minor amounts of other cations, particularly Mg, Mn, Al, Cr and V are commonly present in the naturally occurring minerals of the ilmenite-

hematite series and can be expected to influence the phase relation-
ships. These aspects have not yet been investigated in detail and
studies of this nature cannot be contemplated until the phase relation-
ships of the synthetic end-members are fully understood.

The slowly cooled, intermediate members of the ilmenite-hematite solid
solution series are characterised by the development of a variety of
exsolution textures as described in section 4.3.1. The nature of the
exsolution mechanisms operating in this system has not been investi-
gated in detail in spite of the recent interest that has developed in
this field (Brett, 1964; Yund and Hall, 1970; Yund and McCallister,
1970; Champness and Lorimer, 1976). The application of transmission
electron microscopy techniques to this problem as reviewed by Champness
and Lorimer (1976) should provide many of the answers once studies
have been carried out on a wide range of synthetic and natural crystals
exhibiting all stages of exsolution.

It has been recognised that exsolution can proceed in various stages
due to heterogeneous nucleation and growth, homogeneous nucleation and
growth,and spinodal decomposition processes. These mechanisms operate
under progressively decreasing temperature conditions and varying de-
grees of supersaturation while large regions of metastability can exist,
(Yund and McCallister, 1970; Champness and Lorimer, 1976). These
features do not only have application in microstructural studies, but
suggest that the actual recognition of equilibrium conditions in exp-
erimental studies might be extremely difficult. The operation of
these various exsolution mechanisms is also a function of the cooling
rate with the result that microstructural interpretations require cau-
tion unless information is available on the composition of the co-

existing phases and their thermal history.

The similarity in crystal structure and cell-dimensions between ilmenite and hematite suggest that exsolution might take place via the spinodal decomposition mechanism (Cahn, 1968; Hilliard, 1970; Christie and Olsen, 1974) under suitable cooling conditions. This mechanism would be particularly applicable if the solid solutions are inhomogeneous and consist of Fe- and Ti-rich domains as suggested by Lindh (1972). Heterogeneous and homogeneous nucleation and growth mechanisms might, however, be more important at higher sub-solvus temperatures.

4.3.4 Conclusions

Ilmenite and hematite form a complete solid solution at elevated temperatures, but although the consolute temperature of the miscibility gap is not known, it is certainly below 800°C and might possibly be as low as 700°C (or even lower). The members of this series are sensitive to changes in oxygen fugacity and are only stable over a relatively narrow range of oxygen fugacities. It is, however, possible to set limits on their stability field since ilmenite-rich solid solutions are oxidised at conditions along the HM and $MnO-Mn_3O_4$ buffers while hematite-rich solid solutions are reduced under conditions along the NNO buffer (Lindsley, 1962, 1963).

Members of the ilmenite-hematite solid solution series commonly co-exist in equilibrium with members of the magnetite-ulvospinel solid solution series in nature and Lindsley (1963) has shown that their composition is largely a function of oxygen fugacity and temperature. This information can consequently be used to delimit the approximate stability field of the intermediate members of this solid solution series as indicated by the shaded area in figure 11. A more detailed version of

this diagram is presented as figure 8.
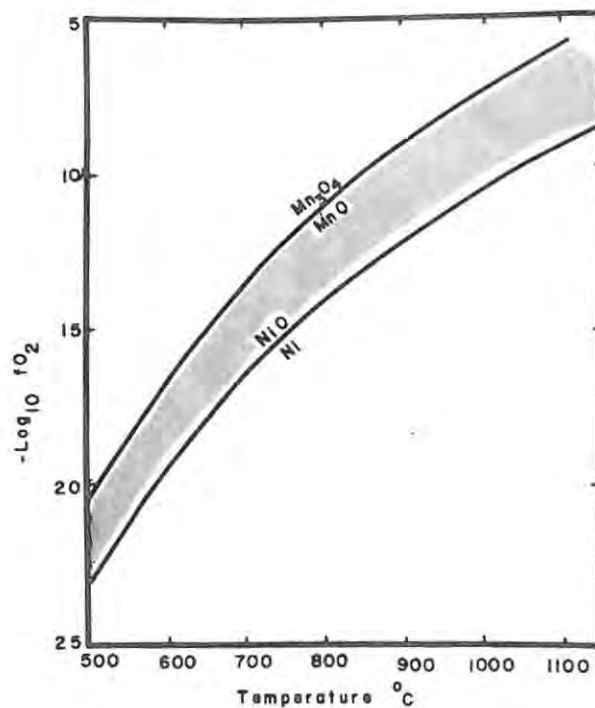
FIGURE 11   Plot of fO$_2$ versus temperature showing the approximate

stability field (shaded area) for intermediate members

of the ilmenite/hematite series (modified after Lindsley,

1963).

The nature of the microintergrowths produced in the intermediate memb-

ers of the ilmenite-hematite solid solution series is dependent larg-

ely on the initial composition of the solid solution and the rate of

cooling.   Homogeneous minerals can be produced over the whole comp-

ositional range between ilmenite and hematite by quenching from high

temperatures, but slower cooling rates result in exsolution.   The low-

temperature solid solution limits have not been firmly established,

but values of approximately 6 per cent Fe$_2$O$_3$ in ilmenite and 10 per

cent FeTiO$_3$ in hematite given by Ramdohr (1926) and Edwards (1938)

still appear to fit the available data.

Intermediate members of the ilmenite-hematite solid solution series will exsolve on slow cooling and the nature of the exsolution mechanisms involved in the formation of their intergrowths can be interpreted in terms of current views on this subject as summarised by Yund and McCallister (1970) and Champness and Lorimer (1976). The first exsolution bodies will be formed at a slight undercooling below the solvus by the heterogeneous nucleation and growth mechanisms at disloc $\cdot$-ions and other discontinuities along grain boundaries and within the crystals. This process gives rise to a small number of widely spaced nuclei that are able to grow into large lamellae or discs due to the higher degree of ionic mobility at elevated temperatures. Concentration gradient will build up in the areas between the large lamellae and the ionic mobility will continue to decrease as the temperature decreases. Areas of sufficient supersaturation will ultimately arise between the large lamellae and a further set of nuclei will in turn grow into a set of more abundant, but much smaller lamellae and concentration gradients will also be set up between them. Similar processes would also be operative within the larger, earlier formed lamellae as they also continue to adjust towards more equilibrium compositions.

Ionic diffusion will continue to slow down with decreasing temperature so that concentration gradients will again build up in the areas between the smaller exsolution lamellae. The supersaturation might ultimately become high enough for the formation of a further, even finer set of exsolution lamellae, either by homogeneous nucleation and growth or spinodal decomposition. Exsolution would then continue at a progressively slower rate until the diffusion rates become so slow that the process effectively ceases. Similar processes would also operate within the earlier-formed lamellae. The largest exsolution bodies will be formed towards the centres of these earlier lamellae

since migration of unwanted ions would take place out of their marginal areas into their hosts.

Exsolution lamellae might not have the opportunity to form via either the heterogeneous or homogeneous nucleation and growth mechanisms under conditions of rapid cooling so that the intergrowths might form only by spinodal decomposition at lower temperatures. The nature of the intergrowths developed under various intermediate cooling rates would form via combinations of these three processes.

These mechanisms can account for the various size-ranges and relative abundance of exsolution bodies in this system, but they do not necessary account for their decrease in size towards grain boundaries. It is possible that external exsolution may have occurred in their marginal areas at places where these grains are in contact with other Fe-Ti oxides, but the explanation is not so obvious when they are in contact with silicates. Edwards (1938) suggested that this feature might be due to compositional zoning, but this is unlikely to be the case in slowly cooled rocks. Grain boundary dislocations provide ideal sites for heterogeneous nucleation and result in the growth of either external granules or or exsolution lamellae that develop inwards into their hosts. These features are apparently rarely developed in exsolved hemo-ilmenites which suggests that this mechanism might not be as important as the others in developing exsolution lamellae in this system.

This literature survey indicates the need for a detailed examination of the sub-solidus phase relationships in the ilmenite-hematite system under suitably buffered hydrothermal conditions and for the compilation of an accurate phase diagram. The effect of minor amounts of foreign

ions on the phase relationships also requires investigation while studies of the exsolution mechanisms that give rise to the wide variety of microstructures are needed to provide additional data on the subsolvus phase relationships. It can consequently be concluded that the past 50 years of research into the ilmenite-hematite solid solution series has provided an understanding of many of the problems involved in studying this system, rather than in providing the required answers.

4.4 The Titaniferous Magnetites

4.4.1 Introduction

Titaniferous magnetites from slowly cooled igneous rocks commonly contain crystallographically oriented microintergrowths of ilmenite or ulvospinel or both. The relationships between these microintergrowths are complex and depend largely on oxygen fugacity and cooling rates. The ilmenite microstructures were recognised long before ulvospinel was discovered so that it is pertinent to consider the magnetite-ilmenite subsystem before dealing with the magnetite-ulvospinel system and their mutual relationships.

4.4.2 The titaniferous magnetite microstructures

Naturally occurring titaniferous magnetites from slowly cooled igneous (and some metamorphic) rocks exhibit the development of a wide range of titanium-bearing microintergrowths. Two extreme types can be recognised, one characterised by the presence only of lamellar ilmenite and the other by the development of micrometre-sized ulvospinel microintergrowths. The majority of titaniferous magnetites, however, generally exhibit varying combinations of these two types of intergrowths. A series of photomicrographs illustrating various aspects of these

microstructures is given in Ramdohr (1969, p. 899-904), and in Parts
2 and 3 of the present work.

Titaniferous magnetites commonly show the development of narrow ilmen-
ite lamellae that are oriented parallel to their octahedral planes
and form a well-defined trellis network. These lamellae are commonly
present in two or more distinct size ranges. The ilmenite lamellae
may intersect each other without any marked change in thickness at
their intersections, but they often narrow towards their mutual con-
tacts and display lens-shaped forms. The sets of smaller lamellae
occupy the areas between the larger, more widely spaced ones and very
small, rounded to irregular-shaped ilmenite grains are sometimes in
turn developed in the areas between the finer ilmenite lamellae.

A small number of relatively large and sparsely distributed ilmenite
lamellae that extend to the grain boundaries of their magnetite hosts
is also sometimes present. These lamellae are also oriented parall-
el to (111) and often show a slight thickening towards the grain boun-
daries of their hosts. Numbers of small, irregularly shaped ilmenite
grains are also commonly developed around the periphery of the titani-
ferous magnetites and are occasionally connected to the large lamellae.

Ulvospinel is characteristically present in micrometre-sized, lamellar
networks that are oriented parallel to the cubic planes of their hosts
and form cloth-like textures. These networks exhibit 3-fold axes of
symmetry when viewed perpendicular to (111) of their hosts. The ulvo-
spinel microintergrowths may be developed throughout the magnetite
crystals, or may be confined to relatively small areas between larger
ilmenite lamellae. The areas of ulvospinel development also sometimes
merge imperceptably with areas in which extremely fine ilmenite lam-

ellae are present.

4.4.3 Mineralogical investigations of the Fe_3O_4-$FeTiO_3$ system

The first detailed ore-microscopic investigations of titaniferous magnetites were carried out by Singewald (1913a, b) who also published a series of photomicrographs illustrating many of their relationships. Singewald (1913a, b) reported the presence of both regular ilmenite lamellar intergrowths and irregular ilmenite grains in the magnetite and noted that the lamellae are oriented parallel to the octahedral planes of their hosts. He also noted a wide variation in the size and distribution of these lamellae, and concluded that they were normally too fine-grained to allow for their complete separation, even during fine grinding. He also reported the presence of homogeneous titanium-bearing magnetites which he termed titanomagnetites and concluded that "the magnetite molecule itself may carry titanium".

Warren (1918) described ilmenite intergrowths in titaniferous magnetites from numerous areas and concluded that limited solid solution with a eutectic existed between ilmenite and magnetite. Lindley (1925) described homogeneous skeletal titaniferous magnetite from basalts and noted that grains containing lamellar ilmenite intergrowths parallel to (111) are less common. He concluded that ilmenite and magnetite form a continuous solid solution series at high temperatures and that the solid solutions would not exsolve if cooling was rapid enough. He suggested that sub-microscopic exsolution bodies were formed during slightly slower cooling and that this accounted for the distinct anisotropy shown by some magnetites, while the lamellar ilmenite intergrowths formed during slow cooling.

Ramdohr (1926) described ilmenite-magnetite intergrowths from a large

number of localities and carried out heating experiments , in both air and nitrogen, on titaniferous magnetites containing ilmenite lamellae oriented parallel to (111). He reported that resorption of the finest lamellae commenced at $600^{\circ}C$ and that the intergrowths were homogenised at $800^{\circ}C$. He concluded that there was considerable mutual solubility of ilmenite in magnetite above $800^{\circ}C$ and that exsolution of ilmenite took place on slow cooling to between 700° and $800^{\circ}C$. He noted that the solubility of $FeTiO_3$ in magnetite and Fe_3O_4 in ilmenite at low temperatures amounted to only a few per cent.

Osborne (1928) studied titaniferous magnetites from numerous localities and observed that the basal planes of the ilmenite lamellae are oriented parallel to (111) of the magnetite. He concluded that ilmenite showed considerable solubility in magnetite at the crystallisation temperatures of these minerals and that the apparently constant relationship between the amount of TiO_2 and Fe in magnetite might be the result of limited solubility of ilmenite in magnetite at their temperatures of formation.

Kamiyama (1929, quoted in Dunn and Dey, 1937) reported that typical ilmenite intergrowths were produced in an originally homogeneous magnetite during heating experiments. He also reported that the ilmenite lamellar network in another titaniferous magnetite became more prominent during heating up to $1150^{\circ}C$, but then decreased in size as the temperature was increased to $1390^{\circ}C$ when melting commenced. He concluded that titaniferous magnetite is metastable at ordinary temperatures and that magnetite and ilmenite form a solid solution series above $1150^{\circ}C$ with a eutectic at a composition of about 25 per cent ilmenite, 75 per cent magnetite.

Gruner (1929a) confirmed that the basal planes of the ilmenite lam-
ellae are oriented parallel to the octahedral planes of their magne-
tite hosts. He concluded that this orientation is structurally
controlled since every third and seventh (111) structure plane of
magnetite consists of oxygen ions while every third plane parallel
to (0001) in ilmenite also consists only of oxygen ions. The inter-
growth is thus stabilised by the sharing of a common oxygen plane i~
both ilmenite and magnetite.

Ödman (1932) reported the presence of homogeneous magnetite grains
exhibiting brownish-violet colours in volcanic rocks which he inter-
preted as being due to the presence of ilmenite in solid solution.

Dunn and Dey (1937) reviewed the available data on ilmenite-magnetite
microintergrowths and concluded that it was doubtful whether any true
solid solution of ilmenite and magnetite could exist under normal
temperatures and pressure conditions. They suggested that the suppos-
ed solid solutions were in fact extremely fine-grained intergrowths.
They suggested that ilmenite might exist in a cubic form analogous to
gamma-Fe_2O_3 (maghemite) at high temperatures and postulated that the
original high-temperature titaniferous magnetite might consist of a
stable solid solution of cubic Fe_3O_4, $FeTiO_3$ and Fe_2O_3. They conclud-
ed that the Ti ions would concetrate along the octahedral planes on
cooling and that the cubic $FeTiO_3$ would become unstable and invert
to form rhomohedral ilmenite.

Edwards (1938) reported that ilmenite and magnetite form a solid solu-
tion series at elevated temperatures and that it unmixed on slow cool-
ing. He concluded that the exsolution takes place at higher tempera-
tures than the unmixing of hematite and ilmenite and that pure end-

members are produced rather than further solid solutions. He also ascribed the more regular shapes of the ilmenite lamellae to their having formed as a pure mineral at high temperatures under conditions of more rapid diffusion.

Ramdohr (1939) reaffirmed the existence of high temperature miscibility between ilmenite and magnetite and reported that exsolved titaniferous magnetites can be readily homogenised by heating. He also reported the presence of fine ilmenite lamellae parallel to (100) in $FeTiO_3$-rich magnetites that crystallised at high temperature. Ramdohr (1940) repeated his earlier views on the existence of extensive miscibility between ilmenite and hematite at elevated temperatures.

Chevallier and Girard (1950) synthesised cubic solid solutions of the type yFe_3O_4 $(1-y)FeTiO_3$ that contained up to 37 mole per cent $FeTiO_3$ and concluded that they were intermediate members of the magnetite-ilmenite solid solution series. Basta (1953, unpubl. Ph.D. thesis, Bristol Univ., quoted in Nicholls, 1955), however, reported that mixtures of magnetite and ilmenite could not be homogenised, even after heating at $1100^{\circ}C$ for 48 hours. He concluded that very limited miscibility exists between magnetite and ilmenite at magmatic temperatures, and is less than 5 per cent of either end-member in the other at $1050^{\circ}C$.

Wilson (1953) reported that an ilmenite-bearing titaniferous magnetite from the Bushveld Complex was homogenised by heating at $970^{\circ}C$ for 3 hours followed by quenching. He concluded that the titaniferous magnetite precipitated as a cubic spinel and that the ilmenite separated out on cooling. Roy (1954) also reported that magnetites containing lamellar ilmenite intergrowths were completely homogenised by heating in air at $1200^{\circ}C$ for 24 hours. He reported that the quenched homo-

geneous products represent "titanomagnetites" with optical properties that are intermediate between those of ilmenite and magnetite.

Chevallier et al. (1955) extended their investigations into the magnetite-ilmenite solid solutions. They noted that rhombohedral ilmenite would probably not form a solid solution series with cubic magnetite, because of differences in crystal structure. They synthesised a series of homogeneous titanomagnetites that appeared to be intermediate members of the ilmenite-magnetite solid solution series and postulated that ilmenite might exist in a high temperature cubic gamma-form analogous to cubic gamma-Fe_2O_3 (maghemite). This would enable it to form a solid solution with magnetite. Exsolution of this solid solution would then occur in the normal manner on slow cooling and the gamma-$FeTiO_3$ would invert to its more stable rhombohedral form to form the characteristic intergrowths.

Nicholls (1955) reviewed the available data on the Fe_3O_4-$FeTiO_3$ sub-system and concluded that limited miscibility existed between these two minerals at magmatic temperatures. He compiled a schematic phase diagram for this series under dry conditions (figure 12), but noted that the liquidus and solidus might be depressed in the presence of volatiles with the result that the maximum range of possible solid solution would be restricted even further. Nicholls (1955) concluded that attempts to homogenise magnetite-ilmenite intergrowths by heating would most probably be unsuccessful since the solid solutions from which the intergrowths formed are probably metastable intermediate members between magnetite and cubic gamma-$FeTiO_3$ that cannot be produced by heating rhombohedral ilmenite.
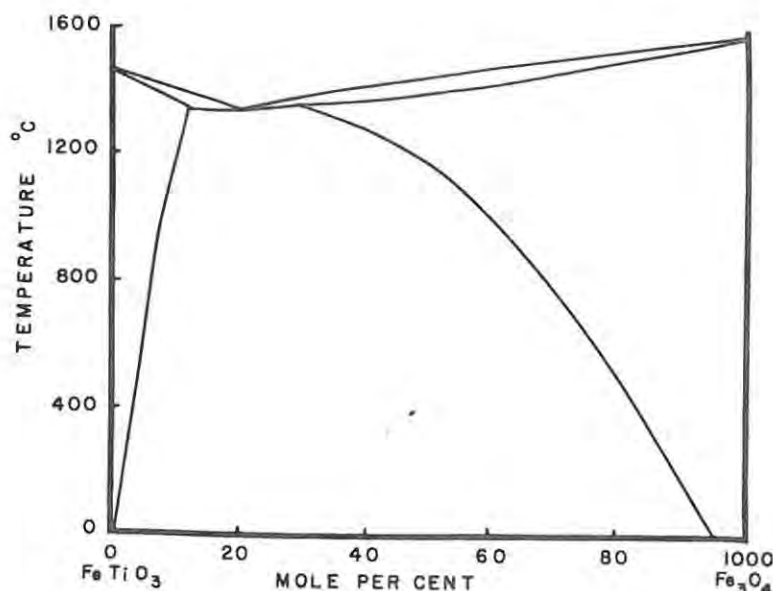
FIGURE 12   Schematic phase diagram for the dry pseudobinary
Fe_3O_4-$FeTiO_3$ system (from Nicholls, 1955).

Buddington et al. (1955) noted that titanium compounds (ilmenite and ulvospinel) normally occur as microintergrowths in magnetite from plutonic rocks, but that they remain in solid solution in magnetite from compositionally equivalent volcanic rocks.   They concluded on this basis that the typical ilmenite and ulvospinel intergrowths formed by exsolution during slow cooling.   Buddington (1956) reaffirmed his views that extensive solid solution existed between ilmenite and magnetite and concluded that their intergrowths are formed by exsolution.

Vincent et al. (1957) conducted an extensive series of heating experiments on a titaniferous magnetite from the Skaergaard Complex that contained extremely fine lamellar ilmenite intergrowths.   Heating was carried out under vacuum in sealed silica ampoules with as little free space as possible.   No changes were noted in samples heated at 600° for 12 hours.   They failed to homogenise the samples even after heating at 950°C for 3 weeks, and concluded that the original ilmenite lamellae

change in composition towards hematite on heating to produce members of the rhombohedral ilmenite-hematite solid solution series. Samples heated to between 1250° and $1300^{\circ}C$ under similar conditions also failed to homogenise, but showed slight oxidation to pseudobrookite.

Vincent et al. (1957) considered that ilmenite might exist as a high-temperature cubic gamma-form that might possibly form solid solutions with magnetite, but noted that it had not been identified in nature or even synthesised. They concluded that a homogeneous spinel intermediate in composition between magnetite and ilmenite could possibly exist and that it would initially unmix into two spinels. The one spinel would be close to a member of the $FeTiO_3$-Fe_2O_3 binary series in composition and would rapidly undergo a monotropic inversion to a rhombohedral phase that would then change in composition towards $FeTiO_3$ on slow cooling, while the other spinel phase would change towards Fe_3O_4, thus forming the typical magnetite-ilmenite intergrowths.

MacChesney Muan (1959) investigated the phase relationships in the iron oxide-titanium oxide system, but did not report any miscibility between ilmenite or magnetite, although they recognised the existence of the other 3 solid solution series.

Akimoto and Katsura (1959) reported the presence of homogeneous titano-magnetite of a composition intermediate between magnetite and ilmenite in volcanic rocks from Japan. They also reported analyses of numerous natural homogeneous titanomagnetites that plotted on either side of the magnetite-ilmenite join on the TiO_2-FeO-Fe_2O_3 ternary diagram and suggested that their composition might be related to their degree of oxidation.

Basta (1960) pointed out that many reports of the successful homogeni-

sation of magnetite-ilmenite intergrowths during heating (Ramdohr, 1926; Kamiyama, 1929; Wilson, 1953; Roy, 1954) were based only on microscopic observation and that no attempts were made to check on the homogeneity of the samples by x-ray diffraction or other techniques. In view of this Basta (1960) carried out a series of heating experiments on both natural ilmenite-magnetite intergrowths and synthetic materials. Heating was carried out under vacuum in sealed silica tubes and the products were examined by x-ray diffraction.

Basta (1960) reported that a titaniferous magnetite containing lamellar ilmenite intergrowths, and with a composition on the Fe_3O_4-$FeTiO_3$ join, failed to homogenise after heating at $1100^{\circ}C$ for 72 hours. He estimated that not more than 5 per cent of the ilmenite had dissolved in the magnetite under these conditions. Similarly, he was unable to obtain homogeneous minerals by heating suitable artificial mixtures of finely powdered magnetite and ilmenite in vacuo at $1050^{\circ}C$ for between 24 and 48 hours. He concluded that not more than 4 per cent of $FeTiO_3$ had dissolved in the magnetite under these conditions.

Basta (1960) reviewed the available data on the ilmenite-magnetite intergrowths and concluded that only very restricted solid solution is possible between magnetite and ilmenite (alpha-$FeTiO_3$) at magmatic temperatures. He suggested that not more than 5 to 10 per cent alpha-$FeTiO_3$ would be soluble in magnetite in view of the difficulty in accomodating the rhombohedral ilmenite in solid solution in the cubic magnetite.

Basta (1960) noted the possibility that some ilmenite might enter into solid solution with magnetite in the form of the hypothetical cubic gamma-$FeTiO_3$, but stressed that the existence of this phase had not yet

been proved. He also reviewed the available data on the chemical compositions of naturally occurring homogeneous titanomagnetites and concluded that samples which were intermediate in composition between Fe_3O_4 and $FeTiO_3$ probably did not exist in nature.

Wright (1961) concluded that the granular aggregates of ilmenite and titaniferous magnetite that are commonly present in basic rocks are the products of exsolution from high temperature solid solutions. He postulated that the original mineral separated from the magma as a single crystalline phase which then exsolved and could thus account for the clustering of smaller ilmenite grains around larger titaniferous magnetites.

Experimental investigations into the $FeO-Fe_2O_3-TiO_2$ systems at $1200^{\circ}C$ (Webster and Bright, 1961) and at $1300^{\circ}C$ (Taylor, 1964) showed extremely limited solid solution between ilmenite and magnetite at these temperatures. Verhoogen (1962a) calculated that the free energy transition of alpha-$FeTiO_3$ to the hypothetical gamma-form would be greater than for the transition of alpha-$FeTiO_3$ to gamma-Fe_2O_3. He concluded that the solubility of $FeTiO_3$ in magnetite would consequently be much less than that of Fe_2O_3. The solubility of Fe_2O_3 in magnetite is about 10 per cent at $1200^{\circ}C$ and is negligable at $800^{\circ}C$. The solubility of ilmenite in magnetite would consequently be very small.

Lindsley (1962) investigated the phase relationships in the $FeO-Fe_2O_3-TiO_2$ system and concluded that the stable solubility of ilmenite in magnetite between 600° and $1300^{\circ}C$ is much less than that required to produce many natural intergrowths. Buddington and Lindsley (1964) reviewed the available data on magnetite-ilmenite intergrowths and

concluded that titanomagnetites contained only minor $FeTiO_3$ in solid
solution at the time of their formation.

The conclusions by Vincent et al. (1957) and subsequent investigators
that ilmenite-magnetite microintergrowths could not be rehomogenised
by simple heating, together with demonstrations of limited miscibility
of ilmenite in magnetite during experimental studies, led to the
development of other theories on the formation of these intergrowths.
The proposal that ilmenite could exist in a hypothetical cubic form
at high temperatures and consequently form solid solutions with magn-
etite, has been appealed to, but has not yet been substantiated.

During the 1950's it became recognised that ulvospinel forms an exten-
sive solid solution with magnetite and that ilmenite can be produced
from it by oxidation.   This led to the realisation that the bulk of
the ilmenite microintergrowths in magnetite might have formed in this
manner.   The development of ilmenite lamellae in titaniferous magnetite
is discussed further after a consideration of the phase relationships
between magnetite and ulvospinel.

4.4.4 <u>Mineralogical investigations of the Fe_3O_4-Fe_2TiO_4 system</u>
Ulvospinel made a rather late entry into the mineralogical literature,
but has since been recognised as an important component in titaniferous
magnetites and the evolution of their microstructures.   Goldschmidt
(1926) synthesised the compound Fe_2TiO_4 and noted that it is isomorph-
ous with magnetite.   He suggested that titanomagnetite might represent
a solid solution series between Fe_2TiO_4 and magnetite by analogy with
the solid solutions of Mg_2TiO_4 and $MgAl_2O_4$.

Foslie (1928) described titaniferous magnetites from Storgangen in
Norway and noted that analyses of this mineral showed 4,49 per cent

excess FeO when their TiO_2 contents were recalculated in terms of il-
menite. Following Goldschmit's (1926) views that miscibility between
rhombohedral ilmenite and cubic magnetite is not possible on crystallo-
graphic grounds, Foslie (1928) stated that only limited miscibility
exists between these two phases at all temperatures. He suggested
that Fe_2TiO_4 would form solid solutions with magnetite since the two
phases are isomorphous at high temperatures and concluded that the TiO_2
contents of the magnetite depended on the formation of Fe_2TiO_4 at high
temperatures in the magma.

Foslie (1928) noted that the formation of Fe_2TiO_4 would be possible
only if Fe_2O_3 is not present in excess compared with TiO_2 and FeO
since it would decompose to yield ilmenite and magnetite as follows:

$$Fe_2TiO_4 + Fe_2O_3 = FeTiO_3 + Fe_3O_4$$
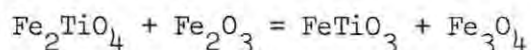
He concluded that Fe_2TiO_4 is unstable at lower temperatures since it
is not found in nature and suggested that it decomposes to yield ilmen-
ite + FeO as follows:

$$Fe_2TiO_4 = FeTiO_3 + FeO$$
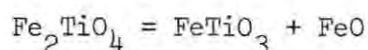
He concluded that the FeO entered into solid solution in the magnetite
and accounted for the excess FeO noted in the analyses.

Barth and Posnjak (1932) synthesised Fe_2TiO_4 and concluded that it has
an inverse spinel structure with a cell edge of 8,50 Å. Ernst (1943)
also reported the synthesis of Fe_2TiO_4 with a spinel structure and a
cell edge of 8,494 Å during a study of the phase relationships in the
$FeO-Fe_2O_3-TiO_2$ system.

Ramdohr (1939, 1940) described networks of "ilmenite" intergrown with magnetite in titaniferous magnetite containing approximately 50 per cent by volume of ilmenite. He concluded that these minerals had crystallised at high temperatures and reported that this "ilmenite" is present as exsolution lamellae parallel to (100) rather than parallel to (111) as it is the usual case.

Mogensen (1946) investigated titaniferous magnetites from Södra Ulvön and noted that they appeared inhomogeneous under high magnification. He recognised that they were composed of extremely fine intergrowths of two minerals in approximately equal proportions. He investigated this intergrowth by means of x-ray diffraction and found that it consisted of two spinels, one having a cell edge of a = 8,40 Å and the other of a = 8,47 Å. He reported that the intergrowth became homogenised during heating at $600^{\circ}C$ under vacuum and yielded a single spinel with a cell edge of a = 8,43 Å.

Morgensen (1946) reported that the chemical analysis of the ore showed an excess of FeO that could be accounted for by recalculating the analysis in terms of Fe_2TiO_4. He concluded that the exsolved phase was Fe_2TiO_4 (ulvospinel).

Pouillard and Michel (1949) and Pouillard (1950) synthesised a series of solid solutions between Fe_3O_4 and Fe_2TiO_4 by heating suitable mixtures of TiO_2 and FeO in vacuo and by reduction of TiO_2 and Fe_2O_3 at $900^{\circ}C$. They expressed these solid solutions by means of the general formula:

$$\left[Fe^{3+}_{2-2x} , Ti^{4+}_{x} , Fe^{2+}_{1+x} \right] O_4$$
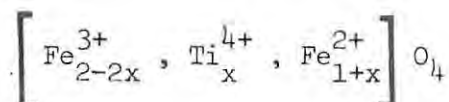
They also reported a regular variation in unit cell parameter with an increasing Ti^{4+} content and noted that the substitution involved the replacement of Fe^{3+} by $Ti^{4+} + Fe^{2+}$.

Ramdohr (1953) subsequently described naturally occurring ulvospinel microintergrowths in titaniferous magnetites from various localities and concluded that it is a much more common mineral than previously recognised. He noted that ulvospinel is characteristically exsolved parallel to (100) of its magnetite host and that it can readily be oxidised to form ilmenite according to the equation:

$$3Fe_2TiO_4 + O = 3FeTiO_3 + Fe_3O_4$$
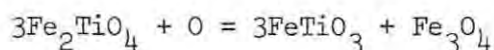
He reported that the ilmenite formed by oxidation of the ulvospinel retained its orientation along (100), but exhibited oblique extinction and could thus be distinguished.

Girault (1953) also reported ulvospinel microintergrowths in Canadian titaniferous magnetites and published several exceptionally good photomicrographs of these textures which clearly illustrated the orientation of the exsolved ulvospinel parallel to (100) of its host.

Akimoto (1954, 1955) noted that titanomagnetite represented a solid solution between magnetite and ulvospinel and reported that analyses of naturally occurring titanomagnetites plotted around the Fe_3O_4-Fe_2TiO_4 compositional join. He also reported the approximately linear relationship between the lattice parameter, Curie point, intensity of saturation magnetisation and composition in naturally occurring titanomagnetites.

Kawai et al. (1954) also synthesised a series of Fe_3O_4-Fe_2TiO_4 solid
solutions and concluded that they formed a continuous series at elev-
ated temperatures, but unmixed on slow cooling. They proposed a
schematic phase diagram (similar to that in figure 14) in which the
crest of the solvus is located at approximately $750^{\circ}C$. Intermediate
solid solutions would exsolve below this temperature to form two solid
solutions, one ulvospinel-rich and the other magnetite-rich. Each
of these solid solutions would then continue to change in composition
towards their end-members as cooling progressed.

Vincent and Phillips (1954) reported the presence of extremely fine-
grained ulvospinel microintergrowths in the titaniferous magnetites of
the Skaergaard Complex. They concluded that the fine cloth-like
microintergrowths of magnetite and ulvospinel are formed by eutectic
crystallisation and noted their similarity to eutectoids formed in cer-
tain metals. They constructed a hypothetical phase diagram for the
Fe_3O_4-Fe_2TiO_4 system (figure 13) and provisionally placed the eutectic
point at a temperature of approximately $500^{\circ}C$ and at a composition of
approximately 40 per cent Fe_2TiO_4.

Vincent and Phillips (1954) noted that the degree of oxidation of the
iron would determine whether solid solutions between Fe_3O_4 and Fe_2TiO_4
or between Fe_3O_4 and $FeTiO_3$, or mixtures of both types would be form-
ed at high temperatures from a given amount of iron and titanium in the
melt. They noted that oxidation-reduction relationships between Fe_3O_4,
Fe_2TiO_4 and $FeTiO_3$ might be feasible and suggested that the oxidation
of Fe_2TiO_4, or an Fe_3O_4-Fe_2TiO_4 solid solution, to a product containing
ilmenite might occur. They concluded that oxidation and the early
stages of exsolution might proceed concurrently.
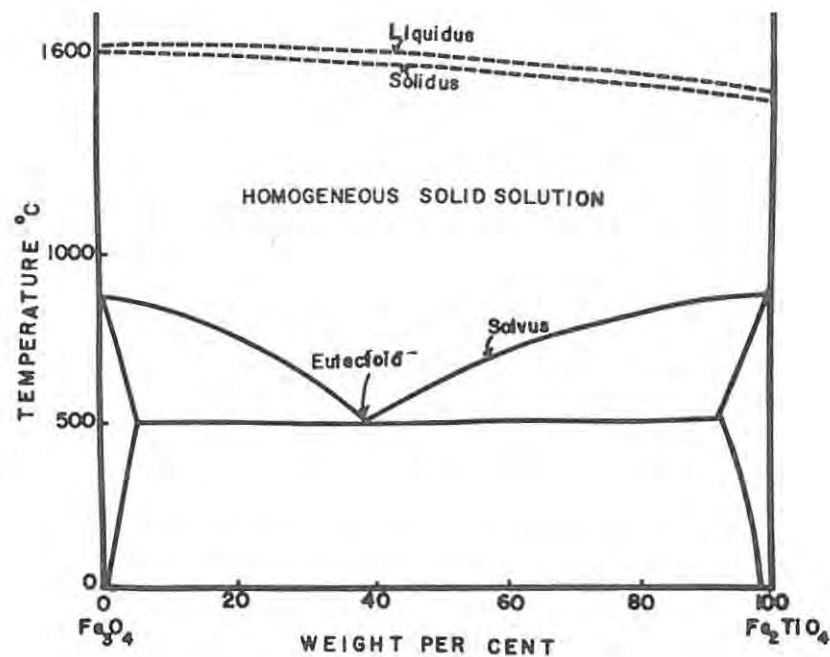
FIGURE 13   Hypothetical sub-solidus phase relationships in

Fe$_3$O$_4$-Fe$_2$TiO$_4$ system (from Vincent and Phillips, 1954).

Nicholls (1955) reviewed the available data on the magnetite-ulvospinel

series and concluded that they are completely miscible at elevated

temperatures.   He compiled a sub-solidus phase diagram (figure 14)

based largely on an earlier version by Kawai et al. (1954) and conclud-

ed that exsolution of an intermediate member of this series would

commence on slow cooling below 750°C.

Kawai (1956) re-examined the phase relationships in the Fe$_3$O$_4$-Fe$_2$TiO$_4$

system by studying synthetic materials.   He found no evidence for

the existence of a eutectic as proposed by Vincent and Phillips (1954)

and produced a modified version of his earlier phase diagram in which

he placed the crest of the solvus at 600°C and 42 mole per cent Fe$_2$TiO$_4$.

Vincent et al. (1957) heated natural grains containing extremely fine

and relatively coarse magnetite-ulvospinel microintergrowths under

vacuum and noted that samples held at 500°C for 15 hours showed little

change. Samples heated at 450°C for 14 days, however, showed a

slight increase in the amount of exsolved ulvospinel at the expense

of magnetite. Complete mutual solution of the magnetite and ulvospinel

was reported in samples heated at 800°C for 12 hours. They also ex-

amined the magnetic properties of these minerals at various stages

of the heating process and compared their results with those obtained

for synthetic systems.
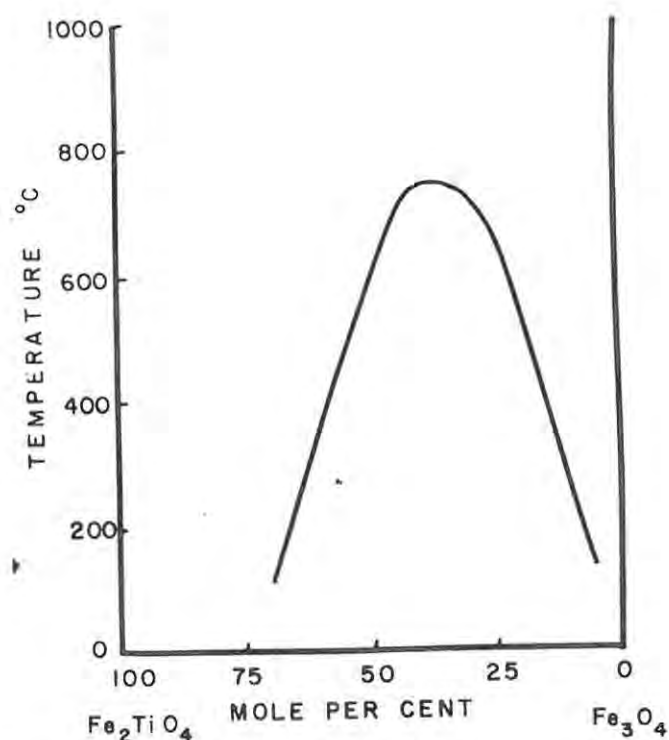
FIGURE 14   Proposed sub-solidus relationships in the Fe_3O_4-Fe_2TiO_4

system (modified after Kawai et al., 1954 by Nicholls,

1955).

Vincent et al. (1957) concluded that there is no real evidence for

the existence of a eutectic in the sub-solidus phase diagram for the

magnetite-ulvospinel series as proposed by Vincent and Phillips (1954).

They noted that magnetite dissolved in ulvospinel during their heating

experiments without itself taking much Fe_2TiO_4 into solution. They

produced a schematic phase-diagram showing a hoop-shaped solvus with a crest at about $600^{\circ}C$ (figure 15).
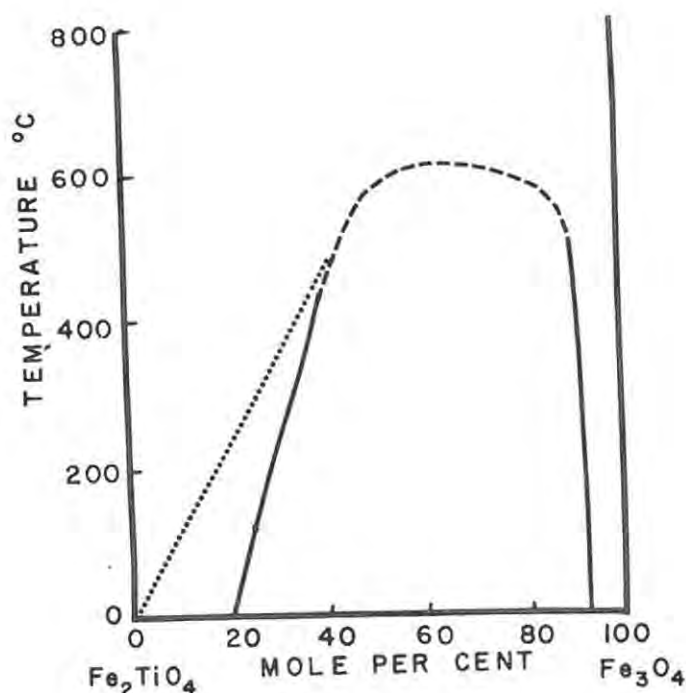
FIGURE 15   Proposed sub-solidus relationships in the Fe_3O_4-Fe_2TiO_4
system.   The dotted portion of the solvus on the
Fe_2TiO_4-rich side of the diagram is from Vincent et al.,
(1957) while the solid line is from Basta (1960).

Vincent et al. (1957) concluded that fairly extensive solid solution probably exists over a great deal of the magnetite-ulvospinel-ilmenite compositional field at elevated temperatures and that intermediate members might be preserved as homogeneous titanomagnetites by quenching. They concluded that a Fe_3O_4-Fe_2TiO_4 solid solution would remain homogeneous under strongly reducing conditions down to much lower temperature than a similar solution in the Fe_3O_4-Fe_2TiO_4 series.   They noted that an original Fe_3O_4-Fe_2TiO_4 solid solution might be changed to a member of the Fe_3O_4-$FeTiO_3$ series by oxidation.   They also reported that the larger ilmenite lamellae exsolved earlier than the ulvospinel

intergrowths in titaniferous magnetites containing both phases.

Akimoto et al. (1957a) prepared homogeneous solid solutions over the whole range from Fe_3O_4 to Fe_2TiO_4 by sintering finely powdered mixtures of Fe_2O_3, TiO_2 and electrolytic Fe in evacuated silica tubes for 6 hours at $1150^{\circ}C$. They reported a linear relationship between the lattice parameter and composition from $8.39 \, \overset{o}{A}$ for Fe_3O_4 to $8.53 \, \overset{o}{A}$ for Fe_2TiO_4. They also reported an approximately linear relationship between Curie point and composition in this series.

Nickel (1958) described magnetite-ulvospinel intergrowths in magnetite from Quebec and produced a series of scanning electron microscope photographs of etched polished section surfaces showing small oriented magnetite cubes set in a groundmass of ulvospinel. He noted that these intergrowths are present in the grains right up to their bound- aries and concluded that the **intergrowth** had formed from the exsolution of a Ti-rich magnetite-ulvospinel solution.

Wright (1959) described the heating at between 1250° and $1300^{\circ}C$ in a reducing atmosphere of titaniferous magnetite containing ilmenite lame- llae. He reported that the ilmenite growth had changed to a uniform pale yellow colour and that x-ray and chemical data indicated that it had reduced to an almost pure magnetite-ulvospinel solid solution. He also noted that an ilmenite-magnetite intergrowth in a silicate rock chip became homogenised when heated to $940^{\circ}C$ under vacuum. He conclud- ed that this occurred because of a reducing atmosphere created by vola- tiles released from the rock during heating.

Akimoto and Katsura (1959) analysed homgeneous titanomagnetites from

volcanic rocks and noted a range in compositions between the Fe_3O_4-Fe_2TiO_4 and Fe_3O_4-$FeTiO_3$ joins and concluded that these compositions might be obtained by the oxidation of an original magnetite-ulvospinel solid solution.

Vincent (1960) described magnetite-ulvospinel (and ilmenite) microintergrowths from the Skaergaard Complex and concluded that both magnetite-ulvospinel and magnetite-ilmenite formed solid solutions at high temperatures. He noted that ilmenite can form from the sub-solidus oxidation of ulvospinel and described various intergrowths displaying these features. He concluded that the iron-titanium oxides would be sensitive to local changes in oxygen fugacity either during slow cooling or subsequently so that the resulting textures might be difficult to interpret.

Basta (1960) synthesised solid solutions belonging to the magnetite-ulvospinel series by heating suitable mixtures of Fe_3O_4 and TiO_2 in evacuated silica tubes for 24 hours at $1000^\circ C$ followed by quenching in water. On the basis of his observations and the available data he concluded that ulvospinel could contain up to 20 mole per cent Fe_3O_4 in solid solution at normal temperatures. He modified the earlier sub-solidus phase diagram of Vincent et al. (1957) to take into account this feature (figure 15).

Basta (1960) also concluded (contrary to the results of Akimoto and Katsura, 1959) that natural titanomagnetite analyses clustered around the Fe_3O_4-Fe_2TiO_4 compositional join which supported the natural occurrence of solid solutions of this nature. He also noted that ilmenite can be formed via the oxidation of exsolved ulvospinel.

Experimental investigations into the $FeO-Fe_2O_3-TiO_2$ system by Mac-
Chesney and Muan (1959, 1961), Webster and Bright (1961) and Taylor
(1964) confirmed the existence of complete solid solution between mag-
netite and ulvospinel at elevated temperatures.

Lindsley (1962) synthesised a series of magnetite-ulvospinel solid
solutions hydrothermally at $800^{\circ}C$ and under conditions of the wüstite-
magnetite (WM) buffer (figure 7). He termed these solid solutions
the beta-series and also investigated the compositions of titaniferous
magnetite in equilibrium with ilmenite for conditions provided by the
NNO, WM and quartz-fayalite-magnetite (QFM) buffers. He observed that
the following reactions occurred:
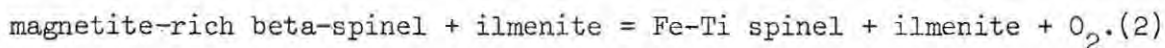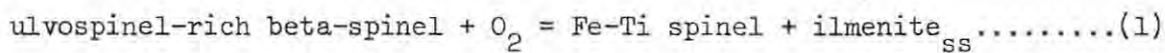
ulvospinel-rich beta-spinel + O_2 = Fe-Ti spinel + ilmenite$_{ss}$.........(1)
magnetite-rich beta-spinel + ilmenite = Fe-Ti spinel + ilmenite + O_2.(2)
where ilmenite$_{ss}$ = ilmenite with Fe_2O_3 in solid solution and

Fe-Ti spinel = a general term to indicate both the beta- and gamma
spinel phases.

Lindsley (1962) concluded that ilmenite is only sparingly soluble in
magnetite. He noted that, although his data did not disprove that
ilmenite intergrowths could form by exsolution from a primary magnetite-
ilmenite solid solution, they strongly supported the hypothesis that
these intergrowths may have formed from the oxidation of magnetite-
ulvospinel solid solutions. He also reported the synthesis of magne-
tite-ilmenite intergrowths via the controlled oxidation of ulvospinel
and ulvospinel-magnetite solid solutions at temperatures between 600°
and $1000^{\circ}C$ and noted that the process is reversible upon reduction.

Verhoogen (1962a) demonstrated thermodynamically that ulvospinel is more

readily oxidised at all temperatures than magnetite. He noted, how-
ever, that a solid solution of magnetite and ulvospinel of the type
$(Fe_2TiO_4)_q(Fe_3O_4)_{1-q}$ would oxidised less readily than would be pre-
dicted from a linear interpolation of the data between the two end-
members since the free energy of mixing would lower the free energy
in the solid solution.

Lindsley (1963) provided additional data on the magnetite-ulvospinel
solid solutions and demonstrated that the compositions in this series
in equilibrium with ilmenite-hematite solid solutions are also funct-
ions of temperatures and oxygen fugacity (figure 16). He noted that
these data can be applied to natural systems if the assumption is made
that the Fe-Ti oxide pairs formed in equilibrium did so during the
crystallisation of the rock and that the minor impurities present do
not markedly influence the phase relationships. He concluded that
the bulk of the ilmenite present in titaniferous magnetites probably
formed via the sub-solidus oxidation of ulvospinel.

Buddington and Lindsley (1964) evaluated the available data on magnet-
ite-ilmenite and magnetite-ulvospinel solid solutions and concluded
that miscibility between magnetite and ilmenite did not have to exist
since all the observed intergrowths could be accounted for by the oxid-
ation of ulvospinel. They calculated that an original titaniferous
magnetite ($Mt_{50}Usp_{50}$) in equilibrium with an ilmenite-hematite solid
solution at $1000^{\circ}C$ in a cooling magma would become oxidised to a ferr-
ian ilmenite and a titaniferous magnetite richer in magnetite than
$Mt_{90}Usp_{10}$ at $500^{\circ}C$. They concluded that this oxidation mechanism
would operate over a variety of magmatic conditions and could account
for the wide variety of magnetite-ilmenite and/or -ulvospinel inter-
growths encountered in nature.
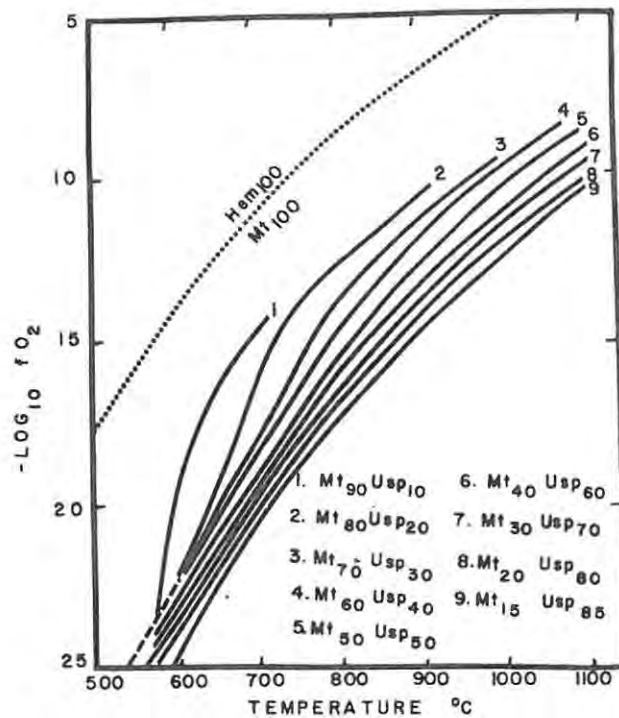
FIGURE 16   Projection parallel to the composition axis of the surface
             in fO_2-T-X space of the magnetite-ulvospinel solid solu-
             tion series that co-exists in equilibrium with ilmenite-
             hematite solid solutions (from Lindsley, 1963).

Buddington and Lindsley (1964) reported that unusually reducing condi-
tions are required to maintain the Fe_2TiO_4 in solid solution during
slow cooling down to the magnetite-ulvospinel solvus.   An ulvospinel-
rich phase is then either exsolved along the cube directions of the
host magnetite at sub-solvus temperatures during slow cooling or else
remains in solution when the cooling is too rapid.   They suggested
that the low oxygen fugacities required for the magnetite-ulvospinel
stability might possibly result from high concentrations of hydrogen
or sulphur in the interstitial fluids or from an excess of FeO relat-
ive to fluids.   They concluded, however, that under more "normal"
conditions where water-rich fluids are abundant relative to ferrous
minerals in cooling magmas, a great deal of the Fe_2TiO_4 in solid solu-

tion would be oxidised directly to ilmenite$_{ss}$ and magnetite$_{ss}$. The Fe$_2$TiO$_4$ would remain in solution at temperatures above the magnetite-ulvospinel solvus, but the ilmenite$_{ss}$ would "exsolve" as lamellae parallel to the (111) planes of the host. They concluded that it is therefore possible to develop both ilmenite lamellae parallel to (111) by partial oxidation and ulvospinel lamellae parallel to (100) by true exsolution under conditions of intermediate oxygen fugacity.

Buddington and Lindsley (1964) also concluded that the small ilmenite grains present around the periphery of titaniferous magnetites might have formed at high temperatures by the oxidation of an original homo-genous ulvospinel-magnetite solid solution. They noted that the amount of granular ilmenite associated with titaniferous magnetite in igneous rocks is, however, highly variable and that both these phases would co-precipitate during the crystallisation of most magmas.

Buddington and Lindsley (1964) concluded that the microintergrowths in natural Fe-Ti oxides can be divided into the following five classes on the basis of increasing degrees of diffusion and oxidation:

1). a single-phase homogeneous spinel; through

2). trellis intergrowths of thin ilmenite lamellae in all sets of (111) planes of the hosts;

3). sandwich intergrowths of thick ilmenite lamellae predominantly in one set of (111) planes;

4). granules of ilmenite within the magnetite, termed "internal granule exsolution";

5). granules or occasional lamellae of ilmenite on the external border of the magnetite, termed "external granule exsolution", or recryst-allised granular aggregates of ilmenite and titaniferous magnetite.

Buddington and Lindsley (1964) noted that the different "exsolution" intergrowths are probably formed at variable temperatures and depend on the rate of cooling, the activity of volatile components and other factors. They suggested that external granule "exsolution" might effectively cease at temperatures between 760° and 890°C, while the development of the trellis or sandwich intergrowths might continue to lower temperatures, possibly below 500°C. They concluded that exsolution would effectively cease at temperatures of "several hundred degrees".

Wilkinson (1965) acknowledged that ilmenite-magnetite intergrowths could be formed by the oxidation of magnetite-ulvospinel solid solutions, but nevertheless, concluded that the bulk of these intergrowths are formed via the exsolution and inversion of gamma-$FeTiO_3$ from Fe_3O_4-gamma-$FeTiO_3$ solid solutions. Rao and Rao (1965) also ascribed the formation of magnetite-ilmenite intergrowths to both of these mechanisms.

Basta and Takla (1968), in contrast to the prevailing views, described ilmenite trellis intergrowths in titaniferous magnetites from Abu Ghalaga and suggested that they had formed from the direct exsolution of an original magnetite-ilmenite solid solution. They also described coarse sandwich- and internal granule-intergrowths as well as composite magnetite-ilmenite grains and concluded that they could not be accounted for by any exsolution process and must consequently have formed via a late-stage, contemporaneous crystallisation of ilmenite and magnetite.

Anderson (1968b) investigated the mineralogy of titaniferous magnetites from the LaBlache Lake Deposit in Canada and undertook oxygen isotope studies with the aim of elucidating the causes of oxidation-exsolution of ilmenite from titaniferous magnetites in plutonic rocks. He noted

that about 0,5 weight per cent excess oxygen can be contained in tit-
aniferous magnetite at 1300°C (Taylor, 1964) and less than 0,3 weight
per cent at 1200°C (Webster and Bright, 1961) which correspond to
about 15 and 8 per cent ilmenite respectively. He concluded that a
maximum of about 10 per cent ilmenite$_{ss}$ could therefore exsolve (sensu
stricto) from igneous titaniferous magnetites. He calculated that the
LaBlache Lake titaniferous magnetite contained the equivalent of about
5 weight per cent of ilmenite$_{ss}$ as excess oxygen. He noted that this
would be exsolved as ilmenite at temperatures above about 800°C, result-
ing in an ideal R_3O_4 stoichiometry in the titaniferous magnetite.

Anderson (1968b) concluded that an additional 7 per cent of ilmenite
might have formed via oxidation-exsolution of a magnetite-ulvospinel
solid solution by trapped water during cooling from approximately
1100° to about 800°C in a closed system. He noted that ilmenite in
excess of approximately 10 weight per cent would have resulted from the
action of either an introduced oxidising agent or by hydrogen loss
from entrapped water. He also concluded that all the ilmenite in the
deposit could be accounted for by the oxidation of an original magnetite-
ulvospinel solid solution.

Duchesne (1970) concluded that the ilmenite intergrowths in titanifer-
ous magnetites are formed via the oxidation of ulvospinel and suggested
that the wide variety of textural types might be due to the oxidation
having occurred at different temperatures. He assumed that the ulvo-
spinel oxidation can occur a wide range of temperatures, either above
or below the magnetite-ulvospinel solvus. When the oxidation of Fe_2TiO_4
in solid solution occurs at supersolvus temperatures, supersolvus ilmen-
ite is formed and migrates to form a trellis-like pattern of lamellae
parallel to (111) of the magnetite. Under conditions of partial super-

solvus oxidation, the non-oxidised Fe_2TiO_4 residue exsolves parallel to (100) of the magnetite host on slow cooling below the solvus.

Conditions are not favourable for ionic diffusion at relatively low subsolvus temperatures with the result that ilmenite forms from the ulvospinel that has already exsolved, preserving the (100) orientation. Ionic diffusion is greater under higher sub-solvus temperatures, and the ilmenite formed from the ulvospinel oxidation is able to migrate and form lamellae parallel to (111). Duchesne (1970) concluded that the wide variety of microintergrowths developed in titaniferous magnetites could be accounted for by various combinations of these processes.

Lindh (1973a) reported difficulties in the experimental exsolution of homogeneous magnetite-ulvospinel solid solutions. He noted that magnetite-ulvospinel intergrowths produce poorly defined x-ray diffraction peaks and suggested that the compositions of the two phases are not clearly defined, possibly due to slow diffusion rates.

Lindh (1973b) reported that the oxide minerals are, however, transformed into stable low-temperature assemblages (magnetite + ilmenite) under lower temperature conditions and higher oxygen fugacities, while the co-existing silicates remain unaffected.

Lindh (1973a) reported that the form of the magnetite-ulvospinel solvus curve prepared by Basta (1960) (figure 15) is essentially correct and is in agreement with his own data. He also noted that ulvospinel intergrowths are preferentially developed in magnetites from basic to ultrabasic rock types that are of high-temperature magmatic origin. He concluded that temperature is an important factor governing the

formation of ulvospinel and that other factors must also be involved since synthetic ulvospinel-magnetite solid solutions can be prepared at temperatures as low as 700°C. He also noted that the oxygen fugacity of the magma would influence the crystallisation paths of the oxide minerals and suggested that a depletion of Ti in the spinel phase would result under conditions of relatively high oxygen fugacity according to the equation:

$$3(Fe_2TiO_4)_{ss} + \tfrac{1}{2}O_2 = (Fe_3O_4)_{ss} + 3FeTiO_3$$
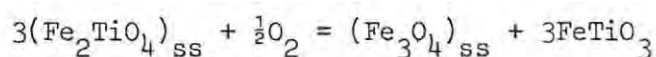
These conditions would give rise to the crystallisation of ilmenite and a titaniferous magnetite with a low Ti-content.

Lindh (1973a) and Annersten et al. (1973) suggested that some of the Ti in ulvospinel might be in the form of Ti^{3+} since, although Ti^{4+} ions have no d-electrons (and consequently have no octahedral crystal field stabilization energy) 90 per cent of the Ti atoms nevertheless occupy octahedral sites (Forster and Hall, 1965). Ti^{3+}, however, has one d-electron and its presence in octahedral sites can be explained by its octahedral crystal field stabilization energy (Burns, 1970). Lindh (1973a) also suggested that the line broadening observed in Mössbauer spectra of these minerals observed by Banerjee et al. (1967) and Annersten et al. (1973) might be due to the presence of some Ti^{3+}.

Lindh (1973a) noted that the formation of a natural magnetite-ulvospinel solid solution required two conflicting processes, namely the presence of sufficient Fe^{3+} to form the Fe_3O_4 component and simultaneously low oxygen fugacities to allow for the Fe_2TiO_4 stability. He also noted that the iron in ilmenite is present as Fe^{2+} and that the titanium is in the form Ti^{4+}. He suggested that since iron and titanium are the

only major elements present that can be expected to occur in more than one oxidation state in magnetite-ulvospinel solid solutions, the following electron exchange might take place:

$$Fe^{3+} + Ti^{3+} = Fe^{2+} + Ti^{4+}$$
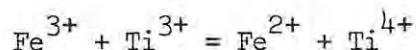
Annersten et al. (1973) suggested that the oxidation of Ti^{3+} to Ti^{4+} might proceed at very low oxygen fugacities and might explain the sensitivity of ulvospinel to oxidation. Lindh (1973a) concluded that the evidence for the existence of Ti^{3+} in the magnetite-ulvospinel solid solutions had not been proved, but that it should be investigated further. Lindh (1977, personal communication) reported that he is continuing with investigations into the magnetite-ulvospinel series using more sophisticated equipment.

Bowles (1977) stressed that the mechanism of lamellar ilmenite formation in magnetite is not yet fully understood, and in particular, posed the question as to why distinct size-ranges of lamellae are commonly developed when the cooling is an essentially continuous process. He suggested that an "oxidation threshold" might have to be exceeded before ilmenite could be produced from a magnetite-ulvospinel solid solution. Bowles (1977) noted that the cooling path followed by a normal magma through the temperature-oxygen fugacity field exhibits an extremely rapid decrease in fO_2 for a small fall in temperature. This oxygen must consequently either escape from the system or be taken up by the iron oxide phases. He concluded that continuous cooling would imply a continuous oxidising influence that would result in the formation of ilmenite in distinct generations if an oxidation threshold had to be exceeded before the ilmenite could be formed.

4.4.5 Discussion

The nature and diversity of investigations carried out on both natural and synthetic members of the magnetite-ilmenite, magnetite-ulvospinel and magnetite-ilmenite-ulvospinel series clearly indicate the complexities that exist within these mineral groups. The later studies also indicate that assumptions based purely on microscopic observations of textures alone are not necessarily valid and should at least be substantiated by x-ray diffraction procedures.

The members of the magnetite-ulvospinel series are extremely sensitive to changes in oxygen fugacity with the result that they cannot be investigated in many of the temperature and pressure ranges required for the complete elucidation of their phase relationships. Their subsolidus relationships are not known with any accuracy and the schematic phase diagram of Basta (1960) (figure 15) should be used with caution until the position of the miscibility gap has been more clearly demarcated.

The degree of miscibility between ilmenite and magnetite is very low, even at elevated temperatures and this has been demonstrated experimentally on numerous occasions. In order to overcome this it was postulated that ilmenite could exist as a cubic, high temperature gamma form analagous to maghemite. This phase has, however, not been synthesised or recognised in nature. Its existence must be doubted and it has not been considered in the literature as a possible solid solution compon-

ent since Basta and Takla (1968). The recognition that ilmenite can be formed by oxidation of ulvospinel has also obviated the necessity to invoke this hypothetical phase as the explanation for lamellar ilmenite intergrowths.

4.5 The Microstructural Evolution of the Titaniferous Magnetites

4.5.1 Introduction

The titaniferous magnetites from slowly cooled igneous rocks display a wide variety of microstructures as outlined in section 4.4.2. The bulk of these intergrowths can be interpreted as having formed either by the exsolution or oxidation -exsolution of an original magnetite-ulvospinel solid solution, the nature of the intergrowth being controlled by both changes in oxygen fugacity and rate of cooling (Buddington and Lindsley, 1964; Duchesne, 1970). The formation of these intergrowths is, however, also governed by the factors controlling exsolution in minerals and any proposed mechanism for their development has also to account for the following features:

1. The wide variety of microstructures developed, often within a single titaniferous magnetite grain.

2. The various combinations of microstructures developed in a particular grain and their significance.

3. The presence of distinct size ranges (or "generations") of exsolution bodies in a particular grain.

4. The relationship between the degree of oxidation and the microstructures.

5. The relationship between the stage at which oxidation occurs and the microstructures produced.

6. The exsolution mechanism by which the intergrowths developed.

7. The temperatures at which the various microstructures developed.

4.5.2 Composition of the initial magnetite-ulvospinel solid solution

The nature of the exsolution bodies that will develop depends initially on the composition of their original magnetite-ulvospinel solid solution. Buddington and Lindsley (1964) have shown that this ranges from approximately 25 to 80 mole per cent ulvospinel for a wide range of basic rock types. The lower values for basic rocks are, however, regarded as "suspect" by these authors because of the effects of external granule exsolution. A lower limit in excess of 35 mole per cent might consequently be more appropriate. Published analyses of titaniferous magnetites also rarely show TiO_2 values exceeding 25 per cent (corresponding to 70 mole per cent ulvospinel). This suggests that solid solutions containing more than approximately 80 mole per cent ulvospinel are unstable under magmatic conditions and do not form.

The lower TiO_2 limit appears related to lower crystallisation temperature in the more SiO_2-rich rocks (Buddington and Lindsley, 1964). The initial composition of the majority of magnetite-ulvospinel solid solutions probably lies between 35 and 70 mole per cent (equivalent to 12.5 to 25 per cent TiO_2). These values also correspond reasonably well to the range of bulk analyses of titaniferous magnetite ores presented in Part 3 of this thesis. Solid solutions in this compositional range would be expected to exsolve on slow cooling below 600°C.

4.5.3 The effect of oxidation

The magnetite-ulvospinel solid solutions are extremely sensitive to changes in oxygen fugacity and the ulvospinel component becomes oxidised to ilmenite which exsolves along (111) of the host (Buddington and Lindsley, 1964). The latter authors recognised 5 classes of microintergrowths on the basis of increasing degrees of oxidation and diffusion. This scheme

was extended by Duchesne (1970) who concluded that the oxidation of ulvospinel can occur over a wide range of temperatures, either above or below the magnetite-ulvospinel solvus and he recognised that a greater variety of intergrowths could be developed in this manner. The actual variety of intergrowths encountered in the titaniferous magnetites are far more complex than those outlined by Duchesne (1970) and their development can also be ascribed to variable degrees of oxidation occurring at different stages of cooling.

4.5.4 Exsolution mechanisms

Exsolution in the magnetite-ulvospinel-ilmenite system is complicated by the role of oxidation which results in the formation of ilmenite lamellae by a complex oxidation-exsolution process that is not well understood. In view of the lack of evidence to the contrary, it is assumed that if the magnetite-ulvospinel solid solution is oxidised at temperatures above the magnetite-ulvospinel solvus, the ilmenite that is formed will exsolve parallel to (111) since it is only sparingly miscible with magnetite. At sub-solvus temperatures, the exsolving ulvospinel-rich phase can be either oxidised as it exsolves and the resulting ilmenite migrate to form lamellae along (111) or else it can be oxidised after exsolution and maintain its orientation along (100).

The "oxidation threshold" mechanism of Bowles (1977) suggests that the oxidation of ulvospinel and consequent exsolutions of ilmenite is a discontinuous process although the cooling rate is itself continuous. The distinct size ranges of exsolution bodies can, however, be accounted for by the usual exsolution mechanisms reviewed by Brett (1964); Yund and McCallister (1970) and Champness and Lorimer (1976). Only the broader aspects of the exsolution mechanisms necessary for the understanding of the proposed processes are discussed here. Readers are

directed to the original papers for a more detailed synthesis of the factors involved.

The crystal structures of ilmenite (rhombohedral) and magnetite (cubic) are very different so that exsolution can proceed only by nucleation and growth mechanisms. The formation of a nucleus is, however, an energetically unfavourable process that involves the formation of a critical-sized particle of the exsolved phase that can subsequently grow with a decrease in free energy. Champness and Lorimer (1976) have shown that the free energy change accompanying precipitation, ΔG_{total}, is composed of 3 terms:

$$\Delta G_{total} = \Delta G_{volume} + \Delta G_{surface} + \Delta G_{strain}$$

where ΔG_{volume} = volume free-energy difference between the parent and product phases: this is the driving force for the reaction.

$\Delta G_{surface}$ = the free energy increase accompanying the creation of an interface between the matrix and the precipitate.

ΔG_{strain} = strain energy due to the difference in volume between the precipitate and matrix.

Champness and Lorimer (1976) note that both $\Delta G_{surface}$ and ΔG_{strain} are positive terms and oppose the nucleation event. The variation in ΔG_{total} as a function of the size of the nucleus, r, is illustrated in figure 17 (from Champness and Lorimer, 1976).

It can be seen from figure 17 that the nucleus has to reach a critical size, r^*, which is an energetically unfavourable process before further growth can proceed with a decrease in free energy. The initial value of $\Delta G_{total} = \Delta G^*$ represents the activation-energy barrier to precipitate

nucleation that has to be overcome before homogeneous nucleation can occur. This is normally achieved by a large amount of undercooling of the supersaturated solid solution.
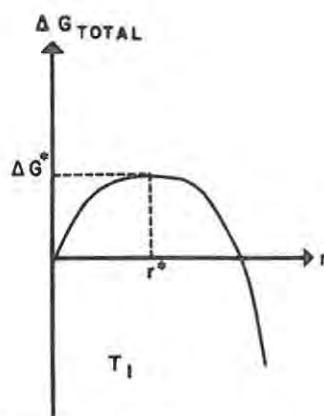
FIGURE 17   Schematic variation in free energy change, ΔG, as a function of the radius of the nucleus. ΔG^* represents the activation barrier to nucleation and r^* is the critical size of the nucleus (from Champness and Lorimer, 1976).

Nicholson (1970) has shown that when the misfit between the matrix and precipitiate is more than about 2 per cent, the strain free-energy will be so large that it will be impossible to form a critically sized nucleus of the equilibrium phase, even for large undercoolings with the result that homogeneous nucleation cannot occur.   This prohibitively high energy-barrier can, however, be overcome by heterogeneous nucleation at either planar or linear defects (Champness and Lorimer, 1976).

Champness and Lorimer (1976) also noted that a grain boundary (an incoherent planar interface) represents a potent nucleation site since the strain free-energy can be reduced because the misfit between the precipitate and matrix can be accommodated in the disordered structure of the boundary.   The surface free-energy can also be reduced if the

the precipitate "wets" the grain boundary. Dislocations (linear defects) provide less favourable nucleation sites than grain boundaries since they can only relieve strain in one dimension, but are in turn better sites than the matrix. Champness and Lorimer (1976) concluded that heterogeneous nucleation will occur at grain boundaries at under-coolings of a few degrees C, but undercoolings of several tens or hundreds of degrees C might be required for the initiation of homogeneous nucleation. Nucleation on dislocations will take place under conditions of intermediate undercoolings.

Anderson (1968b) concluded that a maximum of approximately 10 per cent ilmenite$_{ss}$ could conceivably exsolve from titaniferous magnetites due to the expulsion of excess oxygen. He estimated that approximately 5 per cent by mass of the ilmenite in the LaBlache Lake Deposit formed in this way. By analogy, it might be assumed that up to 10 per cent, but probably less ilmenite can form by true exsolution from titaniferous magnetites depending on the crystallisation temperature and excess oxygen content of the primary spinel. This process would most likely be initiated at points along the grain boundaries via the heterogeneous mechanism giving rise to external granules and occasional large lamellae that nucleate at grain boundaries and grow inwards into their hosts along their (111) planes.

The formation of these lamellae depletes their immediate surroundings of suitable ions and sets up a concentration gradient in which the required ions must migrate over a certain distance to reach the exsolved phase. Ionic mobility, however, decreases with falling temperature so that long range diffusion processes slow down and the supersaturation again increases in the median areas furthest away from the exsolved lamellae. Champness and Lorimer (1976) have also noted that growth

perpendicular to the length of the exsolution bodies is an energetically
unfavourable process (hence their relatively thin nature) with the re-
sult that the slow acceptance of suitable ions from regions parallel
to the lamellae will also contribute to the increase in supersaturation
in these areas during cooling.

Additional evidence for the existence of concentration gradients is
afforded by the general absence of other finer-grained titanium-rich
phases from narrow zones surrounding the larger-sized lamellae.   The
ilmenite lamellae also commonly taper towards their mutual intersect-
ions and exhibit the overall classic "oleander leaf" exsolution form
described by Schwartz (1931).

A sufficiently large degree of supersaturation (and hence under cooling) is
necessary in the regions between the large lamellae before the activa-
tion energy barrier can be overcome and a further episode of nucleation
and growth can be initiated.   This results in a time lag during which
the supersaturation increases so that when nucleation occurs, a second
series of exsolution lamellae is formed.   These lamellae will be dist-
inctly smaller than the earlier-formed set because they have formed at
much lower temperatures under conditions of lower ionic mobility.   The
exsolution process will thus be of a cyclic nature and can theoretically
occur several times during the slow cooling of a solid solution giving
rise to several sucessivily smaller sets of exsolution bodies, each set
developing in the areas between the next larger set.

The presence of more than approximately 5 per cent lamellae and external
granule ilmenite in a titaniferous magnetite indicates that oxidation of
the ulvospinel component has occurred.   Ilmenite formed in this way,
particularly at lower temperatures, will be virtually immiscible in the

magnetite and it is conceivable that the exsolution processes will continue in essentially the same manner even though an oxidation stage is involved. The high degree of immiscibility between these two phases suggests that the nucleation activation-energy barrier might be overcome at relatively low supersaturations thus accounting for the common development of several distinct size ranges of ilmenite lamellae in a single titaniferous magnetite grain.

A slowly cooled magnetite-ulvospinel solid solution will exsolve at subsolvus temperatures. In view of the similarity in crystal structure and unit cell dimensions between these two phases it is conceivable that exsolution might occur either via the homogeneous nucleation and growth process, or even via spinodal decomposition. The development of concentration gradients between the earlier-formed ilmenite lamellae (particularly the closer-spaced sets) might favour spinodal decomposition since this process involves compositional fluctuations within a solid solution (Cahn, 1968; Hilliard, 1970; Christie and Olsen, 1974).

4.5.5. Proposed sequence of microstructural development.

Exsolution is an essentially continuous process that is initiated during slow subsolvus cooling and continues down to temperatures that are too low to allow for effective ionic migration, even over geological time. Growth or precipitate coarsening will normally continue throughout the entire cooling period of solid solution, but the amount of growth will decrease as the required diffusion distances increase and the ionic mobilities decrease with falling temperature. Consequently it can be reasoned that the bulk of any exsolution body will be formed over a limited period following nucleation and that growth then slows down drastically once suitable ions have been removed from the immediate surroundings. Subsequent long-range diffusion of ions from further

afield will take place, but at a progressively slower rate with falling temperature. The ilmenite formed during the supersolvus oxidation of ulvospinel is immediately available for exsolution and will continue to exsolve as cooling continues. Should the oxygen fugacity be lowered for some reason during this period the ulvospinel might no longer be oxidised and the exsolution of ilmenite will consequently cease. In view of this feature and the foregoing discussion on the generation of distinct size ranges of exsolution bodies, the exsolution process can be conveniently divided into a number of distinct stages. It should be noted, however, that there will be a certain degree of overlap between the end of one stage and the beginning of the next and that growth of each exsolved phase will continue at successively slower rates down to the freezing temperature.

The nature of the titanium-bearing bodies produced in the titaniferous magnetites depends not only on the changes in oxygen fugacity and initial composition, but also on the cooling rate. Homogeneous titanomagnetite crystals can be formed via the quenching of a high-temperature solid solution, whereas slow cooling results in a wide range of microstructures. Intermediate cooling rates result in the telescoping of the various stages and make the interpretation of the resulting microstructures more difficult. The following scheme is presented for titaniferous magnetites from slowly cooled rocks and is based on the available literature and the results of microscopic examination of a wide range of titaniferous magnetites described in Parts 2 and 3 of this thesis. This scheme takes into account most of the more commonly observed microstructures in the titaniferous magnetites.

Stage 1. The crystallisation of a high temperature magnetite-ulvospinel solid solution, probably containing between 35 and 70 mole per cent

or more ulvospinel.

Stage 2. This is represented by the exsolution of ilmenite due to the expulsion of excess oxygen and results in the formation of approximately 5 per cent by mass of ilmenite. Ionic mobility is extremely high at these elevated temperatures and ilmenite granules are formed by heterogeneous nucleation and growth at grain boundaries while occasional large lamellae grow inwards into the grains along (111). The frequency of lamellae . is essentially a function of the original oxygen content of the spinel. They are rarely present in sufficient numbers to form trellis networks and sandwich textures are more common. This process continues down to temperatures of approximately $800^{\circ}C$ (Anderson, 1968b) by which time expulsion of the excess oxygen is complete. These features are illustrated schematically in figure 18.
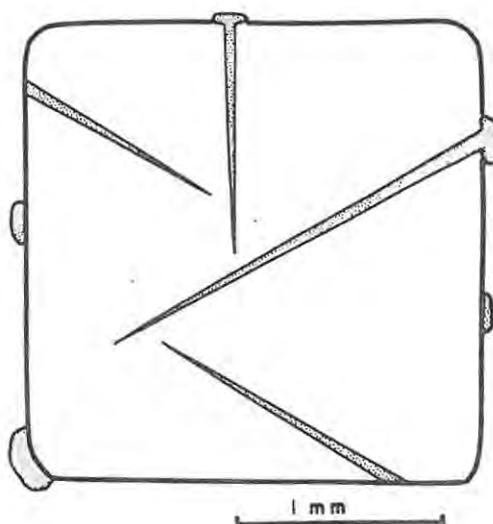
FIGURE 18   Schematic representation of stage 2 showing the development of sparsely distributed ilmenite lamellae oriented parallel to (111) and several external granules (shaded). The widths of the lamellae have been exaggerated for clarity.

Stage 3. This stage encompasses a wide temperature range from the commencement of cooling down to the magnetite-ulvospinel solvus at approximately $600^\circ C$. It consequently overlaps with part of stage 1. The ionic mobility is high and the nature of the microstructures produced depends largely on the prevailing oxygen fugacities. A number of possibilities exist and are illustrated schematically in figure 19.

(b) 0,5 mm   (c) 0,5 mm
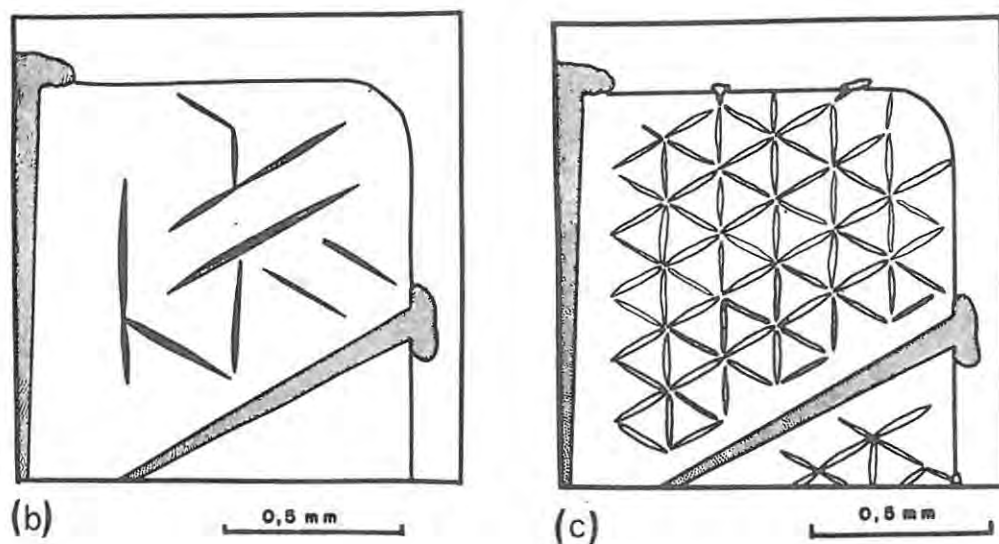
FIGURE 19. Schematic representation of stages 3(b) (left) and 3(c) (right) showing the development of a second set of finer ilmenite lamellae parallel to (111) in the areas between the earlier-formed exsolution bodies. The lamellar development is much more pronounced under higher oxygen fugacities and a smaller set of external granules may also develop. The widths of the lamellae have been exaggerated for clarity.

a) Low fO_2:   the magnetite-ulvospinel solid solution remains stable and no exsolution occurs.

b) Intermediate fO_2:   some oxidation of the ulvospinel will occur resulting in the formation of ilmenite which will exsolve. The amount

of ilmenite produced will be function of the degree of oxidation and at the highest temperature will probably contribute to the formation of the sparse ilmenite granules and lamellae of stage 2. The growth of these earlier bodies will slow down as the temperature decreases and once the nucleation activation-energy barrier has been exceeded, a further set of smaller ilmenite lamellae will be formed parallel to (111) of their hosts. The size, frequency and spacing of the lamellae is a function of the oxygen fugacity. Only a few sandwich lamellae will form at relatively low fO_2, while there will be a more abundant development of trellis networks under more oxidising conditions. The exsolution will take place via the heterogeneous mechanism at elevated temperatures. It is possible that both heterogeneous and homogeneous nucleation and growth processes might be operative at lower temperatures. The unoxidised ulvospinel will remain in solution on cooling down to the solvus.

c) High fO_2: complete oxidation of the ulvospinel-magnetite solid solution occurs resulting in the formation of abundant lamellar ilmenite. This ilmenite will initially contribute to the growth of the sparsely developed lamellae and granules of stage 2. At lower temperatures a further set of well-defined, but very much smaller, trellis lamellae will be formed as discussed above. It is also possible that a second series of finer external granules might be formed when oxidation occurs at higher temperatures. Exsolution occurs via the heterogeneous mechanism at higher temperatures, but the homogeneous mechanism might become operative at lower temperatures.

It is conceivable that a further, smaller set of trellis lamellae might form during the closing stages of this lengthy cooling interval from magmatic temperatures down to approximately 600°C. The development

of these lamellae could take place under conditions of intermediate to high oxygen fugacity and they would develop in the areas between the earlier formed lamellae via the mechanisms discussed above. Three size-ranges of supersolvus ilmenite lamellae are present in some titani- ferous magnetites, but this number is not commonly encountered in the materials examined during this study.

Stage 4. This stage operates in the higher-temperature region immed- iately below the solvus and may continue down to approximately 500°C. It might also conceivably overlap slightly with stage 5. The ionic mobility is still moderately high under these conditions and a number of possibilities of microstructural development exist depending on the oxygen fugacity. The major types are illustrated schematically in figure 20.

a) Low fO_2: exsolution of ulvospinel commences along the (100) direct- ions of the host after a suitable degree of undercooling has been achieved. The exsolution mechanism might well operate via spinodal decomposition, but heterogeneous and homogeneous processes are more likely to be operative in the higher sub-solvus region. The ulvospinel network will be developed in the magnetite in the areas between the pre-existing ilmenite lamellae, or if none is present, the ulvospinel development will be uniform throughout the grain.

The initial, and coarser ulvospinel exsolution, commonly takes place in the immediate vicinity of earlier formed transparent spinel lamellae that are oriented parallel to (100). It develops as a characteristic box-like structure around the spinel lamellae as described by Ramdohr (1953). This ulvospinel is never in direct contact with the transpar-

ent spinel, but its location and relative coarseness suggests that it may have been the earliest exsolution of this phase. It most probably forms via the heterogeneous nucleation and growth mechanism at dis- locations caused by the presence of another phase.

b) Intermediate fO_2: some ulvospinel exsolves, possibly along (100), but is oxidised directly to ilmenite which migrates to form a set of very fine ilmenite lamellae oriented parallel to (111) under these temperatures. It is also possible that portions of the ulvospinel remaining in solid solution under these conditions might be oxidised and exsolve directly as (111) ilmenite lamellae. The abundance of lamellae and the density of the trellis network is again a function of the degree of oxidation.

c) High fO_2: both the exsolving ulvospinel and that portion of it remaining in solid solution are oxidised to form ilmenite which exsolves as a well-developed trellis network parallel to (111). Small internal ilmenite granules might be formed under the highest oxygen fugacities and small internal/external granules will be formed along cooling cracks, fractures, partings and other permeable features that traverse the grains. Exsolution takes place via the heterogeneous- and homogeneous-nucleat- ion and growth processes.

Stage 5. The boundary between this and stage 4 is not clearly defined and is a result of a progressive reduction in the ionic diffusion rates. It is operative over the temperature range from approximately $500^{\circ}C$ to $400^{\circ}C$, but may extend to considerably lower temperatures over long per- iods of time. A number of possibilities exist for microstructural development depending on the prevailing oxygen fugacity. The major types are illustrated schematically in figure 21.

(a)

20 μm

(b)   0,25 mm

(c)   0,25 mm
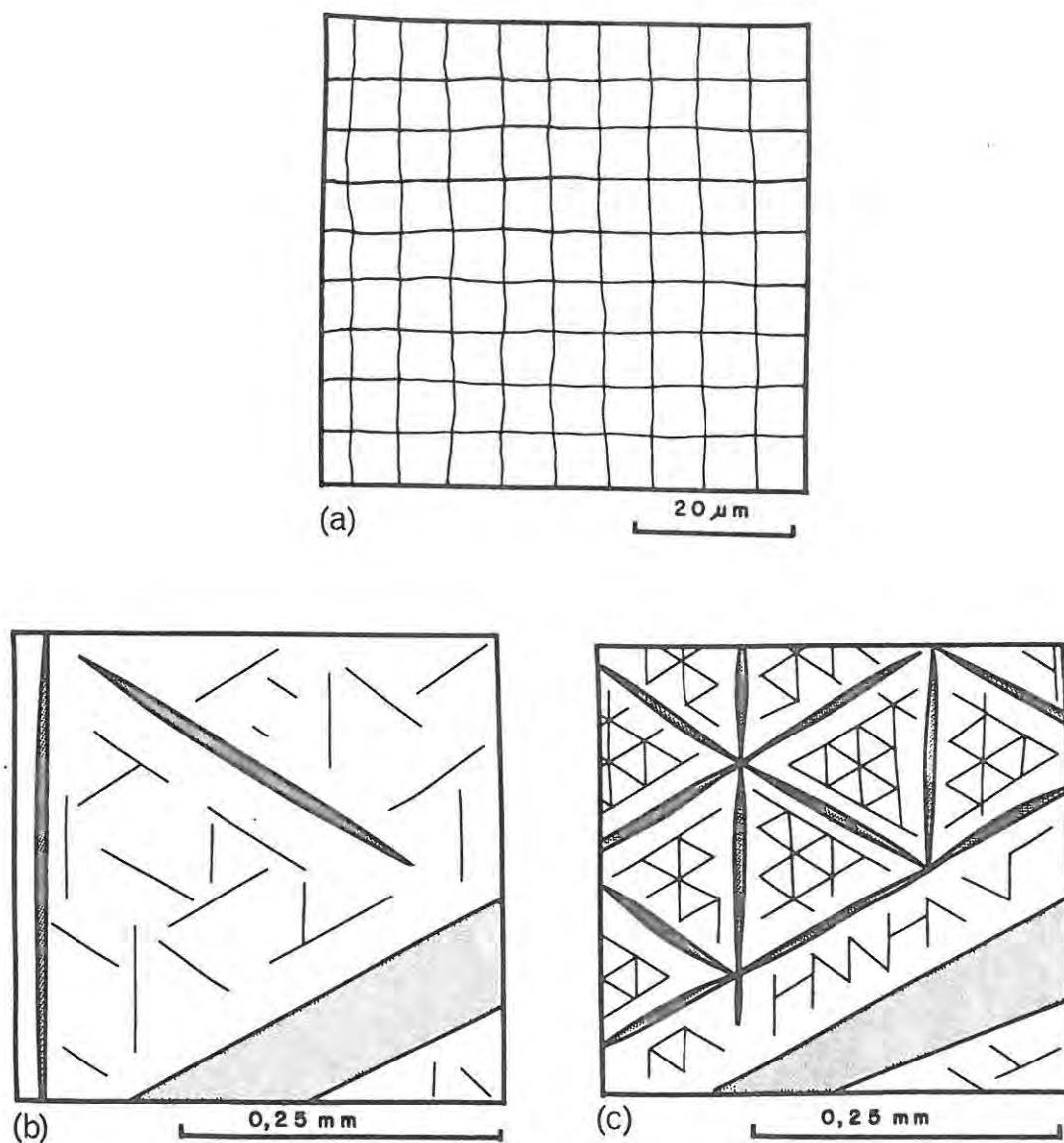
FIGURE 20. Schematic representation of stages 4 (a), (b) and (c).

(a) Ulvospinel begins exsolving parallel to (100) under

low fO_2.   The ulvospinel is oxidised to ilmenite with

increasing fO_2 resulting in a finer set of lamellae.

(b) and (c)   The relative abundance of ilmenite lamellae

produced is a function of the oxygen fugacity.   The widths

of the larger ilmenite lamellae have been exaggerated for

clarity.

a) Low fO_2: ulvospinel continues to exsolve along (100) but at a slower rate than before. A certain degree of precipitate coarsening occurs and the magnetite breaks up into a myriad of tiny, micrometre-sized cubes that are set in a matrix of ulvospinel.

b) Intermediate fO_2: pre-existing exsolved ulvospinel along (100) will become oxidised or partially oxidised to form ilmenite. This ilmenite is, however, not in its stable (111) lamellar arrangement. Breakdown of the (100) lamellae will consequently occur and there will be a tendency for the ilmenite to migrate towards the octahedral planes. The degree of ionic mobility will have decreased so that the development of completely lamellar intergrowth is not attained. The result is an irregular area of micrometre-sized ilmenite grains that form a sieve-like mass containing abundant cubic- to rounded-magnetite inclusions. The degree of alteration of ulvospinel and the breakdown of the original cubic microstructure is also a function of the oxygen fugacity and temperature. Any ulvospinel remaining in solid solution will be oxidised to ilmenite which will exsolve and contribute to the formation of these irregularly shaped bodies rather than form lamellae.

c) High fO_2: the ulvospinel remaining in solid solution will be oxidised resulting in ilmenite exsolution. The conditions of ionic mobility might, however, not be suitable for lamellar growth with the result that the ilmenite forms large numbers of internal granules in the areas between the earlier lamellae rather than the usual forms.
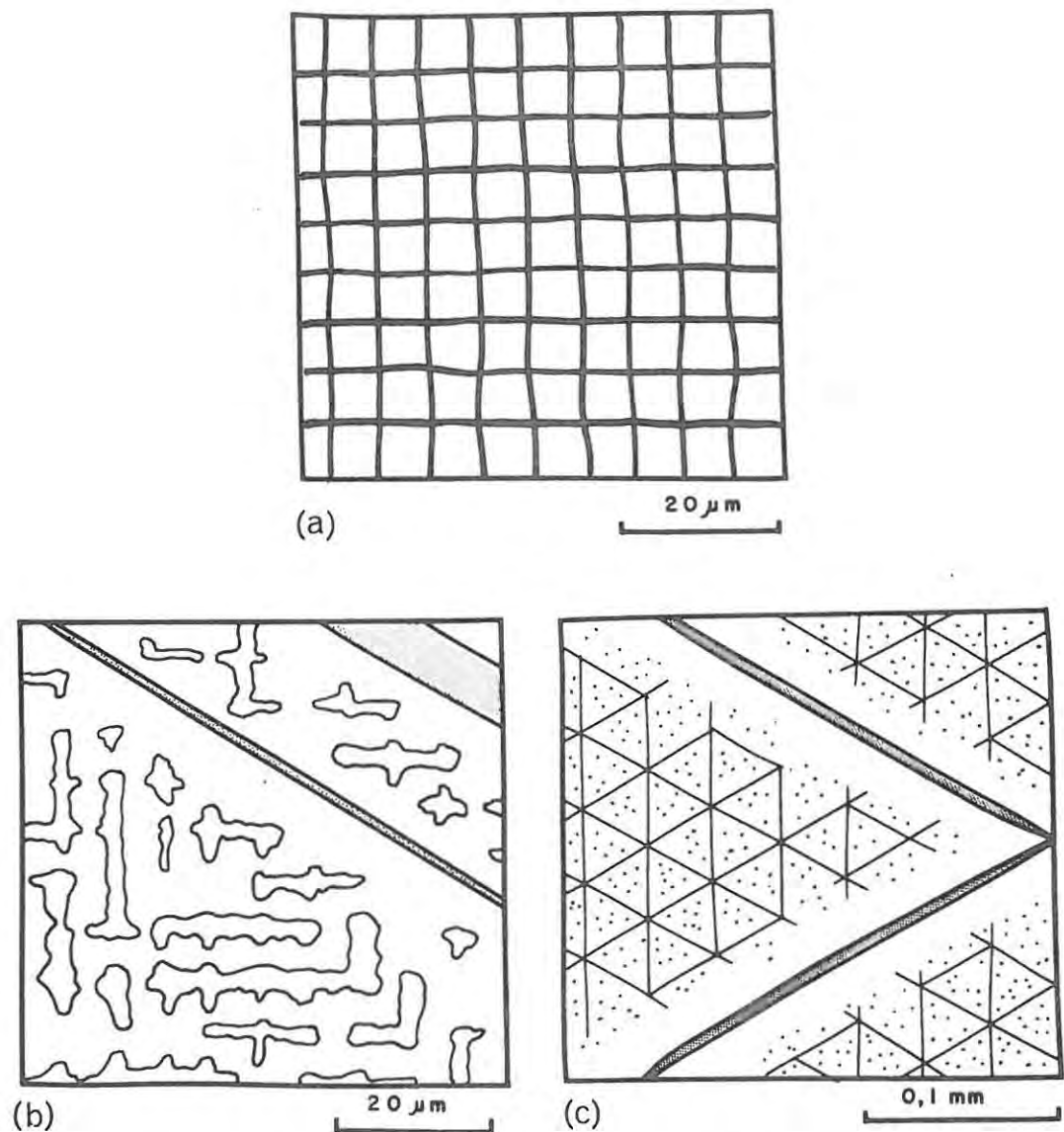
FIGURE 21. Schematic representation of stages 5 (a), (b) and (c).

(a) The (100) ulvospinel lamellae become coarser through continued exsolution under low fO_2.

b) Under higher fO_2 conditions the ulvospinel previously exsolved parallel to (100) becomes oxidised to ilmenite, but this arrangement is crystallographically unstable and recrystall-ization occurs under the prevailing conditions. This leads to the development of tiny irregular ilmenite grains as shown.

c) Internal ilmenite granules are formed in the areas between lamellae under the highest oxygen fugacities.

Stage 6. This represents the lowermost sub-solvus temperature range from approximately $400^{\circ}C$ down to the temperatures at which ionic diffusion becomes infinitely slow and exsolution effectively ceases.

a) Low fO_2: the final stages of precipitate coarsening occur and the ulvospinel network reaches its maximum development, displaying the characteristic cloth microtextures.

b) Intermediate fO_2: oxidation of the pre-existing ulvospinel lamellae occurs, but the resulting ilmenite lamellae preserve their original cubic arrangement since the ionic mobility is too low for migration. Most of the ulvospinel remaining in solid solution oxidises to ilmenite which ex-solves in the form of internal granules.

c) High fO_2: Most of the ulvospinel remaining in solid solution is oxidised and exsolves in the form of ilmenite granules.

Stage 7. Low temperature oxidation of the exsolved ulvospinel can occur at any stage during the subsequent history of the titaniferous magnetite. This results in the oxidation of the ulvospinel micro-intergrowth, but its crystallographic orientation is retained. Sub-sequent oxidation of the titaniferous magnetite during weathering is dealt with in section 6.

4.5.6 Application to natural microintergrowths.

The foregoing scheme can account for the development of a wide range of the titanium-bearing microintergrowths encountered in titaniferous magnetites, but it must be noted that conditions in nature are commonly more complex than outlined here. The common co-existence of titani-ferous magnetite and ferrian ilmenite in a wide range of igneous rocks suggests that the prevailing oxygen fugacities were largely

buffered in the range between the magnetite-wüstite and Mn_3O_4-MnO buffers (figure 7) according to the data of Lindsley (1963). This is supported by data on the Skaergaard Complex suggesting that the oxygen fugacities were buffered near the QFM buffer (Buddington and Lindsley, 1964; Williams, 1971). Similar results were reported for the Dufek Intrusion (Himmelberg and Ford, 1977), but Mathison (1975) concluded that the oxygen fugacities in the Somerset Dam Intrusion were nearer the NNO buffer curve.

In spite of the overall buffering of oxygen fugacities during cooling in the intrusions, considerable local variation in oxygen fugacity can exist over small distances within the same complex. Bowles (1976) reported variations of this nature in the Freetown Complex. Changes in oxygen fugacity can occur at any stage of the cooling process as discussed in section 4.5.5. Equilibration will also take place between the various exsolved phases at successively lower temperatures.

The results of these oxygen fugacity variations are reflected in the wide variety of microstructural combinations observed in natural titaniferous magnetites. An example of this is afforded by the presence of narrow zones of very fine, stage 5 ilmenite lamellae that are commonly developed on either side of narrow fractures or along grain boundaries of titaniferous magnetite while the interiors of the grains exhibit well-defined ulvospinel textures. The development of internal granules also often occurs in these marginal areas while the interiors of the grains show the development of lamellar intergrowths. These features suggest that higher oxygen fugacities exist in the interstitial fluids during these stages resulting in a higher degree of oxidation in the neighbouring areas.

The larger-scale fluctuations in oxygen fugacity also control the nature of the microintergrowths. For example, relatively high oxygen fugacities might exist at elevated temperatures during stage 2 leading to the formation of a well-defined set of large ilmenite lamellae. Should the oxygen fugacity be lowered sufficiently at this stage, exsolution of ilmenite will cease and the solid solution will remain stable until cooled below the solvus when ulvospinel will exsolve. By analogy, fluctuating oxygen fugacities during cooling can produce an extremely wide range of textural types based on various combinations of the processes outlined in stages 2 to 6.

Naturally occuring titaniferous magnetites form complex solid solutions with other spinels and minor amounts of MgO and Al_2O_3 are commonly present. These oxides generally form a transparent spinel that also exsolves on slow cooling and further serves to complicate the microstructural development. This topic is discussed further in section 5.6.

The titaniferous magnetites of igneous rocks contain a detailed record of the various changes in oxygen fugacity that occurred at different stages during their cooling history. Some of this information will inevitably have been lost or blurred due to external granule exsolution and re-equilibration at lower temperatures, but the preserved

microstructures will contribute a great deal of petrogenetically important information once their development is completely understood.

This synthesis of exsolution behaviour is based largely on the available published data and on the microscopic examination of a wide range of titaniferous magnetites, largely from rocks of basaltic affinity. It is intended to illustrate the petrogenetic significance of these microstructures ----- a hitherto neglected field of research.

4.6 Oriented Intergrowths of Magnetite in Ilmenite.

4.6.1 Introduction.

Small magnetite platelets are occasionally developed along the basal planes of certain ilmenites, but are normally present in relatively small numbers. These bodies can be distiguished from hematite intergrowths on the basis of their colour, isotropic properties and morphology. They are distinctly more platelike in contrast to the lensoid hematite. This magnetite may also occasionally exhibit various degrees of martitisation and the completely oxidised martite pseudomorphs can normally be distinguished from hematite on morphological grounds (personal observation).

The occurrence of these intergrowths has been noted from numerous localities, but they have not been investigated in as much detail as the other microintergrowths in this system. The experimental data reviewed in sections 4.4 and 4.5 indicate that only limited solubility exists between magnetite and ilmenite, even at elevated temperatures. The development of these intergrowths is consequently problematical and requires further investigation.

4.6.2 <u>Mineralogical investigations.</u>

Warren (1918) described a magnetic ilmenite from Arendal, Norway and reported that its magnetic properties were due to the presence of thin intergrown magnetite plates. Ramdohr (1926) also reported the occurrence of magnetite platelets in ilmenite and suggested that it might, in part, have formed from exsolved hematite. Ramdohr (1939) reported that ilmenites contain up to 5 per cent exsolved Fe_3O_4, but noted that these intergrowths are not developed in ilmenites containing between 5 and 50 per cent Fe_3O_4. He noted the existence of rare cases of ilmenites containing more than 5 per cent intergrown magnetite, but concluded that they had, in all cases, formed from pre-existing hematite. He also reported that the magnetite is oriented with its octahedral planes parallel to (0001) of the ilmenite hosts.

Ramdohr (1939) concluded that the formation of magnetite from exsolved hematite lamellae in ilmenite might be more common than previously re-cognised. He concluded that the magnetite forms from hematite under reducing conditions and noted that the original lens- and disc-shaped hematite bodies are transformed to magnetite platelets.

Ramdohr (1956) suggested that between 5 and 10 per cent Fe_3O_4 might dissolve in ilmenite at high temperatures and this would account for the very thin magnetite lamellae having formed by exsolution. He also re-affirmed that some of the magnetite bodies are formed from hematite and noted that it is extremely difficult to distinguish between genuine exsolved magnetite and that formed by reduction.

Buddington et al. (1963) described the local occurrence of magnetite platelets in ilmenites from regionally metamorphosed gneisses. They concluded that these intergrowths do not normally form during crystall-

isation of these minerals, but might be produced by the contemporaneous reduction of exsolving hematite lamellae. They suggested that this would take place locally under lower oxygen fugacities by the following reaction:

$$2(FeO.TiO_2) + 3Fe_2O_3 \xrightarrow[\text{during exsolution}]{\text{reduction}} 2Fe_3O_4 + 2(FeO.TiO_2) + O$$
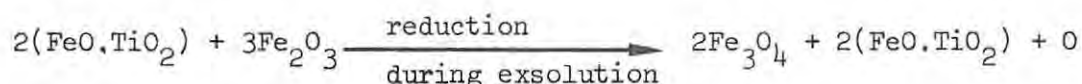
Buddington et al. (1963) reported in support of this mechanism that magnetite intergrowths developed in ferrianilmenite during high temperature contact metamorphism in a gneiss adjacent to a basaltic dyke. He concluded that magnetite intergrowths were formed in the ferrianilmenite by the partial reduction of exsolved Fe_2O_3 that was originally dissolved in the ilmenite.

Buddington and Lindsley (1964) reported the synthesis of magnetite lamellae in ilmenite by reducing Fe_2O_3-rich ilmenites in fO_2-buffered hydrothermal experiments. They reported that this magnetite developed along the basal planes of the magnetite and concluded that magnetite lamellae would develop in ilmenite by the contemporaneous subsolidus reduction of exsolving Fe_2O_3.

Czamanske and Mihalik (1972) described the occurrence of magnetite lamellae in ilmenites in granodiorite and granite from the Finnmarka Complex in Norway. They based their interpretation of these microstructures on the data of Vincent et al. (1957) and Taylor (1964). These data suggest that cooling in a closed, water-bearing system will result in the reduction of the Fe_2O_3 component of the hematite-ilmenite solid solution series while oxidation of the Fe_2TiO_4 component of the co-existing magnetite-ulvospinel solid solution series occurs. Czamanske and Mihalik (1972) concluded that the magnetite rodlets in

the central areas of ilmenite grains are formed by reduction of ilmenite crystals containing Fe_2O_3-rich cores.

Gasparrini and Naldrett (1972) described the presence of fine magnetite rods confined to the central areas of ilmenite grains from the South Range of the Sudbury Irruptive. The marginal areas of these grains contain finer hematite lamellae. They noted that the magnetite would occur along grain margins and near fractures in the ilmenite if it formed by a reduction process since the removal of oxygen from the exsolution sites would be facilitated. They suggested that the presence of magnetite might imply that the Sudbury ilmenites were not stoichiometric at high temperatures. Gasparrini and Naldrett (1972, p. 613) reported in a footnote that D.H.Lindsley (in a personal communication) had objected to the postulate of a cation excess or deficiency in the high temperature ilmenite. He suggested that the cores of the original ilmenites had originally been richer in Fe_2O_3 and were therefore more susceptible to reduction.

4.6.3 Discussion.

Any mechanism invoked to account for the formation of magnetite platelets in ilmenite must account, not only for their generally sparse distribution, but also for their characteristic development in the central areas of their hosts. The available data suggest that these bodies can be developed from pre-existing exsolved hematite by reduction during metamorphism or even by reduction of Fe_2O_3 in solid solution (Ramdohr, 1939; Buddington et al., 1963; Buddington and Lindsley, 1964). The magnetite bodies developed near the marginal areas of these grains might migrate externally during this process, provided temperatures are high enough, and have contributed to the development of other Fe-rich

minerals. This process would conceivably produce magnetite-free rims around the ilmenite grains.

The development of magnetite lamellae in ilmenites from slowly cooled, unmetamorphosed igneous rocks is more problematical. Lindsley (1963) and Buddington and Lindsley (1964) have shown that the compositions of co-existing ilmenite-hematite and magnetite-ulvospinel solid solutions are functions of both the temperature and oxygen fugacity. These minerals co-exist in a wide range of igneous rock types and suggest that cooling took place within these rocks under closely buffered oxygen fugacities that generally lie somewhere in the region demarcated by the $MnO-Mn_3O_4$ and QFM buffers (figure 7) (Buddington and Lindsley, 1964). The compositional ranges of the co-existing ilmenite-hematite solid solutions are clearly defined under these conditions as illustrat-ed in figure 8. The fugacities required for the stability of the different ilmenite-hematite solid solutions are much lower than those required for the reduction of hematite to magnetite (figure 8).

The conditions prevailing in cooling igneous rocks imply that the exsolved hematite in an ilmenite-hematite solid solution cooling to-gether with co-existing members of the magnetite-ulvospinel series under suitably buffered fO_2 conditions might conceivably be reduced to mag-netite. This would most probably occur at temperatures that were too low to allow for large scale ionic migration and the mainten-ence of compositional equilibrium between the co-existing spinel and rhombohedral phases. The previously exsolved hematite-rich solid sol-ution would no longer be within its stability field with respect to the prevailing oxygen fugacity and would be reduced to magnetite.

This process might also operate at higher temperatures with the result

that portion of the Fe_2O_3 in solid solution would be reduced to in-
soluble magnetite which would in turn "exsolve" via a contemporaneous
reduction/exsolution process. The magnetite produced at higher temp-
eratures might migrate out of the ilmenite, particularly from the mar-
ginal areas and become incorporated into the co-existing titaniferous
magnetite or other mafic silicates. The overall iron content of the
ilmenite would therefore be reduced.

The operation of this contemporaneous reduction/exsolution mechanism
during sub-solidus cooling indicates that these magnetite intergrowths
in ilmenite might be more common than previously recognised, as suggest-
ed by Ramdohr (1939). The ilmenites from many igneous rocks are,
unfortunately, not normally very iron-rich with the result that micro-
intergrowths of either hematite or magnetite are not common.
This feature might be due, in part, to the preferrential incorporation
of the Fe^{3+} ion required for Fe_2O_3 formation into the magnetite crystal
structure during crystallisation of these co-existing phases.

The existence of both magnetite and hematite microintergrowths in ilmen-
ite co-existing with titaniferous magnetite indicates the very delicate
control exerted by the oxygen fugacity on phase relationships in this
mineral system and serves to emphasise the complexities. The reduct-
ion of an exsolved hematite microintergrowth in an ilmenite depends
not only on the oxygen fugacity and temperature, but is also controlled
by diffusion rates, the composition of exsolved hematite-ilmenite solid
solution, the presence of volatiles and the effect of impurities. The
data of Lindsley (1963) indicate that the more ilmenite-rich the exsolved
hematite phase is, the lower the oxygen fugacities under which it will
be stable at a given temperature (figure 8).

The possibility that a minor amount of magnetite might be soluble in ilmenite at elevated temperatures should also not be overlooked. Cooling of a solid solution of this nature under suitable oxygen fugacities would certainly produce several per cent of exsolved magnetite in the ilmenite host.

4.6.4 Conclusions.

The occurrence of crystallographically oriented magnetite lamellae along the basal planes of ilmenite crystals is difficult to interpret in view of the low degree of mutual solubility that exists between these two phases. The presence of these lamellae in ilmenites from metamorphic rocks can be ascribed to a solid-state reduction of original exsolved hematite lamellae or Fe_2O_3 in solution during metamorphism under sufficiently low oxygen fugacities.

The occurrence of these intergrowths in primary ilmenites from unmetamorphosed, slowly cooled igneous rocks is more problematical. They might conceivably be produced by the reduction of earlier exsolved hematite lamellae during sub-solidus cooling under low oxygen fugacities. This process might also operate at higher sub-solidus temperatures resulting in the reduction of portion of the Fe_2O_3 in solid solution which would then "exsolve" as lamellae.

A lack of data exists on the natural occurrence of magnetite lamellae in ilmenites and the phase relationships in this respect have not yet been thoroughly investigated. The possibility that up to several per cent (less than 5) of magnetite might be present as a true exsolution product should also not be overlooked.

4.7 Titaniferous Magnetites: Overall Conclusions.

The phase relationships in the magnetite-ulvospinel-ilmenite series have not yet been clearly defined, but it is known that limited miscibility exists between magnetite and ilmenite at all temperatures (Webster and Bright, 1964; Taylor, 1964; Buddington and Lindsley, 1964). Magnetite and ulvospinel, however, form a continuous solid solution series at temperatures above approximately $600^{\circ}C$ (Basta, 1960; Buddington and Lindsley, 1964). The magnetite-ulvospinel solid solutions are unstable under conditions of relatively high oxygen fugacity and decompose to yield less Ti-rich magnetite solid solutions and Ti-rich members of the hematite-ilmenite solid solutions series according to the following equation (Carmichael et al., 1974).
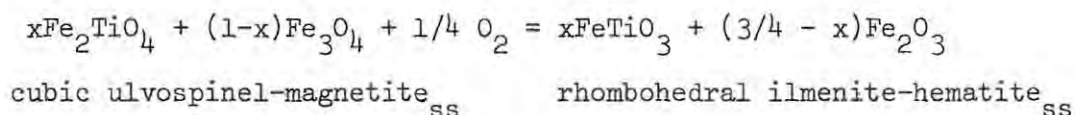
$$xFe_2TiO_4 + (1-x)Fe_3O_4 + 1/4\ O_2 = xFeTiO_3 + (3/4 - x)Fe_2O_3$$

cubic ulvospinel-magnetite$_{ss}$ rhombohedral ilmenite-hematite$_{ss}$

Members of the magnetite-ulvospinel solid solution series commonly coexist in equilibrium with members of the ilmenite-hematite solid solution series in nature and Lindsley (1963) has shown that their compositions are largely functions of oxygen fugacity and temperature. These data can be used to delimit their approximate stability fields as indicated in figure 16.

The nature of the microintergrowths produced in the intermediate members of the magnetite-ulvospinel solid solution series is dependent largely on the initial composition of the solid solution, the prevailing oxygen fugacities at different stages of cooling and the rate of temperature decrease. Homogeneous minerals (titanomagnetites) can be produced over the whole compositional range between magnetite and ulvospinel by

quenching, but terrestrial minerals containing more than 80 mole per cent ulvospinel are rare in nature. Slower cooling rates result in the exsolution of ulvospinel or the contemporaneous oxidation-exsolution of ilmenite as described in section 4.5. The low-temperature solid solution limits of magnetite in ilmenite and *vice versa* are negligable, while those of magnetite and ulvospinel have not been firmly established. Values of 20 mole per cent Fe_3O_4 in ulvospinel and approximately 6 per cent Fe_2TiO_4 in magnetite given by Basta (1960) represent the most recent estimate.

The titaniferous magnetites are extremely sensitive to changes in oxygen fugacity and temperature during cooling and these features are reflected in the wide range of microstructures that are developed. These microstructures consequently contain a detailed record of the cooling history of their host rocks and represent an important key to the petrogenesis of the rocks concerned. The conditions and mechanisms involved in the formation of these exsolution bodies are too imperfectly understood at present for more than their qualitative use as petrogenetic indicators. More detailed studies might, however, result in the quantitative application of this microstructural evidence to petrogenetic studies as envisaged by Bowles (1977).

This literature survey indicates the need for a detailed examination of the sub-solidus phase relationships in the magnetite-ulvospinel system under suitable buffered hydrothermal conditions and for the compilation of an accurate phase diagram. The complex oxidation/exsolution process requires investigation and this should be extended to cover the various exsolution mechanisms operating in this system. These studies should provide additional information that would be of use not only in understanding the phase relationships, but would have important applications in

petrogenetic studies. The effects of both major and minor impurity
ions also have to be evaluated in order that the available data can
be applied to natural mineral systems.

A vast amount of data has accumulated on the titaniferous magnetites
during the past 50 years, but it is only really since the pioneering
work of Lindsley (1962, 1963), and Buddington and Lindsley (1964) that
their nature and behaviour has been appreciated. The basic ground-
work has been completed, but a great deal of detailed study on both
natural and synthetic systems is required before the mineralogical
relationships are fully understood.

4.8 The Orthorhombic Pseudobrookite-Ferropseudobrookite Series.
Complete solid solution exists between Fe_2TiO_5 (pseudobrookite) and
$FeTi_2O_5$ (ferropseudobrookite) at temperatures above $1150^{\circ}C$ (Akimoto
et al., 1957b; Haggerty and Lindsley, 1969). Ferropseudobrookite
decomposes to $FeTiO_3$ + TiO_2 at $1140^{\circ} \pm 10^{\circ}C$ on slow cooling and
pseudobrookite breaks down to yield Fe_2O_3 + TiO_2 at $585^{\circ} \pm 10^{\circ}C$
(Haggerty and Lindsley, 1969). The intermediate members decompose at
temperatures between 700° and $800^{\circ}C$, but the decomposition curve is
not linear between the end members.

Members of the pseudobrookite solid solution series are typically found
as high temperature oxidation products of titanomagnetite and ilmenite
in igneous rocks (usually lavas) (Haggerty and Lindsley, 1969). Min-
erals of Fe_2TiO_5-$FeTi_2O_5$ solid solution series were not encountered
during this study and their phase relationships are not discussed.
Readers requiring additional information are directed to the articles
by Akimoto et al. (1957b), Lindsley (1965b), Wilson and Haggerty (1966),

Watkins and Haggerty (1967), Haggerty (1971a), Johnson et al. (1971),
Lipin and Muan (1974), and Navrotsky (1975b).

5. SOLID SOLUTION BETWEEN THE IRON-TITANIUM OXIDES AND OTHER RELATED SYSTEMS.

5.1 Introduction.

Chemical analyses of the iron-titanium oxides invariably indicate the
presence of small, but variable amounts of elements other than Fe and
Ti (e.g. the analyses of various Fe-Ti oxides presented in Deer et al.,
1962b). These additional elements are normally only minor constituents,
but they can occasionally become major components of the mineral in
question. These analyses indicate that a wide range of ionic sub-
stitutions is possible in the various Fe-Ti oxides and that extensive
solid solution exist between them and certain other related mineral
systems. A detailed consideration of the factors governing ionic
substitutions in minerals is beyond the scope of this review and only
the major features are outlined here. Readers requiring additional
information are directed to the references mentioned in section 5.2.

5.2 The Features Governing Ionic Substitution in the Iron-Titanium Oxides.

The factors governing ionic substitution in minerals are complex and
have not yet been fully determined. Goldschmidt (1937) presented a
set of empirical rules governing the distribution of elements in rocks
and minerals based largely on ionic radius and electronic charge.
Wilson (1953) demonstrated that Goldschmidt's rules could be used to
explain many of the ionic substitutions observed in the iron-titanium
oxides as well as their order of crystallisation from magmas. He
concluded that extensive ionic substitution would occur if the ionic
radii of the elements did not differ by more than 15 per cent. Sub-
stitution of elements with ionic radii differing by more than 15 per

cent could take place, but only at elevated temperatures.

Further investigations led to the recognition of numerous cases in which Goldschmidt's rules did not hold and various modifications were made. Among the more important contributions was that made by Ringwood (1955) who recognised that the electronegativity of the ions is also an important factor governing their distribution and substitution properties. Lister (1966) reviewed the available literature and concluded that the amount of cationic substitution in the iron-titanium oxides is largely governed by the following factors:

1). The crystallisation temperature of the oxides.

2). The amounts of suitable cations available in the medium from which the minerals are precipitated.

3). The relative electronegativity of the cations.

4). The size and charge of the ions relative to the iron and titanium ions.

5). The oxygen fugacity during and after crystallisation.

6). The structure of the minerals being formed.

7). The cooling history.

Burns (1970) published an extensive criticism of the application of Goldschmidt's and Ringwood's rules to the distribution of elements in minerals and noted the existence of numerous exception to these rules. He proposed that the crystal field theory could be used more satisfactorily to explain the observed element distribution, particularly in the more complex silicates. He also demonstrated that the distribution of transition elements in minerals is governed by their octahedral site preference energies. Both the rhombohedral and cubic iron-titanium oxides contain octahedral sites in their crystal structures with the result that the octahedral site preference energy will also be an import-

ant factor governing ionic substitution in these minerals.

Ionic substitutions invariably take place in the same structural sites
in individual iron-titanium oxides with the result that ionic size,
charge and electronegativity would also exert some control on the sub-
stituting ion. Burns (1970) noted that the crystal field stabilisation
energy contributes less than 10 per cent to the total energy of a trans-
ition metal compound. He stated (1970, p. 112) "It cannot be assumed
that the crystal field energy is the sole determiner of cation distri-
bution in the spinel structure, but it evidently cannot be ignored".

It can be concluded that the ionic substitutional processes involved in
the iron-titanium oxides are complex and involve the interplay of num-
erous factors. The seven controls given by Lister (1966) are certainly
applicable to these ionic substitutions and it is possible to add a
further one, namely the octahedral site preference energy for the tran-
sition metal ions. The more important ionic substitutions in the Fe-Ti
oxides are discussed in sections 5.3 to 5.7.

5.3 The Ilmenite-Geikielite-Pyrophanite Series.

5.3.1 Introduction.

Ilmenite ($FeTiO_3$), geikielite ($MgTiO_3$) and pyrophanite ($MnTiO_3$) are
isostructural (Posnjak and Barth, 1934) with the result that consider-
able substitution of Mg^{2+} and Mn^{2+} for Fe^{2+} can theoretically occur in
natural ilmenites. In spite of this, however, ilmenites from a wide
variety of igneous rocks contain only minor amounts of Mg and Mn while
the two end-members are in fact extremely rare (Deer et al., 1962b).
Numerous electron microprobe analyses of ilmenites have been published
since the data compilation of Deer et al. (1962b), but their conclusion
that these minerals normally only contain minor Mn and Mg remains valid.

5.3.2 <u>The MnO content of ilmenite and its distribution between co-</u>
<u>existing ilmenite and titaniferous magnetite.</u>

Only limited experimental data are available on the solid solution re-
lationships between $FeTiO_3$ and $MnTiO_3$, but it is usually assumed that
extensive substitution of Mn^{2+} for Fe^{2+} can occur (Deer et al., 1962b).
Grey et al. (1974) reported that complete miscibility exists between
$MnTiO_3$ and $FeTiO_3$ at $1200^\circ C$. The ilmenite-pyrophanite solid solutions
appear to be stable at low temperatures and no exsolution features have
been reported. Ilmenite forms a complete high temperature solid solu-
tion with Fe_2O_3, but Ishikawa and Akimoto (1958) reported the presence
of a miscibility gap between pyrophanite and hematite over the composi-
tional range between 40 and 60 mole per cent pyrophanite.

Naturally occuring, optically homogeneous, intermediate members of the
ilmenite-pyrophanite solid solution series have been reported over the
whole compositional range as shown in Table 1. These analyses are all
of ilmenites from igneous rocks, but it should be noted that ilmenites
with values of MnO greater than 5 per cent are relatively rare. This
rarity does not reflect any bias in the selection of analyses, but
appears to be a common feature of this solid solution series.

The first investigation into the MnO contents of ilmenites and their
significance was undertaken by Buddington (1964) who noted that the
amount of MnO in igneous rocks decreases from gabbroic through to
granitic types. The MnO contents of the silicate and oxide minerals
in contrast, increase over this compositional range because of the
decrease in the quantity of mafic minerals in these rock types that
can accommodate the MnO. He also reported that the MnO is preferent-
ially incorporated into the ilmenite rather than into the co-existing
titaniferous magnetite.

TABLE 1

SELECTED ANALYSES OF MANGANOAN ILMENITES

OXIDE	1	2	3	4	5	6	7	8	9	10	11	12	13	14
TiO_2	52,65	48,79	47,77	52,00	47,90	52,02	49,10	51,60	52,97	48,17	51,06	52,86	51,50	52,97
FeO	47,35	38,83	37,65	40,40	31,15	33,05	29,34	31,40	26,29	22,38	17,14	16,25	6,60	–
MgO	–	1,60	0,13	0,04	0,03	–	0,03	0,01	0,07	0,10	0,07	0,07	–	–
MnO	–	2,16	5,01	6,94	10,80	12,77	14,70	17,20	19,83	20,49	28,43	30,20	41,00	47,03
Fe_2O_3	–	7,94	9,90	–	8,94	–	5,51	–	0,00	8,32	2,69	0,00	–	–
Al_2O_3	–	0,00	0,00	0,04	0,00	0,36	0,00	–	0,00	0,00	0,00	0,00	–	–
TOTAL :	100,00	99,32	100,46	99,42	99,82	98,20	98,68	100.21	99,16	99,46	99,39	99,38	99,10	100.00

Sources of analyses and the nature of their host rocks

1. Theoretical ilmenite

14. Theoretical pyrophanite.

2,3,9,10,11,12. Olivine monzodiorite to granite (Neumann,1974)

4,8. Adamellite. (Tsusue, 1973)

5,7. Granodiorite. (Czamanske and Mihalik, 1972).

6. Granite (Elsdon, 1975b).

13. Nepheline syenite pegmatite (Neumann and Bergstol, 1964).

Buddington(1964) summarised the situation as follows: "the data show that there is in general a successive systematic increase in the ratio of MnO in ilmenite to MnO in the titaniferous magnetite of igneous rocks from a low in diabase and gabbro through intermediate values for pyroxene, quartz-bearing syenite and granite to a high in granite pegmatite". He also reported that the MnO contents of ilmenites in metamorphosed igneous rocks are systematically higher than those in their unmetamorphosed equivalents. He concluded that this is due to the decrease in MnO of the co-existing titaniferous magnetites during recrystallisation.

Buddington (1964) concluded that the increasing MnO content of ilmenite is related to a decrease in the temperature of crystallisation and that the distribution of MnO between co-existing ilmenite and titaniferous magnetite is also temperature dependent. He also noted that oxygen fugacity might also play an important role in controlling the MnO distribution, but mentioned that Mn^{2+} is stable over a much wider range of oxygen fugacities than Fe^{2+}. On this basis he concluded that temperature is a more important controlling factor than fO_2.

Anderson (1968b) reported that a fair correlation exists of the distribution of MnO between ilmenite and titaniferous magnetite in the LaBlache Lake Deposit and the minimum oxidation temperature. He suggested that this relationship is, however, fortuitous and could be explained by the fractionation law. He concluded that Fe_2TiO_4 would be oxidised at a lower oxygen fugacity than Mn_2TiO_4 with the result that fractional oxidation of a manganese-bearing titaniferous magnetite would lead to an enrichment in MnO in the unoxidised magnetite.

Snetsinger (1969) described manganese-rich ilmenites (up to 14,4% MnO) from an adamellite and concluded that their formation is associated with

later-stage magmatic processes. He suggested that the larger size of the Mn^{2+} ion (0,80 Å) relative to Fe^{2+} (0,74 Å) and Mg^{2+} (0,66 Å) would result in its concentration in the later, more silicic residual liquids according to Goldschmidt's rules. This manganese becomes incorporated into the late-stage ilmenite in the absence of sufficient Fe^{2+}.

Evans and Moore (1968) reported that the MnO contents of ilmenite lamellae in titaniferous magnetites of the Makaopuhi basaltic lava lake are systematically higher than those of the co-existing coarse grained ilmenites. They concluded that this is consistent with the changing distribution of Mn between co-existing ilmenite and magnetite with decreasing temperature. Smith (1970) noted a similar relationship in the opaque oxides of a diabase sill and reported that the Mn contents increase towards the margins of the ilmenite lamellae, reaching their maximum values at the contact. These values fall noticeably on passing into the magnetite host and remain much lower than the corresponding values in the lamellae. Smith (1970) concluded that these compositional gradients built up during exsolution, but became "frozen in" as the temperature dropped.

Dasgupta (1970) reviewed the available data on MnO distribution between co-existing ilmenite and magnetite. He was unable to show any clear relationship between the temperatures and oxygen fugacities and the distribution of MnO between the co-existing cubic and rhombohedral phases. He concluded that the MnO distribution is, however, a reflection of its temperature dependence.

Lipman (1971) reported the preferential incorporation of Mn into ilmenite co-existing with titaniferous magnetite in a series of volcanic rocks ranging from quartz latites to rhyolites. The MnO contents of

these minerals are unusually high, ranging from 1,29 to 4,65 per cent in the magnetite and between 1,55 and 8,97 per cent in ilmenite. He also demonstrated that increasing Mn content in both minerals is related to decreasing temperatures of crystallisation from approximately $950^{\circ}C$ in the quartz latite to $650^{\circ}C$ in the rhyolites. He also noted that MnO contents of ilmenite lamellae are higher than those of the co-existing ilmenites.

Czamanske and Mihalik (1972) reported the strong enrichment of MnO in ilmenite relative to co-existing titaniferous magnetite with increasing oxidation in the Finnmarka Complex. They noted that enrichment of Mn relative to Fe in ilmenites occurred progressively in the more silicic rock units that crystallised under high oxygen fugacities. They concluded that the Fe^{2+} is more readily oxidised out of the ilmenite structure than Mn^{2+} and postulated that oxidation and subsequent extraction of Fe^{2+} from the ilmenites would be reflected in the Mn-enrichment of a steadily decreasing amount of ilmenite in the succeeding differentiates.

Czamanske and Mihalik (1972) also explained the preferential fractionation of MnO into co-existing ilmenite on crystal chemical grounds and noted the following pertinent features in support of their model:

1). Complete solid solution exists between Mn_3O_4 and Fe_3O_4 above $1160^{\circ}C$, but is reduced to 46 mole per cent Fe_3O_4 and 54 per cent Mn_3O_4 at room temperature (Mason, 1943; van Hook and Keith, 1958).

2). Fe_3O_4 has a cubic, inverse spinel structure in which Fe^{3+} occupies the tetrahedral sites while Fe^{3+} and Fe^{2+} share the octahedral sites.

3). Mn_3O_4 is tetragonal, but inverts to the spinel structure at elevated temperatures.

4). $FeTiO_3$ and $MnTiO_3$ are both rhombohedral and contain only octahedral

cation sites in which the equivalent (Mn, Fe) and Ti sites are
ordered into like-atom layers.

5). They used the following ionic radii for octahedral co-ordination
from Whittaker and Muntus (1970): $Fe^{2+} = 0,86$ Å; $Fe^{3+} = 0,73$ Å;
$Mn^{2+} = 0,91$ Å;   and $Ti^{4+} = 0,69$ Å.   They also used the radius of
$Fe^{3+} = 0,57$ Å and $Mn^{2+} = 0,75$ Å for tetrahedral co-ordination.

6). Fe^{3+} and Mn^{2+} both have identical electron configurations with 5
electrons in their 3d orbitals and 0,0 crystal field stabilisation
energy in either the octahedral or tetrahedral sites.

7). Fe^{2+} has a relatively low crystal field stabilisation energy and an
octahedral site preference energy of 4,0 kcal/mole.

8). The octahedral site preference energy of Fe^{2+} is of greater signi-
ficance in the spinels since Fe_3O_4 is an inverse spinel while
$MnFe_2O_4$ is a near normal spinel with Mn^{2+} occupying 81 per cent of
its octahedral sites (Hastings and Corliss, 1956).

Czamanske and Mihalik (1972) noted that although extensive solid solu-
tion is possible in the series Mn_3O_4-Fe_3O_4 and $MnFe_2O_4$-Fe_3O_4, the diff-
erences in crystal symmetry and spinel type must reflect a less ideal
solid solution for these series than for $MnTiO_3$-$FeTiO_3$.   The result
of this is that the Mn exhibits a preference for a phase with a rhombo-
hedral structure and will partition into this phase when conditions
are favourable.   They reported a written communication by C.O.Hutton
who suggested that the larger Mn^{2+} ion might be more readily substituted
in the ilmenite structure because the symmetry elements require only
one plane of metal ion close-packing.   The spinel structure of magnetite,
in contrast, requires that four distinct planes of metal ion close-pack-
ing be maintained.   Czamanske and Mihalik (1972) concluded that the
dominant control is one of relative ionic radii constrained by the

preference of Fe^{2+} for octahedral co-ordination. They also noted that if the Mn^{2+} must dominantly occupy tetrahedral sites in the magnetite structure, the resulting mismatch between Fe^{3+} (0,57 Å) and Mn^{2+} (approximately 0,75 Å) would disrupt the magnetite structure. The Mn^{2+} would consequently be incorporated into the ilmenite structure where the metals are in octahedral co-ordination and have similar ionic radii (Fe^{2+} = 0,86 Å; Mn^{2+} = 0,91 Å).

Duchesne (1972) also reported the preferential enrichment of MnO in ilmenite relative to co-existing titaniferous magnetite from an anortho-site-mangerite suite and noted that the Mn^{2+}/Fe^{2+} ratio in ilmenites increases as differentiation proceeds. He concluded that the MnO distribution between co-existing ilmenite and magnetite is temperature dependent and that the distribution factor is exponential rather than linear as suggested by Anderson (1968b).

Prins (1972) reported the presence of higher MnO contents in ilmenites co-existing with titaniferous magnetites in carbonatites. He noted that MnO is strongly enriched in ilmenite lamellae in titaniferous magnetite. Elsdon (1972) also reported increased MnO contents in ilmenites from the upper layered series of the Kap Edvard Holm Intrusion and noted that the manganese distribution might be a function of equi-libration temperature. He also mentioned that the MnO distribution might be related to fractional oxidation since Fe_2TiO_4 is oxidised at lower oxygen fugacity or increasing temperature. He noted that his data might support a slight fractionation of MnO into magnetite with increasing temperature.

Tsusue (1973) described the occurrence of manganoan ilmenites from granitic rocks in Japan. He noted that the MnO content of the ilmenite

increases with an increase in the differentiation index (normative Q
+ or + ab + ne + lc + ks) of the host rocks while the actual amount
of ilmenite present tends to decrease with an increase in the same index.
He also reported that some of the ilmenite grains are compositionally
zoned and that their Mn/Fe ratio increases regularly from the core
outwards.

Neumann (1974) reviewed the available data on the distribution of Mn^{2+}
and Fe^{2+} between ilmenites and magnetites in igneous rocks and investi-
gated this phenomenon in a suite of rocks ranging from olivine mon-
zodiorite to granite. She noted the following features that are a
common feature of these minerals:

1). Ilmenites in silicic rocks are often strongly enriched in manganese
    compared to their co-existing magnetites.

2). The concentration of MnO in ilmenites often differs markedly from
    grain to grain within single samples of silicic rock even though
    each grain is homogeneous.

3). Exsolution lamellae of ilmenite in magnetite are generally richer
    in MnO than separate co-existing ilmenite grains with the result
    that the magnetite host is depleted in MnO relative to the assumed
    original homogeneous magnetite.

4). There is a definite relationship between the Mn/Fe^{2+} ratio in
    ilmenites and the same ratio in their host rocks.

5). The Mn/Fe^{2+} ratio in the ilmenites increases with increasing differ-
    entiation index of their host rocks.

6). There is no clear relationship between the Mn/Fe^{2+} ratio in what
    is assumed to be the original homogeneous magnetite composition
    and the Mn/Fe^{2+} ratio of the host rocks.

Neumann (1974) based her investigation into the MnO distribution on a

method described by Jensen (1973) who plotted the partition coefficients
for certain minerals/rocks against their ionic radii in various silicates
(Onuma diagrams). Jensen (1973) demonstrated that elements of the
same valency fall on a fairly simple curve and that the different val-
ency curves for one mineral all peak at the same point or points against
ionic radii. She concluded that these peaks define the optimum size
of the cations entering a certain structure and that the optimum size
of a structural position is determined by the silicate or oxygen frame-
work. The valency and effective size of the cations competing for a
structural position are consequently the dominant factor in determin-
ing the partioning of elements beween co-existing phases. The peak
positions remain constant, irrespective of the nature of the ions sub-
stituting in the mineral structure.

Neumann (1974) plotted the partition coefficients (ilmenite/rock)
against the ionic radii for divalent elements for 6 ilmenites (2 of
her own, 2 from the Skaergaard Complex (Williams, 1971) and 2 manganoan
ilmenites (Tsusue, 1973)) and demonstrated that the apex of the peaks
fall between 0,89 and 0,90 Å. She noted that the peaks might, however,
be slightly low due to uncertainties in the Mn^{2+} plot. She concluded
that the Mn^{2+} ionic radius of 0,91 Å would fit into the available
octahedral site better than Fe^{2+} (0,86 Å) and is consequently preferent-
ially incorporated into that structure.

Neumann (1974 noted that the peak heights and slope curves in her plots
increase with increasing differentiation index and/or decreasing temp-
erature. She concluded that this indicates that the Mn preference
increases strongly with decreasing temperature. She also noted that
the increasing Mn content towards grain boundaries in zoned ilmenites
indicates that the preference for Mn^{2+} over Fe^{2+} increases with de-

creasing temperature. The increase in MnO/FeO ratio in the host rocks might be due to the preferential incorporation of Fe^{2+} in other cryst-allising minerals.

Neumann (1974) reported that insufficient data were available to pro-duce similar curves for the titaniferous magnetites, but concluded that Mn fits more readily into the ilmenite structure than into magnetite at the conditions of formation of her analysed samples. She noted that her results are inconclusive in respect to the controls exerted by oxygen fugacity, but suggested that only very limited amounts of Mn_2O_3 would be able to enter into solution in ilmenite. She concluded that Mn^{3+} in tetrahderal co-ordination would have a radius between 0,58 and 0,59 Å which is only slightly larger than Fe^{3+} (0,57 Å) with the result that it can be readily **accomodated in the magnetite structure.** On these grounds she concluded that the amount of Mn^{3+} would increase in magnetite with increasing oxygen fugacity.

Neumann (1974) concluded that the $Mn^{2+}_{ilmenite}/Mn^{2+}_{magnetite}$ ratio will be higher for oxides crystallising at a given temperature and oxygen fugacity from a magma with a relatively high Mn^{2+}/Fe^{2+} ratio than for oxides crystallising from a magma with a lower Mn^{2+}/Fe^{2+} ratio. The $Mn^{2+}_{ilmenite}/Mn^{2+}_{magnetite}$ ratio would also increase more strongly with an increase in the Mn^{2+}/Fe^{2+} ratio in the magma at low temperatures than at high temperatures.

Mathison (1975) reported higher MnO contents in ilmenites co-existing with titaniferous magnetites in the Somerset Dam Layered Intrusion. He noted that the Mn content decreases in magnetite from the base to the top of a zone whereas it increases in the co-existing ilmenite. He demonstrated that the MnO content of secondary ilmenite (derived by

oxidation/exsolution) is higher than that in the primary ilmenite.
He also examined the Mn distribution between titaniferous magnetites
and the contact with a large ilmenite lamella by means of electron
microprobe analyses. The Mn content exhibits a steady decrease in the
magnetite towards the ilmenite contact and a depletion zone is developed
immediately adjacent to the ilmenite interface. The Mn content reaches
a maximum in the ilmenite at the magnetite interface and then decreases
towards the centre of the ilmenite lamella. He reported that the
concentration gradients are steepest in a 20-30 micrometre wide zone
parallel to the ilmenite-magnetite contact. He concluded that this
distribution is a result of oxidation of the magnetite and reflects
the different preferences of this element for the two phases. He
also concluded that the concentration gradients are caused by the
homogenisation processes becoming increasingly difficult during progressive
oxidation.

Elsdon (1975b) described manganoan ilmenites from a granite and noted
that their occurrence could not be satisfactorily explained on the
basis of late-stage manganese-enrichment or as a result of oxidising
conditions during crystallisation or the post-crystallisation history.

Himmelberg and Ford (1977) also reported that the MnO contents of the
ilmenites are greater than those of their co-existing titaniferous
magnetites in the Dufek Intrusion. They furthermore demonstrated
that the highest MnO contents are shown by the ilmenite lamellae in the
titaniferous magnetites. They refer to a written communication by
D.H. Lindsley and state "the manganese content of successive generations
of ferrian ilmenite is consistent with the experimentally-determined
distribution of MnO between magnetite and ilmenite with decreasing

temperature, and suggests that each generation of ferrian ilmenite was closed and did not re-equilibrate during later stages".

Bohlen and Essene (1977) and Bowles (1977) also reported higher MnO contents in ilmenites relative to their co-existing titaniferous magnetites. They also reported higher MnO contents in the ilmenite lamellae than in the larger co-existing ilmenite grains. These authors offered no explanation for the phenomenon.

5.3.3 The MgO content of ilmenite and its distribution between co-existing ilmenite and titaniferous magnetite.

Ilmenite and geikielite form a complete solid solution series above $1300^{\circ}C$ (Johnson et al., 1971) and also above $1160^{\circ}C$ (Speidel, 1970).

The ilmenite-geikielite solid solutions appear to be stable at low temperatures and no exsolution features have been reported (Cervelle, 1967; Cervelle et al., 1971). Ilmenite forms a complete high temperature solid solution with Fe_2O_3, but Ishikawa and Akimoto (1958) reported the presence of a miscibility gap over the compositional range between 50 and 80 mole per cent $MgTiO_3$. Woermann et al. (1969) also noted the presence of a gap in the solid solution series in this range and reported that it breaks down to yield spinel plus pseudobrookite. They concluded that two rhombohedral solid solutions (ilmenite-geikielite) and hematite would probably co-exist in equilibrium at temperatures below approximately $700^{\circ}C$. The presence of this gap in the solid solution series has been noted by Speidel (1970) at $1160^{\circ}C$ and by Johnson et al. (1971) under higher temperature conditions.

Naturally occurring, optically homogeneous, intermediate members of the ilmenite-geikielite solid solutions have been reported over the whole compositional range as depicted in Table 2. Analyses of ilmenites from the usual range of igneous rocks commonly show the presence of less

TABLE 2

SELECTED ANALYSES OF MAGNESIAN ILMENITES

OXIDE	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
TiO_2	47,92	52,20	53,10	51,90	52,29	49,48	51,75	54,61	55,90	56,40	57,52	60,70	64,61	64,9	66,46
FeO	39,76	41,00	40,10	36,45	33,77	28,72	26,40	21,79	16,59	19,90	12,30	8,40	5,68	1,4	–
MgO	2,00	3,30	4,32	5,76	7,07	8,72	11,16	15,14	18,86	20,23	21,57	24,40	27,90	31,8	33,54
MnO	1,13	–	–	–	0,59	–	–	–	–	0,52	1,27	0,91	–	0,4	–
Fe_2O_3	8,33	1,68	1,11	6,39	6,07	11,68	8,82	5,30	6,78	1,91	2,82	6,20	2,50	–	–
Al_2O_3	0,60	0,77	0,26	0,02	0,13	0,18	0,38	0,34	0,25	0,30	1,22	–	–	1,3	–
Cr_2O_3	0,11	0,05	–	0,05	0,17	0,92	0,40	2,05	0,49	1,13	0,65	–	–	–	–
TOTAL :	99,85	99,00	98,89	100,57	100,09	99,70	98,91	99,23	98,87	100,39	97,35	100,61	100,69	99,8	100,00

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Sources of analyses and the nature of their host rocks

1. Troctolite (Mathison, 1975)

2. Nepheline hawaiite (Wass,1973)

3,4. Alkali olivine basalt (Wass,1973)

5. Titaniferous iron ore, Kaffirskraal Complex (this thesis)

10. Kimb rlite (Haggerty, 1973b)

11. Serpentinite (Efremov, 1954)

12. Magnesium Marble (Hounslow and Chao, 1967)

13. Gem gravels, Ceylon (Crook and Jones, 1906).

14. Magnesian marble (Murdoch and Fahey, 1949).

15. Theoretical geikielite.

than 4 per cent MgO (Thompson, 1976) although this may occasionally reach as high as 6 per cent (Wass, 1973). Anderson (1968a) has reported values up to 10 per cent in ferrian ilmenites intergrown with titaniferous magnetites in trachybasalts. Ilmenites from kimberlites typically contain between 8 and 20 per cent MgO and these features are discussed more fully in Part 2 of this thesis. Ilmenites exhibiting higher MgO contents are extremely rare and have only been reported from Mg-rich marbles or serpentinites (analyses 11-14, Table 2).

Sahama and Torgeson (1949) investigated the stability of ilmenite and geikielite in rocks and concluded that geikielite in association with olivine or orthopyroxene represents a high temperature paragenesis. They noted that ilmenite is, however, more common since the Mg/Fe ratios in most rocks favour the formation of ilmenite under the prevailing crystallisation temperatures. They suggested that Mg-rich ilmenites might be more common in dunitic or peridotitic rocks than previously recognised.

Chemical analyses indicate a preferential partitioning of Mg into the ilmenite rather than the co-existing magnetite, but this feature has not been studied in as much detail as the MnO distribution. The first systematic study of minor element variations in co-existing ilmenites and titaniferous magnetites was undertaken by Vincent and Phillips (1954) on the Skaergaard Complex. They noted the MgO contents are consistently higher in the ilmenites than their co-existing titaniferous magnetites. They also noted that there is an overall decrease in MgO contents in both of these phases with increasing height in the complex.

The preferential incorporation of Mg into ilmenites co-existing with titaniferous magnetites from a wide range of igneous rocks was also reported by Carmichael (1967a, b). Anderson (1968b) also reported similar partitioning of MgO between co-existing cubic and rhombohedral phases in the LaBlache Lake Deposit.

Smith (1970) reported higher MgO contents in coarse grained ilmenite than in titaniferous magnetites from a diabase sill. He also noted that the MgO contents of both phases decrease with progressive crystallisation and that the ilmenite lamellae in the titaniferous magnetites contained more MgO than their corresponding coarse-grained ilmenites. He presented data on a one micrometre-step microprobe traverse across a portion of a titaniferous magnetite grain containing a broad ilmenite lamella. These data showed that the Mg content of the magnetite is low, but decreases towards the ilmenite interface where it increases dramatically. It continues to increase, but less steeply over the first 20 micrometres of the ilmenite after which its content increases less markedly until the maximum value is obtained at the centre of the lamella.

Lipman (1971) reported higher MgO values in ilmenites co-existing with titaniferous magnetites in a variety of rocks ranging from quartz latites to rhyolites. He indicated that the ilmenite lamellae in the co-existing titaniferous magnetites contain the highest MgO contents. Essentially similar relationships have been reported for MgO distribution between co-existing cubic and rhombohedral phases by Wass (1973), Mathison (1975), Bowles (1976, 1977), and Himmelberg and Ford (1977). This behaviour is essentially the same as that of MnO and appears to be a typical feature of these co-existing oxides.

Lovering and Widdowson (1968) reviewed the available data on the MgO contents of ilmenites from a variety of rock types and demonstrated a crude relationship between this and the MgO/FeO ratios of their host rocks. They concluded that this distribution is not influenced markedly by temperature and pressure conditions. Mitchell (1973) noted a variation of between 6 and 19 per cent MgO in kimberlitic ilmenites and concluded that this ilmenite crystallised from melts unusually rich in Ti and Mg.

Speidel and Osborn (1967) investigated the phase relationships in the $MgO-FeO-Fe_2O_3-SiO_2$ system and noted that the composition of olivine, pyroxene and magnesioferrite (spinel) in equilibrium with vapour at sub-solidus temperatures changes as a function of temperature and oxygen fugacity. They concluded that the Mg/Fe ratio would increase in olivine, and also to a lesser extent in orthopyroxene, but would simultaneously decrease in magnetite.

Speidel (1970) extended these experiments to include TiO_2 and noted that the MgO content is higher in the spinel phase than the co-existing rhombohedral one at high temperatures and moderately high oxygen fugacities. He demonstrated that this relationship is, however, reversed at lower oxygen fugacities and corresponds to the situation in naturally occurring minerals. He also suggested that the presence of minor Al, V and Mn might also be important in controlling the partitioning of Mg between co-existing phases.

Haggerty (1972a, b, 1973a) reported the presence of Mg-rich ilmenites in lunar materials returned by Luna 16 and Luna 20. Hagerty (1973a) concluded that the high MgO contents of certain lunar ilmenites are due to crystallisation from an ultrabasic liquid under high pressures.

Brett et al. (1973) reported the presence of up to 8,1 per cent MgO in lunar ilmenites and suggested that they may have formed by early precipitation from a melt relatively rich in TiO_2, or by later crystallisation from a melt rich in MgO. Nehru et al. (1974) also reported high MgO values in certain lunar ilmenites and noted that the MgO content of the ilmenite increases with increasing Mg/(Mg + Fe) in the bulk rock. They concluded that the MgO content of the ilmenite is controlled by the composition of the magma from which it crystallised rather than by high pressure. Haggerty (1975) described a variety of MgO-rich ilmenites from kimberlites and concluded that the MgO content is related to high pressure during crystallisation.

Wass (1973 noted that the high MgO contents (2-6%) of ilmenites from basalts of low-pressure origin are related to the high MgO/FeO ratios of their parent magma. She noted that the lower MgO contents of the co-existing titaniferous magnetites might be due to restriction by a partitioning factor with the associated ilmenite. She reported that the high MgO content of megacryst spinel phases of high pressure origin would, however, imply that pressure favours the introduction of Mg into the spinel lattice.

Studies of lunar ilmenites by Steele (1974) and Nehru et al. (1974) have shown that a systematic relationship exists between their MgO/FeO ratios, those of their co-existing minerals and their host rocks. Smith and Steele (1976) reviewed the available data on lunar mineralogy and concluded that the Mg/Fe ratios of the ilmenites increases with an increase in the Mg/Fe ratios of their host rock. They also noted that Mg is transferred to the ilmenites from the co-existing silicates with increasing temperature.

Mathison (1975) reported the preferential incorporation of Mg into ilmenite co-existing with titaniferous magnetite in the Somerset Dam Intrusion and noted that the intergrown ilmenite lamellae contained the highest concentrations of this element. He concluded that a redistribution of Mg must occur during the oxidation of magnetite due to the different preferences of the two phases for this element.

Green and Sobolev (1975) synthesised ilmenites at temperatures between 900° and 1100°C under pressure conditions that varied from 21 to 40 kb. They used an olivine basanite and a pyrolite (less 40 per cent olivine) with variable water contents as their starting materials. They reported that the synthesised ilmenites display compositions similar to those in kimberlites and have distinctive ranges of Mg and Cr when produced from the two parent materials. They also demonstrated that the Mg/Fe ratios of the crystallised ilmenites vary systematically with temperature and display a constant relationship to the Mg/Fe ratios of the co-existing garnets.

Thompson (1976) investigated the chemistry of ilmenites crystallised within the anhydrous melting range of tholeiitic andesite at pressures between 5 and 26 kb and noted variations in their MgO contents. He demonstrated that the MgO contents of the crystallised ilmenites are not related to either their temperatures or pressures of formation. He noted that the $Mg/(Mg + Fe^{2+})$ ratios of the ilmenites decrease during equilibrium crystallisation at a given temperature and concluded that this behaviour is controlled solely by the Mg/Fe^{2+} distribution between co-existing ferromagnesium minerals and the interstitial liquid.

Mitchell (1977) examined the geochemistry of magnesian ilmenites from kimberlites in more detail and concluded that their differing Fe/Mg

ratios do not reflect large Fe/Mg **variations in the liquid.** He suggested that this variation might be due to the change in some other parameter such as temperature , oxygen fugacity or silica activity.

No attempt has been made to interpret the distribution of Mg between co-existing ilmenite and magnetite in terms of crystal chemistry as has been done in the case of Mn. The Mg content of magnetite is variable and the experimental results of Speidel (1970) indicate that this content will decrease on cooling. The data of Speidel and Osborn (1967) indicate that oxygen fugacity might play an important role, while a number of authors note that the Mg/Fe^{2+} ratios of the original liquid might also be important.

Magnesium is not only present in the ilmenite associated with titaniferous magnetite, but also in a wide variety of transparent spinel intergrowths (see next section) with the result that the sub-solidus partitioning of Mg between co-existing rhombohedral, cubic and silicate phases is probably more complex than is the case for Mn.

Complete solid solution exists between $MgFe_2O_4$ (magnesioferrite) and magnetite at temperatures above $160^{o}C$ (Muan and Osborn, 1956; Speidel, 1967; Speidel and Osborn, 1967). Deer et al. (1962b) noted that extensive replacement of Mg by Fe^{2+} can occur in this system. Both magnetite and magnesioferrite exhibit the inverse spinel structure (Barth and Posnjak, 1932) with the result that substitution of Mg for Fe^{2+} occurs in the octahedral sites (Verwey and Heilmann, 1947). The cation sites in the ilmenite structure are all octahedrally co-ordinated with the result that the substitution of Mg^{2+} for Fe^{2+} will also occur in this position in the ilmenite-

geikielite series.

The Onuma diagram of Neumann (1974, p. 1085) indicates that the size of the octahedral site in ilmenite is approximately 0,895 Å. The size of the corresponding site in magnetite is not known and cannot be accurately determined from the available data (Neumann, 1974). The ionic radius for Mg^{2+} in octahedral co-ordination is given as 0,80 Å by Whittaker and Muntus (1970) which implies that Fe^{2+} would fit into the ilmenite structure more readily than Mg^{2+}. The size of the octahedral site in the magnetite structure is uncertain, but by analogy with the behaviour of Mn (Neumann, 1974), the Mg^{2+} might be less well accomodated at lower temperatures on account of its smaller size. This Mg^{2+} is subsequently expelled into the co-existing ilmenite and other spinel phases on slow cooling. This mechanism is supported by the experimental data of Speidel (1970).

5.3.4 Discussion.

Virtually no information is available on the solid solution relationships between geikielite and pyrophanite and there are no published analyses of intermediate members in this series. The analyses in Tables 1 and 2 indicate an almost antipathetic relationship between Mg and Mn in ilmenites. This is easily understood in terms of the fractional crystallisation of magma in which these two elements are often mutually exclusive since the early formed mafic minerals are enriched in MgO whereas the later formed crystals are relatively depleted in Mg, but may show an increased Mn content.

This feature is clearly demonstrated by ilmenites from rocks ranging in composition from gabbroic through to granite types as shown by Buddington (1964). This is also reflected in the crystallisation

trends of co-existing ilmenites and titaniferous magnetites that exhibit decreasing MgO and increasing MnO values with the increasing stages of differentiation of their host rocks.

Members of the ilmenite-pyrophanite solid solution series appear more common than those of the ilmenite-geikielite series (excluding kimberlites) and this might also, in part, reflect the smaller differences in ionic size between Mn^{2+} and Fe^{2+}. The smaller size of Mg^{2+} might be an important factor in its incorporation in ilmenites formed under high pressure conditions as for expample in the typically Mg-rich kimberlitic ilmenites. The Mg-content of titaniferous magnetites is discussed further in the following section.

5.3.5 Conclusions.

Complete solid solution is theoretically possible between ilmenite-geikielite-pyrophanite, but naturally occurring ilmenites from igneous rocks that contain more than 6 per cent MgO and 5 per cent MnO are rare. Kimberlitic ilmenites typically contain between 8 and 20 per cent MgO. Magnesium and manganese also apear to exhibit an antipathetic relationship in that high Mg-ilmenites are generally low in Mn and vice versa.

Both Mg and Mn are enriched in ilmenites relative to their co-existing titaniferous magnetites. The Mn and Mg contents of ilmenite lamellae are generally higher than those of the associated coarse-grained ilmenites and are very much higher than those in their titaniferous magnetite hosts. These features indicate that considerable migration of Mg takes place from the titaniferous magnetite into the co-existing and "exsolving" ilmenite lamellae during sub-solidus cooling. This partitioning becomes more marked with falling temperature. Certain amounts of Mn^{2+} and Mg^{2+} may be accomodated in the spinel structure

at high temperatures, but these ions are expelled during sub-solidus cooling and become incorporated in the co-existing or "exsolving" rhombohedral phases. It also is possible that some migration of Fe^{2+} from the rhombohedral phase to the cubic phase might occur in order to maintain the stoichiometry of the phases. (Note that Johnson et al. (1971) report large departures from stoichiometry for all phases in the MgO-"FeO"-TiO_2 system).

The preferential incorporation of Mn into the rhombohedral phase rather than into the cubic phase has been explained in terms of crystal chemistry by Czamanske and Mihalik (1972) and Neumann (1974). There is also a large amount of data to support Buddington's (1964) hypothesis that the Mn distribution is a function of temperature. The MnO/ FeO ratios of the host rocks and relative abundance of opaque oxides together with other mafic minerals are also important controls, particularly in the more silicic rocks. Oxygen fugacity might also be an important factor, but its role remains to be thoroughly investigated.

The preferential incorporation of Mg into ilmenite rather than the co-existing titaniferous magnetite is not as easily explained as in the case of Mn. It is more difficult to account for on crystal chemical grounds in view of the larger difference in ionic radius between Fe^{2+} and Mg^{2+} in octahedral co-ordination, but certain analogies can be drawn between its behaviour and that of Mn. The low Mg values commonly reported for ilmenites and titaniferous magnetites in a wide range may be largely due to the preferential incorporation of this element into co-existing mafic silicate phases as suggested by the experimental data of Speidel and Osborn (1967) and Speidel (1970). The MgO/FeO ratios of the magma also influence the compositions of the oxide phases that crystallise from them.

The effect of pressure may be important in the formation of high Mg-ilmenites, particularly in kimberlites and associated mantle-derived nodules, but additional experimental data are required to clarify this point. The oxygen fugacity might also influence the amount of MgO partitioned into the ilmenite, since portion of it might be present in the form of Mg_2TiO_4. These features also require further investigation.

5.4 Ilmenite: Solid Solutions with Other Phases.

Ilmenite analyses normally show the presence of small, but variable amounts of other oxides, notably Al_2O_3, Cr_2O_3 and Nb_2O_3. The presence of smaller amounts of SiO_2, V_2O_3, CaO and ZrO_2 has also been reported. Limited experimental data are available on either the solubility of these phases, or the solubility of solid solutions containing these oxides, in ilmenite.

The highest Cr_2O_3 contents (up to 5,6%) and Al_2O_3 contents (up to 1,3%) have been reported from kimberlitic ilmenites (Haggerty, 1975). Ilmenites from slowly cooled basic intrusions also occasionally contain transparent Al_2O_3-rich spinel lamellae oriented parallel to their basal planes (Gierth and Krause, 1973; this thesis, Part 3). These intergrowths have also been reported in ilmenites from pegmatites (Mukherjee et al., 1972). Danchin and D'Orey (1972) and Haggerty (1975) reported that the solid solubility of Cr_2O_3 or Al_2O_3 in $FeTiO_3$ is small according to one-atmosphere experimental phase equilibria studies. Haggerty (1975) noted that a trivalent substitution of the type $Cr^{3+} \longrightarrow Fe^{3+}$ or $2Cr^{3+} \longrightarrow Fe^{2+} + Ti^{4+}$ might occur in the rhombohedral structure and that it might be pressure dependent. The possibility of pressure control and limited solubilities might account for the low Al_2O_3 and Cr_2O_3 reported for ilmenites from a wide range of igneous rocks (excluding

kimberlites). Al_2O_3 and Cr_2O_3 are preferentially incorporated into titaniferous magnetite relative to the co-existing ilmenite (Gjelsvik, 1957; Mathison, 1975).

Niobium is known to substitute in the ilmenite structure, but data are limited. Whitney and Stormer (1976) reported up to 4 per cent Nb_2O_3 in ilmenites from granites while Mitchell (1977) reported that kimberlite ilmenites are "unusually rich in Nb" (up to 6024 ppm). The presence of small amounts of Nb in granites and other late-stage differentiates can be ascribed to the concentration of this element in the late-stage crystallising phases. Mitchell (1977) reported that increasing Nb contents in kimberlite ilmenites "increase with increasing FeO and decreasing MgO and TiO_2 as might be expected if the nodules were formed by crystal-liquid differentiation".

Wet chemical analyses of V_2O_5 (often expressed as V_2O_3) indicate that it is preferentially incorporated into the cubic phase rather than into the co-existing ilmenite (e.g. Vincent and Phillips, 1954; Gjelsvik, 1957; Lister, 1966; Duchesne, 1972). The determination of vanadium in the presence of appreciable titanium by electron microprobe or x-ray fluorescence techniques is made difficult by the interference of the k-beta line of Ti with the k-alpha line of V. Analyses of V in the presence of Ti can, however, be made provided the necessary corrections are made (Carmichael, 1967a; Snetsinger et al., 1968; Cameron and Glover, 1973). Numerous microprobe analyses of V_2O_3 in co-existing ilmenites and titaniferous magnetites are given in the literature and they also illustrate the preferential partioning of V into the cubic, rather than the rhombohedral phase, even when allowances are made for possible analytical inaccuracies (e.g. Carmichael, 1967a, b; Evans and Moore, 1968; Lipman, 1971; Elsdon, 1972; Mathison, 1975; Himmelberg and Ford,

1977).

The partitioning of vanadium into the cubic, rather than the rhombohedral phase, and its presence in only small amounts in ilmenite indicate the limited nature of any possible solid solutions between ilmenite and any vanadium-bearing phases. The minor substitution that occurs is probably of the type $V^{3+} \longrightarrow Fe^{3+}$ or $2V^{3+} \longrightarrow Fe^{2+} + Ti^{4+}$. The V_2O_5 contents of these minerals vary according to the degree of fractionation of their parent magma and must reflect its vanadium content and rate of depletion. The trend of decreasing V_2O_5 content with progressive fractionation is also one of decreasing temperature which suggests that the V_2O_5 content and distribution might also be temperature dependent.

The ZrO_2 content of ilmenites was first recognised in lunar samples (Arrhenius et al., 1971) while Brett et al. (1973) have reported contents of up to 0,47 per cent ZrO_2. Taylor and McCallister (1972) reported that the Zr content of the lunar ilmenites is always higher than in their co-existing phases (chromian ulvospinel). They also noted that values are higher than those in terrestial ilmenites.

Taylor and McCallister (1972) experimentally investigated the partitioning of Zr between ilmenite and ulvospinel. They reported that ZrO_2 contents are always higher in ilmenite and that the ratio (Zr in ilmenite)/ (Zr in ulvospinel) is strongly temperature dependent. They also noted that this ratio increased with decreasing temperature and suggested that it might be a sensitive indicator of differences in cooling histories of lunar rocks. They reported that the ionic size of Zr^{4+} is approximately 20 per cent greater than that of Ti^{4+} with the result that it would be expected to be admitted by Ti^{4+}-bearing minerals during crystallisation.

Mitchell et al. (1973) reported on enrichment of Zr in kimberlitic ilmenites (up to 1190 ppm.) relative to a value of 300 ppm. in all terrestial ilmenites as reported by Arrhenius et al. (1971). Mitchell (1977) reported up to 1950 ppm. Zr in additional analyses of kimberlitic ilmenites. He noted that Zr increases with increasing FeO and decreasing MgO and TiO_2 as might be expected if the **ilmenites were** formed by crystal-liquid differentiation. The behaviour of Zr during fractional crystallisation (Carmichael et al., 1974) and its temperature-dependent distribution between co-existing cubic and rhombohedral phases (Taylor and McCallister, 1972) suggest that it might prove to be an important petrogenetic indicator.

Minor amounts of Si and Ca are commonly reported in both ilmenite and titaniferous magnetites and cannot always be ascribed to the presence of silicate impurities. Vincent and Phillips (1954) reported similar relationships for these minerals from the Skaergaard Complex and noted that a minor amount of substitution of $Si^{4+} \longrightarrow Ti^{4+}$ and $Ca^{2+} \longrightarrow Fe^{2+}$ could concievably occur.

5.5 Trace Elements in Ilmenite.

Limited data are available on trace element contents of ilmenite and titaniferous magnetites and their distribution between these phases. Vincent and Phillips (1954, p. 22) presented graphical data on the variation of Co, Ni, Zn and Cu in both phases and noted that the Zn content of magnetite is very much higher than in the co-existing ilmenite. Co and Ni contents decrease with progressive crystallisation as would be expected while Cu increases initially and then decreases. Gjelsvik (1957) reported that Cr is strongly concentrated in magnetite relative to co-existing ilmenite and that Ni and V are distributed between magnetite and ilmenite in a ratio close to 4:1. Duchesne (1972)

noted that Zn and Ga are always distinctly less abundant in ilmenite than in co-existing titaniferous magnetite.   Vincent and Nightingale (1974) also reported that Ga is strongly enriched in magnetite relative to ilmenite and concluded that "the more or less octahedral cation sites in ilmenite appear singularly unreceptive towards Ga^{3+}".   Mathison (1975) also reported details of Ni, Co, Cu and Zn contents of co-existing ilmenites from the Somerset Dam Layered Intrusion.   His data indicate that Ni shows no clear partitioning relationship, but that Co and Cu are preferentially incorporated into ilmenite while Zn is partitioned into magnetite.

Mitchell (1977) reported Ni contents of between 173 and 1285 ppm. for kimberlitic ilmenites and noted that they are enriched in this element relative to ilmenites from the other igneous rocks.   He reported a strong positive correlation of Ni contents with MgO in these minerals. He also presented data for Cu, Zn and Co contents of kimberlitic ilmenites.   Data on Sc, Hf and Ta in kimberlitic ilmenites are given by Mitchell et al. (1973).

It is obvious that there is a lack of data on trace element distributions in ilmenite and co-existing titaniferous magnetite from a wide range of igneous rock types.   The minor element fractionation trends and the available trace element data suggest that studies of this nature should provide valuable petrogenetic information that would be of use in petrological studies, particularly if analyses of their host rocks are also available.   The distribution of trace elements between the various exsolved phases should also provide data that might reflect the magmatic processes that are operative during crystallisation and the conditions under which they occur.

5.6 <u>Solid Solution Relationships between Magnetite and Other Spinels</u>.

5.6.1 <u>Introduction</u>.

The spinel group of minerals is characterised by an extremely wide range of ionic substitutions that can take place in the octahedral and tetrahedral sites in both their normal and inverse structural types (Verwey and Heilmann, 1947; Deer et al., 1962b; Navrotsky and Kleppa, 1967, 1968). Magnetite forms extensive solid solutions with a number of other spinels at elevated temperatures and transparent exsolved spinel bodies are commonly developed in magnetites from slowly cooled igneous rocks.

The commonly occurring spinels in igneous rocks exhibit a wide compositional range and are complex solid solutions that are composed largely of the oxides of Fe^{2+}, Fe^{3+}, Ti, Mg, Mn, Al, Cr, and V. These features are reflected in the analyses of essentially homogeneous, unexsolved titaniferous magnetites from a variety of igneous rocks presented in Table 3. Bulk chemical analyses of exsolved titaniferous magnetites (nos.10-14) that have been separated from their host rocks and electron microprobe analyses of the magnetite between ilmenite lamellae in complex grains (nos. 15-18) are also given in Table 3 for comparison.

5.6.2 <u>Solid solutions between magnetite and the aluminous spinels</u>.

Titaniferous magnetites from a wide variety of slowly cooled igneous rocks commonly contain transparent spinel microintergrowths. These spinels are present in a variety of forms ranging from distinct grains, commonly associated with ilmenite lamellae, through to lamellar intergrowths that are oriented parallel to cubic planes of their hosts. They are also present in various size ranges and exhibit complex relationships towards the other intergrown Ti-rich phases as discussed in section 5.6.3.

TABLE 3

SELECTED TITANIFEROUS MAGNETITE ANALYSES

OXIDE	HOMOGENEOUS TITANOMAGNETITE									BULK ANALYSES OF "EXSOLVED" TITANIFEROUS MAGNETITES					MICROPROBE ANALYSES OF TITANIFEROUS MAGNETITE BETWEEN ILMENITE LAMELLAE			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
SiO_2	0,21	0,2	-	0,28	0,05	0,13	0,05	0,05	0,18	0,23	-	0,58	0,23	1,00	-	0,71	0,56	-
TiO_2	26,70	21,1	19,5	17,62	15,70	12,60	10,30	7,10	23,80	23,74	12,12	15,40	12,38	8,00	16,82	9,44	5,42	2,53
Al_2O_3	1,06	2,1	2,7	7,50	1,97	0,94	-	5,88	3,14	0,91	2,23	0,90	11,52	3,51	0,06	0,15	2,17	1,68
Cr_2O_3	-	1,3	0,1	0,00	0,05	0,01	-	0,05	0,01	NIL	0,52	0,09	0,00	-	0,02	0,02	0,64	-
V_2O_3	1,01	0,7	-	0,31	1,80	-	-	0,16	-	0,40	1,24	1,59	0,65	0,36	-	-	-	-
Fe_2O_3	13,70	23,4	30,2	30,71	35,60	43,50	49,00	50,04	20,80	31,26	44,67	42,14	41,00	52,47	37,10	50,00	52,80	62,40
FeO	53,90	49,1	42,4	35,99	42,90	41,90	40,30	32,33	48,10	41,69	36,82	37,23	30.03	30,57	45,80	40,80	35,90	32,90
MnO	1,03	0,5	0,3	0,52	0,42	0,86	0,40	0,23	0,63	0,45	0,46	0,33	0,28	0,59	1,03	0,43	0,27	0,18
MgO	0,22	0,9	4,3	3,02	1,18	0,18	0,05	4,02	3,40	1,12	2,16	1,23	3,90	3,30	0,07	0,01	0,20	0,58
ZnO	0,08	-	-	-	0,08	0,17	-	-	-	tr	-	-	-	-	-	-	-	-
CaO	0,36	0,1	-	0,15	0,01	0,02	0,01	0,14	-	tr	-	0,30	0,03	0,10	-	0,04	0,11	-
TOTAL:	98,27	99,4	99,5	96,10	99,76	100,31	100,11	100,00	100,06	99,80	100,22	99,79	100,02	99,90	100,90	101,60	98,07	100,27

Sources of analyses and nature of their host rocks

1. Tholeiite (Carmichael, 1967b).

2. Alkali olivine basalt (Stout and Bayliss, 1975).

3. Fractionated basalt (Anderson and Wright, 1972).

4. Trachyandesite (Aoki, 1966).

5. Dacite (Carmichael, 1967a).

6. Rhyolitic obsidian (Carmichael, 1967a).

7. Quartz syenite (Whitney and Stormer, 1976).

8. Plutonic blocks (plagioclase, olivine, salite and hastingsite) (Lewis, 1970).

9. Tholeiitic andesite (Thompson, 1975).

10. Hortonolite ferrogabbro (Vincent and Phillips, 1954).

11. Titaniferous magnetite plug at Kennedy's Vale (Molyneux, 1972).

12. Hypersthene olivine gabbro (Vincent and Phillips, 1954).

13. Trachyandesite (Aoki, 1966).

14. Ironsands derived from volcanic rocks (Wright, 1964).

15. Micropegmatite (Gasparrini and Naldrett, 1972).

16. Granophyre (Himmelberg and Ford, 1977).

17. Plagioclase-cumulate (Himmelberg and Ford, 1977).

18. Leucogabbro (Mathison, 1975).

Electron microprobe analyses and other mineralogical determinations of
the transparent spinel microintergrowths indicate that they are normally
in the compositional range between pleonaste and hercynite (e.g. Nickel,
1958; Wright and Lovering, 1965; Lister, 1966; Anderson, 1966, 1968b;
Hollander, 1968a, b; Lister, 1966; Molyneux, 1970a, 1972; Cameron and
Glover, 1973; Basta and Shalaan, 1974; Mathison, 1975; Bowles, 1977).
The available data suggest that these spinels might be compositionally
closer to pleonaste than hercynite, but their compositions might con-
ceivably vary according to the nature of their hosts.   Other compo-
sitional variations have also been reported and Bose and Roy (1966)
noted the presence of spinel $(MgAl_2O_4)$ microintergrowths in titanifer-
ous magnetites from norites and anorthosites.   Duchesne (1972)
reported the development of **Zn-bearing** pleonaste in titaniferous
magnetites from the Bjerkrem-Sogndal Massif, while Prins (1972) noted
the presence of spinels with a wide compositional range in titaniferous
magnetites from carbonatites.   Prins (1972) noted that the most common-
ly developed types are either Al-poor hercynite or magnesioferrite
while a Mn-rich spinel is present in one magnetite.   The probable
distribution of Mg and Al in the magnetite structure has been discussed
by Creer and Stephenson (1972).

Complete solid solution exists between magnetite (inverse spinel struct-
ure) and hercynite (normal spinel structure, $FeAl_2O_4$) above $1000^{\circ}C$
(Richards and White, 1954; Atlas and Sumida, 1958).   Turnock and Eugster
(1962) investigated the phase relationships amongst the Fe-Al oxides
at temperatures below $1000^{\circ}C$ and reported the presence of a miscibility
gap between magnetite and hercynite at temperatures below $860^{\circ}C$.   They
also noted that portion of the magnetite-hercynite solvus curve is sen-
sitive to oxygen fugacity and that hercynite-bearing titaniferous mag-
netite assemblages are oxidised to corundum-bearing magnetite and

hematite-ilmenite assemblages under high oxygen fugacities.

A continuous replacement series exists between hercynite and spinel $(MgAl_2O_4)$ and the intermediate members of this series having an Mg/Fe^{2+} ratio between 3 and 1 are termed pleonaste (Deer et al., 1962b). These minerals all have the normal spinel structure.   Complete solid solution exists between magnetite and magnesioferrite $(MgFe_2O_4)$ (Muan and Osborn, 1956; Speidel, 1967) and it is conceivable that an analogous extensive high temperature solid solution series exists between pleonaste and magnetite.   The development of pleonaste lamellae in aluminous titaniferous magnetite and the analyses of "exsolved" titaniferous magnetites, however, indicate the presence of an extensive miscibility gap between magnetite and pleonaste at lower temperatures. Kwestroo (1959) and Ulmer (1969) reported the presence of a miscibility gap between magnesioferrite and spinel at temperatures above $1250^\circ C$. Fleischer (1965) reviewed the available data on magnetites from carbonatites and noted that large amounts of Al_2O_3, MgO and MnO are commonly present in these minerals.   Aoki (1966) reported the presence of high Al_2O_3 (6,6-11,5%) and MgO (2,3-4,5%) contents in titanomagnetite phenocrysts from Japan.   He concluded that these abnormally high values are due to the presence of spinel-hercynite components in solid solution in the titanomagnetite.   He suggested that these titanomagnetites might have crystallised from a trachyandesite magma under higher water vapour pressures and lower temperatures than usual.

Lewis (1970, 1973) reported the occurrence of homogeneous titanomagnetites containing up to 6 per cent Al_2O_3 and 43 per cent MgO in ejected plutonic blocks from the Soufriere Volcano.   Lewis (1970) reviewed the available data on aluminous magnetites and noted the lack of published analyses of similar materials.   He concluded that "extensive

substitution of Al, Mg and Ti might be expected in magnetite separat-
ing at a high temperature from a polycomponent system such as a natur-
al basalt magma".

Wass (1973) has reported high Al_2O_3 and MgO contents in titanomagnetite
phenocrysts in lavas of an inferred high-pressure origin. She suggest-
ed that the Al substitution in these ulvospinel-titanomagnetites might be
extremely pressure-sensitive. She discussed the Al-rich titanomagnetites
described by Aoki (1966) and Lewis (1970, 1973) and stated that "both
these types of magnetite are inferred to be products of deep intratelluric
crystallisation, allowing considerable amounts of Al_2O_3 to be incorporated
in the titanomagnetite lattice". Wass (1973) also noted that the spinel
phases from rocks with an alkali basalt affinity contained significantly
larger amounts of Al_2O_3 and MgO than those from tholeiites.

Carmichael et al. (1970, 1974) reported that titanomagnetites from
basic lavas of low silica activity frequently contain more Al_2O_3
(3-5%) and MgO (1-3%) than those from tholeiitic lavas (1-2% Al_2O_3
and 0,5-1,5% MgO). In contrast to the pressure controls postulated
by Wass (1973), they suggested that the Al_2O_3 content of titanomagne-
tite is governed by a reaction of the type:-

$$MgAl_2O_4 + SiO_2 \longrightarrow MgAl_2SiO_6$$

    spinel   glass   pyroxene component

where $MgAl_2SiO_6$ is in solid solution in the pyroxene. They concluded
that the formation of pleonaste is favoured in magmas of low silica
activity and that titanomagnetites crystallising under these conditions
would be relatively enriched in MgO and Al_2O_3. Ridley (1977) noted
that the Al_2O_3 contents of spinels are reduced by a peritectic reaction
during the crystallisation of plagioclase. He noted that the Al_2O_3

content could also be reduced by reactions involving the intercumulus liquid.

5.6.3 The development of aluminous spinel microintergrowths in titaniferous magnetite.

Transparent aluminous spinel bodies are commonly developed in titaniferous magnetites from a wide variety of slowly cooled rocks. These bodies have been described by numerous investigators as indicated in section 5.6.2 and have been illustrated by Ramdohr (1969 p. 892-911). Numerous illustrations are also given in Part 3 of this thesis.

The transparent spinel microintergrowths appear to have formed via the exsolution of a member of the pleonaste-hercynite solid solution series from an originally homogeneous high-temperature titanomagnetite. The compositions of the exsolved spinels are variable and might reflect differences in composition of their host titaniferous magnetite phases. The exact phase relationships are uncertain and are complicated by the large number of ionic substitutions that take place. Certain analogies may, however, be made between the behaviour of these solid solutions and the magnetite-hercynite solid solution series described by Turnock and Eugster (1962).

The nature of the solid solution mechanisms operating in this system and the processes involved in the formation of the various morphological types of spinel microintergrowth have not been investigated in detail. Wright and Lovering (1965) noted that exsolved transparent spinels are only developed in titaniferous magnetites that have been oxidised to some extent. They noted that these spinel grains are commonly located close to rhombohedral ilmenite lamellae and suggested that, in at least some cases, the exsolution of spinel closely followed the commencement

of oxidation. They concluded that the exsolution of transparent spinels might be dependent on the cooling history of their titaniferous magnetite hosts, rather than on their composition.

The development of transparent spinel exsolution bodies does appear to be related to the Al_2O_3 contents of their host titaniferous magnetites, at least in the case of magmatic titaniferous iron ores (Part 3 of this thesis). The spinel exsolution bodies can be broadly divided into three types as follows: 1) External granules, 2) internal granules, and 3) lamellae. Each of these categories in turn exhibits a variation in size and morphology. The following descriptive generalisations are based on published descriptions and the author's own observations (Parts 2 and 3 of this thesis).

5.6.3.1 External granules of transparent spinel.

Numbers of small rounded to subhedral transparent spinel grains are commonly present around the peripheries of exsolved titaniferous magnetite grains and most probably represent externally exsolved material. The interfaces between co-existing ilmenite and titaniferous magnetite grains are commonly spinelliferous and contain large numbers of rounded to more irregularly shaped grains. Duchesne (1970, 1972) has described these intergrowths in detail and concluded that they form by exsolution from the titaniferous magnetite in the immediate vicinity.

5.6.3.2 Internal granules of transparent spinel.

These vary from rounded, through all intermediate types, to completely euhedral grains and are present either as independent grains or in close association with ilmenite intergrowths. Numbers of small rounded grains are commonly arranged along the interfaces between the larger ilmenite lamellae and the titaniferous magnetite. Smaller sized grains

are found less frequently in a similar association with the smaller ilmenite lamellae that might be present.

Large euhedral spinel grains are commonly present in the titaniferous magnetite in areas away from ilmenite lamellae and are most commonly developed in grains showing extensive ulvospinel development. The larger spinel grains occasionally contain small lath-shaped sulphide crystals (normally pyrrhotite) and appear to have precipitated around these nuclei.

5.6.3.3 Transparent spinel lamellae.

Aluminous titaniferous magnetites commonly display the development of well defined transparent spinel lamellae that are oriented parallel to the cubic planes of their hosts. These lamellae vary in size and spacing and appear to reflect the overall Al_2O_3 contents of their hosts. These lamellae reach their maximum development in titaniferous magnetite grains that are largely devoid of ilmenite lamellae and are character- ised by ulvospinel microintergrowths.

The spinel lamellae decrease in size and become closer spaced towards grain boundaries and a very much finer set is sometimes developed in the areas between the larger lamellae. The lamellae are also gener- ally absent from a narrow zone surrounding larger spinel grains.

5.6.4 Exsolution of aluminous spinel in titaniferous magnetite.

The various spinel microintergrowths are all commonly encountered in a single titaniferous magnetite grain and any exsolution mechanism must be able to account for this feature as well as their common association with ilmenite lamellae. The development of these bodies can be inter- preted in terms of the current developments in exsolution theory as

reviewed by Brett (1964), Yund and McCallister (1970), and Champness and Lorimer (1976). Exsolution is an essentially continuous process, but the nucleation and growth of the various bodies occur at different times. The arguments put forward in section 4.5.5 with regard to the exsolution processes occurring in a number of distinct stages are also applicable here. It is consequently proposed that the microstructural evolution of transparent spinel microintergrowths in titaniferous magnetites can be accounted for by the following model.

Stage 1. The crystallisation of a titaniferous magnetite containing more than approximately 5 mole per cent of pleonaste-hercynite solid solution.

Stage 2. Cooling of the homogeneous titanomagnetite solid solution results in the development of Ti-rich exsolution and oxidation/ exsolution bodies as discussed in section 4.5.5. The transparent spinel would, however, probably remain in solid solution until much lower temperatures, possibly down to 700°C (Lewis, 1970) during which time various sized ilmenite lamellae have commonly developed.

The transparent spinel supersaturation increases on cooling below the titaniferous magnetite-spinel solvus and exsolution will be initiated. This will normally occur at small undercoolings via the heterogeneous nucleation and growth mechanism resulting in the development of external granules. This depletes the marginal areas of the grain in spinel and sets up concentration gradients that cause migration of the required ions towards the grain boundaries.

Grain boundaries are also present between the ilmenite lamellae and their hosts and these also provide suitable nucleation sites. Trans-

parent spinel grains consequently develop along the ilmenite/titaniferous magnetite interfaces leading to the development of the typical spinelliferous ilmenite lamellae as illustrated in figure 22 (a). Concentration gradients are also set up in the areas around these grains.

Ilmenite lamellae are not always well developed in titaniferous magnetite grains at this stage and it is possible that nucleation and growth of spinel bodies will occur at dislocations that are irregularly distributed within the grains. This leads to the formation of small euhedral spinel grains at these points as illustrated in figure 22 (b). External granules are developed in the normal manner.
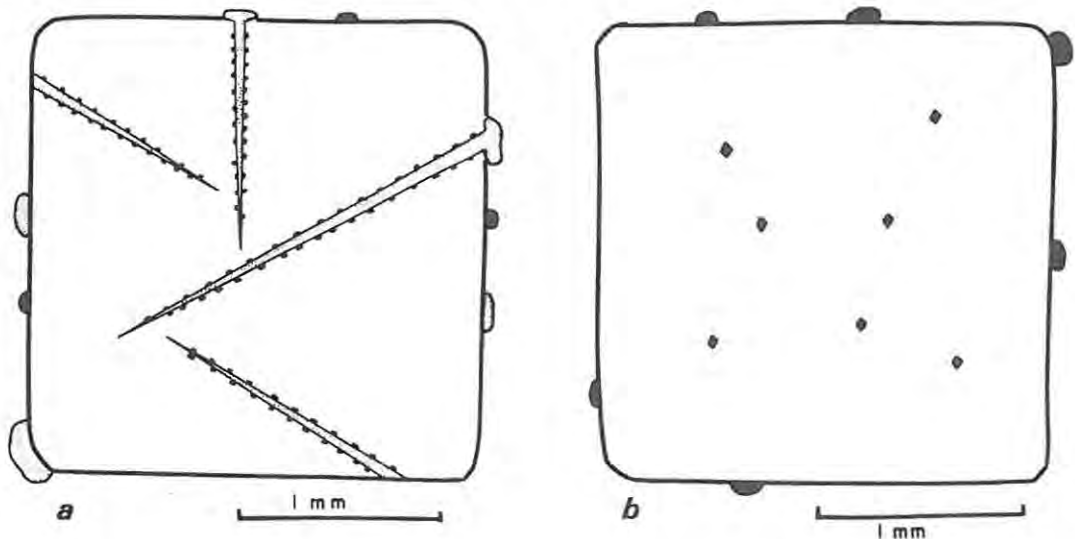
FIGURE 22. Stage 2 (a). Schematic representation showing the development of external spinel granules and spinelliferous ilmenite lamellae (black). (b). Schematic representation showing the development of spinel grains in areas devoid of ilmenite lamellae. Several external grains are also present.

The spinelliferous ilmenite rims develop during this stage and can be regarded as a special case of external granule exsolution. These grains develop in the normal manner along the interface between co-existing ilmenites, but grain-boundary adjustment takes place between these phases and the ilmenite grain continues to grow due to the addition of suitable material being expelled from the titaniferous magnetite.

The spinel grains interfere with grain boundary migration. Coble and Burke (1963) reported that a grain boundary has difficulty in migrating past an inclusion because an area of boundary equal to the cross sect-ioanl area of the inclusion has to be reformed in the boundary on the far side of the inclusion. The inclusion impedes grain boundary move-ment since the surface energy of this area of boundary has to be pro-vided by a decrease in the area of the rest of the boundary. The spinel grains thus tend to remain along the ilmenite/titaniferous mag-netite interfaces and varying degree of complex grain boundary con-figuration arise due to the pinning of one component of the interface while continued growth of the next segment occurs as illustrated in figure 23.

Stage 3. The transparent spinel supersaturation increases in the areas away from the various spinel grains with falling temperature and decreas-ing ionic mobilities. Additional smaller ilmenite lamellae developing through these areas provide suitable nucleation sites which lead to the development of a smaller series of spinel grains along these lamellae as illustrated in figure 24(a).

Nucleation might also take place at various structural discontinuities in areas devoid of ilmenite lamellae, also leading to the development of small equant spinel grains. These grains are commonly octahedral and their apices commonly develop into lamellae that are oriented

along the cubic planes of their hosts as illustrated in figure 24 (b).

0,1 mm
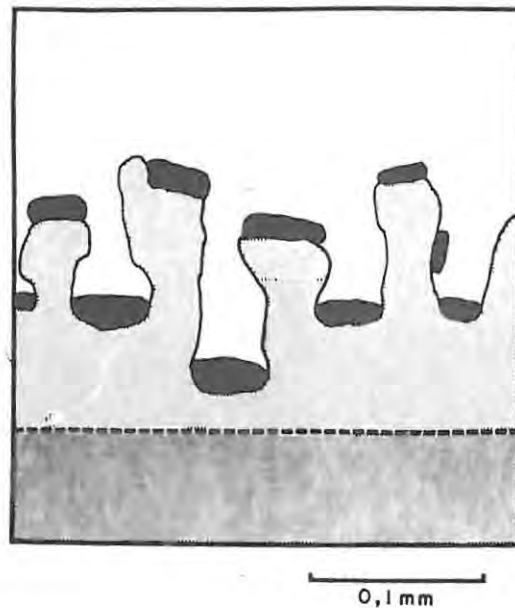
FIGURE 23.   Schematic representation of the development of a spinelli-
             ferous ilmenite rim between ilmenite and titaniferous
             magnetite.   The position of the original grain bound-
             ary is indicated by the dashed line.   The ilmenite is
             shaded   and the spinel grains are black.

Stage 4.   Development of small spinel grains along newly formed ilmen-
ite lamellae continues, but this stage is characterised by the develop-
ment of lamellar spinel intergrowths parallel to the cubic planes of
their hosts.   This form of exosolution probably takes place via the
homogeneous nucleation and growth mechanism.   Concentration gradients
have already been established between the previously formed spinel
exsolution bodies.   The supersaturation consequently attains critical
levels in the areas furthest away from the pre-existing exsolution
bodies resulting in the formation of relatively large, and more widely
spaced lamellae.   Concentration gradients subsequently develop between
these lamellae.
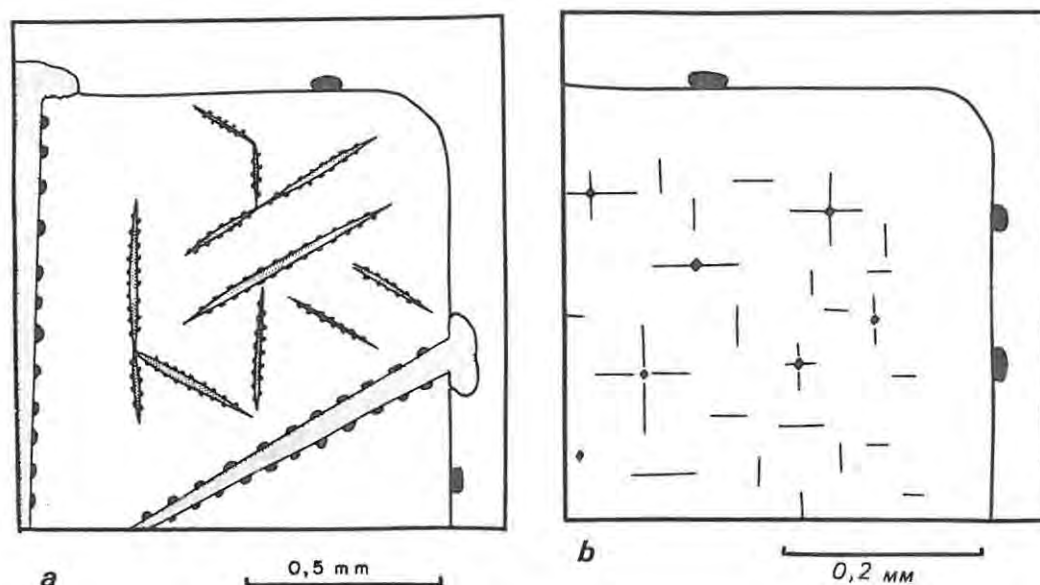
FIGURE 24. Stage 3: (a) Schematic representation of a further series of smaller spinel exsolution bodies (black) oriented along ilmenite lamellae. (b) The formation of equant spinel grains and occasional lamellae in areas devoid of lamellar ilmenite.

Critical supersaturations are reached at lower temperatures in areas containing smaller amounts of spinel in solid solution with the result that smaller and more closely spaced spinel lamellae are formed. This results in a variation in size and relative spacing of lamellae as illustrated in figures 25 (a and b) that reflect not only the original concentration gradients in their host grains, but also the lower temperatures and ionic mobilities under which the smaller lamellae developed.

Stage 5. Continued cooling might conceivably result in the development of a further series of extremely fine spinel lamellae in the areas between the larger and more widely spaced spinel lamellae due to de-

creased ionic mobility. Small spinel grains will also continue to
develop along newly formed ilmenite lamellae. These processes remain
effective until the temperature conditions are reached at which ionic
diffusion becomes too slow and exsolution effectively ceases. Spin-
odal decomposition mechanisms might be operative during this stage of
lamellar development.
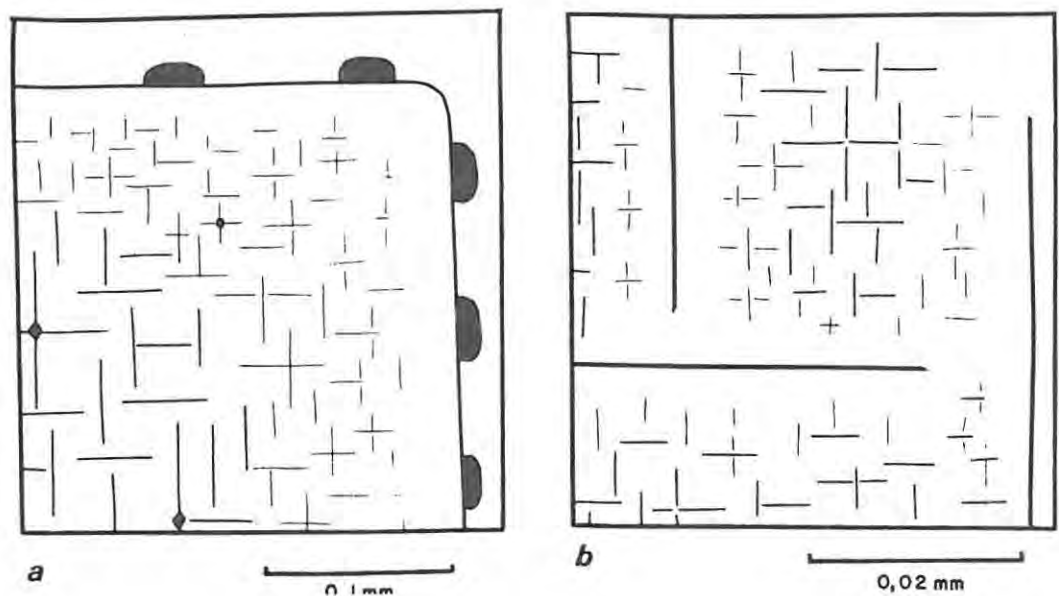
FIGURE 25. Stage 4 (a and b): Schematic representations illustrat-
ing the development of lamellar spinel intergrowths and
their size distribution.

5.6.5 Application of the exsolution model to natural transparent spinel microintergrowths.

The above model can account for the majority of features displayed by
transparent spinel microintergrowths in titaniferous magnetites and
is consistent with their having developed by exsolution during slow
cooling. The relative abundance of exsolution bodies reflects the
original spinel content of the titaniferous magnetite which is highly
variable as indicated by the analyses in Table 3 and Part 3 of this

thesis. The relative abundance of lamellar and granular spinel ex-
solution bodies is partially governed by the presence of ilmenite lam-
ellae that act as nucleation sites.

The effect of oxidation on the development of the spinel exsolution
bodies is not easily evaluated. Oxidation results in the development
of ilmenite lamellae which provide suitable nucleation sites for the
transparent spinel and favour the growth of exsolution bodies. This
feature corresponds to the model proposed by Wright and Lovering (1965)
in which exsolution of spinel follows oxidation of the titaniferous
magnetite host. This process will operate at lower supersaturations
(hence at higher temperatures) when ilmenite lamellae are present,
since it involves the heterogeneous nucleation and growth mechanism.

5.6.6 Solid solutions between magnetite and the chromium-bearing spinels.
Naturally occurring titaniferus magnetites from a wide range of igneous
rocks normally contain only minor amounts of Cr (Table 3). Analyses
of spinels from several plutonic environments (e.g. Frankel, 1942; Stevens,
1944; Beeson and Jackson, 1969; Henderson and Suddaby, 1971; Frisch, 1971;
Cameron and Glover, 1973; Henderson, 1975) and volcanic basalts (e.g.
Evans and Moore, 1968; Gunn et al., 1970; Thompson, 1973; Arculus, 1974;
Ridley, 1977) have indicated the existence of minerals intermediate in
composition between magnetite and chromite. These minerals are,
in most cases, not primary crystallisation products, but appear to have
formed via the reaction of early-crystallised chrome-spinel with late-stage
or other fluids. A large degree of miscibility has, however, been found
to exist between magnetite and a wide range of Cr-bearing spinels at elevated
temperatures (Irvine, 1967; Ulmer, 1969; Cremer, 1969; Navrotsky, 1975a).

Katsura and Muan (1964) reported the existence of complete miscibility between magnetite and chromite at $1300^{\circ}C$ and noted that an extensive cation-deficient solid solution is also developed between these two end-members. Cremer (1969) reported the complete miscibility between magnetite and chromite at $900^{\circ}C$. He experimentally determined that exsolution commenced below this temperature and his data indicate that magnetite can hold approximately 10 mole per cent $FeCr_2O_4$ in solid solution at $500^{\circ}C$.

Irvine (1967) concluded that chromite, spinel and picrochromite ($MgCr_2O_4$) exhibit extensive mutual solubility but noted that solid solutions between these three end-members and the magnetite-magnesioferrite series are not common in natural systems. Cremer (1969) reported that chromite and hercynite form a complete solid solution series above $950^{\circ}C$. Ulmer (1969) reviewed the available data on Cr-rich spinel solubilities at $1300^{\circ}C$ and concluded that complete solid solution exists between magnesioferrite, spinel, picrochromite, magnetite, hercynite and chromite. He noted that these solid solutions might, however, involve defect spinels that contain trivalent ions in excess of the 1:2 divalent to trivalent ratio.

The complex phase relationships between the various Cr-bearing spinels have been reviewed by Muan (1975). He noted that a miscibility gap originates at the titanate-aluminate join below $1400^{\circ}C$ in each of the spinel solid solutions $MgAl_2O_4-Mg_2TiO_4-MgCr_2O_4$ and $FeAl_2O_4-Fe_2TiO_4-FeCr_2O_4$. He also reported that the miscibility gap gradually closes as chromite is added as a third component. Navrotsky (1975a) also reported complete miscibility between magnetite-chromite-hercynite above $1000^{\circ}C$, but noted that exsolution would be initiated on slow cooling. He reported that the behaviour of this system is complex

and concluded that chromite, magnetite and hercynite can co-exist stably at low temperatures.

Analyses of lunar spinels have shown the existence of an exceptionally wide compositional range in this group of minerals, and in particular, they suggest the presence of extensive solid solution relationships between chromite and ulvospinel (e.g. Haggerty and Meyer, 1970a, b; Haggerty, 1971b; 1972a,b;1973a; Busche et al., 1972; Nehru et al., 1974; Smith and Steele, 1976). These spinels often appear to be primary crystallisation products of the lunar lavas and their abundance is in direct contrast to the apparent scarcity of similar phases in terrestrial basalts.

Thompson (1973) described the occurrence of titanium chromite and chromian titanomagnetite from a basalt and suggested that they might represent terrestrial analogues of the lunar spinels. He concluded that the original chemistry of these spinels was preserved by the rapid quenching of their host rock and that they were not involved in any post-precipitation changes. The absence of spinels of intermediate composition between chromite and magnetite is a common feature of the more slowly-cooled basic igneous rocks and has been ascribed to reaction between the spinel and liquid (e.g. Irvine, 1967; Henderson, 1975).

Hill and Roeder (1974) investigated the experimental crystallisation of spinels from a basaltic liquid as a function of oxygen fugacity and succeeded in synthesising spinels that are intermediate in composition between chromite and magnetite. They reported that "the continuous variation in colour, morphology, modal amount, and composition of the spinel all suggest there is continuous solid solution between what is called magnetite and chromite at basaltic liquidus temperatures".

They concluded that the compositional gap between chromite and titano-magnetite in basalts or basic layered intrusions is due to a reaction relation between chromium spinel, clinopyroxene and liquid. This topic is not reviewed here and readers are also directed to papers by Busche et al. (1972), Nehru et al. (1974), and Ridley (1977) for additional information.

The available analyses and experimental data indicate the existence of a large degree of mutual solubility between magnetite or titanomagnetite and a variety of Cr-bearing spinels. The presence of minor amounts of Cr_2O_3 in the titaniferous magnetite analyses can therefore be accounted for and is a result of a substitution of $Cr^{3+} \longrightarrow Fe^{3+}$ or possibly even $Cr^{3+} \longrightarrow Al^{3+}$ in the more aluminous varieties.

It might be expected that the Cr_2O_3 content of titaniferous magnetite would decrease with progressive fractional crystallisation in a similar manner to V_2O_5. This feature is, however, not as marked and has not been well documented. The titaniferous magnetites of the North Range of the Sudbury Nickel Irruptive show a progressive decrease in Cr_2O_3 content from 9,03 per cent at the base to 0,04 per cent near the top (Gasparrini and Naldrett, 1972). Analyses from other intrusions such as the Skaergaard (Vincent and Phillips, 1954), Bushveld (Schwellnus and Willemse, 1943; Molyneux, 1970a, 1972) and Dufek (Himmelberg and Ford, 1977) Complexes do not show such a marked trend, although they do exhibit a slight overall decrease in Cr_2O_3 with increasing height. Mathison (1975) reported a decrease in the Cr_2O_3 contents of titaniferous magnetites with increasing heights in zones 2 and 4 of the Somerset Dam Layered Intrusion.

5.6.7 <u>The presence of vanadium in titaniferous magnetite.</u>

Titaniferous magnetites commonly contain small amounts of vanadium
and it is occasionally present in sufficient concentrations to warrant
recovery (e.g. the Main Seam of the Bushveld Complex).   Dunn and Dey
(1937) described some Indian vanadium-bearing titaniferous iron ores
and noted that the vanadium is largely present in the titaniferous
magnetite. They reported that the vanadium is concentrated in cer-
tain areas of the magnetite grains and that it is optically similar
to maghemite.   They proposed the name coulsonite for this phase and
concluded that it might have a formula $FeO.(Fe,V)_2O_3$ which is analogous
to that of magnetite with part of the Fe^{3+} replaced by V^{3+}.   They
also noted that the formula $(Fe,V)_2O_3$ would be applicable if the
element is present in a vanadiferous maghemite.

These phases were subsequently searched for in numerous vanadium-
bearing titaniferous magnetites, but were never unequivocally identi-
fied.   For example, Frankel and Grainger (1941) suggested that the
vanadium in the Bushveld titaniferous iron ores might be due to the
presence of vanadiferous maghemite, but Schwellnus and Willemse (1943)
failed to detect the presence of any discrete vanadium mineral in these
ores.   Subsequent investigations of these ores also failed to detect
any vanadium-rich phases (Hiemstra and Liebenberg, 1964; Willemse,
1969b; Molyneux, 1970a, b).   Discrete vanadium-bearing phases were not
identified in titaniferous magnetites from five other South African
basic intrusions or from a wide range of igneous rocks (this thesis,
Parts 2 and 3).

Mathewson et al. (1931) reported the synthesis of $FeO.V_2O_5$ which exhibits
a spinel structure.   Radtke (1962) reported the presence of a vanadium-
rich spinel, FeV_2O_4, and suggested that it be termed coulsonite after

the original proposal by Dunn and Dey (1937). The phase relationships between FeV_2O_4 and magnetite have not been investigated experimentally, but the published analyses of titaniferous magnetites indicate that up to 2,5 per cent V_2O_5 can be accommodated in titaniferous magnetite at low temperatures (this thesis, Part 3).

Cameron and Glover (1973) reported an analysis of an optically homogeneous vanadium-rich spinel (10,2% V_2O_5; 6,2% Al_2O_3; 5,3% Cr_2O_3; 10,4% TiO_2; 41,8% FeO; 27,4% Fe_2O_3) in a mafic replacement pegmatite from the eastern Bushveld Complex. This analysis suggests that a large degree of miscibility might exist between coulsonite and magnetite as well as between various other spinels.

The vanadium content of titaniferous magnetites can be used as a petrogenetic indicator in the study of suites of differentiated igneous rocks. Schwellnus and Willemse (1943) reported that the V_2O_5 contents of the titaniferous magnetite-rich seams in the Bushveld Complex decrease with increasing height in the intrusion. This feature was subsequently confirmed by Molyneux (1964, 1970a, b, 1972) and Willemse (1969b). Similar trends in the V_2O_5 contents of titaniferous magnetites were also reported from the Skaergaard Complex (Vincent and Phillips, 1954), certain zones in the Somerset Dam Layered Intrusion (Mathison, 1975), the Dufek Intrusion (Himmelberg and Ford, 1977) and the Rooiwater and Mambula Complexes (this thesis, Part 3).

The behaviour of vanadium during the fractional crystallisation of a wide range of igneous rocks is well documented (e.g. Wager and Mitchell, 1951; Wager and Brown, 1968; Carmichael et al., 1974). The vanadium is preferentially incorporated into the opaque oxides during crystallisation with the bulk entering into the spinel rather than the

rhombohedral phases. Minor amounts enter the pyroxenes and possibly the plagioclase (Wager and Mitchell, 1951).

The V-content of the residual magma begins to increase after cessation of chrome-spinel crystallisation, since vanadium is not readily incorporated into the major rock-forming minerals. This vanadium then becomes incorporated into the titaniferous magnetite once precipitation of this phase commences, thus depleting the residual magma of this element. The amount of vanadium incorporated into the titaniferous magnetite will depend not only on the concentration of vanadium in the magma, but also on the amount and rate of magnetite precipitation. A decrease in the vanadium contents of titaniferous magnetites with increasing fractional crystallisation in a differentiated basic intrusion is thus expected.

5.6.8 Magnetite: solid solutions with other phases.

Magnetite and titaniferous magnetite analyses commonly show the presence of small, but variable amounts of other oxides, notably NiO, ZnO, MnO, CaO and SiO_2 (Deer et al., 1962b). The presence of smaller amounts of Co and Cu has also been reported (e.g. Vincent and Phillips, 1954; Mathison, 1975).

The spinels trevorite ($NiFe_2O_4$) (de Waal, 1972), franklinite ($ZnFe_2O_4$) and jacobsite ($MnFe_2O_4$) are rare, but have been reported to occur naturally (Deer et al., 1962b). These phases together with $CoFe_2O_4$ and $CuFe_2O_4$ (tetragonal below $760^{o}C$, Dunitz and Orgel, 1957), have been synthesised and shown to have the spinel structure (e.g. Verwey and Heilmann, 1947; Gorter, 1957; Dunitz and Orgel, 1957; Navrotsky and Kleppa, 1967; 1968). The high-temperature phase relationships between these spinels have not been investigated in detail and their

degree of mutual solubility with magnetite or titaniferous magnetite is uncertain.

Substitution of minor amounts of Ni, Zn, Mn, Co and Cu into the titaniferous magnetite would be expected to occur readily in view of the ionic substitutions that can take place in the spinel structure. Stout and Bayliss (1975) reported that Fe^{2+} occupies both tetrahedral and octahedral sites in natural titanomagnetite with the result that substitution of Fe^{2+} by Ni, Zn, Mn, Co or Cu can take place. The site preference data of Navrotsky and Kleppa (1967) indicate that Zn^{2+}, Mn^{2+} and Co^{2+} will preferentially substitute in the tetrahedral sites while Ni^{2+} and Cu^{2+} will enter the octahedral positions. Duncan and Taylor (1968) noted that the octahedral site preference energies of Ni^{2+} and Co^{2+} exceed that of Fe^{2+} and concluded that these elements will be enriched in the early crystallising titaniferous magnetites relative to the later crystallising magnetites.

The analytical data of Vincent and Phillips (1954) indicate that Mn contents of the titaniferous magnetites increase sharply in the later crystallisation products of the Skaergaard Complex. This is the usual behaviour of this element (see section 5.3.2). The data of Vincent and Phillips (1954) indicate that both Ni and Co contents of the magnetite decrease upwards in the titaniferous magnetites of the Skaergaard Complex, but that the Ni-depletion occurs much earlier than that of Co. Zn and Cu contents of the oxides increase with increasing height in the Skaergaard Complex and then decrease rapidly in the later crystallisation products. Mathison (1975) also reported a decrease in Ni and Co contents in titaniferous magnetites with increasing height in certain zones in the Somerset Dam Layered Intrusion.

5.6.9 Trace elements in magnetite.

Very little published data are currently available on the distribution of trace elements in magnetites and titanferous magnetites from igneous rocks. The elements analysed by Wager and Mitchell (1951) and Vincent and Phillips (1954) have been largely discussed above. Vincent and Nightingale (1974) reported that Ga is preferentially incorporated into magnetite and is due to substitution of Ga^{3+} for Fe^{3+} in the magnetite structure.

5.6.10 Conclusions.

The minor element variations in titaniferous magnetites reflect changes in the magma from which they crystallised. The magnetite compositions provide additional petrogenetic data that can be used in an analogous way to plagioclase and pyroxene analyses in tracing the crystallisation history of fractionated igneous rocks. This aspect of the titaniferous magnetite compositions has not been used to any extent in this manner and the subject requires further investigation.

It is concluded that the TiO_2 and MnO contents of the titaniferous magnetites of basic igneous rocks will increase during progressive fractional crystallisation whereas MgO, NiO, Co, Al_2O_3 and V_2O_5 will decrease. The behaviour of trace elements in these minerals has not been studied, but should also provide information that would be of use in petrogenetic studies.

6. OXIDATION OF THE IRON-TITANIUM OXIDES.

6.1 Introduction.

The iron titanium oxides are sensitive to changes in oxygen fugacity and any marked increase in fO_2 causes their oxidation. This oxidation may take place at various stages during the cooling of an igneous complex

as illustrated by the sub-solidus oxidation of magnetite-ulvospinel solid solutions discussed in section 4. It can also occur in other ways, the most important being:

1). Low temperature oxidation that occurs during weathering under surface and near-surface conditions.

2). High temperature oxidation that occurs in sub-aerially erupted lavas when the hot magma comes into contact with the atmosphere.

3). High temperature oxidation that occurs in sub-aqueous eruptive lavas when the hot magma comes into contact with oceanic water.

4). Oxidation during metamorphism.

5). Late-stage deuteric oxidation due to the action of interstitial fluids during the final stages of crystallisation.

6.2 The Low-Temperature Oxidation of Magnetite and Titaniferous magnetite.

6.2.1 Introduction.

The oxidation of magnetite and titaniferous magnetite has been the subject of considerable debate in the geological literature and a degree of confusion still exists. The debate has largely centred around the degree of solubility of Fe_2O_3 in Fe_3O_4, the presence of maghemite as a possible intermediate phase in the oxidation of Fe_3O_4 to Fe_2O_3 (martite) and the various oxidation mechanisms involved.

6.2.2 Magnetite oxidation microstructures.

The oxidation of magnetite produces certain distinctive microstructures and the following descriptions are based on published descriptions as well as the author's own observations. The textures have been illustrated by Ramdohr (1969, p. 904-911) while numerous illustrations are also given in Part 3 of this thesis.

Magnetite is commonly oxidised directly to martite and this process

produces a very distinctive texture. Oxidation commences around grain boundaries, along fractures and more rarely around inclusions or intergrowths such as ilmenite lamellae and moves inwards into the grain. Oxidation takes place preferentially along the octahedral planes of the magnetite and results in the formation of narrow Fe_2O_3 lamellae that appear to migrate into the magnetite and resemble exsolution lamellae. These lamellae thicken and coalesce until the entire magnetite grain is ultimately converted to martite.

THe martite (hematite) is readily distinguished from the magnetite on the basis of its white colour, anisotropy and other optical properties. The direct martitization of titaniferous magnetite is most commonly observed in grains that are relatively free from extremely fine-grained microintergrowths. This oxidation process also tends to disrupt the finer-grained intergrowths.

The oxidation of magnetite to maghemite is not as distinctive as in the case of martitization. Maghemite is slightly lighter coloured and has a distinct bluish colour, but is isotropic and otherwise microscopically indistinguishable from magnetite. Maghemitization also commences at grain boundaries and fractures, but moves into the magnetite in an irregular fachion that does not appear to be crystallographically controlled. The interface between the magnetite and maghemite is diffuse and appears to be gradational. A narrow transitional zone that varies in colour from that of magnetite to maghemite generally separates the two phases.

Maghemitization is most frequently observed in titaniferous magnetites containing abundant fine-grained microintergrowths (e.g. ulvospinel cloth textures). These delicate microstructures are not disrupted by

the maghemitization process and are in fact more readily seen because of the lighter colour of the maghemite groundmass.

The maghemite in turn often shows alteration to martite and this also takes place in an irregular fashion commencing at grain boundaries and along fractures. Composite grains consisting of an unaltered magnetite core surrounded by an intermediate maghemite zone and an outer martite zone are commonly encountered in weathered rocks.

6.2.3 Mineralogical investigations.

Sosman and Hostetter (1916) investigated the phase relationships in the Fe_2O_3-Fe_3O_4 system and concluded that extensive, if not complete, solid solution exists between these two end members. They also noted that oxidation of Fe_3O_4 results in the formation of Fe_2O_3 that is indistinguishable from hematite.

Sosman and Hostetter (1918) reported that many natural iron oxides are solid solutions between Fe_2O_3 and Fe_3O_4 and concluded that their magnetic susceptibilities are a function of their FeO contents. They noted that the high temperature oxidation of magnetite resulted in the formation of Fe_2O_3 (martite), but that a magnetic ferric oxide (Fe_2O_3) was produced when the oxidation was carried out at normal temperatures. The magnetism of this phase was, however, destroyed on heating at $750^{O}C$. They also reported the natural occurrence of a magnetic ferric oxide and concluded that the oxidation of magnetite to form martite would only occur at elevated temperatures in nature.

The first ore-microscopic observations of the relationships between naturally occurring magnetites and hematites were published by Broderick (1919). He criticised the work of Sosman and Hostetter (1918) on the

grounds that they had not checked the homogeneity of their postulated magnetite-hematite solid solutions by means of microscopic examination. Broderick (1919) reported that microscopic examination had shown that many minerals of intermediate composition between magnetite and hematite in fact consisted of intergrowths of these two phases. He concluded that the most common intergrowth is represented by a replacement of magnetite by hematite that takes place along the octahedral planes of the host.

Gruner (1922) reported that the alteration of magnetite to hematite in the Mesabi ores is caused by the action of meteoric water. He expressed doubts as to the existence of a solid solution series between magnetite and hematite. Gilbert (1925) described the presence of microscopic hematite lamellae oriented parallel to (111) of magnetite. He noted that these lamellae increased in size and abundance towards the grain boundaries where a continuous zone of hematite was often present. He concluded that these hematite intergrowths were formed by the hydrothermal replacement of magnetite.

Sosman and Posnjak (1925) partially oxidised synthetic magnetite in air at $105^{o}C$ and by using a solution of NH_4SO_4. The chocolate-brown oxidation product was deficient in FeO, but remained highly magnetic and produced an x-ray diffraction pattern that was identical to magnetite. This material remained stable under normal conditions but inverted irreversibly to hematite when heated at between 500° and $600^{o}C$. They also reported the natural occurence of magnetic oxidised magnetite in a gossan from Iron Mountain, California.

Welo and Baudisch (1925) heated synthetic magnetite in a stream of oxygen at $220^{o}C$ and produced a material that contained no ferrous iron,

but remained magnetic. Further heating of this oxidised material to 550°C in a nitrogen atmosphere resulted in the inversion of the oxidation product to hematite. They concluded that the oxidation of magnetite involved a two-stage process in which the magnetite was first converted to oxidised magnetite containing no FeO at about 200°C and that this material inverted to hematite at 550°C. They demonstrated that the low-temperature oxidised magnetite retained the spinel structure and concluded that the extra oxygen ions introduced during oxidation could be accommodated without due strain. Heating at 550°C resulted in a collapse of the spinel structure and inversion to the hematite structure occurred.

Gruner (1926) investigated the oxidation of magnetite by heating polished sections of this mineral in air at temperatures between 150° and 200°C for periods of up to 330 days. He confirmed that oxidation occurred and resulted in the formation of hematite (martite) lamellae that migrated into the magnetite along its octahedral planes. He confirmed that martite and hematite are identical by means of x-ray diffraction. He concluded that oxidation occurred along the octahedral planes of magnetite because of the atomic arrangement and that it led to a volume increase of 5,2 per cent. The introduction of additional oxygen results in a distortion of the cubic structure with the result that its symmetry changes to the rhombohedral form of hematite.

Ramdohr (1926) disagreed with the conclusions of Sosman and Hostetter (1918) and concluded on crystallographic grounds that only limited solubility could exist between magnetite and hematite. He suggested that the intermediate compositions between magnetite and hematite represent magnetites in various stages of martitization. He further reported that martitisation of magnetite is a very common feature of

these minerals.

Twenhofel (1927) investigated the oxidation of both natural and arti-
ficial magnetite by heating the material in steam of oxygen at differ-
ent temperatures for variable lengths of time. She concluded that
oxidation first resulted in an oxidised magnetic phase and that this
process occurred over a range of temperatures. She noted that the
oxidised artificial magnetite inverted to hematite at $500^{\circ}C$, but that
the natural magnetite did not invert until $800^{\circ}C$ was reached. She
noted that the oxidised magnetite is always formed as an intermediate
phase in the oxidation of magnetite and that its rate of formation and
stability is dependent on the temperature and duration of the oxidation
event.

Gilbert (1927) discussed the available data on magnetite oxidation and
stressed the need for a thorough investigation of the processes involved.
Newhouse and Callahan (1927) reported the natural occurrence of a brown-
ish magnetic oxidised magnetite from several localities and noted that
it replaced portions of pre-existing magnetite crystals. They also
noted that this material could be produced artificially by heating
portions of the unoxidised magnetite in the oxidising flame of a blow
torch at very low red heat.

Gruner (1927) discussed the results of previous investigators and stress-
ed that he had not yet identified magnetic oxidised magnetite. He
concluded that oxidised magnetite would be "unstable except under very
special conditions and for short periods of time, such as obtained in
the laboratory". Wagner (1927, 1928) reported that the bulk of the
titaniferous magnetite from surface exposures in the Bushveld Complex
has been replaced by a very strongly magnetic form of ferric oxide.

He noted that this mineral is structurally identical to magnetite, but has the chemical composition and physical properties of hematite. He concluded that it is the product of the normal atmospheric weathering of magnetite and proposed the name maghemite in order to distinguish it from martite. This term was adopted and has become firmly entrenched in the geological literature (Basta, 1959).

Newhouse (1929) examined a large number of lodestones (natural material exhibiting polarity) from various localities and reported that they are almost all composed of magnetic ferric oxide rather than magnetite as he had initially assumed. He concluded that lodestone is generally formed from oxidised magnetite which has a higher magnetic remanence than ordinary magnetite. Gruner (1929b) criticised Newhouse's (1929) work and presented data that suggested that certain lodestones are in fact composed of magnetite.

The first detailed crystal structure determination of maghemite was carried out by Thewlis (1931). He synthesised the maghemite and termed it gamma-Fe_2O_3 by analogy to gamma-Al_2O_3. He concluded that maghemite is cubic and has a cell edge of 8,4 Å. He reported that the iron and oxygen atoms occupy the same positions as in the unit cell of magnetite, but that 4 additional oxygen atoms are present. The structure could consequently be regarded as intermediate between magnetite and hematite.

Ödman (1932) reported that maghemite is a common alteration product of magnetite in the lavas of Mount Elgon. He described the optical properties of this mineral and suggested that it might be a common alteration product of magnetite in lavas. He also reported the alteration of magnetite to hematite and described the association of maghemite and

hematite as alteration products of the same magnetite grain.

Welo and Baudisch (1934) presented a historical review of research into gamma-Fe_2O_3 over the period 1838 to 1925. They repeated their earlier conclusions (Welo and Baudisch, 1925) on the two-stage transformation of magnetite to hematite via the formation of intermediate maghemite. They also supported Thewlis's (1931) interpretation of the crystal structure of maghemite.

Grieg et al. (1935) published the results of an extensive investigation into the phase relationships between Fe_3O_4 and Fe_2O_3 at elevated temperatures. They reviewed the earlier experimental work in this system (data largely not discussed here since they are not relevant) and concluded that only limited miscibility exists between magnetite and hematite, e.g. magnetite can contain only 8 mole per cent Fe_2O_3 at $1075^{\circ}C$.

The crystal structure of maghemite was re-examined independently by Hägg (1935), Kordes (1935) and Verwey (1935). They concluded that maghemite differs from magnetite in having a defect lattice in which 1/9 of the iron positions in the crystal structure are vacant. The unit cell consequently contains 32 oxygen ions and 21 and 1/3 cations, while 2 and 2/3 vacant positions are statistically distributed over the 24 cation positions in the inverse spinel structure. Hägg (1935) demonstrated that the cell edge decreased continuously from 8,390 $\overset{o}{A}$ for Fe_3O_4 to 8,322 $\overset{o}{A}$ for gamma-Fe_2O_3 and concluded that the oxidation is also a continuous process.

Newhouse and Glass (1936) reported the results of further investigations into maghemite and concluded that it is cubic and has a crystal structure

similar to magnetite, but with a smaller cell edge. They suggested that it might range in composition from $(Fe,Ti)_2O_3$ to Fe_2O_3 in order to include the titaniferous varieties described by Wagner (1927, 1928). They concluded that it forms as an alteration product of titaniferous and non-titaniferous magnetite and that it is commonly, but not always, a weathering product.

Newhouse (1936) reported the presence of fine hematite exsolution lamellae oriented parallel to the octahedral planes of **magnetite in** basalt from Mount Edna. He concluded that their morphology and distribution indicated an exsolution rather than an oxidation origin.

The crystal structure of maghemite was investigated further by Haul and Schoon (1939) who noted the presence of several additional weak lines on the x-ray powder photographs of this mineral. They suggested that this might indicate either a lower symmetry or larger unit cell than had been previously deduced for this phase. Additional data were presented by Starke (1939).

Mason (1943) reviewed the available data on the system Fe_2O_3-Fe_3O_4 and concluded that gamma-Fe_2O_3 is a metastable phase with respect to hematite. He noted that maghemite cannot be formed from hematite, but that maghemite readily inverts to hematite under suitable temperature and pressure conditions. He noted a common association between maghemite and limonitic material and suggested that oxidation and hydration worked together in the alteration process. He also noted that oxidation of magnetite to hematite can take place directly, usually along the octahedral planes, but that maghemite formation occurred in an irregular fashion.

Edwards (1949) described a fine intergrowth of hematite lamellae along
the octahedral planes of a waterworn magnetite pebble and in magnetites
from some beach sands. He concluded that they represented exsolution
lamellae rather than oxidation products since they were evenly developed
throughout the grain. Baker (1952) reported similar intergrowths in
magnetites in peridotites and amphibolites. Both these authors noted
that the temperatures required for the formation of these intergrowths,
based on the data of Grieg et al. (1935), were much too high for the
formation of magmatic rocks. They concluded that some other factor
must therefore have been involved.

Schmidt and Vermaas (1955) investigated the oxidation of natural magne-
tite by means of DTA. They concluded that the oxidation of magnetite
in air is a two-stage process. The first stage involves the surface
oxidation to hematite while the second stage involves complete oxida-
tion of the sample to hematite. They did not detect the formation of
gamma-Fe_2O_3 at any stage.

David and Welch (1956) studied the oxidation of magnetite under a var-
iety of conditions. They noted that magnetite which produced gamma-
Fe_2O_3 invariably contained appreciable percentages of water, while
oxidation of magnetite under dry conditions never resulted in gamma-
Fe_2O_3. They concluded that the gamma-Fe_2O_3 itself contained a small
percentage of water which could not be removed without destroying the
characteristic spinel structure.

Lepp (1957) also examined the oxidation of magnetite by means of DTA
and concluded that the process involved the following three stages
during rapid oxidation: 1) The formation of gamma-Fe_2O_3 which commences
at approximately $200^{\circ}C$ and culminates at about $375-400^{\circ}C$. 2) The

inversion of gamma-Fe_2O_3 to alpha-Fe_2O_3 which commences at about $375^{\circ}C$ and terminates between 525°-$550^{\circ}C$. 3) The oxidation of magnetite to hematite that commences at between 550° and $575^{\circ}C$. He noted that the rate of oxidation of magnetite at a given temperature and oxygen fugacity is a function of the specific surface of the material and the degree of perfection of the crystal lattice. The finer grain size of the synthetic magnetite would therefore account for its oxidation at lower temperatures.

Finch and Sinha (1957) reported that the transition from alpha-Fe_2O_3 to gamma-Fe_2O_3 would take place above $700^{\circ}C$ under suitable conditions. They suggested that intermediate beta-Fe_2O_3 might also exist.

Basta (1959) reviewed the available data on magnetite oxidation and presented his own results. He concluded that the oxidation of magnetite to maghemite is a continuous process that involves the removal of iron atoms from the magnetite lattice. The oxidation of magnetite to hematite is, in contrast, a discontinuous process and involves a different mechanism. He noted that both maghemite and martite were not developed together in any of his samples. He also suggested that the presence of impurity atoms might influence the formation of these phases.

Gokhale (1961) investigated the oxidation of magnetite and concluded that it changes continuously to maghemite of variable composition. The maghemite then alters to hematite via a discontinuous change. He suggested that the oxidation of magnetite could be considered as a gradual solid solution of magnetite with hematite, the hematite increasing at the expense of the magnetite.

Katsura and Kushiro (1961) reported the natural occurrence of titano-

maghemite in a variety of Japanese volcanic rocks. They concluded that it formed via the oxidation of titanomagnetite during cooling of the lava. They suggested that this phase might be more common than previously recognised and noted that the titanomagnetite contains two or three metal ion vacancies per unit cell.

Verhoogen (1962a) reviewed the available data and concluded that partial oxidation of magnetite-ulvospinel solid solutions is a complicated process that involves the formation of unstable or metastable gamma-phases as an intermediate step.

Colombo et al. (1964, 1965) examined the oxidation of both synthetic and natural magnetite and reported that hematite is always formed at temperatures above $600^{o}C$. They noted that synthetically precipitated magnetites are altered to gamma-Fe_2O_3 at temperatures below $400^{o}C$ via a topotactic oxidation to a solid solution of gamma-Fe_3O_3 in Fe_3O_4. They concluded that oxygen is absorbed and ionised by electrons derived from the oxidation of Fe^{2+} to Fe^{3+}. This oxidation causes a diffusion of Fe ions from the interiors of the magnetite crystals thus forming a solid solution. They noted that the spinel lattice is stabilised by reticular impurities and other crystalline imperfections with the result that oxidation occurs rapidly in the imperfectly crystalline precipitated magnetites.

Colombo et al. (1964, 1965) suggested that the natural magnetites are less imperfect than the synthetically precipitated types. Oxidation of these grains at temperatures between 200° and $500^{o}C$ results in the formation of an outer protective layer of hematite that forms via the disproportionation of a previously formed solid solution. They also noted that the surface areas of the grains (i.e. grain size) might also

be an important factor in the oxidation process.

Elder (1965) investigated the particle-size effect in the oxidation of magnetite by ball-milling natural magnetite in a water slurry and then oxidising the various size fractions. He reported that the less-than-one micrometre-sized material was oxidised to maghemite by heating in air at $250^{\circ}C$. The same material with a grain size of more than 25 micrometres was partially converted to hematite below $400^{\circ}C$. He concluded that the maghemite formed from the fine-grained material is stabilised by adsorbed or hydrated water since similar material produced by grinding under acetone oxidised directly to hematite.

O'Reilly and Banerjee (1966) extended the oxidation mechanisms proposed by Colombo et al. (1964, 1965) to include the titaniferous magnetites and discussed the probable cation distributions in the phases. O'Reilly and Banerjee (1967) also carried out oxidation experiments and concluded that "single-phase oxidation products are only obtained for very small grain sizes, usually produced by precipitation from an aqueous solution and that in such cases oxidation proceeds rapidly at low temperatures due to large specific surface areas, high degree of crystalline imperfection and possibly absorbed water".

Ozima and Larson (1967) reported that naturally occurring titanomaghemites are often intermediate in composition between titanomagnetite and ilmenite-hematite. They noted that pure titanomaghemite decomposes to the alpha phase on heating, but that the alteration of titanomaghemite of intermediate composition at elevated temperatures requires some form of internal redistribution. They postulated that the oxygen vacancies in the intermediate titanomaghemite migrate freely to some concentration centres to form groups of molecules of nearly pure

titanomaghemite that would decompose to the alpha-phase at elevated temperatures. The Fe ions would simultaneously migrate and fill the positions left by the migrating vacancies to produce essentially un-oxidised titanomagnetite. They concluded that this results in a final product consisting of a relatively pure titanomagnetite in which a fine intergrowth of the alpha-hematite-ilmenite series is developed.

Sakamoto et al. (1968) reported the formation of cation-deficient spinels by oxidation of fine-grained synthetic titanomagnetite that had been wet-ground to a grain size of less than 1 micrometre. They noted that the gamma-phases are formed at approximately $300^{\circ}C$ and that they in-verted to the alpha-form at about $500^{\circ}C$. Schult (1968) noted that the various heating experiments probably did not represent natural oxidation conditions and suggested that natural titanomagnetites and titano-maghemites should be studied.

Gallagher et al. (1968) reported that maghemite is always produced when pure magnetite grains smaller than 3000 Å are oxidised at temperatures below $220^{\circ}C$. They noted that larger particles are first oxidised to a composition intermediate between Fe_3O_4 and Fe_2O_3 and then undergo disproportionation into Fe_3O_4 and alpha-Fe_2O_3. The Fe_3O_4 which re-appeared is oxidised directly to alpha-Fe_2O_3 in the last stages of the reaction. They concluded that the metastable gamma-Fe_2O_3 trans-forms to the thermodynamically stable alpha-form at temperatures above $250^{\circ}C$. Colombo et al. (1968) and Gazzarini and Lanzaveccia (1969) criticised the results of Gallagher et al. (1968) and presented addit-ional experimental evidence which indicates that stoichiometric magne-tite can be oxidised to maghemite when its grain size is larger than 3000 Å. They concluded that magnetite containing stacking faults would oxidise partially to hematite, via solid solution, even when the

particle size is less than 3000 $\overset{\circ}{A}$. They stressed that the grain size
of the magnetite only plays a kinetic role and that it is the presence
of nuclei or crystals of alpha-Fe_2O_3 that determine the low temperature
oxidation of magnetite to hematite.

Davis et al. (1968) examined the atom positions and symmetry details of
the magnetite and hematite structures. They concluded that the oxida-
tion process consists of initial iron atom diffusion through an oxygen
framework that remains essentially intact resulting in the formation
of maghemite. The maghemite subsequently inverts to hematite result-
ing in the development of distorted octahedra. The iron from the
diffusion process is oxidised and precipitates around the margins of
the grains.

Prevot et al. (1968) investigated a crystal of titanomagnetite that ex-
hibited a rim of titanomaghemite. They noted that the amount of Fe
decreased in the oxidised zone, but that the contents of Ti and Mn in-
creased. They concluded that the maghemitisation is not a simple
process, but involves the diffusion of some cations and results in a
partial occupation of some theoretically vacant positions in the crystal
structure. (These features might also be interpreted as normal compo-
sitional zoning in the original titanomagnetite, see section 5).

Creer et al. (1970) investigated the oxidation of titanomagnetite to
titanomaghemite and suggested the following mechanisms. "Two ferrous
ions at the edge of the crystal become oxidised to ferric when an
oxygen atom from the surroundings adds itself to the close packed
oxygen structure of the spinel. As time goes by, the Fe ions migrate
within the larger lattice so as to distribute the vacancies uniformly

and the Ti atoms also distribute themselves uniformly so creating a new homogeneous phase".

Readman and O'Reilly (1970) and Sanver and O'Reilly (1970) examined the oxidation of titanomagnetites in more detail and confirmed that different oxidation products are obtained when the same materials are wet- and dry-ground. They concluded that coarse-grained titanomagnetites might oxidise to cation-deficient spinels at low temperatures over geological time. Such changes cannot be observed in the laboratory because of extremely slow oxidation rates at low temperatures. Readman and O'Reilly (1971, 1972) confirmed their earlier observations and calculated that the oxidation of coarse-grained titanomagnetite would require approximately 10^6 years at $20^{\circ}C$. They noted that burial to a depth of a kilometer under slightly elevated temperatures and the presence of water would accelerate this process considerably.

The magnetic properties of titanomagnetite and its various oxidation products have also been examined in detail. A review of this topic is beyond the scope of this review and readers are directed to papers by Ozima and Larson (1970), Ozima and Sakamoto (1971), Readman and O'Reilly (1971, 1972), Johnson and Merril (1972, 1973, 1974) and Kropacek (1974).

The writer has observed the formation of both titaniferous martite and maghemite as oxidation products in titaniferous magnetites from a wide variety of igneous rocks that have been subjected to atmospheric weathering. The oxidation preferrentially occurs via the formation of intermediate titanomaghemite in samples containing abundant fine-grained ulvospinel intergrowths. In contrast, titaniferous magnetites containing larger intergrowth-free areas (i.e. absence of micrometre-

sized intergrowths) oxidised directly to martite along their (111) planes. Similar relationships have been reported in titaniferous magnetites from the Bushveld Complex (Molyneux, 1970a). The diffuse boundary between the magnetite and maghemite suggests that the oxidation is a gradual process and that members intermediate in composition between these phases exist.

The fine grain size of the magnetite cubes (often micrometre- to sub-micrometre-sized) in the ulvospinel-type microintergrowths might render them more susceptible to maghemitization as suggested by the experimental evidence of Colombo et al. (1964, 1965), Elder (1965), and Sakimoto et al. (1968). Water is freely available in the zone of weathering and fulfils another apparent requirement for maghemite stability. The presence of minor impurities in the original titanomagnetite structure might also contribute to the stability of the oxidised defect cubic form.

The presence of the abundant fine-grained Ti-rich lamellae will also impede the development of hematite lamellae along the (111) planes of the titaniferous magnetite since these intergrowths disrupt the crystal structure. This feature is illustrated by the titaniferous magnetites of the Kaffirskraal Complex (Part 3 of this thesis). In this case the titaniferous magnetites exhibit a typical ulvospinel cloth texture and on weathering become oxidised to martite via the intermediate formation of maghemite. Veinlets of optically homogeneous magnetite cutting across the same grains are, however, oxidised directly to martite. Compositional differences between the two types of magnetite might also be important in this respect. Willemse (1969b) suggested that the presence of oxidised ulvospinel (ilmenite) might strengthen the magnetite against the formation of martite.

6.2.4 <u>Conclusions</u>.

The magnetite oxidation mechanisms remain a topic for debate in spite of the extensive amount of research that has been carried out in this field. The natural occurrence of titaniferous maghemite is well established and it is generally accepted that it represents a meta-stable, low-temperature, cation-deficient, oxidation product of titani-ferous magnetite. It forms as an oxidation product at temperatures below $250^{\circ}C$ and this appears to be favoured by the presence of water and an extremely fine-grain size. The presence of impurities and structural defects might also contribute to the stability of this phase. Maghemite inverts irreversibly to the more stable rhombohedral form on heating at temperatures between 250° and $300^{\circ}C$. Maghemite can also invert to martite at much lower temperatures as illustrated by an examination of titaniferous magnetite weathering products.

Rhombohedral martite (hematite) is the common high-temperature oxida-tion product of magnetite and forms either directly on oxidation at temperatures above $300^{\circ}C$ or via the inversion of previously formed maghemite. Martite can also form directly from magnetite during oxidation at low temperatures. The direct martitization of magnetite occurs via the formation of hematite "oxidation lamellae" along grain boundaries and other permeable features of the magnetite. These lamellae migrate into the magnetite along its (111) planes, broaden and coalesce until the whole grain is transformed.

6.3 <u>The Weathering of Magnetite</u>.

The weathering of magnetite initially involves oxidation as discussed in the foregoing section. The subsequent alteration and hydration of magnetite has, however, received only limited attention. Bachmann (1954) reported the formation of goethite as a weathering product of

martites from Taberg, Sweden. Deer et al. (1962b) also reported that goethite is a common weathering product of magnetite.

The Ti-bearing components of titaniferous magnetites are altered to leucoxene (see section 6.5) while the martitised magnetite becomes hydrated to goethite (Molyneux, 1970a). This behaviour is confirmed by the writer's observations on weathering products from a wide range of igneous rocks and titaniferous iron ores (Parts 2 and 3 of this thesis). Fitzpatrick and le Roux (1975) reported that the weathering of titaniferous magnetites results in the formation of titano-hematite. They also noted that goethite forms from these oxidation products in the soil, but that increasing amounts of Ti inhibit the formation of this phase.

6.4 The High-Temperature Oxidation of Titaniferous Magnetite.

The high temperature oxidation of titaniferous magnetite usually occurs during the sub-aerial eruption of lavas. The high atmospheric oxygen fugacities and cooling lava temperatures result in the oxidation of the iron-titanium oxides and the formation of hematite and pseudobrookite assemblages (Lindsley, 1962, 1963). Oxidised titaniferous magnetites of this type were not encountered during this study and readers are directed to the following papers for a detailed discussion of this topic: Wilson and Haggerty (1966), Watkins and Haggerty (1967), Wilson et al. (1968), Ade-Hall et al. (1968), Gromme et al. (1969), Ozima and Larson (1970), Ade-Hall and Lawley (1970), Ade-Hall et al. (1971), Negendank (1972).

6.5 <u>The Low Temperature Oxidation and Weathering of Ilmenite</u>.

6.5.1 <u>Introduction</u>.

Ilmenite is present in economically important concentrations in many sedimentary heavy mineral deposits, particularly beach sands. The ilmenite in these deposits (and in many weathered igneous rocks) commonly exhibits varying degrees of low-temperature alteration due to the effects of weathering under atmospheric conditions. This alteration of ilmenite has been the subject of considerable debate in the geological literature and the subject has been recently reviewed by Dimanche and Bartholome (1976). The debate centres both on the alteration mechanism and the nomenclature of the alteration products.

6.5.2 <u>Mineralogical investigations</u>.

The term leucoxene was introduced by Gumbel in 1874 in order to define a greyish mineral that was associated with ilmenite, titaniferous magnetite and rutile (Tyler and Marsden, 1938). The term has subsequently been loosely applied as a descriptive name for dull, fine-grained, yellowish to brown high-titania alteration products that are formed from the breakdown of a variety of titanium minerals such as ilmenite, sphene and perovskite (Palache et al., 1944). This terminology has persisted to the present, although several detailed investigations have been undertaken in order to determine the true nature of these alteration products.

Palmer (1909) described a monoclinic mineral with the composition $Fe_2O_3.3TiO_2$ which he named arizonite. He also reported the analysis of a "titanic iron sand" from Brazil that approximated his arizonite analysis. He thus concluded that arizonite was the dominant phase in the concentrate. The name arizonite consequently became entrenched in the literature and has been reported as a constituent in numerous

ilmenite deposits even though it has never been positively identified.
Attempts by Ernst (1943) to synthesize this compound also failed.
Numerous attempts have since been made to discredit it as a distinct
mineral species, but the name, like the proverbial bad penny, keeps
re-appearing in the literature.

McCartney (1931) investigated the occurrence of leucoxene in sandstones
and reported that it consists of amorphous calcium titanium silicate
which altered to brookite, anatase and rutile.   Coil (1933) investi-
gated the optical properties and chemical composition of leucoxene in
sandstones and concluded that it is an amorphous, hydrated titanium
oxide.

Tyler and Marsden (1938) carried out x-ray powder diffraction studies
and detailed microscopic examinations on leucoxenes from a wide var-
iety of rock types.   They reported that the leucoxene consisted of
microcrystalline TiO_2 in the form of rutile, anatase and possibly
brookite and suggested that these phases develop at the expense of
leucoxene.   They concluded that leucoxene forms as an alteration pro-
duct of titanium-bearing minerals (generally ilmenite) and that it is
often related to the surface weathering of igneous and sedimentary rocks.

Miller (1945) described ilmenite concentrates from Florida beach sands
and noted that their chemical analyses were similar to those reported
for arizonite.   He examined these ilmenite concentrates by means of
x-ray diffraction and concluded that the Ti-rich alteration products
are essentially amorphous and are therefore structurally different from
arizonite.   Creitz and McVay (1949) also studied the opaque minerals
in the Florida beach sands and concluded that they are leucoxenes that
varied both in specific gravity and titania content.   They noted that

the amount of iron present in these minerals was less than that contained in either arizonite or ilmenite and suggested that they might be derived from the weathering of ilmenite.

Allen (1949) concluded that leucoxene is an amorphous material that varies in both chemical and mineralogical composition. He demonstrated that x-ray powder patterns of leucoxene are similar to those of anatase, sphene and rutile and that small amounts of water are present. He proposed that the term leucoxene be retained as a petrographic term for the alteration products in which titania occurs in rocks and that it should not be used as a mineral name implying a definite mineral species.

Overholt et al. (1950) reported that the physical properties of arizonite could be duplicated by heating ilmenite sand to $900^{\circ}C$ overnight. This treatment destroyed the ilmenite structure. They also reported that pseudobrookite and rutile are produced when finely ground ilmenite is oxidised and that the final products depend on the oxidation temperature. They concluded that Fe_2O_3 and anatase would be formed at low temperatures.

Overholt et al. (1950) re-examined the original x-ray data on arizonite and demonstrated that it consisted of an impure mixture of hematite, ilmenite, anatase and rutile. They concluded that arizonite is weathered ilmenite and suggested that ilmenite oxidation would occur in months at $100^{\circ}C$ and in years at room temperatures. They also supported the idea that arizonite might occur in beach sands that are exposed to strongly oxidising conditions.

Lynd et al. (1954) examined ilmenite concentrates from North Carolina, Florida, Brazil and India by means of ore microscopic and x-ray powder

diffraction techniques. They described the progressive nature of the
ilmenite alteration as seen in polished sections and reported that the
ilmenite decomposes to form hematite and finely crystalline aggregates
of anatase and rutile. They noted that the TiO_2 contents of the ilmen-
ite concentrates increased with progressive oxidation due to the re-
moval of iron by leaching. They concluded that "there is no reason
to postulate the existence of the hypothetical compound, arizonite",
since the various properties of the concentrates could be accounted for
by the progressive alteration of ilmenite.

Bailey et al. (1956) recognised three successive stages in the altera-
tion of ilmenites in beach sands. They noted that progressive alter-
ation is accompanied by a decrease in magnetic suceptibility and an
increase in the ratio of TiO_2 to iron oxides. They reported that the
ilmenite initially decomposes to a lighter-coloured compound consisting
of either an amorphous iron-titanium oxide or a mechanical mixture of
amorphous TiO_2 and iron oxide (stage 1). Once this process is com-
plete (stage 2), the iron is removed and the amorphous material alters
progressively to leucoxene (stage 3).

Bailey et al. (1956) noted that the alteration is progressive and that
all three stages are often observed in single grains. They concluded
that leucoxene commonly consists of oriented aggregates of finely
crystalline rutile, and in some cases, brookite. They noted that the
alteration of the ilmenite grains occurred during the final stages
of transport or perhaps even after deposition. They also reported that
no evidence had been found to substantiate the existence of the mineral
arizonite.

Allen (1956) reviewed the available data on leucoxene compositions and

reported that x-ray powder patterns of leucoxene are similar to those of rutile, anatase, sphene and brookite. He also noted that leucoxene is commonly amorphous and contains a small amount of water. Allen (1956) concluded that "the chemical and mineralogical variability of leucoxene indicates it is not a definite mineral species, but is an alteration product in the same sense as clay".

Bailey and Cameron (1957) provided additional data that illustrate the compositional variablility of leucoxene alteration products of ilmenite. They noted that rutile is the most common constituent of leucoxene and that anatase is less common. They reported that brookite had also been identified as an alteration product and that some leucoxenes consist of mixtures of rutile and anatase or rutile and brookite.

Flinter (1959) investigated the alteration of ilmenite grains from Malaya and confirmed that ilmenite can alter in the solid state to form leucoxene in the manner envisaged by Bailey et al. (1956). Flinter (1959) reported that the alteration results in an increase of TiO_2, Fe_2O_3 and H_2O in the decomposition products, while FeO decreases. He attributed the decrease in FeO contents to the development of Fe_2O_3 and possibly FeO(OH) as a result of oxidation. He also noted that a certain amount of leaching of the iron oxides occurred and that the final alteration products are commonly amorphous. He suggested that this altered ilmenite be termed "hydroilmenite".

Flinter (1959) attempted to recrystallise the amorphous TiO_2-rich ilmenite alteration products by heating and reported that mixtures of rutile and pseudobrookite are formed at temperatures of $1100^{\circ}C$. He suggested that the pseudobrookite represents an unstable high-temperature form that would eventually decompose to yield hematite and anatase.

He considered that the amorphous ilmenite alteration products might themselves recrystallise to form mixtures of rutile, anatase and hematite over long periods of time. He suggested that the term arizonite be retained to indicate these recrystallised phases which would represent an end-product consisting of rutile and/or anatase and/or brookite and hematite.

Karkhanavala et al. (1959) examined a leucoxene concentrate from the beach sands of Quilon, India by means of x-ray diffraction studies on various hand-picked grains. They recognised three types of alteration products consisting chiefly of rutile + pseudobrookite, rutile + pseudobrookite + minor anatase, and rutile + anatase. They interpreted the lack of ilmenite in the leucoxene concentrates as being due to the early destruction of the ilmenite lattice during alteration. They also reported the presence of hematite in all samples and concluded that it is a definite constituent of leucoxene.

Karkhanavala and Momin (1959a) investigated the alteration of ilmenite experimentally by heating ilmenite samples at temperatures between 30° and 1000°C. They reported that heating ilmenite at 650°C for periods of up to 72 hours produced cryptocrystalline mixtures of hematite with small amounts of rutile. Heating at 850°C produced pseudobrookite, rutile and hematite. They concluded that these heating products are identical to naturally occurring leucoxene and suggested that the slow oxidation of ilmenite might occur in a "few hundred years" under the slightly elevated temperature conditions prevailing on tropical beaches.

Karkhanavala and Momin (1959b) investigated the phase relationships in the Fe_2O_3-TiO_2 system under both dry and hydrothermal conditions and attempted to synthesise arizonite ($Fe_2O_3 \cdot 3TiO_2$). They failed to synth-

esise this phase under dry conditions, but reported the formation of a
phase identical to arizonite under hydrothermal conditions. They con-
cluded that this phase is unstable under atmospheric conditions at
temperatures above $500^{O}C$ and noted that it would also probably be un-
stable at lower temperatures.

Karkhanavala (1959) reported that the x-ray powder diffraction data of
the synthetic arizonite prepared earlier (Karkhanavala and Momin, 1959b)
compared favourably with that of the original material. He concluded
that there is no justification for regarding the x-ray pattern of nat-
ural arizonite as being composed of a mixture of hematite, anatase,
rutile and ilmenite. He noted that the limited success he had obtained
in synthesising arizonite under hydrothermal conditions supports its
occurrence as a rare mineral in nature.

Karkhanavala(1959) suggested that arizonite might exist only over within a
limited stability field since the hydrothermal products obtained during
studies of the $Fe_2O_3-TiO_2$ system decompose to pseudobrookite and rutile
on heating to $400^{O}C$ in air. He concluded that arizonite does not form
as a normal atmospheric weathering product, but might form during hydro-
thermal alteration.

Hartman (1959) investigated the alteration of ilmenites in bauxite de-
posits and noted that the process does not operate in the same manner
as in beach sands. He recognised at least three types of alteration
and reported that the leucoxene consists of amorphous material, anatase
and rutile. He did not identify arizonite in his samples but suggested
that mechanical mixtures of finely divided TiO_2 and hematite in the leu-
coxene grains might be chemically equivalent to the hypothetical formula
for arizonite.

Lynd (1960a) published a criticism of the papers by Bailey et al. (1956), Flinter (1959) and Karkhanavala and Momin (1959a). He noted that the starting materials used by Karkhanavala and Momin (1959a) were already highly weathered. They contained 59 per cent TiO_2 and could consequently not be regarded as "ilmenites" in the heating experiments with the result that the value of the reported work is in doubt.

Lynd (1960a) proposed that the terms "altered ilmenite" or "weathered ilmenite" should be used in preference to Flinter's (1959) suggested name of "hydroilmenite". He noted that the chemical and mineralogical composition of these products would vary according to the degree of alteration and that only minor amounts of water are present. He emphasised that the term arizonite should be restricted to the phase $Fe_2O_3 \cdot 3TiO_2$ as originally defined since other uses would be misleading. Lynd (1960a) also recommended that the term "leucoxene" be used as a general term for alteration products containing titanium.

Lynd (1960b) investigated the mechanism and rate of ilmenite weathering by determining the effect of various dilute reagents on originally fresh ilmenite at temperatures between 45 and $50^{\circ}C$. He demonstrated that the weathering process is extremely slow and appears to be favoured by low pH conditions. He noted that the ilmenite is most readily attacked by acid solutions along twin lamellae and the crystallographic (0001) directions. He concluded that the most effective weathering agents are likely to be humic and sulphuric acids in rain and ground water. Sea water and other weakly alkaline solutions do not attack ilmenite appreciably.

Flinter (1960) re-affirmed that the term "arizonite" should be applied to the final recrystallised stages of leucoxene formation. He also

suggested that the pseudobrookite present in the leucoxene samples de-scribed by Karkhanavala et al. (1959) is not an alteration product, but might be a primary phase derived from the source area.

Dyadchenko and Khatuntseva (1960) reviewed the Russian contributions on the subject of ilmenite weathering and concluded that alteration occurr-ed according to the following scheme: ilmenite $\longrightarrow$ hydrated ilmenite $\longrightarrow$ arizonite$\longrightarrow$leucoxene$\longrightarrow$rutile (anatase or brookite). They presented chemical data which indicates that arizonite might exist as an inter-mediate phase in the alteration process. They suggested that leucoxene might be formed as a colloid and that the TiO_2 polymorphs formed during the crystallization of this phase.

Golding (1961) reviewed the nomenclature and **genesis** of leucoxene and suggested that the unqualified term "leucoxene" should be restricted to "material containing at least 75 per cent TiO_2, and consisting pre-dominantly, say 90 per cent by volume, of particles having a maximum short diameter of 5 microns". He noted that the leucoxinization pro-cess usually involves decomposition and differentiation under weather-ing, deuteric or hydrothermal conditions. He concluded that the pro-cess will be controlled by weathering factors such as environmental hydrology, pH and Eh as well as the crystal structure, physical and chemical properties of the ilmenite crystal.

De la Roche et al. (1962) examined ilmenites from south eastern Madaga-scar beach sands and compared them with ilmenites in the country rocks in the hinterland. They concluded that the ilmenite alteration is an extremely slow process that involves the oxidation and removal of the iron while the TiO_2 is retained in an amorphous state.

Teufer and Temple (1966) investigated grains of altered ilmenite from commercial ilmenite concentrates by means of single crystal x-ray diffraction techniques. They identified a new phase with a composition approximating $Fe_2Ti_3O_9$ which they named pseudorutile. They reported that it exhibited hexagonal symmetry and is the major constituent of the alteration products. They also noted that the small amounts of co-existing ilmenite and rutile could easily be distinguished on the basis of their x-ray diffraction patterns.

Temple (1966) investigated the alteration of ilmenite by means of ore-microscopy, electron microprobe and x-ray diffraction techniques. He noted that the process involves oxidation and progressive removal of iron so that the residual product consists essentially of TiO_2. He reported that the alteration process commences along grain boundaries and structural discontinuities in the ilmenite resulting in oxidation and partial removal of the iron from the ilmenite lattice. These changes result in the formation of pseudobrookite which contains between 65 and 70 per cent TiO_2.

Temple (1966) reported that continued alteration resulted in the complete removal of iron from the pseudorutile lattice and the formation of rutile crystallites. He noted that x-ray powder diffraction patterns of altered ilmenites can all be indexed in terms of three minerals: ilmenite, rutile and pseudorutile and this accounts for all the lines present. He did not identify anatase, brookite or pseudobrookite in his samples.

Temple (1966) established that the iron is removed along structural discontinuities during weathering, but noted that the iron might also migrate through the lattice. He concluded that "the removal of iron

from the grain is caused by a migration gradient initiated at the structural interface and facilitated by the slight reduction in size of the Fe atom due to oxidation from the ferrous to the ferric state".

Gibb et al. (1969) examined ilmenites showing various degrees of alteration by means of Mössbauer spectroscopy and concluded that their degree of alteration could be determined by this technique. They also reported the presence of a phase with an x-ray pattern approximating that of $Fe_2O_3 \cdot 3TiO_2$ amongst the alteration products.

Dimanche (1972) investigated the alteration of ilmenites in South African beach sands. He concluded that the process is continuous and recognised four distinct stages of alteration. Each stage is represented by a marked increase in the TiO_2 content of the alteration product and a change in the optical properties. He reported that the cryptocrystalline intermediate materials give the major x-ray diffraction peaks of ilmenite, rutile, goethite and possibly pseudorutile. The final alteration products consist of rutile containing more than 90 per cent TiO_2.

Rao and Rigaud (1974) reviewed the available data on the oxidation and weathering of ilmenite. They experimentally oxidised samples in air and dry oxygen over the temperature range between 500° and $900^{\circ}C$ and investigated the oxidation products by means of x-ray diffraction. They reported that the assemblages hematite + rutile formed between 500° and $750^{\circ}C$; hematite + pseudorutile over the range $770^{\circ}-890^{\circ}C$ while pseudobrookite and rutile formed at temperatures above $900^{\circ}C$.

Grey and Reid (1975) investigated the crystal structure of natural pseudorutile that had been separated from ilmenite concentrates. They

confirmed that it occurs as a major constituent in certain altered ilmenite deposits and represents a distinct intermediate alteration product of ilmenite. All the iron has been oxidised to the trivalent state in this material and one-third of it has been leached out resulting in the stoichiometry $Fe_2Ti_3O_9$.

Grey and Reid (1975) suggested that the stability of pseudorutile is due to the fact that its stoichiometry corresponds to the maximum removal of iron from the ilmenite structure without concomitant removal of oxygen. They noted that oxidation of all Fe^{2+} to Fe^{3+} can occur and that the change in composition can be accounted for by metal ion diffusion and oxidation at the crystal surface as follows:

$$3Fe^{2+}TiO_3 \longrightarrow Fe_2^{3+}Ti_3O_9 + Fe \qquad \dots\dots\dots\dots\dots(1)$$

ilmenite   pseudorutile
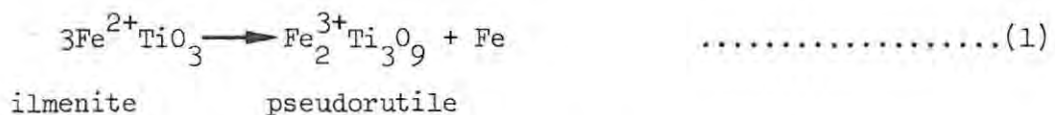
They further noted that the continued removal of iron by leaching to produce rutile must also involve the removal of oxygen as follows:

$$Fe_2Ti_3O_9 \longrightarrow 3TiO_2 \underbrace{+ 2Fe^{3+} + 3O^{2-}}_{Fe_2O_3 (hematite)} \qquad \dots\dots\dots\dots\dots(2)$$

pseudorutile   rutile
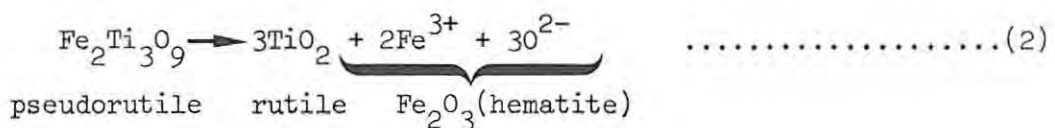
Grey and Reid (1975) concluded that reaction (1) might occur topotactically via the diffusion of iron through an essentially unaltered oxygen lattice while reaction (2) involves a disruption of the anion lattice as both iron and oxygen are removed. They further suggest that reaction (1) occurs predominantly in ilmenite situated below the water table while reaction (2) takes place under conditions prevailing above the water table. They proposed that an **electrochemical corrosion** model could account for the initial alteration of ilmenite to pseudorutile in the zone of saturation while the alteration to rutile in the oxidation zone occurs via a dissolution and reprecipitation process.

6.5.3 <u>Conclusions</u>.

It is evident that the alteration products of ilmenite encompass a wide variety of mineral assemblages, the formation of which is governed largely by the prevailing conditions in each locality. The extremely fine-grained, and often amorphous, nature of the ilmenite alteration products has led to a number of conflicting reports. It is evident that further investigations using electron microprobe and ore-microscope techniques are necessary before theproblem can be satisfactorily solved.

It is generally agreed that the alteration process is essentially continuous and involves the progressive oxidation and removal of iron from the decomposing ilmenite. This results in a breakdown of the ilmenite crystal structure and the formation of amorphous or finely crystalline TiO_2-rich products (usually rutile and/or anatase). Pseudorutile might be formed as an intermediate phase in this process under certain conditions, but the universal occurrence of this mineral has yet to be demonstrated. The alteration process commences along grain boundaries and other permeable features and migrates into the ilmenite, often along (0001). The areas of alteration increase at the expense of the ilmenite until the original grain is completely destroyed.

No universally acceptable system of nomenclature has yet been evolved for the ilmenite alteration products. The existing terminology, especially the word "leucoxene", has been used by various authors to describe various materials. It is suggested that the term "leucoxene" should be retained for use in the widest possible sense to describe fine-grained, TiO_2-rich alteration products as proposed by Allen (1949, 1956). The actual mineral phases present in an ilmenite alteration product should, however, be used whenever their identification is

possible.

7. THE IRON TITANIUM OXIDES AS PETROGENETIC INDICATORS.

7.1 Introduction.

The iron titanium oxides are minor, but important consitutents of the majority of igneous rock types. Their importance has been summarised by Buddington and Lindsley (1964) who stated that "the iron-titanium oxide minerals also provide important paragenetic information on the rocks containing them, and can serve as a useful geological thermometer and oxygen barometer ". Many aspects of the behaviour, compositional variation, microstructural development and mutual relationships between these minerals and their petrogenetic significance have already been discussed in the foregoing sections. This review is confined to a discussion of the Buddington-Lindsley geothermometer which is receiving increasing attention in the geological literature.

7.2 The Buddington-Lindsley Geothermometer.

The phase relationships between co-existing titaniferous magnetite and ilmenite were investigated experimentally by Lindsley (1962, 1963) who demonstrated that their compositions are essentially functions of temperature and oxygen fugacity. Buddington and Lindsley (1964) reviewed the compositions of co-existing iron-titanium oxides in a wide variety of igneous rock types and concluded that Lindsley's (1962, 1963) experimental data could be used to determine the temperatures and prevailing oxygen fugacities under which the oxides crystallised.

Buddington and Lindsley (1964) reported that their inferred temperatures were similar to those obtained by other techniques, but noted that their temperature results for gabbros were too low. They concluded that this

was due to post-crystallisation, external granule exsolution of ilmenite having taken place. They assumed that the minor amounts of foreign elements such as Mg, Al and V present in the oxides would only have a small effect on their phase relationships.

7.3 Application and Criticism of the Buddington-Lindsley Geothermometer.

Amongst the first practical applications of the Buddington-Lindsley geothermometer was that of Carmichael (1967a). He determined the temperatures at which silica-rich volcanic glasses were quenched on the basis of electron microprobe analyses of the iron-titanium oxide phenocrysts. He assumed that the Fe-Ti oxides do not re-equilibrate rapidly with the result that any interaction between ilmenite, titani-ferous magnetite and the magma would cease at the time of quenching.

Carmichael and Nicholls (1967) investigated the application of the Buddington-Lindsley geothermometer to a variety of volcanic rocks and noted that it would only be applicable in cases where the oxidation state of the Fe is controlled only by the oxygen fugacity. They reviewed the available data and concluded that the Fe^{3+}/Fe^{2+} ratios in natural magmas are also controlled by their bulk composition and alkali content in addition to the oxygen fugacity. They noted that this would also influence the compositions of co-existing oxide phases. They suggested that the Buddington-Lindsley geothermometer would have to be calibrated for magmas of varying composition. They noted that the geothermometer might be applicable to a narrow range of basaltic magmas, but that the largest corrections would have to be made for the oxide assemblages in sialic volcanics, particularly the peralkaline rhyolites and phonolites.

Anderson (1968a) applied the Buddington-Lindsley geothermometer in an

investigation of the oxygen fugacities and crystallisation temperatures of alkaline basalts and related magmas from Tristan da Cunha. He determined the compositions of the co-existing oxides by means of the electron microprobe. He based his conclusions on the assumption that any reaction between the phenocrysts and magma that occurred after eruption , but prior to solidification occurred without communication with outside oxidising and reducing agents. He noted that this assumption is consistent with the subsolidus temperature range over which oxidation was shown to occur in Hawaiian and Icelandic basalts by Sato and Wright (1966) and Watkins and Haggerty (1967).

Anderson (1968a) noted that the temperature, fO_2 and TiO_2-activity might vary from place to place within a basaltic magma with the result that it cannot be assumed that separate crystals of ilmenite and titaniferous magnetite crystallised under identical conditions. He also noted that the geothermometer could only be applied if the co-existing oxide phases are in equilibrium. He concluded that mutual saturation and reaction (i.e. equilibrium) would only be attained at the interface between neighbouring opaque oxides so that analyses of these oxides should be made within 10 micrometres of these points.

Anderson (1968a) noted that the iron-titanium oxide phenocrysts changed in composition away from their mutual grain boudnaries and concluded that it is indicative of disequilibrium in terms of fO_2, and TiO_2-activity or both if the temperature remains constant. He stressed that the textural relationships should also be examined in detail before analyses are made since misinterpretations might easily arise. As an example he described the relationships in certain trachybasalts in which the ferrian ilmenite appeared to be unstable with respect to the magma. He noted that this ilmenite is never in direct contact with the ground-

mass or glass, but is separated from it by titaniferous magnetite or augite. He reported that the ilmenite contains magnetite intergrowths which he interpreted as reduced hematite. The hematite content of the ilmenite decreases towards the titaniferous magnetite contact indicating that partial adjustment to relatively reducing conditions had occurred. He concluded that this ilmenite was introduced into the trachybasalt magma as xenocrysts or phenocrysts inherited from a more oxidised magma. The ferrian ilmenite subsequently reacted with the trachybasalt magma and titaniferous magnetite grew as a product of the reduction of the ferrian ilmenite while the magma also gained TiO_2. Utilisation of the analyses of these co-existing, non-equilibrium, oxide phases would obviously yield incorrect results on the Buddington-Lindsley geothermometer.

Anderson (1968b) also investigated the application of this technique to oxide minerals in the plutonic LaBlache Lake titaniferous magnetite deposits. He noted that the oxide assemblage in most plutonic rocks is either three-phase (magnetite + ulvospinel + ilmenite) or two-phase (magnetite + ilmenite) or relict two-phase (ilmenomagnetite + ilmenite). He pointed out that interpretation of equilibrium relationships between the various co-existing and exsolved phases is difficult. He noted that it is necessary to determine whither the discrete or granular ilmenite in a rock last equilibrated with a homogeneous magnetite ancestor or whether equilibrium was attained between the granular ilmenite and the magnetite phase of the complex titaniferous magnetite intergrowths.

Anderson (1968b) reported that the hematite contents of the granular ilmenite and lamellar ilmenite intergrowths are identical and that their oxygen-isotope ratios are also the same. He suggested that the cooling

rates of plutonic rocks are sufficiently slow for the maintenence of
equilibrium between discrete granular ilmenite, ilmenite lamellae in
titaniferous magnetite and the magnetite phase of titaniferous magne-
tite. He concluded that it is therefore not possible to establish the
hematite content of the discrete granular ilmenite that was the
equilibrium associate of the homogeneous ancestral titaniferous magnetite.

Anderson (1968b) noted that the hematite content of ilmenite co-existing
with titaniferous magnetite will decrease if cooling takes place in
a closed system devoid of other oxidising agents. The result of this
is that the hematite contents of the ilmenites represent minima so that
the apparent temperatures and oxygen fugacities are also minima. He
concluded that the LaBlache Lake deposit had cooled under closed condi-
tions and obtained temperatures close to $800^\circ C$ for many of his ilmenite-
poor samples using the geothermometer. He consequently suggested that
the closed system exsolution and/or oxidation-exsolution of ilmenite
from titaniferous magnetite ceased at temperatures above $800^\circ C$.

Anderson (1968b) reported that oxidised specimens of the opaque oxides
are very much more difficult to interpret since the hematite content of
the ilmenite might be augmented. He noted that the augmented hematite
content of the ilmenite will give fictitiously high temperatures and
relative oxygen fugacities when all the ilmenite derived by oxidation-
exsolution is retained as intergrowths in the titaniferous magnetite.
Conversely, the deduced temperatures will be too low, while the corre-
sponding relative oxygen fugacities will be apparently variable when
most of the ilmenite derived by oxidation-exsolution forms granular
ilmenite. He noted that this would depend on the relative importance
of exchange reactions with the titaniferous magnetite and the amount
of hematite produced by oxidation of the magnetite. He concluded that

the application of the Buddington-Lindsley geothermometer to plutonic rocks containing external granule ilmenite will produce evidence of the recrystallisation conditions rather than those of igneous crystallisation.

Gromme et al. (1969) investigated the application of the Buddington-Lindsley geothermometer to basaltic complexes collected from the cooling Alae and Makaopuhi lava lakes. The samples were collected by core-drilling into the solid and semi-solid lava. The drilling fluid effectively quenched the samples which were representative of a temperature range from $25^{\circ}C$ to $1050^{\circ}C$. The corresponding temperatures and oxygen fugacities were determined by measurement down the borehole. The co-existing oxides were analysed by means of electron microprobe and the experimental temperature and oxygen fugacities compared with the true values.

Gromme et al. (1969) noted that the experimentally determined temperatures were approximately $100^{\circ}C$ (and up to $400^{\circ}C$) higher than the directly measured values. They concluded that the re-equilibration temperatures of the oxides exhibit a lag of approximately $100^{\circ}C$ behind the temperature as the lava cools. They also noted that the content of opaque oxides in many lavas is too low for the ilmenite to have reacted with the titanomagnetite to buffer the oxygen fugacity.

Speidel (1970) investigated the phase relationships between co-existing rhombohedral and spinel phases in the $MgO-FeO-Fe_2O_3-TiO_2$ system at temperatures between 1300° and $1160^{\circ}C$ under various oxygen fugacities. He noted that small amounts of MgO influence the phase relationships in this system at elevated temperatures and noted that 4 per cent by mass of MgO in titanomagnetite at $1160^{\circ}C$ is sufficient to change the

oxygen fugacity by one order of **magnitude**. This suggests that the presence of small amounts of other elements might not be negligable as is usually assumed. He noted that the effect is less **apparent** at lower temperatures and can be partly offset by allocating the Mg to both $MgTiO_3$ and Mg_2TiO_4 in the mineral calculations.

In spite of the problems inherent in using this geothermometer numerous attempts were made to apply this technique to volcanic (e.g. Evans and Moore, 1968; Smith and Carmichael, 1969; Lipman, 1971; Anderson and Wright, 1972; Wass, 1973; Fodor, 1975) and plutonic rocks (e.g. Gasparrini and Naldrett, 1972; Duchesne, 1972; Elsdon, 1972; Grapes, 1975; Barker et al., 1975; Mathison, 1975; Buchanan, 1976). Very much lower temperatures than expected were obtained for the plutonic rocks and the authors concluded that they represented temperatures at which re-equilibration between the oxide phases ceased.

Thompson (1975) examined the one atmosphere liquidus oxygen fugacities of some tholeiitic intermediate, alkalic and ultra-alkalic lavas experimentally and compared the results with those obtained using the compositions of natural oxides. He concluded that the iron-titanium oxide phenocrysts in lavas undergo partial sub-liquidus re-equilibration during the further crystallisation and quenching of the rock, even when it is very fine grained. He discussed various aspects of the application of the Buddington-Lindsley geothermometer and concluded that the compositions of phenocrysts cannot be used without reservation to determine the liquidus conditions under which they formed.

Bowles (1976) obtained different temperature results for several ilmenite-titaniferous magnetite pairs in the same polished section. He concluded that different oxygen fugacities can exist, at least locally

within an igneous rock. He suggested that this might be due to the existence of small pockets of residual fluids in the interstices between grains after the bulk of crystallisation and these would control the oxygen fugacity directly. He noted that many of the earlier reports had assumed that the compositions of theco-existing oxide phases in a rock were identical and should be regarded with caution.

Whitney and Stormer (1976) compared the results of the Buddington-Lindsley geothermometer with those obtained using a two-feldspar technique in epizonal granitic intrusions. They obtained similar results from both those techniques and concluded that the oxides re-equilibrate on cooling to the solidus.

Bohlen and Essene (1977) obtained comparable results using both the oxide and feldspar techniques in an investigation of granulites. They reported that the titaniferous magnetites contain ilmenite intergrowths, but they successfully calculated the bulk compositions of these grains by analysing the two phases and determining their relative amounts by point counting. Gasparrini and Naldrett (1972) had also used a similar technique to determine the bulk compositions of the Sudbury titaniferous magnetites.

Himmelberg and Ford (1977) examined the co-existing oxide assemblages in the Dufek Intrusion and obtained a range of temperatures using the Buddington-Lindsley geothermometer. They attempted to determine the original compositions of the high-temperature unexsolved oxide phases. These attempts were generally unsuccessful and they concluded that reconstructions of this sort are very difficult due to the complex post-crystallisation changes that occur in the oxide minerals. They noted that the lower temperatures reflected equilibration at different

stages during cooling in agreement with other results on plutonic rocks (e.g. Anderson, 1968b; Duchesne, 1972; Mathison, 1975).

Bowles (1977) suggested that the compositions of different sized ilmenite lamellae in an exsolved titaniferous magnetite grain might be useful in determining the temperature conditions under which they formed. His technique involves modal analyses and microprobe analyses of the various phases and then a reconstruction of their compositions at different stages of the cooling process. He determined the compositon of a grain of granular ilmenite and calculated the bulk composition of a co-existing titaniferous magnetite. He concluded that the corresponding temperature represents the temperature at which external granule exsolution ceased. Similarly he determined the compositions of coarse lamellar ilmenite and the bulk composition of the remainder of the titaniferous magnetite host. This gives the temperature at which coarse lamellar development ceased.

The accuracy of these results is in doubt because of the inherent problems associated with modal analyses of these fine-grained intergrowths and the limited number of grains in a polished section. Similarly certain assumptions have to be made regarding what represented original co-existing grains. Bowles (1977) mentions a discussion of probable errors in this method that is "in the press", but this is unfortunately not yet available. He also pointed out that various schemes can be used to recalculate the electron microprobe analyses and that the temperature and oxygen fugacity values obtained can differ depending on the re-calculation procedure used. This feature makes the direct comparison of results difficult.

Powell and Powell (1977) noted that the intersecting contours on the

widely-used temperature-oxygen fugacity diagram of Buddington and Lindsley (1964) intersect at low angles and are almost sub-parallel in places. This results in uncertainties, particularly in the case of co-existing $FeTiO_3$-rich ilmenites and Fe_2TiO_4-rich magnetites. They reformulated the experimental data of Buddington and Lindsley (1964) on a thermodynamic basis in such a way that this problem is largely overcome. They produced a graphical determination method in which the concentration of ulvospinel in magnetite is plotted against the concentration of ilmenite in the ilmenite-hematite solid solution. The temperature is indicated on the graph by means of sets of univariant isotherms and the system is independent of oxygen fugacity. They also produced a similar diagram that is independent of temperature in which the oxygen activity is plotted against the mineral compositions.

Powell and Powell (1977) stressed that their results are strictly only applicable to binary solid solutions and should only be used for Fe-Ti oxides that are close to the theoretical end-members in composition. They also commented on the possiblety of obtaining different results when using different methods of recalculating the electron microprobe analyses. They suggested that the analyses be recalculated in such a way as to yield maximum and minimum values so that the differences between them can be taken as an indication of the maximum uncertainty in the determinations.

7.4 Conclusions.

The Buddington-Lindsley geothermometer represents a petrogenetically important method for determining the temperature and oxygen fugacities in igneous rocks. The method suffers from the same inherent problems

as many other techniques that require the extrapolation of experiment-
ally determined data on simple systems to more complex, multi-component
natural situations. The technique is most easily applied to pheno-
crysts or microlites in quenched lavas, but even here, equilibrium
problems arise as discussed by Carmichael and Nicholls (1967),
Anderson (1968a) and Thompson (1975).

The application of the technique to more slowly cooled oxide grains
requires assumptions as to what were co-existing equilibrium assem-
blages at various stages during cooling. The lack of suitable methods
for determining bulk mineral compositions of complex grains with the
microprobe provides added problems. The temperature results obtained
from plutonic rocks are inevitably low and are usually inferred to
represent temperatures at which re-equilibration ceased (usually between
600° and 800°C).

Results obtained by the Buddington-Lindsley geothermometer are being in-
creasingly reported in petrologic studies and it can now be regarded
as a standard technique. Unfortunately there is a tendency to quote
the determined temperatures and oxygen fugacities without presenting
the analytical data, let alone a detailed microscopic description of
the opaque oxides. It is apparent from the foregoing review that many
pitfalls await those who attempt this technique without a thorough
understanding of the behaviour of the iron-titanium oxides during sub-
liquidus cooling of igneous rocks.

8. CONCLUDING REMARKS.

This literature review has highlighted some of the complex problems
posed by the iron-titanium oxides encountered during the investigations
reported in Parts 2 and 3 of this thesis. It conveys some idea of the

present state of knowledge about certain aspects of these minerals and it is evident that a great deal of research is necessary before this system is completely understood.

The theoretical models of microstructure development proposed in this review have direct application to natural systems and form the framework within which interpretations in the following sections are based. The nature and behaviour of the iron-titanium oxides in a wide variety of igneous rocks are interpreted in terms of their development being controlled, not only by the initial crystallisation conditions, but also by various post-crystallisation processes.

PART II

THE CO-EXISTING IRON-TITANIUM OXIDES IN SOME SOUTH AFRICAN INTRUSIVE IGNEOUS
ROCKS AND BEACH SANDS.

1. INTRODUCTION.

The iron-titanium oxides occur as primary accessory phases in a wide variety
of igneous rocks. Ilmenite and titaniferous magnetite are the most common-
ly encountered primary members of this mineral group and are present in a
wide range of intrusive igneous rock types ranging from ultrabasic through
basic to SiO_2-rich types. The high-temperature oxidation products of these
minerals (pseudobrookite and hematite) are encountered in some sub-aerially
erupted lavas while their secondary alteration products (hematite and
leucoxene) are common in the zone of atmospheric weathering.

The iron-titanium oxides are becoming increasingly important as petrogenetic
indicators, but surprisingly little is known about their compositional varia-
tion and mutual relationships in certain igneous rock types. The aim of
this section is to present new data and summarize the available information
on the co-existing iron-titanium oxides (largely ilmenite and titaniferous
magnetite) in a variety of igneous rock types ranging from kimberlite to
granite.

2. THE ECONOMIC SIGNIFICANCE OF THE IRON-TITANIUM OXIDES.

Ilmenite is the most economically important iron-titanium oxide in many
igneous rocks, but it is only rarely present in sufficient concentrations to

warrant consideration as an ore. Ilmenite is, however, released during weathering and it is incorporated as a common detrital heavy mineral constituent in many sandstones and other sedimentary deposits as it is relatively stable under normal transportation and weathering conditions. Natural processes often concentrate this ilmenite along with other heavy minerals to such an extent that their exploitation becomes economically feasible.

An increased demand for ilmenite as a raw material for TiO_2-pigment manufacture (Roskill, 1971) has led to the investigation of many ilmenite-bearing sedimentary deposits in South Africa. Interest has been focussed largely on deposits in the Ecca sandstones of the Transvaal and Free State (Behr, 1965) as well as the coastal sand dunes that are developed in certain localities (Coetzee et al., 1957; Nel and Koen, 1960; Dimanche, 1972). The coastal dunes contain the most economically viable deposits. Ilmenite has been produced at Umgababa on the Natal South Coast (Nel and Koen, 1960) and at Morgan's Bay in the Transkei. Production of high-titania slag and and pig iron from ilmenite concentrates has recently commenced at Richard's Bay and utilizes material recovered from coastal dunes in the vicinity.

The presence of minor quantities of Cr, Mn and Mg in the ilmenite concentrates is undesirable since these elements, particularly Cr, can adversely effect the colour of the TiO_2-pigment and consequently decrease the value of the ore. These elements are often present in the ilmenite and can not always be ascribed to the presence of other associated minerals such as chromite, with the result that they cannot be removed by conventional ore-dressing techniques. A knowledge of the compositional range of these ilmenites and their probable source rocks would consequently be of importance in the appraisal of beneficiation tests on ilmenite concentrates produced from secondary deposits.

The ilmenites from kimberlites are characteristically Mg-rich and, although

they are of no economic importance in themselves, they are widely used as indicator minerals during prospecting operations (e.g. Besson, 1967; Cervelle et al., 1971; Frick, 1973a). A thorough knowledge of the chemical variablity of ilmenites from a wide range of igneous rock types is also essential in this context.

Titaniferous magnetite also becomes concentrated along with ilmenite in these heavy mineral deposits but is not usually of any economic significance. Primary titaniferous magnetite is found concentrated in discrete layers in some stratiform basic intrusions and this topic is covered in Part 3 of this thesis.

3 SCOPE OF THE PRESENT INVESTIGATION.

The principal aim of this study is to investigate the nature and occurrence of the iron-titanium oxides, in particular ilmenite, in a variety of South African intrusive igneous rocks. The co-existing opaque oxides in a number of rock types ranging from kimberlite to granite pegmatite were investigated microscopically using incident light techniques. The compositional ranges of the ilmenites from the different rock types were established by means of wet-chemical and electron microprobe analyses. Additional data were obtained from the literature.

The ilmenites from the various rock types were characterized by means of reflectivity and micro-indentation hardness measurements while their unit cell dimensions were determined using x-ray diffraction techniques. The possibility of determining the chemical composition of the ilmenites by means of one or more of these properties was also investigated. The small compositional range shown by the ilmenites from most common igneous rocks prevented the application of these indirect measurement techniques except in the case of the kimberlitic ilmenites which can readily be distinguished

on the basis of a number of parameters.

The co-existing titaniferous magnetites are, in contrast, characterized by the extensive development of complex microintergrowths. These intergrowths, often on a micrometre scale, interfere with the measurement of reflectivity and micro-indentation hardness so that the value of the measurements is doubt-ful. These properties were consequently not determined. These grains were not analysed by means of electron microprobe in view of the problems present-ed by the extremely fine-grained intergrowths. Bulk chemical analyses of titaniferous magnetite concentrates, although desirable, were not undertaken in view of the large number of analyses presented in Part 3 and the costs involved.

The analytical data presented in this section are confined largely to the discrete ilmenite grains in the various rock types. The data presented for the co-existing titaniferous magnetites are largely of a descriptive nature and are concerned mainly with microstructural development in view of the difficulties in determining their other parameters accurately.

This study was confined to the mineralogical investigation of the opaque oxides in the rocks examined. Thin sections of rocks were examined in transmitted light in order to confirm their identity and check for possible post-crystallization alteration. The co-existing silicates were not examined in detail since the compositional variations and optical properties of the major rock-forming silicates are already well known. The composition-al variations between the ilmenites from the basic and SiO_2-rich rock types also proved to be much less than those exhibited by their co-existing feld-spars and pyroxenes. No attempt was made to relate the compositional var-iations of the Fe-Ti oxides to similar changes in their co-existing silicates

in view of the large number of mineral analyses that would be required and the costs involved.

Trace element studies, particularly of Ni, Cu, Co, Zn, Zr and Nb would have been invaluable in this study since these elements might be expected to show a much greater variation than the major and minor elements for which analyses were made. Analyses of this nature were, unfortunately, beyond the scope of this study.

4. METHODS OF INVESTIGATION.

1). Samples of suitable host rocks were collected from surface outcrops during field excursions or were obtained from reliable sources. Iron-titanium oxides from the following rock types were examined: kimberlites (ilmenite only), gabbros, norites and gabbronorites, Karroo dolerites, diabases, syenites, granophyres, granites, and pegmatites. The ilmenites in ten Eastern Cape beach sands were also investigated.

2). Thin sections were prepared for microscopic examination in transmitted light in order to confirm the identity of the host rock and check on the possible presence of post-crystallisation alteration features.

3). Polished sections of the host rock were prepared for microscopic examination in incident light. These sections were used to examine the mutual relationships between the co-existing opaque oxides and their micro-structures.

4). Representative portions of the rocks were crushed and ilmenite and titaniferous magnetite concentrates prepared as described in Appendix 1.

5). Polished sections of the ilmenite and some of the titaniferous magnetite concentrates were prepared. These sections were used for reflectivity and micro-indentation hardness determinations as well as for electron microprobe analyses.

6). Wet chemical analyses were carried out on 38 of the ilmenite concentrates

for which sufficient material (more than 0,5 g) was available.

7). The unit cell dimensions of the Karroo dolerite and kimberlite ilmenites were computed using x-ray powder diffraction data.

5. TECHNIQUES, APPARATUS AND OPERATING CONDITIONS.

5.1 Introduction.

The experimental and analytical studies embodied in this section were largely carried out at Rhodes University and at the National Institute for Metallurgy (NIM) over a period of five years. Additional microscopic investigations, reflectance and micro-indentation hardness determinations were made at University of Port Elizabeth. The nature and types of apparatus available at these three institutions differ and only results that were obtained on similar equipment under similar operating conditions have been compared.

5.2 X-ray Diffraction Studies and the Determination of Unit Cell Parameters.

5.2.1 Introduction.

The objective of the x-ray powder studies was to determine the unit cell parameters of the ilmenites and investigate any dimensional changes caused by compositional variations of this mineral. The possibility of utilising certain peak positions (two-theta angles) as an indicator of ilmenite composition was also investigated. Qualitative x-ray determinations were carried out at Rhodes University while quantitative measurements were made at NIM.

5.2.2 Qualitative x-ray diffraction studies.

Purified ilmenite concentrates covering the range of samples investigated in this study were analysed at Rhodes University using the G.E.C. XRD 3 x-ray diffractometer with a xenon detector available at that time. Fe-filtered Co radiation was used and the samples were run at a scan speed of $\frac{1}{2}^{O}$ 2-theta per minute. The rating of the Co-x-ray tube required operation

at low kV and mA settings in order to keep the output below 600 watts. The diffractometer was calibrated using a pure quartz sample on the basis of the published d-spacings of Frondel (1962). The optimum operating conditions were determined by means of an extensive series of investigations involving the evaluation of variables such as kV, mA, time constant, counting rate, different beam, soller- and receiving-slits and chart speed.

The utilised operating conditions yielded only between 8 and 10 useable reflections, mostly in the low two-theta angular range that correspond to the most intense ilmenite peaks on the diffractogram. Determinations of the weaker high 2-theta reflections were also complicated by the high levels of background caused by secondary radiation and inadequate pulse-height discrimination circuitry. The k-alpha doublet was only poorly resolved, even at the highest 2-theta angle for which useable reflections were obtained (hkl = 2,1,10). The possible use of quartz as an internal standard during the diffractometer runs was investigated, but without success. The presence of the quartz merely reduced the intensity of certain ilmenite peaks so that they were not adequately resolved. Certain quartz peaks also overlap with those of ilmenite.

The unit cell dimensions of the analysed ilmenites were calculated by means of the least-squares refinement of the diffraction data using the computer programme of Appleman and Evans (1973). The results obtained were unsatisfactory and indicated an unacceptably high standard deviation between

the measured d-spacings and those calculated on the basis of the determined unit cell parameters. A relatively large variation in the unit cell parameters of ilmenites that are chemically very similar was also noted, e.g. a variation of 0,008 Å in the a-direction and 0,017 Å in the c-direction was noted for ilmenites from Karroo dolerites. The main reasons for the poor results are ascribed to: (1) the low intensity of the Co x-radiation used and the resulting small number of peaks that were obtained; (2) the limited number of d-spacings particularly in the important high 2-theta range, used in the unit cell calculations; (3) the poor resolution of the measured peaks in the higher 2-theta ranges and the problems involved in their interpretation, and (4) the lack of an internal standard with which the peak positions could be accurately accertained.

The results obtained during these x-ray diffraction studies indicated that the d-spacings and unit cell parameters of the kimberlite ilmenites are different from those of ilmenites from a wide range of other igneous rocks and might serve as a basis for distinguishing between them. The measured d-spacings of the ilmenites from the whole range of other investigated igneous rock types showed a limited variation. Their calculated unit cell parameters also differed by a maximum of 0,01 Å in the a-direction and 0,02 Å in the c-direction. These variations could not be related directly to compositional differences between the ilmenites and are not significantly greater than the range of values shown by the Karroo dolerite ilmenites.

It was concluded that the range of calculated cell dimensions obtained for the non-kimberlite ilmenites is due largely to inaccuracies in the x-ray diffraction studies as discussed above. This conclusion is supported by the chemical analyses of these ilmenites which show only minor compositional differences between those minerals from different rock types. These results also showed that it would not be possible to distinguish minor compositional

differences in the ilmenites on the basis of x-ray powder data. The larger
compositional differences exhibited by the kimberlite ilmenites, are,
however, reflected by noticeable changes in the position of their x-ray
reflections (two-theta angles) and unit cell dimensions. This aspect
appeared sufficiently interesting to warrant a more detailed study and
this investigation was shelved until a diffractometer capable of
greater resolution became available.

5.2.3 Quantitative x-ray diffraction studies.

5.2.3.1 Introduction.

It was decided on the basis of the earlier x-ray diffraction studies to
confine this investigation to ilmenites from kimberlites and one other
igneous rock type. Karroo dolerite ilmenites were selected for this study
since they had been characterised by the other mineralogical techniques
and are compositionally close to the theoretical ilmenite end-member
composition. Their compositional range is also typical of ilmenites from
a wide range of basic igneous rocks. The co-existing titaniferous magnetite
and its intergrown ilmenite were also subjected to detailed x-ray powder
diffraction studies.

5.2.3.2 Apparatus.

The quantitative x-ray diffraction studies were carried out using equipment
in the Mineralogy Division at NIM. A Philips PW 1140/00 3 kw x-ray genera-
tor fitted with a Philips RW 1050/25 wide angle goniometer having a tolerance
of $\pm$ 0,0025° two-theta and a reading accuracy of 0,01° two-theta was used.
The x-radiation was produced by a Philips 2 kw PW 2256/00 broad focus Co
x-ray tube with the instrumentation being provided by a Philips PW 1325

instrument panel. The radiation detector was fitted to an x-ray focussing monochromator using a curved graphite crystal and manufactured by Advanced Metals Corporation, Burlington, Massachussetts.

5.2.3.3 Calibration and operating conditions.

The graphite monochromator was fitted to the diffractometer and the entire instrument was carefully aligned and checked by a trained Philips technichian immediately prior to these series of determinations. The equipment was calibrated using the standard pressed silicon disc supplied with the diffractometer for this purpose. The resolution of the k-alpha doublet for the (311) Si peak at 66° two-theta was checked by comparison with a standard diffractometer trace supplied with the monochromator and made under optimum conditions. The monochromator was adjusted until comparable

results were obtained in which the k-alpha doublet was clearly resolved with the intensity of the k-alpha_1 peak being twice that of the k-alpha_2 peak. The resolution of the k-alpha doublets and their correct intensity ratio represent a sensitive indicator of the correct alignment of the monochromator. This feature was checked repeatedly throughout the course of the determinations which were carried out over a period of approximately three months.

The use of the graphite monochromator resulted in a significant improvement in intensity, resolution and peak to background ratio. This was particularly important in the high two-theta region where it became possible to measure peaks that could otherwise not be resolved. The improvement could be clearly seen when the monochromated x-ray diffractometer traces were compared with those made earlier on the same equipment and under identical operating conditions, but using the standard Fe-filter and slit assemblages.

The x-ray focussing monochromator can be considered as a narrow band pass filter which is set so that it transmits a band of wavelengths slightly wider than the k-alpha doublet (manufacturer's handbook). The increased peak intensity is due to the use of unfiltered x-radiation and different slit assemblages. The improvement in peak to background ratio and resolution was the direct result of the monochromator which effectively discriminates against secondary fluorescent and scattered radiation from the specimen (background radiation).

The optimum operating conditions were determined by experimentation. Unfiltered Co radiation was used and was generated at a setting of 40 mA and 45 kV. A goniometer scan speed of $\frac{1}{4}^O$ two-theta per minute was used since this produced a good resolution of the k-alpha doublet for two-theta angles above 50° and represented a reasonable speed. A chart speed of 10 mm/min was selected to produce a spacing of 10 units per degree on the chart paper for easy measurement.

A time constant of 8 was used in accordance with the operating instructions for the instrument which state that the time constant should be equal to 2/scan speed in $^O 2 \theta$ per min for optimum conditions. The counting rate was adjusted for each peak in such a way that the entire peak was recorded on the chart paper at its maximum possible size.

Optimum resolution of the k-alpha doublets was obtained by using a 1^O divergence slit and a $\frac{1}{4}^O$ (0,125 mm) receiving slit in conjunction with the graphite monochromator (manufacturer's handbook) and these conditions

were used for all 2-theta angles below 90°. The peak intensities are generally very low at higher two-theta values and the use of a 4° divergence slit resulted in an increase in intensity of approximately 45 per cent without any loss in resolution. The intensity could be further increased by using a $\frac{1}{2}$° receiving slit when necessary and these conditions were used for two-theta angles above 90°.

The mineral powders were firmly pressed into glass-backed Philips aluminium sample holders that had been ground down to approximately 0,2 mm in thickness. These holders held approximately 0,2g of sample and care was taken to ensure that the surface of the mineral powder was level and flush with the surface of the surrounding aluminium holder. No problems associated with the preferred orientation of the mineral grains were encountered with either ilmenite or titaniferous magnetite.

5.2.3.4 <u>Internal standard</u>.

The peak positions on the diffractometer traces were checked by means of an internal standard and corrections were applied where necessary. Silicon powder purchased from the United States National Bureau of Standards was used as the internal standard. This represents the official x-ray diffraction standard (SRM 640) that is prepared from electronic grade float-zone prepared silicon boules that are more than 99,99 per cent pure (Hubbard et al., 1974).

The d-spacings and two-theta angles of this silicon standard were calculated for Co radiation using the following wavelengths from Fang and Bloss (1969):

Co k-alpha = 1,79021 Å

Co k-alpha$_1$= 1,78892 Å

Co k-alpha$_2$= 1,79278 Å

The two-theta values calculated for the silicon standard showed no significant variation in the second decimal place over the range between 20 and 138° when compared with the values supplied with the standard Philips pressed silicon disc. The diffractometer could thus be calibrated using either the pressed silicon disc or the standard reference material when necessary.

The silicon standard is in a finely ground form and approximately 20 per cent by mass of it was added to the ilmenite and titaniferous magnetite samples prior to analysis. The samples were then thoroughly mixed with the standard by grinding in an agate mortar under acetone. The samples were packed into the sample holders once the acetone had evaporated.

5.2.3.5 Measurement of peak positions, accuracy and precision.

Measurements of the peak positions of both the Si standard and the ilmenites or titaniferous magnetites were made according to the method suggested by Swanson et al. (1968). The pattern peaks were measured in the centre at a position averaging about 75 per cent of the peak height for low two-theta values. The two separate peaks were measured in the same way when both the k-alpha$_1$ and k-alpha$_2$ peaks were resolved at higher two-theta values.

The k-alpha$_1$ was measured and an averaged k-alpha value determined in cases where k-alpha$_1$ was resolved, but k-alpha$_2$ was imperfectly resolved. The internal standard correction appropriate to each region was then applied to the measured two-theta values. Linear interpolations were used for regions between the standard peaks in cases where the internal standard correction varied along the length of the pattern.

Slight peak overlap occurs between the silicon standard and ilmenite peaks at 66° and 137°. The k-alpha$_1$ peak of both these phases is, however, usually resolved and can be measured. Values for both k-alpha$_1$ and k-alpha$_2$ of ilmenite were obtained at these angles by first measuring the pure ilmenite without any internal standard and using the Si as an external calibration medium. These values were then corrected in the normal manner and were added to the more accurately determined values for computation.

The (800) reflection of titaniferous magnetite overlaps with the 117° peak of the silicon and this was handled in the same way as for ilmenite. The (311), (444), (642) and (555) reflections of titaniferous magnetite at 41°, 95°, 106° and 134° respectively also overlap with their intergrown ilmenite peaks in these regions. Attempts were made to measure either their k-alpha$_1$ or k-alpha$_2$ peaks in places where they were resolved.

The coarse-grained ilmenites produce well defined x-ray diffraction peaks showing very good k-alpha doublet resolution above 72° two-theta. The fine intergrown ilmenite in the titaniferous magnetite, in contrast, exhibits fairly marked peak broadening, particularly in the higher two-theta ranges. The titaniferous magnetite exhibits an even more marked peak broadening and resolution of the k-alpha doublet is rarely achieved at angles below 110°

two-theta.   The main reasons for this line broadening are as follows:

1). lattice distortion and strain caused by the grinding process,

2). the small crystallite size of the two phases since the magnetite is
broken up into sub-micrometre sized cubes due to the presence of an
ulvospinel "cloth structure" (now largely altered to ilmenite),

3). a small amount of unoxidised ulvospinel might be present as a second
spinel phase,

4). partial oxidation (maghemitization) would be responsible for a slight
change in magnetite cell dimensions.

5). broadening of the ilmenite peaks might also reflect compositional
differences between the "exsolved" ilmenite lamellae and those formed by
the oxidation of exsolved ulvospinel. (as illustrated by Mathison (1975),
in the Somerset Dam Intrusion).

The peak positions (two-theta values) were measured directly to the first
decimal place on the diffractometer trace while the value of the second
decimal place was determined by interpolation.   A series of duplicate
measurements indicated that they are readily reproducible to within
$\pm$ 0,01°.   The use of the silicon internal standard provides the necessary
control on the accuracy of the measurements which are considered to be
within 0,02° two-theta of the true values.   Hubbard et al. (1974) state
that the use of the silicon x-ray standard should result in a reproducibility
of 2 parts in 10^5 when using goniometer and interpolating angles to 0,0025°.
The accuracy achieved cannot be greater than that allowed by the measuring
technique which is $\pm$ 0,02° two-theta.

5.2.3.6 Computation of unit cell dimensions.

The problems involved in the determination of unit cell parameters from
diffractometric measurements have been reviewed by Klug and Alexander (1974).

They note that the major sources of error are: 1) instrument misalignment, 2) slight inaccuracies in the gearing of the goniometer drive, 3) errors in the zero degree two-theta position , 4) flat specimen error , 5) specimen transparency, 6) axial divergence, 7) specimen displacement, 8) rate meter recording, and 9) dispersion and the Lorentz factor. The diffractometer goniometer and other settings were carefully checked while the other errors are significantly decreased by the use of the x-ray diffraction standard (Hubbard et al., 1974).

The unit cell parameters were computed by means of a least-squares refinement of the diffraction data (Appleman and Evans, 1973). This programme automatically indexes the x-ray reflections, but this facility was not used. Ilmenite is trigonal and can consequently be indexed according to either rhombohedral or hexagonal axes. The ASTM powder diffraction file data card for ilmenite (3-0781) is indexed according to hexagonal axes and this procedure was followed in this study. It should be noted, however, that the hexagonal cell determined by this method is triply primitive and certain lines that would be present if the lattice were truly hexagonal are absent since the underlying lattice is rhombohedral (Henry et al., 1960). The magnetite reflections were indexed according to the scheme of Basta (1957).

The least-squares refinement requires the maximum available data in order to determine the unit cell constants. An average of 37 values (obtained from 19 reflections) were used for the coarse-grained ilmenites while an average of 32 values (obtained from 18 reflections) were used for the titaniferous magnetites. The number of usable values was decreased to 34 (obtained from 18 reflections) for the fine grained intergrown ilmenites in the titaniferous magnetites.

The refinement program operates via the following steps (Appleman and Evans, 1974):

1) d-spacings are calculated for all allowable hkl values for the space group and approximate unit cell given in the input,

2) each d (calc.) is compared with the d (obs.) from the input. A match is accepted if and only if there is no other observed reflection and no other calculated reflection with a Bragg angle theta less than a specified tolerance different from that of a given reflection,

3) delta-theta values are calculated for the accepted relections and are used to obtain corrections to the unit cell parameters by least-square analysis,

4) the tolerance is set equal to twice the standard error for an observation of theta of unit weight(provided that this is not less than a minimum resolution value, in this case $0,02^{o}$), and the program is returned to (1) for another cycle.

The standard errors calculated for the unit cell dimensions on the basis of the measured two-theta values vary between $\pm 0,00012$ Å and $\pm 0,00024$ Å for the a-dimension of the ilmenites and between $\pm 0,0005$ Å and $\pm 0,001$ Å for the c-dimension. The larger degree of uncertainty in the c-dimension is due to the low number of reflections with indices of 001. It is consequently estimated that the determined a-unit cell dimensions for both ilmenite and magnetite are correct to within $\pm 0,0005$ Å at $25^{o}C$. The uncertainty in the c-unit cell dimension of ilmenite is greater, being $\pm 0,001$ Å.

5.3 Reflectivity Measurements

5.3.1 Introduction

The objective of this study was to determine the effect of compositional

variations on the reflectivity of ilmenite. The possibility of using reflectance measurments as a method of distinguishing between different types of ilmenite was also evaluated. The reflectivities of the co-existing titaniferous magnetites were not measured in view of their highly exsolved nature and the abundance of micrometre-sized intergrowths in these minerals.

Reflectivity measurements were carried out on ilmenite from kimberlites, Karroo dolerites, gabbros, syenites, granites and beach sands at Rhodes University. The results obtained indicated that the Mg-rich kimberlite ilmenites could be readily distinguished from the other types by this technique. This method was, however, not sensitive enough to detect the minor compositional differences between the ilmenites from other sources. These studies were consequently not extended to include the ilmenites from other rock types that were subsequently investigated.

5.3.2 Apparatus and operating conditions

The reflectivity measurements were made on a Zeiss MPM-01 photometer that was fitted to a Zeiss Universal Research Microscope equipped for incident light microscopy as described in Eales and Viljoen (1973). The light source was highly stabilised and the values captured by chart recorder. Measurements were made in modulated monochromatic light at various wavelengths using a Zeiss band-type running filter with a half-height width of 12 nm. Reflectivity values were determined by comparison with a SiC reflectivity standard calibrated by Firma Carl Zeiss and having a reflectivity of 20,8 per cent at 546 nm in air.

5.3.3 Measurement of reflectivity : accuracy and precision.

Ilmenite is uniaxial negative with the result that it has two principal

reflectivities in which the one that corresponds to the ordinary vibration (R_o) is constant for any given wavelength of light in any orientation of the grain (Cervelle, 1967 ; Cervelle et al. 1971). R_o can consequently be determined simply by rotating the microscope stage to obtain the maximum reflectivity for any grain without having to determine its orientation.

The reflectivity corresponding to the extraordinary ray (R_e) is a minimum and can only be determined from sections cut parallel to the optic axis and measured at 90° from R_o. All other sections will produce a minimum reflectivity that has some value intermediate between R_o and R_e and that varies from a maximum (=R_o) in perfect basal sections to a minimum that corresponds to R_e in parallel sections. Measurements were consequently made on sections showing the strongest reflection pleochroism (parallel sections). R_o was measured as described above and the minimum reflectivity measured at 90° from this position. A second value of R_o was measured at 180° from the first and a second minimum value was obtained in the same way. Only measurements in which the two maximum values and two minimum values are identical were used. R_e was taken as the lowest reflectivity measured from a series of sections showing strong reflection pleochroism and having acceptable values for R_o. This is,however, not necessarily the true value of R_e, but should be very close to it.

The problems involved in obtaining accurate reflectivity measurements have been reviewed by Piller and von Gehlen (1964) , Piller (1967) and Galopin and Henry (1972).

The major sources of error and the steps taken to minimise them are as follows:

1. Errors caused by the mechanical properties of the microscope. The

equipment should have outstanding mechanical stability since the photo-
electric equipment is sensitive to vibrations.   The highest quality
Zeiss equipment was used and the extent of vibration during measurements
reduced by the use of a cable operated shutter release in order to
transmit the reflected beam to the photomultiplier.

2. Errors caused by the optical properities of the microscope.   These are
largely due to the scattering of light and reflections (primary glare)
as well as deflection by optical elements that are out of alignment.
The width of the photometer field was stopped down to measure an area
5 micrometers in diameter and the illuminator field was stopped down to
twice this value by the use of special diaphragm stops supplied with
the photometer.   The optical adjustment and centering of the microscope
and photometer were checked at regular intervals while the sharpness of
the focus on the specimen or standard was checked before each measurement.
The primary glare was corrected for by the use of a "black box" reading,
but was negligible at the correct settings.

3. Errors caused by the properties and operation of the supplementary
devices.   This is largely due to fluctuations in current for the light
source and amplifier.   The light source was highly stabilized and
measurements were only made after the apparatus had been switched on
for at least one hour.   The stability of the apparatus was checked by
observing the base line of the recording apparatus in between measurements.
The measurements were recorded for a minimum period of 10 seconds to
allow for the photomultiplier output to stabilize.

4. Errors caused by the specimen.   The polished surface to be measured
has to be perfectly flat and free from imperfections, even at the highest
magnifications.   This represents the largest source of error in these

determinations, but was minimized as far as possible by the following procedures:

i) The samples were given a final polish using 0,25 micrometre diamond paste on a Hyprocell Pellon pad and the quality of the surfaces checked under high power magnification. The samples were buffed for 1 minute on a silk-covered lap immediately prior to measurement using a 0,05 micrometre gamma-alumina aqueous suspension.

ii) The sample was attached to a glass slide with a large lump of plasticine and then carefully levelled using a Leitz levelling press.

iii) Areas in the central portions of the grains were selected for measurement in order to avoid possible curvature of the polished surface towards grain boundaries due to polishing relief.

iv) The measured area was standardized at 5 micrometres in diameter and was carefully selected so as to avoid polishing scratches or other imperfections.

v) Two sets of measurements were made on different areas of five grains in each sample. Each set of measurements consisted of two R_o measurements at 180° to each other and two R_{min} values at 180° to each other, thus giving a total of 40 measurements per sample. The reflectivity of the standard was measured between each set of determinations . The value of R_o used is taken as the average of the measurements of R_o while R_e is assumed to be the minimum value.

vi) The reflectivity measurements were made using monochromatic light with a wavelength of 546 nm in accordance with the recommendations of the International Mineralogical Association (Galopin and Henry, 1972).

vii) The reflectivity values of the calibrated SiC standard (20,8%) are very close to the range of values measured for the ilmenites (18-29%), thus obviating the necessity for dubious extrapolations.

The accuracy of qualitative reflectivity measurements on titanomagnetite over a similar range of values to these ilmenites using the equivalent Leitz apparatus has been calculated by Halfen (1976). He concluded that a relative accuracy of $\pm$ 1 per cent was obtained in his measurements. A similar accuracy in this study is assumed in view of the nature of the apparatus used and the precautions taken.

The refractive index (n) and absorbtion coefficient (k) of ilmenite can be calculated from measurements of reflectivity in air and in oil for a specific wavelength (Piller and von Gehlen, 1964). Determinations of this nature were not made, however, since von Gehlen and Piller (1965) demonstrated that a relatively small error in the measurement of either R_{air} or R_{oil} for ilmenite would result in a relatively large change in the calculated n or k values. This is due to the relatively high refractive index and low absorbtion coefficient of ilmenite which lie close to the limiting values of possible R_{air} and R_{oil} pairs. (Piller and von Gehlen, 1964).

5.4 Micro-Indentation Hardness

5.4.1 Introduction

The micro-indentation hardness measurements were carried out on the ilmenites whose reflectivities had been determined with a view to their possible use (in conjunction with some other parameter such as reflectivity) as a method of distinguishing between the different types of ilmenite. This technique was successful in distinguishing between the Mg-rich ilmenites from kimberlites and other igneous rock types, but was not sensitive enough to determine minor compositional differences. These determinations were consequenty not extended to cover the ilmenites investigated at a later stage and which only showed minor compositional variations. The micro-indentation

hardness of the co-existing titaniferous magnetite grains were not determined in view of their complex exsolved nature.

5.4.2 Apparatus and operating conditions

Measurements were made using a G.K.N.micro-indentation hardness tester using a Vickers diamond indenter. The diamond indenter was lowered manually and the indentation time standardized at 15 seconds as suggested by the International Mineralogical Association (Galopin and Henry, 1972). Measurements were also carried out using the recommended standard load of 100g.

5.4.3 Determination of the Vickers Hardness Number

The subject of micro-indentation hardness measurement has been reviewed by Galopin and Henry (1972) who noted the following pertinent points:

i. There is always a range of values, even for cubic crystals, although the extent of the range varies widely from one substance to another.

ii. The values can vary with the method of polishing used.

iii. The values will depend on load, within limits.

iv. Different values can be obtained with different orientations of the indenter on a given crystal face.

Point (ii) was minimized since all the sections investigated were polished in the same manner. Point (iii) was minimized by expressing all measurements as VHN_{100} where 100 refers to the standard 100g load. The average VHN values for each sample were obtained by measuring the micro-indentation hardness in 10 grains showing random orientation in each polished section.

The indents produced by the 100g load are rarely perfect and one diagonal is always slightly longer than the other. The ilmenite invariably displays a slight amount of fracturing at the corners of the indentation while the sides are generally concave. This aspect was checked using a Leitz

"Mini-load" micro-indentation hardness tester using a hydraulically impelled indenter. The nature of the indentations produced by both the manually and hydraulically lowered diamonds are comparable. The imperfections in the indentations are consequently interpreted as reflecting the brittleness of the ilmenite and might be a characteristic feature of this mineral. Morton and Mitchell (1972) reported that perfect indentations were produced in only 4 of the 24 ilmenite grains that they investigated.

Indentations that resulted in excess fracturing of the grains or were poorly shaped were not measured. The value of the longest diagonal was taken as the lowest micro-indentation hardness for a particular grain while the shortest diagonal represented the highest. The lengths of the indent diagonals were measured in micrometres and the corresponding VHN values obtained from tables supplied with the instrument.

The length of the diagonals can be measured to an accuracy of $\pm$ 0,2 micrometres which is equivalent to approximately a VHN variation of $\pm$ 30 in the range of values measured. The technique is not as sensitive or accurate as other determinative methods (Galopin and Henry, 1972) and the average values reported generally show a variation of approximately $\pm$ 50 in the VHN for an individual sample. The technique is not suitable for detecting small compositional differences between ilmenites in view of the range of values obtained for single samples. Morton and Mitchell (1972) demonstrated that a linear relationship does not exist between the VHN and MgO-contents of magnesium ilmenite from kimberlites.

5.5 Mineral Analyses

5.5.1 Introduction

The ilmenite analyses presented in this section of the thesis were carried out in order to establish the compositional range of this mineral in the

various igneous rocks examined . The relationships between chemical
composition, unit cell dimensions, reflectivities and micro-indentation
hardness were also investigated with a view to their use as possible
indirect means of determining mineral compositions. The analyses are of
two types : (1) bulk wet chemical analyses of ilmenite concentrates and
(2) electron microprobe analyses of discrete ilmenite grains.

5.5.2 Wet chemical analyses

5.5.2.1 Introduction

Electron microprobe facilities were not available at Rhodes University
when this study was commenced (1972) with the result that it was necessary
to analyse purified mineral concentrates in the manner described by Vincent
and Phillips (1954). Thirty eight ilmenite concentrates of which
sufficient material was available were analysed using semi-micro techniques
involving rapid analytical procedures. The determinations were made in
duplicate on 100 to 150 mg portions of sample using mainly colorimetric and
volumetric methods.

5.5.2.2 Sample preparation

The kimberlite ilmenites were in the form of ovoid grains between 10 and 20
mm in diameter. The outer surfaces of some of these grains were coated with
various light-coloured, perovskite-rich alteration products which were ground
off on a diamond cup wheel. The grains were then crushed to less than 85
mesh in a mortar after which they were sealed in sample tubes
until analysis.

The beach sand ilmenite concentrates with a grain size between 85 and 120
mesh were further purified by repeated passes through the electromagnetic
separator. The resulting concentrate was then further purified by means
of heavy-liquid separations using warm saturated Clerici solution with a

specific gravity slightly in excess of 4,2. The concentrate was then washed thoroughly with copious quantities of hot water and finally oven dried at $80^{\circ}C$.

The ilmenite concentrates with a grain size between 120 and 200 mesh obtained from the various igneous rocks were selected for analysis. These grains were also generally cleanly liberated and free from all but minor silicate impurities. These samples were also further purified by means of heavy liquid separations using warm saturated Clerici solution.

All samples were finely ground under acetone in an agate mortar immediately before analysis.

5.5.2.3 Purity of samples

The kimberlite ilmenites represent either simple "xenocrysts" or poly-crystalline aggregates. Considerable care was exercised in removing any secondary alteration products with the result that the analysed material is virtually pure. The beach sand ilmenite concentrates were examined microscopically prior to analysis and grain counting showed them to be more than 98 per cent pure. The major source of contamination in these samples is due to minor intergrown silicate phases. A minor amount of chromite with a similar magnetic susceptibility to the ilmenite might be present, but was not detected in the polished sections examined. The low Cr_2O_3 values obtained, however, indicate that only very minor amounts, if any, of chromite are present.

The ilmenite concentrates prepared from the various crushed igneous rocks contain the highest proportion of impurities in the form of intergrown and imperfectly liberated silicate minerals. This feature is particularly

noticeable in the case of Karroo dolerite ilmenites where the sample
purity is sometimes as low as 95 per cent as determined by grain counting
and based on visual estimates of the volume of unliberated silicates.
The sample purity is generally between 97 and 98 per cent as determined
by these methods.

The silicates remain relatively unaffected during the potassium
pyrosulphate fusions and their content can be largely determined as an
insoluble residue. This aspect was checked by carrying out duplicate
potassium pyrosulphate fusions on samples of finely ground labradorite
and bronzite. The insoluble residue was determined gravimetrically
after fusion and dissolution in dilute H_2SO_4. The labradorite showed
a loss of 6,2 per cent and the bronzite 1,6 per cent when the fusion was
carried out for the same length of time normally required for the complete
dissolution of an ilmenite sample.

A sample containing equal proportions of plagioclase and pyroxene as
contaminants would only lose a total of approximately 4 per cent by mass
of these components during fusion. The largest amount of insoluble
residue found was 5,4 per cent from a dolerite ilmenite concentrate while
the majority of samples contained much less than this. In this extreme
case, the maximum contamination of the sample by decomposed silicates
would only be in the order of 0,2 per cent of the total. At least half
of this contamination would be made up of SiO_2 while the bulk of the
remainder would consist largely of Na_2O, CaO and Al_2O_3 from the plagioclase.
Only minor amounts of FeO and MgO (less than 0,02%) would be introduced
from the pyroxene. The effect of these small amounts of impurities on
the final analytical results is thus very minor and can be neglected.

5.5.2.4 Analytical methods

i) Decomposition of the sample : low temperature fusion carried out in a Pt crucible using potassium pyrosulphate. Fusion cake dissolved in dilute H_2SO_4.

ii) Insoluble residue : determined gravimetrically.

iii) TiO_2 : determined colorimetrically using tiron (disodium-1,2-dihydroxybenzene-3,5 disulphate) (Maxwell, 1968, p382-383).

iv) MnO : determined colorimetrically using potassium periodate (Maxwell, 1968, p387 - 389).

v) Fe_2O_3 : total iron determined colorimetrically as Fe_2O_3 using o-phenanthroline (Maxwell, 1968, p 424 - 425).

vi) Cr_2O_3 : determined colorimetrically using s-diphenyl carbazide (Sandell, 1959, p 388 - 397).

vii) CaO : determined volumetrically using EDTA (Maxwell, 1968, p370-372).

viii) MgO : determined volumetrically using EDTA (Maxwell, 1968, p376-377).

ix) FeO: determined by hot acid decomposition followed by titration with potassium dichromate (modified Pratt method) (Maxwell, 1968, p416-418).

5.5.2.5 Analytical standards

No completely characterized international ilmenite reference standards, against which the accuracy and precision of the analytical methods employed could be checked, are available. Four kimberlite ilmenite samples and one beach sand ilmenite sample were submitted to the South African Geological Survey for wet chemical analysis. These samples were analysed by the General Superintendence Co. S.A. (Pty) Ltd., and served as the primary standards against which the various analytical techniques were evaluated.

These samples were analysed in duplicate together with the unknown ilmenite samples and served as a check on the accuracy of the determinations.

A sample of analysed hemo-ilmenite from the Lac Tio deposit in Quebec was kindly supplied by Dr Z. Katzendorfer of the Quebec Bureau of Natural Resources, Canada and this was also used as a standard. Two partially analysed (TiO_2 only) ilmenite samples and a rutile sample (TiO_2 and Cr_2O_3 only) were purchased from the Bureau of Analysed Samples, Middlesborough, England and were also used for this purpose.

5.5.2.6 Analyses of Standards : accuracy and precision

The compositions of the analytical standards used are given in Appendix 2 together with the averages of duplicate analyses of those samples carried out during the routine ilmenite analyses. Comparison of results indicates a close agreement between the standard values and those obtained during the analytical runs with the exception of FeO and Fe_2O_3. The values for total iron, expressed as Fe_2O_3, are, however, comparable. The general agreement of the results with the standard values and their reproducibility as indicated by duplicate analyses indicate the validity of the analytical methods used.

The discrepancy between the FeO and Fe_2O_3 values reported for the standards and the values obtained are due to problems encountered in the FeO determinations (Fe_2O_3 is determined as total iron less FeO x1,11113). The FeO was determined using the modified Pratt method (Maxwell, 1968) in which the finely ground sample is decomposed by boiling in a mixture of H_2SO_4 and HF for 10 minutes. The boiling period should not be extended since this leads to the evaporation of excess acid and oxidation of the ferrous to ferric iron. This period of boiling was insufficient for the decomposition of the entire sample and a small amount of black residue remained in the crucible causing

determined FeO content to be low.

The optimum conditions were determined by using slightly smaller quantities of sample and boiling for progressively increasing intervals of 5 minutes. The best results were obtained after boiling for 17,5 minutes, but they remained approximately 1,8 per cent lower than those reported for the standards. Variations in the amounts of acids used in the decomposition did not affect the results to any marked extent.

The persistently low values for FeO recorded in these analyses may be due to one or more of the following reasons:

 i) Numerous problems are associated with the determination of the valence states of iron in a rock or mineral and the results obtained are not always perfect (Maxwell, 1968).

 ii) Oxidation of the FeO in the samples may have commenced during the decomposition step of the determination before all the ferrous iron had been taken into solution. This is the most plausible cause for the resulting low FeO values.

iii) The samples were oven-dried at $95^{\circ}C$ for an hour prior to analysis and this may have resulted in slight oxidation.

 iv) The samples were finely ground in an agate mortar and immediately prior to analysis with the result that a minor amount of oxidation may have occurred during this stage.

The FeO and Fe_2O_3 values reported in the analyses have been recalculated assuming stoichiometry using the values obtained for total iron. The total iron was converted to FeO and the calculations carried out as described in section 5.5.3.5 for the microprobe analyses.

5.5.3 Electron microprobe analyses

5.5.3.1 Introduction

The electron microprobe analyses were carried out in two batches on the same equipment, but separated by a period of two years. The first batch represents the bulk of the microprobe analyses presented in Part 2 with the exception of the diabases and several other analyses that are indicated as such in the relevant sections. The second batch is represented by the diabases, the balance of other analyses and all the microprobe analyses reported in Part 3.

5.5.3.2 Apparatus and operating conditions

The analyses were made on an ARL microprobe in the Mineralogy Division at NIM. The first batch of analyses were carried out under the supervision of Mr.P.Mihalik using an acceleration potential of 25 kV, sample current of 0,02 micro-A on brass and an integration time of 10 seconds. Ten points were measured on each sample and the average values computed. The raw data were corrected for background, dead time, absorbtion, atomic number and fluorescence effects by means of a computer programme devised by Beeson (1967).

The second batch of samples was analysed on the same equipment at 15 kV acceleration potential and a sample current of 0,1 micro-A on brass under the supervision of Mr.E.A.Viljoen. The raw data were corrected using the EMPADR V11 computer programme of Rucklidge (1967). Ten points were measured on each sample and the average values computed. Both sets of analyses were made using the same standards.

5.5.3.3 Analytical standards

The following four standards were used:

i) A well analysed ilmenite standard (A236) was kindly supplied by
Dr.K.Snetsinger of NASA, Moffett Field, California and was used
for Ti, Mn and Fe.

ii) An analysed Mg-rich ilmenite from the Naizees 4 kimberlite, Poffadder
obtained from Dr.C.Frick of the Geological Survey. This was used
for Cr, Mg, Ti and Fe in the Mg-rich ilmenites.

iii) A well analysed chromite from the Merensky Reef, supplied by
Dr.S.A. de Waal. This was used for Si, Al, Mg.

iv) A Mg-rich kimberlite ilmenite standard kindly supplied by the
Anglo American Research Laboratories and used to check the Mg-
contents of the high MgO ilmenites present in the Kaffirskraal and
Trompsburg titaniferous iron ores.

Analyses of these standards are given in Appendix 3.

5.5.3.4 Microprobe analyses : accuracy and precision

The quality of a microprobe analysis depends to a large extent on the
standards used and the accuracy with which they have been characterized.
Ilmenite standards were used where practicable in order to facilitate
comparison and eliminate possible sources of error. Mg-rich ilmenites
from kimberlites provide good standards since they are often compositionally
homogeneous and are large enough to be analysed several times by conventional
methods. They are, unfortunately, not ideally suited to analysing ilmenites
that are closer to the end-member composition. This represents a serious
problem since ilmenite standards in this compositional range are not easily
produced.

Microprobe analyses in which the oxides total between 98 and 102 per cent
are usually regarded as "good" and the accuracy of the results is considered
to be within 2 per cent of the values obtained. The analyses reported in

this thesis all lie within this range and duplicate analyses have indicated that the results are reproducible.

5.5.3.5 Calculation procedures

The electron microprobe is unable to distinguish between the oxidation states of the iron present and the total Fe content is generally expressed as FeO. The Fe_2O_3 content of the ilmenites can be calculated if stoichiometry is assumed (Buddington and Lindsley, 1964) and this procedure is widely used in the case of these minerals. Various recalculation schemes are in use and this subject has been discussed by Bowles (1977). The following recalculation scheme is used in this thesis:

i) the chemical formulae of the ilmenites are calculated from the analyses according to the number of ions on the basis of six oxygens following the procedure set out in Deer et al. (1966).

ii) the allocation of oxides in the mineralogical calculations follows the scheme of Buddington and Lindsley (1964), with additional assumptions regarding the treatment of the minor oxides following the procedures of Carmichael (1967a) Anderson (1968b) and Lipman (1971). The method used is as follows:

a) The molecular proportions of TiO_2 and SiO_2 are combined (where SiO_2 values are available).

b) MgO and MnO are allocated to $Mg\ TiO_3$ and $Mn\ TiO_3$.

c) Al, Cr and V are allocated to Al_2O_3, Cr_2O_3 and V_2O_3.

d) The remaining Ti is calculated as $Fe\ TiO_3$ and, if necessary, additional FeO is formed from Fe_2O_3 assuming ilmenite stoichiometry (Buddington and Lindsley, 1964).

e) Any excess FeO is recalculated as Fe_2O_3.

f) Fe_2O_3, Al_2O_3, Cr_2O_3 and V_2O_3 are combined as R_2O_3.

g) In the case of the electron microprobe analyses, total iron is expressed as FeO and any excess is recalculated to Fe_2O_3 following the procedure of Carmichael (1967a).

h) The ilmenites from the beach sands show variable amounts of alteration to "leucoxene" and this is reflected in an excess of TiO_2 and Fe_2O_3 in the analyses. Leucoxene does not have a fixed composition so that this excess is simply combined and expressed as "leucoxer ".

i) The molecular percentage of hematite present in the ilmenites is calculated as :

$$\text{mol. } \% \ Fe_2O_3 \ = \ \frac{\text{mol. prop. } Fe_2O_3}{\text{mol. prop } R_2O_3 \ + \ \text{mol. prop. } RTiO_3}$$

5.5.4 Comparison of wet chemical and electron microprobe analyses

The major obstacle to using wet chemical methods for the analyses of minor mineral phases in igneous rocks is in the preparation of sufficiently pure concentrates. The purity of the analysed samples is better than 95 per cent (section 5.5.2.3), but small smounts of silicate impurities are present as intergrowths and cannot be readily removed. The method also requires a fairly large number of small grains (or portions of larger grains) so that fine-scale compositional fluctuations due to zoning cannot be detected. Similarly, compositional differences between individual grains in the same piece of rock cannot be detected and the values obtained merely represent the average bulk compositions of the minerals present.

The electron microprobe can, in contrast, be used to analyse small areas of individual grains and is suited to the investigation of compositional zoning. Numerous grains in the same sample can also be analysed and checked for compositional homogeneity. A difficulty with this technique arises when only a limited number of analyses can be made (as in this study)

and a large number of grains cannot be analysed in each sample.

The samples examined are largely from plutonic rocks and it has been assumed that their crystallization conditions were sufficiently slow to allow continued re-equilibration down to low temperatures. Compositional zoning, if present, should be of a limited nature and the individual ilmenite grains in each polished section should have a similar composition. (Bowles, 1977, has shown that this assumption is not always valid).

The compositional variations exhibited by ilmenites from a wide variety of igneous rock types are fairly limited (Part 1). This feature is also reflected in the analyses made by both techniques during this study. By analogy, the range of compositional zoning shown by individual ilmenites in relatively slowly cooled igneous rocks might also be expected to be limited. All microprobe analyses were made as close as possible to the cores of the ilmenite grains in order to standardize the comparison of results and minimize the effects of possible zonation.

The Karroo dolerite ilmenites are considered to be the most likely to exhibit compositional zoning since they are from hypabyssal intrusions and were more rapidly cooled than those from plutonic sources. In this case a reasonably good agreement exists between the wet chemical analyses and the values determined by microprobe as shown in Table 8 . Five of the analyses were performed by each method and only minor variation is evident between samples. This feature is also reflected in the unit cell dimensions and reflectivities of these samples.

6. THE CO-EXISTING IRON-TITANIUM OXIDES IN KIMBERLITES.

6.1 Introduction

limited published information on the opaque oxides in kimberlites was

available in the Western literature prior to 1972 when this investigation was commenced. The classic works of Wagner (1914) and Williams (1932) provided very little data on these oxides as did the later pioneering articles by Dawson (1962) and Nixon et al. (1963). The Mg-rich nature of kimberlite ilmenites became widely recognised at this time and these minerals were studied in more detail (Besson, 1967 ; Cervelle, 1967 ; and Cervelle et al. 1971). Considerable progress in kimberlite research was also made in Russia during this period and the data on the opaque oxides has been summarised by Sobolev (1959) and Frantsesson (1970) while additional information is given by Ponomarenko et al. (1972).

Interest in the opaque oxides in kimberlites developed during the International Upper Mantle Project and a number of important publications appeared between 1973 and 1977. The publication of the book "Lesotho Kimberlites" (Nixon, 1973) and the proceedings of the First International Kimberlite Conference (Ahrens et al., 1975), in particular, have contributed a wealth of data on these phases. The bulk of the published information deals with the compositions of the kimberlite ilmenites and the only detailed studies specifically concerned with the Fe-Ti spinels in these rocks are those of Haggerty (1973b,1975) , Smith and Dawson (1975) and Mitchell and Clarke (1976).

The published information indicates that the phase relationships exhibited by the spinels and various smaller-sized ilmenites in kimberlites are extremely complex and require further detailed studies that are beyond the scope of this thesis. The present study was consequently restricted to the characterization of 10 ilmenite xenocrysts from various South African kimberlites in order to facilitate their comparison with ilmenites from other sources.

Cervelle (1967) and Cervelle et al. (1971) suggested that the MgO content

of kimberlite ilmenite might be obtained indirectly by means of reflectivity,

micro-indentation hardness and unit cell determinations.   The relationship

between micro-indentation hardness and the composition of kimberlite

ilmenites was investigated further by Morton and Mitchell (1972) who demon-

strated that there is no direct relationship.   Frick (1973a) presented the

composition of kimberlite ilmenites in terms of their molecular percentages

of $MgTiO_3$, $FeTiO_3$ and Fe_2O_3 as a function of their a-unit cell dimensions

and densities.   He suggested that this might represent a cheap, yet

effective method for identifying kimberlite ilmenites.   These aspects

have been further evaluated in the present study.

6.2 Literature Review

The ilmenites in kimberlites are characteristically Mg-rich, containing

between 6 and 24 per cent MgO (Mitchell, 1977).   They commonly contain

fairly large amounts of Fe_2O_3 (up to 20%) in solid solution and are

characterized by the presence of unusually large amounts of Cr_2O_3 (up to

5%) and Al_2O_3 (up to 1%).   A compilation of analytical data by Mitchell

(1977) also indicates that there is a wide compositional variation in

ilmenites from a particular kimberlite occurrence.   Mitchell (1973,1977)

has also suggested that the range of MgO contents exhibited by the

ilmenites might be characteristic for each pipe   (Table 1).

The ilmenites are present in the kimberlite as discrete grains and

polycrystalline aggregates as well as in a variety of associations with

silicates, ultramafic nodules, alteration products and in the kimberlite

groundmass itself.   Each of these ilmenite types can be distinguished on

the basis of their mode of occurrence and Haggerty (1975) has recognised

the following six types as usually being present in kimberlite:

TABLE 1

TYPICAL ANALYSES OF KIMBERLITE ILMENITES

OXIDE	"XENOCRYSTIC" ILMENITES													ILMENITES FROM ULTRAMAFIC NODULES			ILMENITES FROM LAMELLAR INTERGROWTHS		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
SiO₂	-	-	2,00	-	0,48	-	-	0,40	0,10	0,02	-	-	0,12	0,19	0,07	0,22	0,11	-	0,04
TiO₂	53,79	49,27	50,00	49,32	45,80	48,26	49,35	47,97	46,33	50,60	49,67	48,87	51,70	49,61	56,63	53,01	49,30	48,77	50,22
FeO	29,34	28,18	28,80	28,18	19,15	27,12	27,57	28,00	26,29	21,42	25,55	29,53	29,70	25,70	26,65	19,42	27,00	28,65	30,18
MgO	8,87	9,00	9,00	9,00	15,84	8,65	7,75	9,00	8,60	13,40	10,59	7,44	13,30	10,49	13,52	15,74	9,64	11,82	8,31
MnO	0,29	-	-	-	-	0,26	0,95	-	-	0,24	0,25	0,26	0,20	0,18	0,23	0,26	0,20	0,23	0,23
CaO	0,13	-	-	-	-	-	0,20	tr	tr	0,01	-	-	0,02	-	-	-	0,02	0,08	-
Fe₂O₃	7,05	11,27	10,80	14,30	15,56	17,10	13,71	13,15	17,96	10,53	11,34	11,87	-	8,97	2,93	5,20	13,10	9,63	8,30
Cr₂O₃	-	0,63	-	-	2,63	-	-	0,75	0,41	3,17	0,57	· 0,14	3,10	2,17	1,40	5,04	0,08	0,08	0,07
Al₂O₃	-	-	-	-	-	-	0,33	-	-	-	-	-	0,70	0,69	0,47	1,41	0,61	0,50	0,55
V₂O₃	-	-	-	-	0,57	-	-	-	-	0,62	-	-	-	-	-	-	-	-	-
TOTAL:	99,47	98,35	100,60	100,80	100,30	101,39	99,86	99,27	99,69	100,01	97,97	98,11	99,34	98,00	101,90	100,30	100,06	99,76	97,90

- not reported   tr = trace

Sources of Analyses

1. Kimberley Mine. Wagner (1914)

2. Mukerub Mine, S.W.A. Wagner (1914).

3. Monastery Mine. Williams (1932).

4. Frank Smith Mine. Williams (1932).

5. Wesselton Mine. Williams (1932).

6. Thaba Putsoa Pipe, Lesotho. Dawson (1962).

7. Kao pipe, Lesotho. Nixon et al.(1963).

8. Zarnista pipe, Siberia. Sobolev (1959).

9. Mir pipe, Siberia. Sobolev (1959).

10. Sloan diatreme, Colorado. McCallum and Eggler (1971).

11. Kao pipe, Lesotho. Mitchell (1977).

12. Sekameng pipe, Lesotho. Mitchell (1977).

13. Sloan diatreme, Colorado. McCallum et al. (1975).

14. Nodule in Thaba Putsoa pipe. Boyd and Nixon (1973).

15. Nodule in Matsoku pipe. Boyd and Nixon (1973).

16. Ilmenite in an olivine crystal, Kentucky, U.S.A.Boyd and Nixon (1973).

17. Enstatite-ilmenite intergrowth, Monastery Mine, Boyd (1971).

18. Pyroxene-ilmenite intergrowth. Ringwood and Lovering (1970).

19. Pyroxene-ilmenite intergrowth. Dawson and Reid (1970).

1.   xenocrystic ilmenite

2.   groundmass primary ilmenite

3.   subsolidus oxidation ilmenite in titanomagnetite

4.   ilmenite-spinel-perovskite mantles on xenocrystic ilmenite

5.   recrystallised ilmenite pseudomorphs after spinel

6.   ilmenite-rutile and ilmenite-rutile-armalcolite intergrowths.

Several other types of ilmenite-bearing silicate inclusions, not studied by Haggerty (1975), are also commonly present in kimberlites and have been described by Boyd and Nixon (1973) who distinguished five types, the three most important being :

1.   megacrysts or discrete nodules, with inclusions

2.   lamellar intergrowths

3.   granular intergrowths.

The bulk of the published information on kimberlite ilmenites deals with the "xenocrystic" types and limited data (other than that of Boyd and Nixon (1973) and Haggerty (1975)) are available on the other types of ilmenite. An exception is the case of the lamellar intergrowths of ilmenite and pyroxene which have attracted widespread interest (e.g. Williams, 1932 ; Ringwood and Lovering, 1970 ; Dawson and Reid, 1970 ; Boyd, 1971 ; Boyd and Dawson, 1972 ; Frick, 1973b ; Boyd and Nixon, 1973 ; Gurney et al. 1973 ; Mitchell, Carswell and Brunfelt, 1973 ; Ilupen et al., 1974 ; McCallister et al. 1975;   Wyatt et al. 1975).   The nature, occurrence and possible origin of these intergrowths has been reviewed by Wyatt (1977) and is not discussed further.   Data on the compositions of ilmenites in discrete ultramafic nodules in kimberlites are given by Boyd (1974) and Boyd and Danchin (1974).

The ilmenites investigated in this study are of the "xenocrystic" type
and this summary is concerned largely with these types.   They are generally
present as discrete rounded to ovoid grains that are set in a matrix of
finer-grained kimberlite and range in size from less than 0,05mm up to
more than 10 cm.   These "xenocrysts" are either portions of large single
crystals or are composed of polycrystalline ilmenite aggregates (e.g. Frick,
1973a , Mitchell, 1973 , 1977).   These authors' also reported that these
ilmenites commonly exhibit deformation features such as undulose extinction,
kink banding and deformation twinning.   The polycrystalline aggregates
either exhibit well-defined equilibrium grain boundaries with triple
junctions or are characterized by disequilibrium grain boundaries that are
similar to those developed in highly deformed rocks.   The ilmenites of both
types sometimes exhibit varying stages of re-crystallization.

The rounded ilmenite "xenocrysts" are commonly surrounded by light-coloured
reaction rims of sphene and perovskite (Frick, 1973a).   These rims are of
variable width and the reaction products are also present along fractures
in the single crystals as well as along the grain boundaries in the
polycrystalline aggregates.   Frick (1973a) recognised four stages in the
essentially progressive process of ilmenite reaction -resorbtion that led
to the formation of these rims.   Haggerty (1975) described the presence of
ilmenite-spinel- perovskite mantles around certain xenocrystic ilmenites.

The ilmenites are generally opitcally homogeneous and free from exsolved
phases (Frantsesson, 1970 , Cervelle et al. 1971 , and Danchin and d'Orey,
1972).   The grains commonly contain excess Fe_2O_3 (more than 6%) and the
absence of hematite exsolution lamellae is notable.   Frick (1973a) described
the presence of hematite lamellae in ilmenites from meta-kimberlite in the
Premier Mine, but commented on their extreme rarity in other kimberlites.

Mitchell (1973) suggested that the lack of exsolution lamellae might be due to their formation at high temperatures in the mantle followed by rapid quenching of the crystals during transport of the kimberlite magma towards the surface. Frick (1973a) reported that he had artificially produced hematite exsolution bodies in these ilmenites by heating them at $1200^{\circ}C$. for 36 hours in an argon atmosphere. He concluded that temperature alone was not the controlling factor in inhibiting the exsolution of hematite and suggested that the rapid decrease in confining pressure during emplacement might be an important factor.

Other types of exsolution lamellae are also rare. Danchin and d'Orey (1972) described the development of chromium ulvospinel parallel to (0001) in an ilmenite from the Premier Mine while Mitchell (1973) reported the presence of magnetite lamellae in an ilmenite nodule from the Monastery Mine. Haggerty (1975) reported the presence of titanium chromite and possible titanomagnetite exsolution lamellae in ilmenites from the Kao pipe in Lesotho.

Ilmenite is present is variable amounts up to 40 per cent in the various types of ultramafic xenoliths present in the kimberlite (e.g. Boyd and Nixon, 1972 , 1973 , 1975 ; Frick, 1973a ; Mitchell, 1973 ; Boyd, 1974 ; Harte and Gurney, 1975 ; Meyer and Boctor, 1975). This ilmenite is compositionally similar to the ilmenite in the "xenocrysts" and is present both as discrete grains and in granular aggregates. A portion of the "xenocryst" ilmenites, particularly in the finer-grained sizes, is probably derived from the fragmentation of this type of material. The bulk of the large grains are, however, not generally considered to have been derived from this source. (e.g. Boyd and Nixon, 1973 ; Frick, 1973a ; Mitchell, 1973 , 1977).

The "xenocrystic" ilmenite is generally accepted as having originated
in the upper mantle (e.g. various papers in Nixon, 1973, and Ahrens et al.
1975), but there is no consensus on the stage at which it is formed or
its relationship to the kimberlite magma. The larger ilmenites are
usually assumed to have been brought up by the kimberlite magma, but are
not in equilibrium with it under near-surface conditions as shown by their
well-defined reaction rims. The debate centres around whether these
ilmenites are genetically related to the kimberlite magma (i.e. cognate
inclusions) or are true xenoliths, having been accidently incorporated
into the magma during its ascent.

Boyd and Nixon (1973) suggested that the ilmenite megacrysts might have
originally been present as phenocrysts in crystal-mush magmas that
developed in the upper part of the low Velocity Zone in the Upper Mantle.
These ilmenites were then picked up together with other materials by the
erupting kimberlite magma.

Mitchell (1973) postulated that these essentially monomineralic ilmenite
aggregates formed as cumulates during the high pressure differentiation
of a proto-kimberlite magma. This ilmenite cumulate would become
sheared, broken up and randomly mixed with the kimberlite magma as it
began its ascent from the mantle.

Frick (1973a) concluded that these ilmenites crystallized intratellurically
under high confining pressures from a silicate magma in a cotectic
relationship with orthopyroxene and clinopyroxene. He noted that this
ilmenite fractionation probably took place under high oxygen fugacities
resulting in their high Fe_2O_3 contents. He also reported that these
ilmenites display a geikielite-hematite variation trend and suggested that

this feature is a direct result of crystallization differentiation. Frick (1973a) postulated that the ilmenites are the last phases to crystallise prior to eruption.

Boyd and Nixon (1975) reaffirmed their earlier views that the discrete ilmenite nodules are not indigenous to the kimberlite, but were picked up by the erupting magma in the same manner as the other mantle xenoliths. Mitchell (1977) presented additional geochemical data on kimberlite ilmenites and reviewed the major hypotheses regarding their origin. He favoured the view that these ilmenites are phenocrysts since each intrusion is characterized by ilmenites of a distinct compositional range. He noted, however, that the available data are insufficient to prove conclusively whether or not these ilmenites are true phenocrysts. He stressed that additional data are required before final conclusions can be reached.

The ilmenites in the ultramafic, mantle-derived nodules have been less well studied than their discrete "xenocrystic" counterparts. Boyd and Nixon (1973, 1975) suggested that these nodules are derived from an ilmenite-bearing zone at the top of the Low Velocity Zone in the upper mantle. Harte and Gurney (1975) indicated that some of these ilmenites might have been produced by Ti-metasomatism of garnet lherzolite. These secondary ilmenites, however, appear to be compositionally different to the "normal" kimberlite types.

The high, but variable, MgO-contents of the kimberlite ilmenites are also the subject of debate. Lovering and Widdowson (1968) suggested that the high MgO/FeO ratios of kimberlitic ilmenites could be directly related to high MgO/FeO ratios in the kimberlite magma itself. Frisch (1970) reported a wide variation in the MgO contents of different ilmenite grains in a

single kimberlite hand specimen and concluded that they had not formed in equlibrium with their enclosing rock.

Mitchell (1973) noted that ilmenites within a particular kimberlite pipe exhibit a continuous range in composition which he interpreted as being due to the fractional crystallization of a magma unusually rich in TiO_2 and MgO. Frick (1973a) also suggested that the MgO/FeO ratios of the kimberlite ilmenites are functions of the MgO/FeO ratios of the kimberlite magmas rather than the prevailing pressures during crystallization. Haggerty (1975) in contrast, favoured pressure as the major factor controlling MgO distribution.

Mitchell (1977) noted that the total amount of ilmenite formed is small in relation to the volume of magma. He suggested that the variable Fe/Mg ratios are consequently not a result of large variations in Fe/Mg ratios in the magma, but are influenced by some other variable parameters such as temperature, oxygen fugacity or silica activity. The MgO content of ilmenite is discussed further in Part 1, section 5.3.2 and Part 3, section 10.7.

6.3 Samples Investigated

Ten ovoid ilmenite "xenocrysts" from various kimberlite occurrences were examined and their localities are given in Table 2. The bulk of these samples were kindly supplied by Prof. H.V.Eales who originally obtained them from Mr.J.B.Hawthorn of de Beers Consolidated Mines.

TABLE 2

THE KIMBERLITE ILMENITES INVESTIGATED

Sample Number	Locality
K1	Klipfontein Mine
K2	Frank Smith Mine
K3	Kaal Vallei Pipe
K4	Taylor's Kopjie
K5	Kamfersdam Pipe
K6	Newlands Pipe
K7	Riverton Pipe
K8	Kameeldraai No.2. Pipe
K9	Bull Hill Pipe
K10	Monastery Mine

In addition, a single ilmenite-rich, phlogopite nodule (UN1) was obtained
from Mr.B.Kokkinn who found it "propping up a fence post" at the site of
the old Bultfontein "floors" where the mined kimberlite was left to
weather prior to treatment.

6.4 Description of Samples

The ilmenites are all of the "xenocryst" type, and with the exception of
two samples, are all single crystals.   They exhibit no marked exsolution
textures and do not exhibit undulatory extinction although stress twin
lamellae are occasionally present.   The ilmenites are strongly
anisotropic in incident light and exhibit colours that are distinctly
greyer than the ilmenites from non-kimberlite sources.   Several of the
grains showed the development of white sphene - and perovskite-rich

reaction rims, but their nature was not investigated.

The ilmenite in the phlogopite nodule is in the form of granular aggregates that are restricted to the areas between large phlogopite grains and appear to be transgressive veinlets. The individual ilmenite grains are approximately 0,5 mm in size and the aggregates exhibit an overall polygonal texture with well-defined triple junctions having interfacial angles that approximate 120°. This ilmenite appears to have been re-crystallized and shows no undulatory extinction.

6.5 Unit Cell Dimensions, Reflectivity and Micro-Indentation Hardness

The experimentally determined values for these parameters are presented in Table 3. The values obtained for the unit cell parameters are within the range reported by Cervelle (1967 (a=5,06$\overset{o}{A}$;c=14,10-14,13$\overset{o}{A}$) and Frick (1973a) (a=5,066-5,073$\overset{o}{A}$) for magnesian ilmenites covering this compositional range.

The reflectivity values are not easily compared, but they also fall within the range given by Cervelle (1967) (R_o=17,1-18,8 ; R_e = 15,6-17,0) in air at 546 nm for Mg-rich kimberlites containing between 7,3 and 15,6 per cent MgO. Cervelle et al. (1971) also reported a linear relationship between MgO content and reflectivity for these ilmenites in air in white light. They reported that the reflectivity (R_o) ranges from 18,5 to 16,4 per cent for the compositional range between 7,5 and 20 per cent MgO. Snyman (1974) reported that the reflectivity of kimberlite ilmenites ranges from 15,5 to 21,5 per cent, but gives no corresponding chemical analyses.

Cervelle (1971) reported that the Vicker's Hardness Numbers vary between

TABLE 3

KIMBERLITE ILMENITES : UNIT CELL PARAMETERS, REFLECTIVITIES AND VICKER'S HARNESS NUMBERS.

Sample number	Unit cell dimensions (Hexagonal axes)			Calculated d-spacing for (2.1.10) ($\mathring{A}$)	2-theta angle for co-radiation K-alpha$_1$ for (2.1.10)	Reflectivity in air at 456 nm		Vicker's hardness number
	$a \pm 0,0005 \, \mathring{A}$	$c \pm 0,001 \, \mathring{A}$	volume($\mathring{A}^3$)			R_o(%)	R_e(%)	(VHN$_{100}$)
K1	5,0723	13,969	311,248	1,0689	113,61	17,6	13,6	948 - 1005
K2	5,0689	14,025	312,067	1,0711	113,25	17,6	14,3	723 - 747
K3	5,0729	13,963	311,184	1,0687	113,64	18,5	15,2	825 - 896
K4	5,0734	14,038	312,930	1,0721	113,09	18,1	14,9	860 - 916
K5	5,0711	13,965	311,015	1,0690	113,65	17,5	14,3	968 - 1030
K6	5,0718	13,963	311,064	1,0686	113,66	18,1	14,5	912 - 982
K7	5,0726	14,019	313,266	1,0718	113,51	18,3	14,9	766 - 845
K8	5,0728	14,022	312,496	1,0713	113,21	18,3	14,8	763 - 848
K9	5,0731	13,968	311,345	1,0690	113,60	18,7	15,1	753 - 781
K10	5,0720	13,965	311,118	1,0687	113,64	18,4	15,2	854 - 911
UNI	-	-	-	-	-	17,5	14,2	859 - 977

690 and 1020 for magnesian ilmenites and his data compilation suggests that the micro-indentation hardness increases with increasing MgO content. Morton and Mitchell (1972) investigated this aspect in more detail and reported VHN values of between 639 and 1084 for kimberlite ilmenites containing between 6,5 and 19,5 per cent MgO. They concluded that no linear relationship exists between the MgO content and VHN. The values obtained during this study also fall within this range and appear to be typical of this type of ilmenite.

6.6 <u>Chemical Compositions</u>.

The chemical compositions of the kimberlite ilmenites are presented in Table 4 and can be compared with the analyses of typical kimberlite ilmenites given in Table 1. The wet chemical and electron microprobe analyses are comparable and fall within the typical compositional range of kimberlite ilmenites. Haggerty (1975) investigated the composition of large numbers of kimberlite ilmenites and noted that they typically contain between 10 and 70 mole per cent Fe_2O_3, up to 5,6 per cent by mass Cr_2O_3 and up to 1,3 per cent by mass Al_2O_3.

6.7 <u>Discussion of Results</u>.

A plot of R_o against MgO will illustrate that no linear relationship exists between these parameters, in contrast to the conclusions of Cervelle et al. (1971). The presence of magnesium has the effect of decreasing the overall reflectivity of the kimberlite ilmenites, but this relationship is complicated by the presence of variable amounts of Fe_2O_3, and to a lesser extent Cr_2O_3, in solid solution. Ramdohr (1969) noted that the presence of Fe_2O_3 in solid solution increases the reflectivity of ilmenite and this effect is also evident in the case of these magnesian ilmenites.

TABLE 4

ANALYSES OF KIMBERLITE ILMENITES

	K1	K2+	K3+	K4+	K5	K6	K7	K8	K9	K10	K11	K12	UN1
TiO_2	52,87	53,16	48,86	52,53	53,39	51,16	51,85	50,10	52,44	51,17	52,84	51,96	52,74
FeO	21,80	23,28	28,80	27,28	22,63	21,95	25,52	26,23	32,68	24,12	32,16	24,62	27,51
MgO	14,24	13,65	8,42	10,99	14,13	13,36	11,49	10,44	8,02	12,07	8,41	12,02	10,94
MnO	0,26	0,17	0,17	0,27	0,13	0,11	0,15	0,18	0,12	0,08	0,61	0,23	0,17
CaO	0,11	-	-	-	0,03	0,13	0,38	0,02	0,03	0,12	-	0,32	0,20
Fe_2O_3	7,05	9,98	13,89	5,43	6,66	12,91	9,13	11,82	4,54	12,02	4,87	8,74	5,79
Cr_2O_3	3,14	0,42	0,26	4,17	2,00	0,27	0,20	0,54	1,02	0,12	0,07	1,64	1,81
Al_2O_3	-	0,68	0,55	-	-	-	0,67	0,20	-	-	0,13	-	-
V_2O_3	-	-	-	-	-	-	0,26	0,20	-	-	-	-	-
TOTAL:	99,47	101,34	100,95	100,67	98,97	99,89	99,65	99,73	98,85	99,70	99,09	99,53	99,16

NUMBER OF IONS ON THE BASIS OF 6 OXYGENS

	K1	K2+	K3+	K4+	K5	K6	K7	K8	K9	K10	K11	K12	UN1
V^{3+}	-	-	-	-	-	-	0,017	0,011	-	-	-	-	-
Al^{3+}	-	0,038	0,028	-	-	-	0,038	0,011	-	-	0,006	-	-
Cr^{3+}	0,114	0,016	0,011	0,151	0,072	0,010	0,005	0,023	0,040	0,006	0,006	0,061	0,068
Fe^{3+}	0,242	0,336	0,493	0,189	0,234	0,448	0,318	0,417	0,160	0,426	0,172	0,307	0,202
Ti^{4+}	1,822	1,805	1,734	1,830	1,847	1,771	1,811	1,769	1,900	1,781	1,908	1,816	1,865
Fe^{2+}	0,834	0,880	1,136	1,058	0,870	0,843	0,990	1,030	1,318	0,941	1,284	0,959	1,082
Mg	0,971	0,920	0,592	0,761	0,971	0,916	0,793	0,731	0,576	0,837	0,598	0,832	0,766
Mn	0,011	0,005	0,006	0,011	0,006	0,006	0,006	0,008	0,006	0,003	0,026	0,008	0,006
Ca	0,006	-	-	-	-	0,006	0,022	-	-	0,006	-	0,017	0,011
TOTAL:	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000

NORMATIVE COMPOSITION (MOLE PER CENT)

	K1	K2+	K3+	K4+	K5	K6	K7	K8	K9	K10	K11	K12	UN1
$FeTiO_3$	41,79	44,08	56,80	52,92	43,57	42,30	50,00	51,48	65,80	47,19	64,18	48,31	54,40
$MgTiO_3$	48,69	46,13	29,60	38,02	48,55	45,91	40,14	36,53	28,84	41,99	29,94	41,97	38,49
$MnTiO_3$	0,55	0,27	0,28	0,56	0,28	0,28	0,28	0,42	0,29	0,14	1,29	0,42	0,28
R_2O_3	8,97	9,52	13,32	8,50	7,60	11,51	9,58	11,57	5,07	10,68	4,59	9,30	6,83
TOTAL:	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

N.B. FeO and Fe_2O_3 analyses have been recalculated assuming ilmenite stoichiometry.

+ indicates eletron microprobe analysis.
K11 bulk analysis of an ilmenite concentrate from the de Beers Mine.
K12 bulk analysis of an ilmenite concentrate from the Wesselton Mine.

A survey of the published analyses indicates that both the Fe_2O_3 and MgO contents of kimberlite ilmenites vary between wide limits. Furthermore, there is no apparent direct relationship between these two variables. The presence of the Fe_2O_3 (and possibly Cr_2O_3) also influences the reflectivity of the kimberlite ilmenites with the result that this property cannot be used to determine the MgO content of these minerals in the presence of these solid solution components in the manner envisaged by Cervelle et al. (1971). The reflectivities of the kimberlite ilmenites are, however, consistently lower than those of ilmenites from other igneous rocks and this property might still be useful as an aid in the identification of this type of ilmenite.

The micro-indentation hardness does not show a linear relationship towards the MgO, although there is an overall increase in VHN with increasing MgO content. This feature is in accord with the findings of Morton and Mitchell (1972) and can also be ascribed to the variable amounts of MgO, Fe_2O_3 and Cr_2O_3 in solid solution in these minerals. Morton and Mitchell (1972) unfortunately only provided analyses of MgO and Cr_2O_3 for the ilmenites that they investigated with the result that an evaluation of the effects of Fe_2O_3 on this property is thus hampered by a lack of data.

The unit cell dimensions are distinctly smaller than those recorded for ilmenites that are nearer the theoretical end-member composition. This feature is due to the combined effect of the presence of Mg^{2+} and Fe^{3+} ions in the ilmenite crystal structure. Geikielite has a smaller unit cell (a = 5,054 Å) than ilmenite (a = 5,079 Å) and Cervelle (1967) has shown that the unit cell dimension decreases with increasing Mg content. Similarly, the unit cell dimension decreases from ilmenite to hematite (a = 5,029 Å) with increasing Fe_2O_3 content (Part 1, section 4.3). The use of this method for determining the amounts of MgO or Fe_2O_3 in solid solution can

only be used when dealing with essentially pure members of the ilmenite-geikielite or ilmenite-hematite solid solution series. It cannot be used effectively in the case of the more complex solid solutions as typified by the kimberlite ilmenites which can be regarded as members of the ilmenite-geikielite-hematite solid solution series. The presence of up to 5,6 per cent Cr_2O_3 (Haggerty, 1975) will, in addition, further complicate the observed cell variations.

The combined effect of the presence of MgO and Fe_2O_3 is to decrease the unit cell dimensions of the kimberlite ilmenites and they are consistently small-er than those recorded for ilmenites from other igneous rocks. This feature can thus be used in a qualitative way (preferably in conjunction with some other parameter such as reflectivity or micro-indentation hardness) to identify kimberlite ilmenites in concentrates containing ilmenites from other sources.

The smaller unit cell dimensions of the kimberlite ilmenites are reflected in their d-spacings and the two-theta angles of x-ray reflections. This is particularly noticeable in the high two-theta range where the measurement of a single reflection should be suffcient to indicate the smaller unit cell size. The (2.1.10) reflection is particularly well suited to this purpose since it is the most intense reflection in this high two-theta range and is easily measured. The k-alpha$_1$ peak position of this reflection ranges from 113,09^o to 113,66^o 2 θ in the samples examined, which is distinctly larger than that obtained for the ilmenites closer to the end-member composition (112,59^o to 112,70^o).

Limited data are currently available on the trace element content of kimber-lite ilmenite, but studies of this type should provide additional parameters by which they can be recognized (e.g. Mitchell et al., 1973, Nixon and

Kresten, 1973).

6.8 Conclusions.

1). The kimberlite ilmenites can be distinguished from other igneous ilmenites on the basis of their chemical compositions. They typically contain large amounts of MgO (6-24%) and Fe_2O_3 (0,1-20%), while their Cr_2O_3 (0,1-5,6%) and Al_2O_3 (0,1-1,0%) contents are also unusually high.

2). The compositional range of these ilmenites is such that they can generally be distinguished from ilmenites from other igneous rock types. A slight overlap is evident in the MgO contents of kimberlite ilmenites and magnesian-rich ilmenites from certain titaniferous iron ores (e.g. Kaffirskraal and Trompsburg complexes, this study, Part 3). The hematite content of these ilmenites is, however, often very much lower than those of the kimberlite ilmenites and generally forms exsolution lamellae when present in excess of 6 per cent.

3). The unit cell dimensions, reflectivities and micro-indentation hardness of the kimberlite ilmenites are influenced by their chemical compositions. These properties are sufficiently different from those of ilmenites from a wide range of common igneous rocks and can be used either independently or in various combinations as an aid in the recognition of kimberlite ilmenites. The independent and wide variation in MgO and Fe_2O_3 contents of the kimberlite ilmenites renders these techiques unsuitable for the determination of either MgO or Fe_2O_3 contents.

4). The lack of hematite exsolution lamellae in the Fe_2O_3-rich kimberlite ilmenites is consistent with their having been quenched from high temperatures. The possible effect of pressure on this process is difficult to evaluate since hematite and ilmenite form a complete solid solution series at temperatures above $600^{o}C$ under low pressures (Lindsley and Lindh, 1974).

7. THE CO-EXISTING IRON-TITANIUM OXIDES IN KARROO DOLERITES.

7.1 Introduction.

The Karroo dolerites are encountered over a wide area in southern Africa and have been described in detail by Walker and Poldervaart (1949). They are commonly present in the form of typically hypabyssal intrusions that form sills, dykes and inclined sheets. They are considered to be the intrusive equivalents of the considerable thickness of Karroo basalts that were once present over large areas of southern Africa and in some cases the dykes might represent the original feeder systems of the lavas. The emplacement of these intrusions and their associated volcanism has been related to the early stages of the Gondwanaland fragmentation (e.g. Cox, 1970, 1972).

The associated Karroo basalts have been studied in far greater detail than the dolerites in recent years (e.g. Cox and Hornung, 1966; Manton, 1968; Cox, 1970, 1972; Rhodes and Krohn, 1972; Lock et al., 1974). Some of the larger basic intrusions of this period show evidence of fractional crystall-ization and have begun to attract increasing attention (e.g. Maske, 1966; Eales and Booth, 1974; Eales and Robey, 1976). The Karroo dolerites themselves have, however, remained rather neglected.

The dolerites are typically tholeiitic in composition and usually contain between 1 and 5 per cent of opaque oxides as accessory phases. These minerals are generally located interstitially between the larger silicates or are found intergrown with them. As far as the author is aware, no detailed study of these minerals in the Karroo dolerites has been published.

7.2 Samples Investigated.

The twelve Karroo dolerite samples investigated were obtained from the area between the towns of Cookhouse, Middleburg, Tarkastad and Adelaide in the Eastern Cape. The samples were collected from road cuttings in order to obtain the freshest material for investigation. Microscopic examination of these rocks has shown them to be relatively unweathered and they normally only exhibit incipient alteration. The dolerites consist essentially of pyroxene and plagioclase and exhibit typical ophitic textures. Small amounts of quartz in the form of micropegmatite are present in samples D6, D6A and D10. Sample D13 represents a coarser-grained dolerite pegmatite.

7.3 The Nature and Occurrence of the Opaque Oxides.

The opaque oxides in the Karroo dolerites consist essentially of ilmenite and titaniferous magnetite. The twelve dolerites examined are texturally and mineralogically similar, but their opaque oxides exhibit a wide range in relative abundance and morphology. The titaniferous magnetite is usually subordinate to the ilmenite and is,in some cases, virtually absent.

The titaniferous magnetite is invariably found in close association with the ilmenite and these two phases commonly form complex aggregates that are located interstitially between plagioclase and pyroxene grains (Plate A (1 and 2)). Discrete titaniferous magnetite grains showing no direct association with large amounts of ilmenite are rarely encountered. Ilmenite, in contrast, is commonly present as discrete skeletal grains that commonly enclose silicate inclusions (Plate A (3)).

The ilmenite and titaniferous magnetite aggregates are commonly penetrated by plagioclase laths (Plate A (1, 2 and 4)) and contain abundant small sub-hedral to rounded silicate inclusions. A narrow reaction rim of biotite is occasionally developed between the opaque oxides and the plagioclase.

THE OPAQUE OXIDES IN KARROO DOLERITES.

1). Granular aggregates of ilmenite (white) and titaniferous magnetite (slightly darker, mottled appearance) showing typical relationships with pyroxene and plagioclase (grey). Incident light in air.

2). Similar to (1) but showing a much larger amount of ilmenite (white). The minor titaniferous magnetite (grey, mottled appearance) shows signs of alteration. Incident light in air.

3). Typical ilmenite grain (white) showing an almost euhedral outline and containing minor rounded silicate inclusions. Incident light in air.

4). Titaniferous magnetite grain (grey) containing a broad band of ilmenite (white) and set in a pyroxene-plagioclase groundmass. Incident light, partially crossed nicols in air.

5). The upper portion of the grain represents a completely altered titaniferous magnetite grain in which the "skeleton" of ilmenite lamellae (white) remains set in a matrix of chlorite, sphene and other alteration products. The lower portion of the grain represents a typical skeletal subgraphic-to vermicular-ilmenite intergrowth (white) with hydrous silicates. Incident light in air.

6). Similar to (5), but showing a greater degree of modification of the ilmenite lamellae to form graphic and vermicular morphologies. Incident light in air.

7). Typical skeletal ilmenite grains (white) showing various subgraphic and vermicular forms. This ilmenite is intergrown with secondary hydrous silicates. Incident light in air.

8). Similar to (7), under higher magnification showing the nature of the sub-graphic and vermicular ilmenite intergrowths (white) with secondary hydrous silicates. Incident light in air.

PLATE A
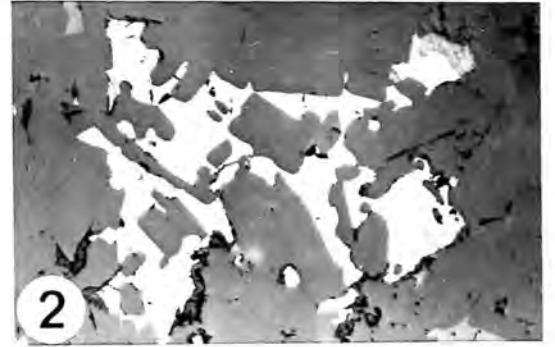
1, 0 mm
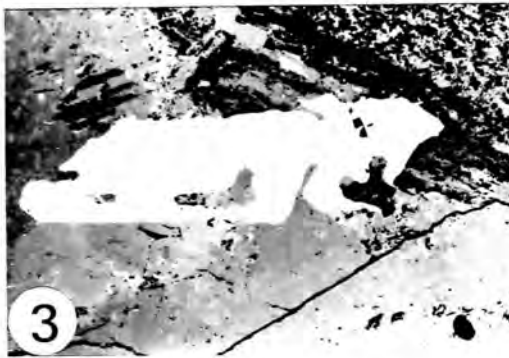
0, 25 mm
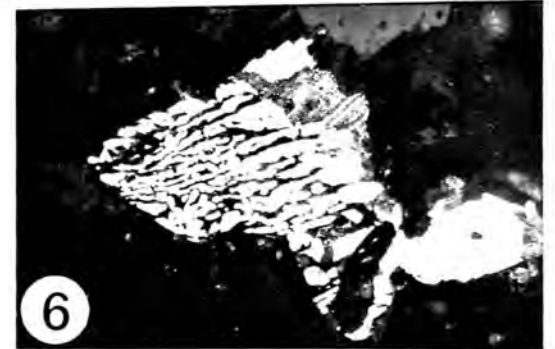
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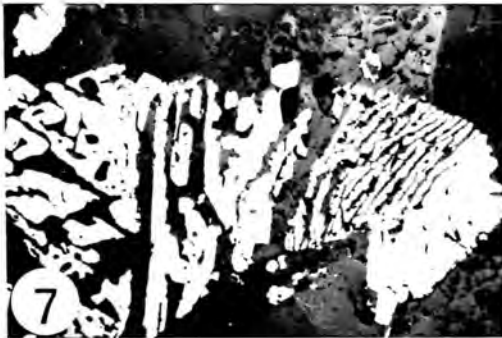
0, 25 mm
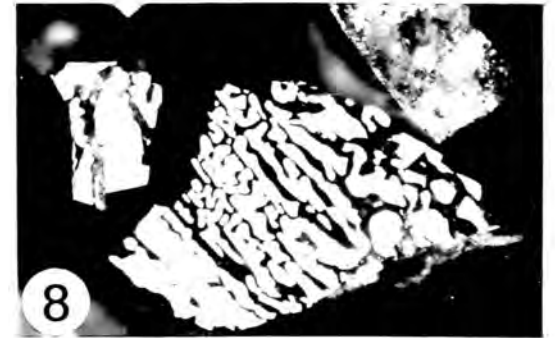
0, 15 mm

Tiny euhedral hexagonal prisms of apatite up to 30 micrometres in size are occasionally present as inclusions in the ilmenite.

The ilmenite exhibits a much greater morphological variation than the titaniferous magnetite and is present in a variety of skeletal forms that can be described as subgraphic or vermicular (Plates A (5-8) and B (1-2)). These ilmenite grains are sometimes associated with altered titaniferous magnetite whose former identity can be recognized by the presence of narrow oriented ilmenite lamellae set in a fine grained groundmass of alteration products (Plate A (5-6)). There is often no direct association between these ilmenite grains and titaniferous magnetite and they are commonly intergrown with fine-grained secondary silicate minerals such as biotite, hornblende and sphene (Plates A (7-8) and B (1-2)).

7.4 The Titaniferous Magnetite.

The titaniferous magnetite is usually present as small grains, less than 0,25 mm in size. They are generally subhedral to anhedral with their external morphologies being dictated by the shapes of the surrounding silicates. The titaniferous magnetites generally show the development of straight-to slightly curved-grain boundaries at places where they are in contact with large ilmenite grains. The titaniferous magnetites characteristically exhibit varying degrees of secondary alteration and invariably contain a variety of exsolved titanium-bearing phases.

The titaniferous magnetite is commonly traversed by numbers of narrow arcuate fractures and incipient maghemitization is usually evident in the narrow zones bordering these fractures. Maghemitization is also commonly evident in regions adjacent to grain boundaries and lamellar ilmenite intergrowths. The titaniferous magnetite also commonly exhibits varying degrees of dissolution and replacement that is also particularly noticeable in the areas adjacent to these fractures and along contacts with silicate minerals.

PLATE B.

OPAQUE OXIDES IN KARROO DOLERITES AND BUSHVELD GABBROS.

1) and 2).   Various forms of skeletal ilmenite (white) showing the ulti-
    mate stages in development of subgraphic and vermicular intergrowths.
    Incident light in air.

3).   Titaniferous magnetite containing trellis networks of narrow ilmenite
    lamellae in 3 orientations.   The ulvospinel in the surrounding titani-
    ferous magnetite has been altered to ilmenite that is in optical con-
    tinuity with the nearby ilmenite lamellae.   This produces the "an
    isotropic" effect illustrated.   Incident light, partially crossed
    nicols, oil immersion.

4).   Similar to (3) but under higher magnification showing the extremely
    fine-grained nature of the oxidised ulvospinel (ilmenite) in optical
    continuity with nearby ilmenite lamellae (darker grey).   Incident
    light, partially crossed nicols, oil immersion.

5).   A typical hemo-ilmenite grain (grey) from the Hendriksplaats norite
    showing abundant hematite lamellae exsolved parallel to (0001)
    (white).   Incident light, oil immersion.

6).   Titaniferous magnetite grains (grey) meeting in well defined triple
    junctions and showing extremely coarse ulvospinel cloth textures in
    an ore-rich Bushveld gabbro.   The mottled effect is due to partial
    maghemitization.   Incident light, oil immersion.

7).   Typical ulvospinel cloth texture in a Bushveld titaniferous magnetite
    (the ulvospinel has been oxidised to ilmenite (dark grey)).   Incid-
    ent light, oil immersion.

8).   Similar to (7), but showing the presence of several transparent spinel
    lamellae (black).   Note the development of coarser ulvospinel "frames"
    around the spinel lamellae.   Incident light, oil immersion.

PLATE B
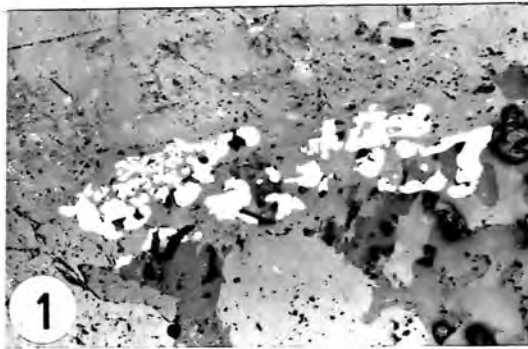
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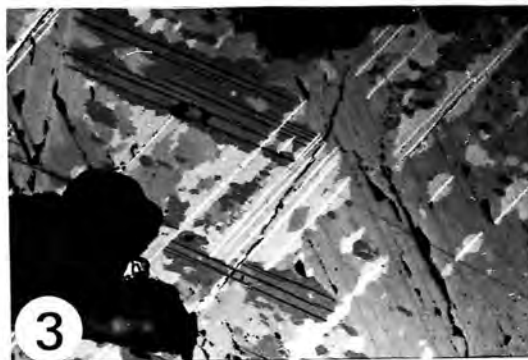
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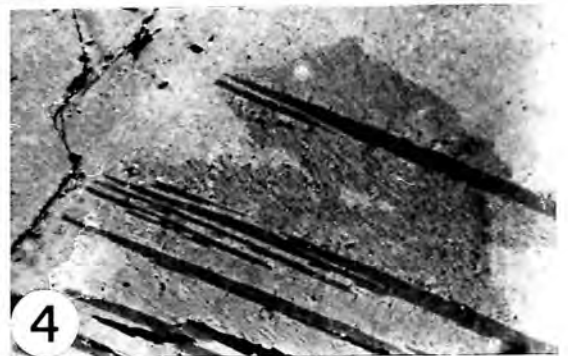
0,015 mm
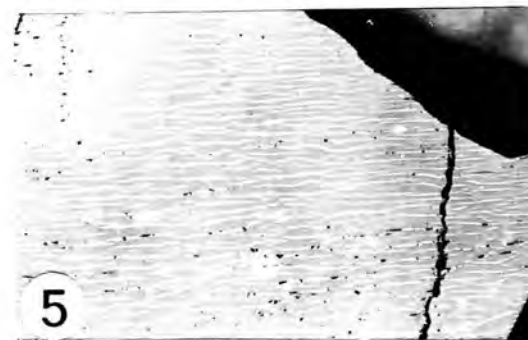
0,1 mm

0,07 mm
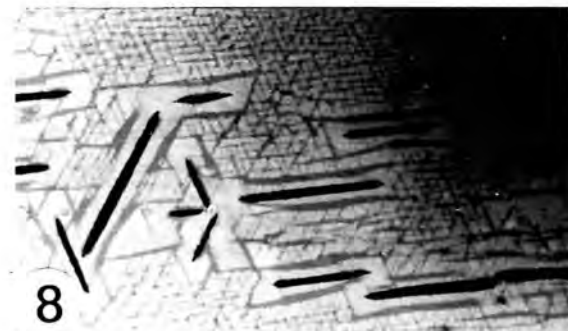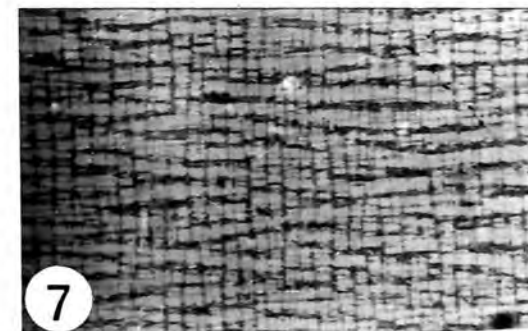
0,015 mm

The commencement of this alteration is characterized by a slight lightening in the colour of the magnetite and the development of micrometre-sized dark mineral aggregates (possibly finely crystalline sphene) in the titaniferous magnetite. This produces a texture with an overall porous appearance. This solution and replacement of titaniferous magnetite by these fine-grained aggregates then progresses to the stage where the original titaniferous magnetite grain is completely destroyed. The ilmenite lamellae appear more resistant to the alteration and are commonly preserved in their original orientation in the alteration products as illustrated in Plate A (5-6).

The amount of titaniferous magnetite in the dolerites is invariably less than that of the associated ilmenite and reaches its maximum in samples exhibiting the relationships shown in Plates A (1-2). A continuous range of textural types exists in which the amount of skeletal ilmenite increases while the titaniferous magnetite decreases until it is virtually absent. This decrease in the titaniferous magnetite content appears to be the result of increasing degrees of alteration rather than any significant decrease in the amount of magnetite that originally crystallized.

The alteration of the titaniferous magnetite can also be seen in thin section, but the fine-grained alteration products are not easily identified. They appear to be largely secondary hydrous silicates such as biotite and amphibole, while sphene is evident in at least two samples. Incipient alteration is noticeable along the contacts between the opaque oxides and the surrounding silicates even in the specimens in which the silicates otherwise appear completely fresh and unaltered. This is also evident in the corresponding polished sections where the titaniferous magnetite shows incipient alteration (Plate A (1-2)) along grain boundaries with silicates.

When the complete suite of samples is examined in thin section it is apparent

that the amount of secondary hydrous silicates increases at the expense of the titaniferous magnetite. The ilmenite morphology also changes from the simple granular form exhibited in Plate A (1, 2 and 3) to the more complex skeletal and poikilitic forms illustrated in Plates A (5-8) and B (1-2) and is related to the decrease in magnetite content. The secondary hydrous silicates are generally confined to the areas immediately surrounding the opaque oxides. The plagioclase in the immediate vicinity may show some alteration to saussurite and the pyroxene some alteration to hornblende. Moderately extensive alteration of the silicates is only evident in samples D5, D6, D6A, and D13.

The titaniferous magnetite is characterized by the virtual absence of transparent spinel exsolution bodies. When present, they form tiny micrometre-sized grains that are located along the interfaces between the titaniferous magnetite and the larger ilmenite lamellae or discrete ilmenite grains.

The titaniferous magnetite generally contains minor, but variable amounts of lamellar ilmenite and is characterized by an extremely fine micrometre- to sub-micrometre-sized ulvospinel cloth texture. This texture is often developed on a scale that is at the limit of optical resolution and its fine scale is presumably related to the more rapid cooling rate of the hypabyssal dolerite intrusions.

The unit cell dimensions of the titaniferous magetite are given in Table 5 together with the corresponding parameter obtained for pure magnetite by Basta (1957).

The titaniferous magnetite exhibits peak broadening in the high 2 θ range. This is in part due to the small particle size of the magnetite caused by the fine-grained ulvospinel exsolutions. It is also partly due to changes

in the cell parameter caused by the presence of some ulvospinel in solid
solution, the possible presence of some discrete unoxidized ulvospinel and
the incipient maghemitization which have all contributed to small changes in
the unit cell dimensions.   The unit cell parameters of some titaniferous
magnetites are larger than those of pure magnetite and this can be ascribed
to the presence of small, but variable amounts of ulvospinel in solid solu-
tion (Basta, 1957).   The remaining magnetites exhibit smaller unit cell
dimensions and this is due to the effects of maghemitization which results
in a decrease in cell size (Basta, 1957).

TABLE 5.

UNIT CELL DIMENSIONS OF EXSOLVED TITANIFEROUS MAGNETITES FROM KARROO DOLERITES.

Sample Number	a($\pm$0,0005 Å	Degree of Altera-tion of the sili-cates around the oxides
Pure magnetite	8,3963	–
D3	8,3950	slight
D4	8,3967	slight
D5	8,3950	moderate
D6	8,3956	moderate
D6A	8,3960	moderate
D7	8,3953	slight
D8	8,3951	slight
D9	8,3993	slight
D10	8,3998	incipient
D11	8,3987	incipient
D12	8,3950	slight
D13	8,3950	moderate

7.5 <u>The Ilmenite.</u>

The ilmenite is present as discrete grains, in skeletal forms and as lamellar microintergrowths in titaniferous magnetite.

7.5.1 <u>Granular ilmenite.</u>

This is the most common type of ilmenite and it is present both as anhedral grains associated with titaniferous magnetite (Plate A (1 and 2)) or as discrete euhedral to subhedral grains that commonly contain small rounded silicate inclusions (Plate A(3)). It is completely free from exsolution lamellae of any kind and does not generally show any secondary alteration features. This type of ilmenite is also present in small amounts in the samples containing the skeletal forms.

The experimentally determined unit cell dimensions, reflections and micro-indentation hardness values for these ilmenites are given in Table 6. The measured cell dimensions are very close to those given by Deer, Howie and Zussman (1962b) for ilmenite (a = 5,089 $\overset{o}{A}$, c = 14,163 $\overset{o}{A}$). They also fall within the range of values for coarse grained ilmenites in the Bushveld Complex (a = 5,074-5,090$\overset{o}{A}$, c = 14,02-14,065 $\overset{o}{A}$) investigated by Molyneux (1970, 1972).

The reflectivity measurements are within the range of values reported by Cervelle (1967) for ilmenites containing no Mg (R_o = 19,5-20,1%, R_e = 16,7-17,6%). The VHN_{100} values obtained also fall within the same general range (VHN_{100} = 560-700) given by Cervelle (1967) for these ilmenites.

A comparison of Table 6 with Table 3 indicates that the kimberlite ilmenites can be readily distinguished from the dolerite ilmenites on the basis of any one of these properties or combinations of these properties. The relatively small variation in each of these parameters between the ilmenites

TABLE 6

DOLERITE ILMENITES : UNIT CELL PARAMETERS, REFLECTIVITIES AND VICKER'S HARDNESS NUMBERS

| Sample number | Unit cell dimensions (Hexagonal axes) | | | Calculated d-spacing for (2.1.10) ($\mathring{A}$) | 2-theta angle for Co-radiation K-alpha$_1$ for (2.1.10) | Reflectivity in air at 546 nm | | Vicker's hardness number |
	$a \pm 0,0005 \mathring{A}$	$c \pm 0,001 \mathring{A}$	volume $\mathring{A}^3$			R_o (%)	R_e (%)	(VHN_{100})
D3	5,0883	14,074	315,561	1,0750	112,62	19,5	17,1	544 – 574
D4	5,0892	14,074	315,673	1,0751	112,61	19,4	16,8	550 – 587
D5	5,0869	14,066	315,216	1,0745	112,70	19,5	16,7	538 – 565
D6	5,0883	14,068	314,434	1,0747	112,66	19,7	16,9	564 – 590
D6A	5,0883	14,073	315,547	1,0749	112,63	19,6	16,5	546 – 583
D7	5,0874	14,072	315,411	1,0748	112,65	19,7	17,2	566 – 598
D8	5,0882	14,072	315,520	1,0749	112,63	20,0	16,6	587 – 640
D9	5,0874	14,071	315,378	1,0747	112,66	19,5	16,4	572 – 616
D10	5,0885	14,070	315,519	1,0749	112,64	19,7	16,5	563 – 595
D11	5,0885	14,074	315,560	1,0750	112,62	19,5	16,4	556 – 583
D12	5,0892	14,073	315,657	1,0750	112,62	19,6	16,4	559 – 612
D13	5,0889	14,077	315,701	1,0751	112,59	19,6	16,8	565 – 595

from different dolerites is also reflected in their relatively small
compositional variation.

7.5.2 Skeletal ilmenite.

The bulk of the dolerites are characterized by the presence of skeletal
ilmenite grains that exhibit complex subgraphic or vermicular intergrowths.
These grains are either associated with titaniferous magnetite that shows
advanced stages of decomposition (Plate A (5 and 6)) or occur in areas that
are devoid of other opaque oxides. They are characteristically surrounded
by a narrow alteration zone of irregular and variable width that
contains fine-grained secondary hydrous silicates. Amphibole and biotite
can often be recognised and fine-grained sphene aggregates have been noted
in at least two samples. These alteration products are also present in the
areas between the individual portions of the grains and form the matrix in
which they are set.

The grain boundaries of this ilmenite appear smooth and curved under low
power magnification, but under high power they are more irregular and show
evidence of replacement. This is particularly noticeable in the samples
in which a narrow zone of sphene surrounds the ilmenite.

The proportion of this type of ilmenite present in any sample is related to
the degree of alteration that has taken place in the associated titaniferous
magnetite. This type of ilmenite is rare in samples containing abundant
titaniferous magnetite, but its relative content increases as the degree of
magnetite alteration increases and the overall magnetite content decreases.

The individual portions of the complex grains are often elongated and are
arranged in a parallel fashion as shown in Plate A (5-8). These individual
portions are generally in optical continuity and combine to form large grains

that have overall dimensions of up to 2 mm, although the average size is in the region of 0,5 mm. The elongated portions of the grains are sometimes present in two or three distinct intersecting orientations, but this type of arrangement is not as common as the parallel kind.

The individual portions of these grains tend to coalesce into larger, more continuous grains in places where they are in contact with altered titaniferous magnetite (Plate A (5 and 6)). These bodies are also very often in optical continuity with the ilmenite lamellae that form the "skeletons" of the altered titaniferous magnetite grains as illustrated in Plate A (5).

The margins of the skeletal ilmenite grains also show evidence of alteration in the more highly altered samples. The ilmenite appears slightly lighter in colour and has a slightly bluish colour similar to that developed during the normal weathering of ilmenite. This appears to be due to the removal of iron from the ilmenite structure and the ilmenite itself shows signs of resorption. Small amounts of sphene are also commonly developed around the peripheries of these ilmenite grains.

7.5.3 Lamellar Ilmenite.

Various size ranges of ilmenite lamellae are present in the titaniferous magnetites. The large relatively unaltered titaniferous magnetites commonly contain two or threee very broad lamellae or sometimes more irregularly shaped ilmenite bodies as illustrated in Plate B (4). These might, in some cases, be very large sandwich lamellae, but in others they have developed as a result of simultaneous crystallization of ilmenite and titaniferous magnetite.

The majority of titaniferous magnetite grains contain several sparsely distributed broad ilmenite lamellae that sometimes extend across the entire

width of the grain.   These lamellae are usually less than 15 micrometres in width, but are up to 0,15 mm in length.   They appear to have nucleated at grain boundary imperfections and to have grown into their hosts. They are developed along all the octahedral planes in the magnetite, but they very often show preferential development along a particular octahedral plane to form typical sandwich textures.   They are rarely present in sufficient quantities to form typical trellis networks.

Smaller-sized ilmenite lamellae are only rarely developed and they are never present in sufficient quantities to form well defined trellis networks.   They are generally between 1 and 4 micrometres in width, but commonly exceed 0,1 mm in length (Plate B (4 and 5)).   These lamellae are commonly slightly lensoid in shape and are occasionally arranged in a closely spaced en echelon fashion as illustrated in Plate B (4).

The bulk of the intergrown ilmenite is represented by the fine-grained oxidised ulvospinel intergrowths that are ubiquitously developed in the areas between the larger lamellae.   The abundance of this material produces a distinct anisotropic appearance in the titaniferous magnetite when viewed between crossed polars. The ilmenite oxidation products have maintained the original morphology of the ulvospinel cloth texture and have developed in optical continuity with neighbouring ilmenite lamellae.   This is particular-ly noticeable between crossed polars where irregularly shaped areas of "an-isotropic" magnetite bordering the ilmenite lamellae also appear to be in optical continuity with them (Plate B (3 and 4)).

The unit cell dimensions of the intergrown ilmenite in the titaniferous magnetite are presented in Table 7.   The values obtained represent averages of the various size ranges of ilmenite present since there is no physical method for separating the various fine-grained types.   The ilmenite

produced by ulvospinel oxidation is the dominant phase present and the values

obtained are probably those of this material. The ilmenite peaks exhibit

a distinct broadening in the high 2 θ range which can be ascribed to the

extremely small ilmenite particle size. It might, in part, also reflect

minor compositional differences between the different size ranges of ilmenite

lamellae.

TABLE 7

UNIT CELL DIMENSIONS OF INTERGROWN ILMENITE LAMELLAE IN TITANIFEROUS

MAGNETITE.

Sample number	Unit cell dimensions (hexagonal axes)			Calculated d-spacing for (2.1.10) (Å)	2θ angle for Co-radiation k-alpha, for (2.1.10)
	$a \pm 0,0005$Å	$c \pm 0,001$Å	volume Å^3		
D3	5,0875	14,073	315,444	1,0749	112,64
D4	5,0885	14,079	315,679	1,0752	112,59
D5	5,0891	14,070	315,570	1,0740	112,64
D6	5,0891	14,077	315,732	1,0752	112,59
D6A	5,0889	14,076	315,687	1,0751	112,60
D7	5,0895	14,073	315,670	1,0751	112,61
D8	5,0886	14,076	315,662	1,0751	112,60
D9	5,087	14,063	315,162	1,0743	112,72
D10	5,0880	14,073	315,516	1,0749	112,63
D11	5,0881	14,074	315,543	1,0750	112,62
D12	5,0887	14,075	315,646	1,0751	112,61
D13	5,0889	14,079	315,754	1,0753	112,57

These cell parameters are essentially the same as those obtained for the coarse-grained ilmenite concentrates (Table 6) which consist of a mixture of granular and skeletal ilmenite types. This feature suggests that the various size ranges of ilmenite, both intergrown and granular, are compositionally similar. A similar relationship was noted by Molyneux (1970, 1972) between the coarse-grained and intergrown ilmenites in the Bushveld Complex. In his samples, the unit cells of the intergrown ilmenites are often slightly larger than those of their corresponding coarse-grained varieties. The variation in the corresponding Karroo dolerite ilmenites appears to reflect no direct relationship and is probably partly due to minor experimental errors.

7.6 Ulvospinel.

The original presence of abundant ulvospinel is clearly illustrated by the development of well defined ulvospinel cloth textures. This has, however, been almost entirely oxidized to ilmenite and it is doubtful whether any ulvospinel is actually present in the samples investigated. The unit cell dimensions of the titaniferous magnetite hosts (Table 5) indicate that at least some ulvospinel has remained in solid solution in the magnetite. The maghemitization of many of the titaniferous magnetites has resulted in a compensating decrease in unit cell parameters with the result that the ulvospinel solid solution content of these minerals cannot be determined by this method.

7.7 Chemical Composition of the Ilmenites.

The chemical compositions of individual granular ilmenites were determined by electron microprobe, while the bulk compositions of ilmenite concentrates were determined by wet chemical methods. The results obtained are presented in Table 8. The literature contains numerous analyses of ilmenite from gabbros and basaltic lavas, but complete analyses of ilmenites from dolerites

TABLE 8

ANALYSES OF DOLERITE ILMENITES

	D3+	D4+	D5	D6	D6A+	D7+	D8+	D9	D10	D11	D12	D13	ILMENITES FROM THOLEIITIC BASALTS (CARMICHAEL, 1967b)					
SiO_2	0,72	1,26	-	-	1,08	0,21	1,90	-	-	-	-	-	0,06	0,10	0,10	0,09	0,07	0,17
TiO_2	51,79	50,90	49,85	50,60	51,26	50,49	50,91	48,77	49,46	49,92	49,65	49,37	50,30	49,80	49,40	50,50	49,80	49,50
FeO	45,59	45,93	44,02	44,15	45,30	44,95	45,87	43,00	43,42	44,25	43,83	43,50	43,80	42,00	42,00	42,70	41,90	42,10
MgO	0,70	0,22	0,22	0,26	0,16	N.D	0,20	0,29	0,32	0,35	0,08	0,22	0,49	1,17	1,00	1,21	1,28	1,09
MnO	0,40	0,44	0,27	0,79	0,41	1,38	0,89	0,21	0,43	0,21	0,60	0,49	0,50	0,47	0,47	0,43	0,53	0,49
CaO	-	-	0,08	0,11	-	-	-	0,05	0,05	0,04	0,05	0,08	0,07	0,27	0,25	0,19	0,11	0,16
Fe_2O_3	-	-	4,42	3,01	-	1,28	-	7,15	5,70	4,36	5,46	5,44	4,40	5,80	6,60	4,80	6,10	6,40
Cr_2O_3	-	-	N.D	0,01	-	-	-	N.D.	0,02	0,04	0,04	N.D.	-	-	-	-	-	-
TOTAL	99,20	98,75	98,86	98,93	98,21	98,31	99,77	99,47	99,40	99,17	99,71	99,10	99,62	99,61	99,82	99,92	99,79	99,91

NUMBER OF IONS ON THE BASIS OF 6 OXYGENS

Cr^{3+}	-	-	-	-	-	-	-	-	-	-	-	-
Fe^{3+}	-	-	0,172	0,116	-	0,064	-	0,275	0,220	0,166	0,208	0,210
Si^{4+}	0,036	0,064	-	-	0,055	0,009	0,096	-	-	-	-	-
Ti^{4+}	1,964	1,944	1,914	1,942	1,964	1,959	1,916	1,863	1,890	1,917	1,896	1,895
Fe^{2+}	1,930	1,950	1,881	1,884	1,930	1,931	1,922	1,829	1,845	1,880	1,863	1,856
Mg	0,052	0,015	0,018	0,018	0,012	-	0,015	0,021	0,024	0,028	0,006	0,015
Mn	0,018	0,018	0,012	0,034	0,018	0,037	0,039	0,009	0,018	0,006	0,024	0,021
Ca	-	-	0,003	0,006	-	-	-	0,003	0,003	0,003	0,003	0,003
TOTAL	4,000	3,991	4,000	4,000	3,979	4,000	3,988	4,000	4,000	4,000	4,000	4,000

NORMATIVE COMPOSITION (MOLE PER CENT)

$FeTiO_3$	96,51	98,30	94,18	94,48	98,43	93,54	97,26	91,59	92,36	94,18	93,28	92,95
$MgTiO_3$	2,58	0,77	0,92	0,82	0,63	-	0,76	1,07	1,22	1,38	0,31	0,77
$MnTiO_3$	0,91	0,93	0,61	1,69	0,94	2,85	1,98	0,45	0,92	0,30	1,22	1,07
R_2O_3	-	-	4,29	2,91	-	3,61	-	6,89	5,50	4,14	5,19	5,21
TOTAL:	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

N.B. FeO and Fe_2O_3 analyses have been recalculated assuming ilmenite stoichiometry. The insoluble residue totals have been subtracted from the wet chemical analyses and the analyses recalculated according to their original totals.

+ indicates electron microprobe analysis - indicates oxide not determined N.D. indicates less than 0,01%.

with which direct comparison can be made are not available. Partial analyses of these types of ilmenite by Jensen (1966) and Smith (1970) indicate the same range of minor element variation.

The microprobe and wet chemical analyses are comparable except that no excess Fe_2O_3 is apparent in the recalculated analyses for samples D3,4,6A and 8. This feature is due to the slightly larger TiO_2 values reported in microprobe analyses and the small, but variable amounts of SiO_2 that have been added to the TiO_2 during the mineral calculations. The values for SiO_2 reported in the microprobe analyses are probably nearly all too high. Vincent and Phillips (1954) concluded that a maximum of 0,50 per cent SiO_2 might be present as a replacement of Ti^{4+} in the crystal structure of ilmenite.

The small amounts of Fe_2O_3 reported in the analyses can be readily held in solid solution in the ilmenite as indicated by the absence of hematite exsolution lamellae. The minor element contents of these ilmenites are also small with the result that they are very close to the theoretical end member composition for ilmenite.

There does not appear to be any direct relationship between the minor compositional variations shown by these ilmenites and their unit cell dimensions, reflectivities or micro-indentation hardness.

7.8 The Development of Subgraphic and Vermicular Ilmenite Intergrowths.

The presence of discrete ilmenite grains displaying subgraphic to vermicular intergrowths in gabbroic rocks of the Bushveld Complex has been reported by Ramdohr (1969) and Molyneux (1970). Jensen (1966) reported the occurrence of similar ilmenite intergrowths with pyroxene that had been altered to biotite in dolerite dykes. He noted that the elongated ilmenite plates were

developed paralllel to (0001) and concluded that they represented a form
of skeletal growth caused by rapid cooling.

Davidson and Wyllie (1968) described an essentially similar series of
ilmenite grains showing various stages of development in a diabase-
granophyre suite from Pennsylvania that is in many respects analogous to
the opaque oxides in Karroo dolerites. They also presented a series of
photomicrographs that are essentially similar to those in Plates A (1-8)
and B (1-2) and noted that the titaniferous magnetite is partially oxidised.
They reported that the skeletal ilmenite is invariably and intimately
associated with hydrous mafic silicates (biotite and hornblende) that also
fill the interstices between the ilmenite arms and noted that all stages of
associated titaniferous magnetite alteration were present.

Davidson and Wyllie (1968) suggested that an aqueous fluid developed within
the crystallizing magma during the iron-enrichment stage of the different-
iation sequence and that this was capable of dissolving iron from the titani-
ferous magnetite leaving skeletal crystals of ilmenite. The ilmenite plates
become enlarged during the removal of the iron and they lose their regular
straight-sided outlines and assume the typical form of the skeletal grains.
They concluded that some or all of this iron was redeposited as a second
generation of Ti-poor magnetite within the host rock or else it escaped to
be deposited elsewhere.

Haselton and Nash (1975) described the occurrence of a similar orthopyroxene-
ilmenite intergrowth from the Skaergaard Complex and reviewed the available
data on the development of these types of intergrowths with particular
reference to their occurrence in kimberlites. They concluded that the
texture in the Skaergaard gabbro was formed by the sub-solidus oxidation of
titanomagnetite that was present as inclusions in the pyroxene. They

estimated the equilibration temperature for this ilmenite-orthopyroxene pair at approximately 700°C.

The dissolution of titaniferous magnetite and its replacement by sphene-chlorite aggregates was noted in Usushwana Complex gabbros and has been widely reported in the literature. This topic is reviewed in Part 3, section 8.8.

The titaniferous magnetites and skeletal ilmenites found in the Karroo dolerites are strikingly similar to those described by Davidson and Wyllie (1968), although no discrete Ti-poor magnetite has been recognised. The increase in skeletal ilmenite is related to the increasing alteration of titaniferous magnetite and an increase in the amount of secondary hydrous silicates in the immediate vicinity. The ilmenite is not present in an eutectic-type intergrowth with pyroxene or other silicate, but appears to be located interstitially between both pyroxene and plagioclase laths. The alteration of the magnetite is widespread and must have occurred during the later stages of magmatic crystallization (deuteric alteration) since these dolerites have not been metamorphosed.

The alteration appears to have taken place at temperatures below the magnetite-ulvospinel solvus since the altered magnetites exhibit typical ulvospinel cloth textures, even in the areas in direct contact with the alteration products. The maghemitization appears related to the alteration of the titaniferous magnetite rather than to surface weathering effects and implies the existence of, at least locally, high oxygen fugacities during altera-tion. This would have caused extensive oxidation of the ulvospinel remain-ing in solid solution resulting in lamellar ilmenite or internal granule development, had it occurred at higher sub-solvus temperatures while the pre-existing ulvospinel lamellae would also show evidence of re-arrangement.

The nature of the solutions responsible for the alteration is not known, but they probably represent late-stage volatile-rich fractions left after the bulk of the crystallization has been completed. Their abundance is highly variable as shown by the different amounts of alteration exhibited by the titaniferous magnetite and they are presumably operative at relatively low temperatures, possibly below $350-400^{\circ}C$ to allow for the development of the unmodified ulvospinel cloth textures. The incipient and restricted degree of alteration in many cases suggests that the fluids responsible might represent the final aqueous crystallization products that are entrapped in the interstices between mineral grains.

The dissolution of the iron in the magnetite leads to the liberation of Ti which is precipitated along with some of the iron as ilmenite overgrowths on the pre-existing ilmenite lamellae and grains and allows for their continued growth to produce the vermicular intergrowths. These secondary ilmenite overgrowths are in optical continuity with the original lamellae and their parallel development can be ascribed to the "sandwich" arrangement of the original ilmenite lamellae. The arms of these intergrowths are also found in two and three different orientations, but they are not as common as the parallel types and this corresponds with the paucity of ilmenite "trellis" networks in the titaniferous magnetite.

Portion of the liberated iron is incorporated into the femic hydrous silicates (biotite and hornblende) that are invariably associated with the alteration products. A minor amount of sphene might also be formed during this process from Ca^{2+} released during the alteration of plagioclase or augite. Any remaining excess iron would presumably be removed in solution and be deposited elsewhere, but no secondary Ti-poor magnetite was recognised in the samples examined. The more highly altered samples typically contain several percent of finely disseminated sulphides, usually pyrrhotite and chalcopyrite, and

it is possible that some of this iron might be precipitated as sulphides.

The oxidation of the titaniferous magnetite and the exsolved ulvospinel lamellae probably took place during this late stage as a result of the relatively high oxygen fugacities associated with the aqueous fluids. This is further supported by the incipient alteration of the skeletal ilmenite grains in the more altered samples. This is not due to atmospheric weathering since the silicates appear fresh in areas not affected by the secondary alteration and there is no evidence of hematite, goethite, clay minerals or other typical weathering products. Moreover, the rock samples were collected from road cuttings and represent the "freshest" material available for study.

7.9 Conclusions.

1). The opaque oxides in the Karroo dolerites consist essentially of titaniferous magnetite and ilmenite. The titaniferous magnetite exhibits variable degrees of late-stage alteration that has contributed to the development of skeletal ilmenite grains with subgraphic and vermicular morphologies.

2). The ilmenites exhibit a restricted compositional range that is also reflected in the relatively small ranges in their unit cell parameters, reflectivities and micro-indentation hardnesses. These ilmenites are very near to the theoretical end member in composition.

3). The dolerite ilmenites appear to be chemically similar to ilmenites from a wide range of basic igneous rocks (section 9) and can readily be distinguished from the MgO- and Fe_2O_3-rich kimberlites. They can also be distinguished from the kimberlite ilmenites by means of unit cell dimensions, d-spacings, reflectivities or micro-indentation hardness measurements.

8. <u>THE CO-EXISTING IRON-TITANIUM OXIDES IN DIABASES ASSOCIATED WITH THE</u>

<u>BUSHVELD COMPLEX.</u>

8.1 <u>Introduction.</u>

The Transvaal Supergroup along the southern and southeastern margin of the
Bushveld Complex has been intruded by large numbers of hypabyssal basic
intrusions that are often in the form of sills. These intrusions are
diabases (i.e. altered dolerites) and are regarded as being genetically
related to the Bushveld Complex. Willemse (1969a) referred to them as the
"Sill Phase" of the Bushveld Complex and suggested that they were intruded
prior to the main mass of Bushveld basic magma. He noted that the sills
commonly consist of saussuritized plagioclase and clinopyroxene that exhibits
varying degrees of alteration to green hornblende and chlorite. Biotite,
"iron ore" and a quartz-potassium feldspar mesostasis are also commonly
present. He also noted that "comparatively little research has been carried
out on these diabase sheets specifically".

Frick (1973c) investigated the "Sill Phase" of the Bushveld Complex in
eastern Transvaal and recognised the presence of an older dioritic group
and a younger doleritic group of differentiated sills. He also noted the
abundant development of a variety of diabase sills composed of green fibrous
amphibole, some quartz, plagioclase, biotite and opaque minerals. He
concluded that these diabases represent metadolerite and noted that the
dolerites are typically tholeiitic in chemical composition. Frick (1973c)
also noted that the "Chill Zone" of the Bushveld Complex is tholeiitic in
nature and suggested that a genetic relationship exists between these sills
and the basic portion of the Bushveld Complex.

The diabases characteristically display variable degrees of alteration that
is in part due to the thermal metamorphic effects associated with the intru-
sion of the Bushveld Igneous Complex, and in part due to any low grade

regional or burial metamorphism that might have subsequently occurred. The diabases are typically tholeiitic hypabyssal intrusions and can consequently be compared with the very much younger and unaltered Karroo dolerites described in section 7. The opaque oxides in these diabases were investigated in order to determine the nature of any possible changes that might have occurred during the alteration of their host rocks as well as to provide data on the compositional range of their ilmenites.

8.2 Samples Investigated.

Diabase sills are commonly encountered in the Transvaal Supergroup sediments around the southern and southeastern margins of the Bushveld Complex. Samples were collected from road cuttings in the area between Pretoria, Delmas and Bronkhorstspruit as well as along the National road between Belfast and Waterval Boven. The rocks exhibit varying degrees of alteration and are characterized by the presence of saussuritized plagioclase and uralitized pyroxene. Several samples contain variable amounts of quartz in the form of micropegmatitic intergrowths, but in others it is virtually absent.

8.3 The Nature and Occurrence of the Opaque Oxides.

The diabases generally contain less opaque oxides than their Karroo dolerite counterparts and some samples are almost devoid of them. The oxides are invariably associated with secondary hydrous silicates and the diabases are characterized by the virtual absence of titaniferous magnetite. The ilmenite also shows varying degrees of alteration to sphene and in some cases rutile.

The suite of samples examined exhibits a complete range of opaque oxide assemblages and relationships that vary from types that are similar to those present in the more altered Karroo dolerite samples to samples in which

only a few highly altered ilmenite grains are present. The increasing
degree of alteration and modification of the primary opaque oxide relation-
ships is also related to increasing amounts of alteration of the associated
silicates.

8.4 Titaniferous Magnetite.

Titaniferous magnetite is a relatively rare constituent of the diabases and
is only present in the least altered samples. It is invariably associated
with granular ilmenite and usually exhibits extensive alteration
to extremely fine-grained aggregates of sphene, chlorite and other femic
hydrous silicates. The magnetite normally contains sparsely distributed
broad ilmenite lamellae and they are commonly preserved in their original
orientation in the magnetite alteration products.

The original nature of the titaniferous magnetite is difficult to establish
on account of its highly altered state. The presence of ilmenite lamellae
and its preferential association with larger ilmenite grains suggest that it
may have been similar to the titaniferous magnetite present in the Karroo
dolerites. The alteration would thus be the result of two episodes, the
one associated with late magmatic-stage processes, and the other related
to the metamorphism responsible for the larger-scale alteration features
exhibited by the diabases.

The late-stage processes would presumably have produced relationships very
similar to those exhibited by the Karroo dolerites while the later meta-
morphism would have been responsible for their extensive alteration and
replacement by sphene and other hydrous silicates. The replacement of
titaniferous magnetite by sphene and chlorite aggregates has also been noted
in gabbros from the Usushwana Complex and has been widely reported in the
literature. This topic has been reviewed by Desborough (1963) and is

discussed further in Part 3, section 8.8.

8.5 Ilmenite.

The ilmenite is present as small discrete grains or as skeletal forms ex-
hibiting subgraphic and vermicular intergrowths that are similar to those
developed in the Karroo dolerites. The skeletal grains are thought to
have developed in essentially the same way as proposed for their counterparts
in the Karroo dolerites (section 7.8). The titaniferous magnetite is con-
spicuously absent in samples containing these skeletal intergrowths and
the ilmenite is usually surrounded by aggregates of secondary biotite,
chlorite, and amphibole.

The ilmenite grains (both discrete and skeletal) usually exhibit
corroded outlines and have been replaced to varying extents by sphene-rich
aggregates of secondary hydrous silicates. The amounts of sphene increase
at the expense of the ilmenite with increasing degrees of alteration while
the skeletal forms of ilmenite are progressively replaced until they are
finally eliminated. The surviving larger ilmenite grains exhibit extensive
alteration to sphene-rich materials and the most highly altered grains are
extensively fractured and show the development of secondary rutile. The
rutile is present in small irregularly shaped masses within the ilmenite and
is usually separated from the sphene-rich areas by a narrow zone of ilmenite.
The interfaces between the ilmenite and rutile are diffuse and a transition
zone is present between the two phases.

Several size-ranges of sparsely distributed ilmenite lamellae are present in
the altered titaniferous magnetites. These lamellae typically show evidence
of solution and partial replacement by sphene. The magnetites have been
eliminated from the more altered specimens, but several small lamellar ilmen-
ite grains are occasionally found enclosed by hornblende. These might re-

present relicts of intergrown ilmenite in original titaniferous magnetite
grains.

8.6 Microprobe Analyses of the Ilmenite.

Electron microprobe analyses of discrete ilmenite grains from eleven diabases
are presented in Table 9 and should be compared with the analyses of Karroo
dolerite ilmenites (Table 8). The analyses are very simialr with the ex-
ception of MnO which is generally between two and four times higher in the
ilmenites from the diabases than in those from the Karroo dolerites. This
feature is in accord with the observations of Buddington (1964) who noted
that the MnO-contents of ilmenites from metamorphosed igneous rocks are in-
variably higher than those of ilmenites from corresponding unmetamorphosed
igneous rock types.

8.7 Alteration of the Opaque Oxides in the Diabases.

The behaviour of the iron titanium oxides in basic igneous rocks during
progressive metamorphism has not been studied in detail. Buddington et al.
(1955, 1963) reported the formation of sphene and hydrous femic silicates
at the expense of titaniferous magnetite and ilmenite in regionally
metamorphosed gneisses. Wilcox and Poldervaart (1958) reported the develop-
ment of granular sphene rims around titaniferous magnetites in metadolerites
and noted that the sphene commonly takes the place of magnetite in some amphi-
bolites. Desborough (1963) reviewed the available literature on the devel-
opment of sphene at the expense of iron-titanium oxides in diabases and con-
cluded that the process would occur under regional metamorphic conditions.

Abdullah and Atherton (1964) reported that the content of ilmenite exceeds
that of titaniferous magnetite by a factor of ten or more in metamorphosed
basic igneous rocks (dolerites) containing hornblende. They also noted
that titaniferous magnetite is often completely absent and suggested that

TABLE 9.

MICROPROBE ANALYSES OF ILMENITES FROM DIABASES.

	SP1	SP 2	SP 3	SP 4	SP 5	SP 6	SP 7	SP 8	IR 213	IR 214	IR 215
TiO_2	50,07	49,56	49,18	49,27	49,18	51,05	48,93	50,61	50,61	50,40	49,87
FeO	43,52	40,32	39,23	39,92	40,46	42,25	40,71	42,51	41,40	41,82	40,11
MgO	0,21	0,70	0,61	0,63	0,67	0,70	0,70	0,68	0,64	0,70	0,70
MnO	1,16	3,00	2,48	3,25	2,60	2,42	2,06	1,67	2,91	2,29	3,45
Fe_2O_3	4,63	5,67	6,94	4,95	6,14	3,35	6,94	3,91	1,84	4,39	5,11
Al_2O_3	0,08	0,13	0,12	0,12	0,13	0,12	0,14	0,13	0,21	0,12	0,12
Cr_2O_3	0,07	0,19	0,19	0,19	0,22	0,21	0,17	0,17	0,17	0,19	0,18
TOTAL	99,74	99,57	98,75	98,33	99,40	100,10	99,65	99,68	97,78	99,91	99,54

NUMBER OF IONS ON THE BASIS OF 6 OXYGENS.

	SP1	SP 2	SP 3	SP 4	SP 5	SP 6	SP 7	SP 8	IR 213	IR 214	IR 215
Al^{3+}	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006
Cr^{3+}	-	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006
Fe^{3+}	0,176	0,212	0,260	0,190	0,230	0,128	0,262	0,146	0,068	0,164	0,194
Ti^{4+}	1,909	1,888	1,864	1,899	1,879	1,930	1,863	1,921	1,960	1,912	1,897
Fe^{2+}	1,845	1,708	1,653	1,708	1,714	1,776	1,723	1,796	1,783	1,764	1,696
Mg	0,015	0,052	0,045	0,049	0,052	0,051	0,052	0,052	0,050	0,051	0,052
Mn	0,049	0,128	0,166	0,142	0,113	0,103	0,088	0,073	0,127	0,097	0,149
TOTAL	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000

NORMATIVE COMPOSITION (MOLE PER CENT).

	SP1	SP 2	SP 3	SP 4	SP 5	SP 6	SP 7	SP 8	IR 213	IR 214	IR 215
$FeTiO_3$	92,24	85,39	82,60	85,38	85,69	88,82	86,17	89,83	89,15	88,18	84,80
$MgTiO_3$	0,76	2,59	2,27	2,46	2,59	2,57	2,58	2,58	2,48	2,58	2,58
$MnTiO_3$	2,44	6,39	8,32	7,08	5,63	5,14	4,41	3,64	6,37	4,85	7,45
R_2O_3	4,56	5,63	6,81	5,08	6,09	3,47	6,84	3,95	2,00	4,39	5,17
TOTAL	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

Fe_2O_3 calculated assuming ilmenite stoichiometry.

the breakdown of pyroxene to hornblende would result in the absorbtion of a considerable amount of the magnetite, thus leaving the ilmenite as the dominant oxide. They also stated that "the metamorphism of ilmenite seems limited to breakdown and the formation of associated products such as sphene, rutile et cetera" (sic).

The experimental data of Schuiling and Vink (1967) indicate that the sphene stability field lies within the temperature range encountered both during the sub-solidus cooling of basic igneous rocks and during low grade metamorphism (less than $500^{\circ}C$). Hunt and Kerrick (1977) also noted that sphene can be formed from ilmenite during metamorphism, but comment on the lack of published experimental data on the possible mechanisms involved. This topic is discussed further in more detail in Part 3, section 8.8.

The reasons for the increased MnO content of the diabase ilmenites in relation to their Karroo dolerite equivalents is not altogether clear since they do not appear to have been recrystallized. Buddington (1964) also noted this feature and it appears that the small amounts of Mn released during the dissolution of the titaniferous magnetite and the alteration of the surrounding mafic silicates might become incorporated into the remaining ilmenite rather than the secondary hydrous silicates. The $MnTiO_3$ component also appears to remain in solid solution in the ilmenite in grains where alteration of the ilmenite has occurred, thus raising the overall MnO content of this phase.

The temperatures at which this MnO re-equilibration takes place are uncertain, but this process is operative at relatively low sub-solvus temperatures as shown by the MnO-enrichment of ilmenite lamellae in titaniferous magnetites (Part 1, section 5.3.2). The MnO- enriched nature of the diabase ilmenites indicates that the MnO re-equilibration can take place in the solid state under low grade metamorphic conditions, possibly at temperatures less than

500^0C.   Rumble (1971, 1973) reported that no detectable Mn is present in
magnetite co-existing with ilmenite in a wide range of metamorphic rocks
unless the host rocks are unusually Mn-rich.   He also noted that the Mn is
preferentially incorporated in the rhombohedral phase.

The presence of rutile as an alteration product of the ilmenite is also in
keeping with the metamorphosed nature of these rocks.   The formation of
hematite + rutile assemblages as high temperature oxidation products of
ilmenite is well known (e.g. Haggerty, 1971), but these reactions have not
been widely studied in metamorphosed basic igneous rocks.   Rumble (1971,
1973) has reported the presence of rutile-ferrianilmenite assemblages in
amphibolites formed during the metamorphism of basic volcanic rocks.

The usual reaction would require the breakdown of ilmenite to form hematite
+ rutile, but no secondary hematite (or magnetite) is present in the altered
samples.   Lindsley (1962) noted that many low grade metamorphic rocks contain
the assemblage magnetite + rutile which is chemically equivalent to hematite
+ ilmenite.

The presence of an intermediate alteration zone between the ilmenite and
rutile suggests that the process is progressive and that the iron content of
the ilmenite might be preferentially lowered during reactions leading to the
formation of the secondary hydrous silicates (e.g. biotite, chlorite or
amphibole).   This process would be analogous to the leaching of iron from
ilmenites during atmospheric weathering (leucoxene formation) and would
almost certainly be accelerated by the higher temperatures of metamorphism.
The slightly altered rims of the skeletal ilmenite grains referred to in
section 7 would represent the incipient stage in this type of alteration
process.

8.8 Conclusions.

1). The titaniferous magnetite and ilmenite in the least altered diabases
   resemble those in the unmetamorphosed Karroo dolerites, and they ex-
   hibit essentially similar modes of occurrence.

2). The opaque oxides in the diabases exhibit varying degrees of alteration
   that commences with the progressive alteration of titaniferous magnetite
   to sphene-rich aggregates. The titaniferous magnetite is gradually
   eliminated and the co-existing ilmenite in turn shows alteration to
   sphene and is also eliminated. The ilmenite also becomes partially
   altered to rutile in some cases.

3). The ilmenites in the diabases are chemically similar to those in the
   Karroo dolerites, but contain between two and four times as much MnO.
   This MnO-enrichment is interpreted as being due to the concentration
   of the available MnO in the remaining rhombohedral phases rather than
   its incorporation in the secondary hydrous silicates during dissolution
   of the opaque oxides.

4). The nature of the alteration processes exhibited by the opaque oxides of
   basic igneous rocks during progressive metamorphism are imperfectly
   understood and require detailed studies.

9. THE CO-EXISTING IRON-TITANIUM OXIDES IN THE GABBROIC ROCKS OF THE
   BUSHVELD IGNEOUS COMPLEX.

9.1 Introduction.

The iron-titanium oxides of the gabbroic rocks of the Bushveld Complex were
studied in order that their properties might be compared with the opaque oxides
from the other rock types presented in this report. An extensive literature
has developed on the vanadium-bearing titaniferous magnetite ores of the
Bushveld Complex (see Part 3, section 6), but considerably less attention
has been given to their occurrence as accessory phases in the Bushveld
gabbroic rocks. Molyneux (1970a, b, 1972) has provided some data on the

ilmenites in these rocks although his studies have been primarily concerned with the ore-rich horizons. The results presented in Part 3 indicate that differences, particularly in the microstructures and ilmenite compositions, exist between the accessory opaque oxides and those present in the ore-rich seams.

Titaniferous magnetite and ilmenite are present in the Chill Zone ⌐ the Complex and are then rarely found until their entrance as cumulus phases at the top of the Main Zone (Willemse 1969a, b; Molyneux, 1970a, b, 1972). They reach their maximum development in the Upper Zone where more than 21 discrete titaniferous magnetite-rich seams are developed. Titaniferous magnetites are also present in discordant plugs, but these are not discussed here.

9.2 Samples Investigated.

The samples investigated were all collected from the eastern lobe of the Bushveld Complex and represent a suite of gabbroic rocks that cover the range from the first appearance of cumulus titaniferous magnetite at the top of the Main Zone to approximately the level of seam number 13. The samples were collected in the vicinity of Roossenekal and along a traverse in the Magnet Heights area. Several samples of the so-called "Hendriksplaats norite" were collected in the vicinity of Steelpoort station and are taken to represent the chill zone of the Complex as suggested by Willemse (1969a). The opaque oxides from the discrete ore-rich seams were not investigated.

9.3 Nature and Occurrence of the Opaque Oxides.

The opaque oxides are present as accessory phases and consist essentially of titaniferous magnetite and ilmenite. They are usually present in amounts ranging from 1 and 10 per cent. Discrete ilmenite grains very often form the dominant phase which is in contrast to the situation in the ore-rich

layers where titaniferous magnetite is dominant.

The oxides are located interstitially between the larger silicates, but may occasionally be interconnected to form larger masses. Narrow reaction rims of biotite or other secondary hydrous silicates are sometimes developed along the contacts between the opaque oxides and the silicates, but the more advanced stages of deuteric alteration noted in the Karroo dolerite opaque oxides were not observed in the Bushveld samples examined.

Distinct differences exist between the oxides developed in the Hendriksplaats norite and those present in the Upper Zone gabbroic rocks. The Hendriksplaats norite is characterized by the presence of abundant hemo-ilmenite grains whereas the gabbroic rocks contain variable proportions of titaniferous magnetite which is texturally similar to that occurring in the ore-rich horizons, and abundant granular ilmenite.

9.4 The Hendriksplaats Norite.

These rocks are generally finer grained than the Upper Zone gabbros and are characterized by the presence of abundant hemo-ilmenite. This phase is present as elongated, irregularly shaped grains up to 1 mm in length and is characterized by the abundant development of fine hematite exsolution lamellae parallel to (0001) of the host ilmenite (Plate B (5)). The samples examined are virtually devoid of titaniferous magnetite. The hemo-ilmenite exhibits embayed outlines and is commonly surrounded by reaction rims of biotite and other hydrous femic silicates.

The highly exsolved nature of these grains prevented the determination of their reflectivities and micro-indentation hardnesses. The chemical compositions of two ilmenite concentrates were determined by wet chemical methods and these results are presented in Table 11. Attempts were made

to analyse two additional grains by means of electron microprobe (IR 107 and 108), but this was complicated by the presence of the hematite lamellae with the result that the totals are anomalous.

The lack of titaniferous magnetite and the abundance of hemo-ilmenite suggest that these rocks crystllised under relatively high oxygen fugacities. Duchesne (1972) reported that hemo-ilmenite is the only oxide present in the lowermost rocks of the Bjerkrem-Sogndal anorthositic massif and noted that the oxygen fugacities decrease with increasing height in the Complex as reflected by a decrease in the degree of oxidation of the opaque oxides. He recognised five rhythms in the noritic phase of this intrusion and noted that the base of each rhythm is characterised by the presence of hemo-ilmenite. No other data are available on the nature of ilmenites from the bases of large basic intrusions with which comparisons can be made. The data of Mathison (1975) indicate the opposite trend with the Fe_2O_3 content of the ilmenites increasing during fractional crystallisation.

9.5 The Bushveld Gabbroic Rocks.

The microstructures exhibited by the iron-titanium oxides are very similar to those displayed by the titaniferous iron ores that have been described by Molyneux (1970a, b, 1972) and are not here discussed in detail. The titaniferous magnetite shows the development of particularly coarse-grained ulvospinel cloth textures as illustrated in Plate B (6 and 7). Broad ilmenite lamellae are only sparsely developed in titaniferous magnetites while the various finer ilmenite lamellae are also comparatively rare.

The titaniferous magnetite is relatively Al-poor and transparent spinel exsolution bodies are completely absent in many samples. When present, they commonly show well-defined lath-like forms that are characteristically

surrounded by a "frame" of coarser-grained ulvospinel (Plate B (8)). Small rounded spinel grains are also developed along the boundaries of the larger ilmenite lamellae at places where they are developed.

The titaniferous magnetite characteristically exhibits varying degrees of oxidation to maghemite while the associated ulvospinel is typically altered to ilmenite (Plate C (1)). The maghemite in turn shows varying degree of oxidation to martite in the more highly weathered samples. Titaniferous magnetites showing the development of only lamellar intergrowths of varying size ranges are occasionally present in some of the samples and these characteristically show direct oxidation to martite (Plate C (2)).

The coarse-grained ilmenites are typically homogeneous, although extremely fine magnetite platelets are developed along the basal planes of certain ilmenites. The reflectivities and micro-indentation hardness of these ilmenites were determined and are presented in Table 10.

The ranges in reflectivities and Vicker's Hardness Numbers are essentially the same as those recorded for the dolerite ilmenites and reflect their similarity in chemical composition.

The chemical compositions of the ilmenites are given in Table 11 and are essentially similar to those reported for the Karroo dolerite ilmenites. The high Fe_2O_3 values for samples IR 9, 10, and 65 reflect the slightly weathered nature of these samples which has resulted in the oxidation of portion of the Fe^{2+} to Fe^{3+}. The MgO values are consistently lower than those reported by Molyneux (1970a, 1972) for discrete ilmenite grains in the titaniferous magnetite seams and reflect a trend that is also shown by ilmenites from other basic intrusions (this thesis, Part 3).

PLATE C.

MISCELLANEOUS OPAQUE OXIDE-BEARING ROCKS.

1). An ulvospinel cloth-textured titaniferous magnetite (medium grey) showing irregular oxidation to maghemite (lighter). There is a large ilmenite grain on the right (dark grey). Incident light, oil immersion.

2). Bushveld titaniferous magnetite surrounded by ilmenite (grey). The titaniferous magnetite shows extensive oxidation to martite (white lamellae parallel to (111))and also contains ilmenite lamellae in the same orientation (dark grey). Incident light, oil immersion.

3). Syenite, Leeufontein Complex: titaniferous magnetite (white) exhibiting a well defined sandwich texture of ilmenite lamellae (grey). Incident light, oil immersion.

4). Syenite, Leeufontein Complex: ilmenite lamellae and internal granules (grey) in titaniferous magnetite. Incident light, oil immersion.

5). Granophyre, Bird's River Complex: composite ilmenite/titaniferous magnetite grain in which the magnetite has been altered leaving a well defined ilmenite sleleton. Incident light in air.

6). Granite, Nelspruit area: the remains of a highly altered ilmenite grain surrounded by secondary silicates. Incident light in air.

7). Dimani granite: complex partially reduced hemo-ilmenite grain. Hematite is white, ilmenite, dark grey and magnetite, a lighter grey. Incident light, oil immersion.

8). A rounded ilmenite grain from an eastern Cape beach sand showing moderate alteration to leucoxene around grain boundaries and fractures. Incident light, partially crossed nicols in air.

PLATE C
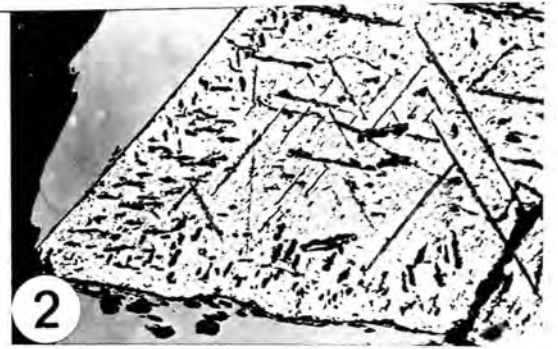
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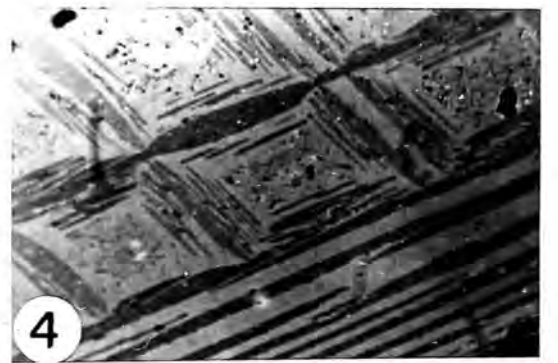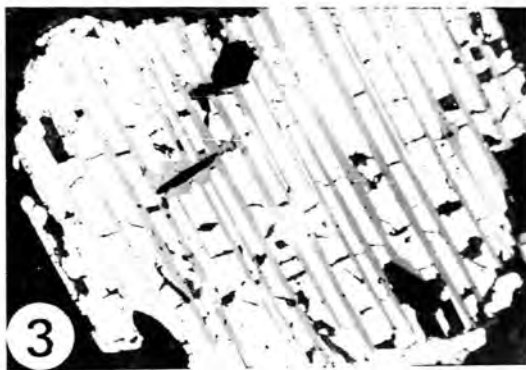
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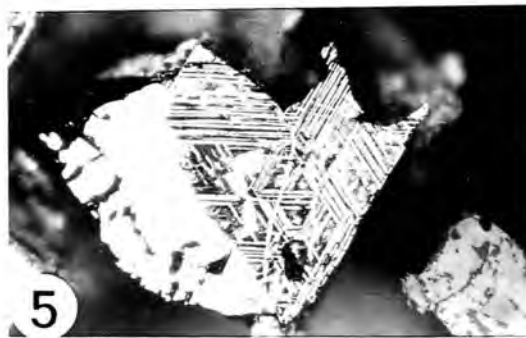
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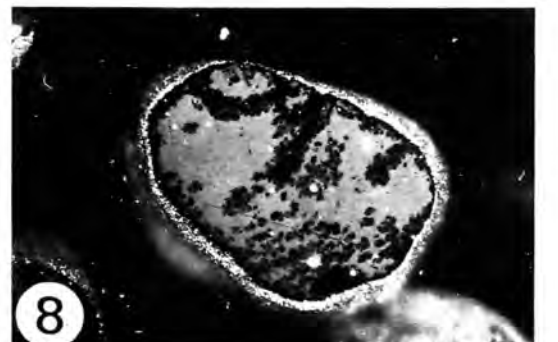
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TABLE 10.

REFLECTIVITIES AND VICKER'S HARDNESS NUMBERS FOR DISCRETE ILMENITES FROM THE

BUSHVELD COMPLEX.

Sample Number	Reflectivity (546nm)		Micro-indentation Hardness (VHN$_{100}$)
	R$_o$ (%)	R$_e$ (%)	
IR 92	19,2	16,4	N.D.
IR 9	19,5	16,4	587-647
IR 8	19,9	16,9	N.D.
IR 65	20,2	17,0	621-674
IR 5	19,6	16,3	613-675
IR 4	19,0	16,2	598-671
IR 10	20,2	17,0	593-632
IR 61	19,7	17,0	603-663

N.D. = not determined

The ilmenite analyses are also comparable with the analyses of ilmenites from a wide range of basic igneous intrusions e.g. Skaergaard (Vincent and Phillips, 1954), the Somerset Dam Intrusion (Mathison, 1975), the Freetown Complex (Bowles, 1976) and the Dufek Intrusion (Himmelberg and Ford, 1977). The ilmenites from a wide variety of basic igneous rocks thus appear to exhibit a relatively narrow compositional range.

9.6 Conclusions.

1). The ilmenites present as accessory phases in the gabbroic rocks of the Bushveld Complex are compositionally similar to those present in Karroo dolerites and are characterised by similar reflectivities and micro-indentation hardness.

2). The ilmenites from a wide variety of basic igneous rocks exhibit a restricted compositional range in which the MnO content is generally less

TABLE 11

ANALYSES OF ILMENITES FROM THE BUSHVELD IGNEOUS COMPLEX

	Hendriksplaat norite sheet				IR192+	IR9	IR8+	IR65+	IR5	IR4+	IR10	IR61	A	B	C	D	E
	IR106	IR107+	IR108+	IR109													
SiO$_2$	-	0,33	0,45	-	1,01	-	1,59	0,23	-	0,21	-	-	0,23	0,51	0,57	0,60	-
TiO$_2$	43,79	41,18	46,52	40,76	50,44	47,48	48,18	47,46	48,38	49,59	46,51	49,68	51,97	50,02	50,31	49,30	50,00
FeO	38,15	35,54	40,39	35,84	44,17	40,59	42,11	39,22	41,39	41,66	39,42	43,20	42,72	42,18	43,30	43,30	43,20
MgO	0,30	0,51	1,03	0,20	1,12	0,61	0,14	1,03	0,87	1,33	0,45	0,49	1,48	0,46	0,62	0,42	0,69
MnO	0,60	0,85	0,04	0,28	0,37	0,84	2,82	1,86	0,53	0,72	1,59	0,57	0,62	1,44	0,65	0,79	0,54
CaO	0,11	-	-	0,09	-	0,19	-	-	0,06	-	0,06	0,04	0,48	0,71	0,46	0,13	-
Fe$_2$O$_3$	15,71	18,68	14,29	22,44	2,96	9,79	4,87	8,62	7,67	7,19	10,97	5,48	2,58	4,19	3,93	5,30	5,08
Cr$_2$O$_3$	1,17	-	0,23	0,08	-	0,15	0,45	-	0,24	-	0,21	-	-	-	-	0,04	-
Al$_2$O$_3$	-	-	0,08	-	-	-	-	0,02	-	-	-	-	-	-	trace	0,21	-
TOTAL:	99,83	97,09	103,03	99,69	100,07	99,65	100,16	99,44	99,14	100,70	99,21	99,46	100,08	99,51	99,84	100,09	99,51

NUMBER OF IONS ON THE BASIS OF 6 OXYGENS

	IR106	IR107+	IR108+	IR109	IR192+	IR9	IR8+	IR65+	IR5	IR4+	IR10	IR61
Al^{3+}	-	-	0,006	-	-	-	-	-	-	-	-	-
Cr^{3+}	0,049	0,012	0,012	0,006	-	0,006	0,018	-	0,012	-	0,006	-
Fe^{3+}	0,599	0,734	0,522	0,866	0,114	0,372	0,182	0,332	0,294	0,268	0,418	0,208
Si^{4+}	-	0,016	0,020	-	0,054	-	0,078	0,018	-	0,009	-	-
Ti^{4+}	1,676	1,617	1,710	1,564	1,889	1,811	1,822	1,816	1,847	1,857	1,788	1,896
Fe^{2+}	1,625	1,554	1,651	1,531	1,844	1,722	1,770	1,674	1,756	1,737	1,683	1,835
Mg	0,021	0,041	0,076	0,015	0,084	0,046	0,009	0,080	0,067	0,099	0,034	0,037
Mn	0,024	0,038	0,003	0,012	0,015	0,037	0,121	0,080	0,021	0,030	0,068	0,024
Ca	0,006	-	-	0,006	-	0,006	-	-	0,003	-	0,003	-
TOTAL:	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000

NORMATIVE COMPOSITION (MOLE PER CENT)

	IR106	IR107+	IR108+	IR109	IR192+	IR9	IR8+	IR65+	IR5	IR4+	IR10	IR61
FeTiO$_3$	81,51	77,71	82,62	76,83	92,20	86,43	88,53	83,74	87,96	86,82	84,34	91,76
MgTiO$_3$	1,07	2,04	3,82	0,77	4,20	2,29	0,45	3,99	3,35	4,94	1,69	1,83
MnTiO$_3$	1,22	1,88	0,15	0,61	0,75	1,83	6,04	3,99	1,07	1,50	3,37	1,22
R$_2$O$_3$	16,20	18,37	13,41	21,79	2,85	9,45	4,98	8,28	7,62	6,74	10,60	5,19
TOTAL:	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

FeO and Fe$_2$O$_3$ analyses recalculated assuming ilmenite stoichiometry.   + indicates electron microprobe analysis.

N.B. Samples IR104-109 are hemo-ilmenites and the poor totals for 108 and 109 are due to the presence of exsolved hematite lamellae.

A,B,C - Ilmenites from the Skaergaard Complex (Vincent and Phillips, 1954).
D,E - ilmenites from the Dufek Intrusion (Himmelberg and Ford, 1977).

than 1,5 per cent while the MgO content is less than 3,5 per cent, although it occasionally reaches 6 per cent. The Fe_2O_3 content is generally less than approximately 6 per cent and hematite exsolution lamellae are characteristically developed when it is higher than this.

3). The typical ilmenites from a wide variety of basic igneous rocks and their metamorphosed equivalents can readily be distinguished from kimberlite ilmenites, not only on the basis of composition, but by the use of parameters such as unit cell dimensions, selected d-spacings, reflectivities and micro -indentation hardnesses.

10. THE CO-EXISTING IRON-TITANIUM OXIDES IN SYENITES.

10.1 Introduction.

There is virtually no published information on the nature of iron-titanium oxides in syenitic rocks which commonly contain large amounts of sphene (e.g. Ramdohr, 1956). Samples of syenite from the Pilanesberg (IR 162) and Leeufontein (IR 16) Complexes were examined and found to contain both titaniferous magnetite and discrete ilmenite grains.

10.2 Nature and Occurrence of the Opaque Oxides.

The opaque oxides are present in granular aggregates of titaniferous magnetite and ilmenite that are invariably associated with larger grains of amphibole and biotite. The external boundaries of both the ilmenite and titaniferous magnetite exhibit evidence of replacement by sphene and secondary hydrous silicates.

The titaniferous magnetite is characterised by the development of abundant broad ilmenite lamellae that are commonly developed in a typical sandwich pattern (Plate C (3)). These lamellae are up to 0,02 mm wide, commonly traverse the entire width of the grain and protrude beyond the present margins of the grain into the alteration products. The titaniferous magnetite

between these broad lamellae also typically contains several sets of ilmenite trellis lamellae and fine ilmenite granules (Plate C (4)). These ilmenite lamellae have a typical "oleander leaf" shape and taper markedly at their mutual intersections.

The titaniferous magnetite appears free from extremely fine-grained exsolution bodies and only shows the development of minor transparent spinel exsolution bodies. The magnetite alters directly to martite without the formation of intermediate maghemite.

The discrete ilmenite grains appear optically homogeneous and show incipient alteration to sphene and hydrous silicates around their margins. The reflectivities of these ilmenites are given in Table 12 and their chemical compositions are presented in Table 13. These data indicate that they are similar in composition to the ilmenites in basic igneous rocks, but additional information is required before definite conclusions can be reached.

TABLE 12.

REFLECTIVITIES AND VICKER'S HARDNESS NUMBERS FOR ILMENITES FROM SYENITES AND A GRANOPHYRE.

Sample Number	Rock Type	Reflectivity in Air (546 nm)		Micro-Indentation Hardness (VHN_{100})
		R_o (%)	R_e (%)	
IR 16	Syenite	19.7	16.7	577-621
IR 162	Syenite	19.5	17.3	563-595
HVE 71/34	Granophyre	19.7	16.6	525-550

Barker et al.(1975) presented analyses of co-existing ilmenite and titaniferous magnetites from a fayalite quartz syenite that indicate a Mn content of between 2,6 and 7,0 per cent in the ilmenite. These values place the syenite ilmenites in the same compositional range as ilmenites from granites (section 12).

The extremely coarse and well-developed broad ilmenite lamellae in the magnetite indicate the presence of relatively high oxygen fugacities during sub-solidus cooling at temperatures above the magnetite-ulvospinel solvus. The sets of smaller ilmenite lamellae indicate that the oxygen fugacities remained constantly high throughout cooling. This is also supported by the presence of fine internal ilmenite granules. The oxygen fugacities may even have been high enough to cause the partial oxidation of the magnetite.

TABLE 13

ANALYSES OF ILMENITES FROM SYENITES, GRANOPHYRES, GRANITES AND PEGMATITES

	SYENITES		GRANOPHYRES			GRANITES										PEGMATITES		
	IR16	IR162+	H.V.E 71/34+	BHPG+	IR236+	G1+	C5+	G9+	IR54+	7326+	7388+	7391+	2M51+	801A2+	801DZ+	REJ287+	A	B
SiO_2	-	-	-	-	-	0,40	-	0,38	0,40	0,14	0,96	1,15	1,06	1,37	1,44	0,02	1,08	0,65
TiO_2	49,25	51,56	49,86	49,87	49,42	51,69	54,49	48,63	49,94	50,80	50,25	50,37	50,16	50,28	50,60	48,77	44,18	43,25
FeO	42,60	44,98	44,00	40,98	38,80	42,92	43,32	39,18	41,89	44,72	43,68	40,20	42,27	44,64	44,21	37,41	31,22	32,25
MgO	0,12	0,57	0,22	0,59	0,63	-	0,16	0,44	N.D.	N.D.	0,14	0,15	N.D.	0,17	0,10	0,53	0,43	0,19
MnO	1,32	0,40	0,47	4,04	4,46	3,38	1,05	4,22	3,48	1,11	2,63	6,00	4,10	1,60	2,84	5,51	5,63	5,60
CaO	0,08	-	0,08	-	-	-	-	-	-	-	-	-	-	-	-	-	0,10	0,10
Fe_2O_3	5,83	-	4,84	4,15	5,43	-	0,02	7,34	2,40	3,19	1,44	0,40	1,84	-	0,16	6,87	15,72	15,65
Cr_2O_3	N.D.	0,02	0,05	0,17	0,17	-	-	-	-	-	-	-	-	-	-	-	-	-
Al_2O_3	-	0,36	-	0,17	0,17	-	-	-	-	-	-	-	-	-	-	-	0,55	1,25
TOTAL:	99,20	97,89	99,52	99,97	99,08	98,39	99,04	100,19	98,11	99,96	98,90	98,27	99,43	98,06	99,35	99,11	98,91	98,94

NUMBER OF IONS ON THE BASIS OF 6 OXYGENS

	IR16	IR162+	H.V.E 71/34+	BHPG+	IR236+	G1+	C5+	G9+	IR54+	7326+	7388+	7391+	2M51+	801A2+	801DZ+	REJ287+	A	B
Al^{3+}	-	0,024	-	0,006	0,006	-	-	-	-	-	-	-	-	-	-	-		
Cr^{3+}	-	-	-	0,006	0,006	-	-	-	-	-	-	-	-	-	-	-		
Fe^{3+}	0,226	-	0,184	0,156	0,208	-	-	0,278	0,094	0,120	0,056	0,012	0,066	-	0,006	0,262		
Si^{4+}	-	-	-	-	-	0,021	-	0,018	0,021	0,007	0,049	0,058	0,055	0,070	0,073	-		
Ti^{4+}	1,887	1,988	1,908	1,916	1,890	1,991	2,056	1,843	1,932	1,933	1,923	1,936	1,912	1,933	1,924	1,869		
Fe^{2+}	1,820	1,927	1,869	1,701	1,649	1,827	1,823	1,649	1,802	1,891	1,859	1,721	1,790	1,909	1,869	1,596		
Mg	0,009	0,043	0,015	0,045	0,049	-	0,012	0,033	-	-	0,009	0,012	-	0,012	0,006	0,040		
Mn	0,058	0,018	0,021	0,170	0,192	0,147	0,045	0,179	0,151	0,049	0,104	0,261	0,177	0,071	0,122	0,233		
Ca	-	-	0,003	-	-	-	0,009	-	-	-	-	-	-	-	-	-		
TOTAL:	4,000	4,000	4,000	4,000	4,000	3,986	3,945	4,000	4,000	4,000	4,000	4,000	4,000	3,995	4,000	4,000		

NORMATIVE COMPOSITION (MOLE PER CENT)

	IR16	IR162+	H.V.E 71/34+	BHPG+	IR236+	G1+	C5+	G9+	IR54+	7326+	7388+	7391+	2M51+	801A2+	801DZ+	REJ287+	A	B
$FeTiO_3$	90,96	96,90	93,59	85,07	82,44	83,95	*	82,45	90,11	94,53	92,97	86,02	89,30	95,84	93,47	79,79		
$MgTiO_3$	0,46	2,17	0,76	2,24	2,44	-	-	1,66	-	-	0,46	0,61	-	0,61	0,30	1,99		
$MnTiO_3$	2,91	0,93	1,07	8,51	9,62	16,05	-	8,92	7,57	2,43	5,20	13,06	8,83	3,55	6,08	11,64		
R_2O_3	5,67	-	4,58	4,18	5,50	-	-	6,97	2,32	3,04	1,37	0,31	1,67	-	0,15	6,58		
TOTAL:	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00		

FeO and Fe_2O_3 analyses recalculated assuming ilmenite stoicheometry.

+ indicates microprobe analysis

A,B - analyses of pegmatite ilmenites from Puffer (1975).

N.D. = not detected.

* excess TiO_2 in analysis,

11. THE CO-EXISTING IRON-TITANIUM OXIDES IN GRANOPHYRES.

11.1 Introduction.

The amount of published information on the co-existing iron-titanium oxides
in granophyres is also fairly limited. Himmelberg and Ford (1977) have
described the oxide mineral assemblages in the granophyre of the Dufek
Intrusion and it appears that they are not markedly different from those in
the associated basic rocks which consist of discrete ilmenite and multi-
phase titaniferous magnetite grains.

11.2 Samples Investigated.

Granophyres from the Bushveld and Trompsburg Igneous Complexes were examined
and proved to contain no titaniferous magnetite or ilmenite. Opaque oxides
were found in three samples of granophyre from the following localities:
(a) the Bird's River Complex (H.V.E 71/34) supplied by Prof. H.V. Eales,
(b) a small occurrence of granophyre west of Bronkhorstspruit (BHP-G) and,
(c) the Usushwana Complex (IR 236).

11.3 Nature and Occurrence of the Opaque Oxides.

The opaque oxides in the Bird's River granophyre closely resemble the ilmen-
ite-titaniferous magnetite aggregates in the Karroo dolerites in which the
magnetite has been largely replaced by sphene and hydrous silicates. The
titaniferous magnetite typically contains extremely well developed ilmenite
trellis networks and these are commonly present as "skeletons" in the replac-
ed magnetite (Plate C (5)).

The larger ilmenite grains are optically homogeneous and contain no exsolved
phases. They also generally show varying amounts of alteration and
sphene development around their margins.

The remaining two samples are virtually devoid of titaniferous magnetite due

to extensive alteration and the ilmenite shows advanced replacement by sphene and rutile so that they resemble those in the highly altered diabases. Both these samples appear to have been slightly metamorphosed with the result that their primary features have been largely destroyed and the effects of deuteric alteration are not readily recognizable.

The chemical compositions of the ilmenites in these three granophyres are presented in Table 13. The composition of the ilmenite from the Bird's River granophyre is similar to the ilmenites from basic igneous rocks while the MnO contents of the other two are closer to the range shown by granitic ilmenites. The reflectivity and micro-indentation hardness values of H.V.E 71/34 are also in the same range as those for ilmenites from basic igneous rocks (Table 12).

The absence of iron-titanium oxides in many of the granophyres examined can be attributed to a combination of factors including the low Fe and Ti contents of these rock types, the conditions of crystallisation of which may have favour- ed the crystallisation of other phases (e.g. Carmichael·et al., 1974), the deuteric alteration of these phases and their replacement by sphene and hydrous femic silicates. Additional data are also required before definite conclusions can be reached on the nature and compositional variations of the opaque oxides in granophyres.

12. THE CO-EXISTING IRON-TITANIUM OXIDES IN GRANITIC ROCKS.

12.1 Introduction.

Iron-titanium oxides are present as minor accessory phases in a wide range of granitic rocks. The magnetite in these rocks is typically Ti-poor (e.g. Buddington and Lindsley, 1964), while the ilmenites commonly contain several percent MnO. The MnO contents of these ilmenites have attracted much attention and the literature contains many analyses of MnO-rich ilmenites

(e.g. Czamanske and Mihalik, 1972, Tsusue, 1973, Neumann, 1974, Elsdon, 1975b).
The normal compositional range of the ilmenite is, however, less well known
and the data of Whitney and Stormer (1976) indicate the presence of both
ilmenites with lower MnO contents and others containing as much as 4 per cent
Nb_2O_3.

Numerous analyses of opaque oxide phenocrysts from SiO_2-rich volcanic rocks
are also available in the literature (e.g. Carmichael, 1967a, Lipman, 1971).
These analyses also show that the magnetites are characteristically Ti-poor
and the ilmenites, Mn-rich. Limited data are available on the microstruct-
ural relationships exhibited by the opaque oxides in granitic rocks.

The most detailed studies of the iron-titanium oxides in a wide range of
granititc rocks are those of Buddington et al., (1955, 1963) and Balsley
and Buddington (1958). Buddington and his co-workers have provided a wealth
of data on the nature of these phases, but unfortunately only presented part-
ial analyses the oxides. Their pioneering work did, however, serve to focus
attention on the relationship between the degree of oxidation of the iron-
titanium oxides and the nature of their associated silicates.

Buddington et al. (1963) noted that the least oxidised iron-titanium oxide
assemblages are present in igneous granitic rocks of the green pyroxenic
facies while the most highly oxidised types occur in granites of the pink
K-rich microperthitic microcline facies. They also noted that the oxide
assemblages in granitic orthogneisses are more highly oxidised than those
of corresponding syenitic and quartz-syenitic types. They also recognised
the replacement of ilmenite by sphene-bearing assemblages in certain gneisses.

12.2 Samples Investigated.

Iron-titanium oxides are usually very minor constituents of granitic rocks

and are not present in certain granites. A wide variety of granites were examined but relatively few were found to contain opaque oxides. Dr. E.J. Oosthuyzen of NIM kindly provided heavy mineral concentrates from a number of granites which he had investigated during routine age determinations carried out at the C.S.I.R. in Pretoria. Only the ilmenites in these concentrates were examined and no data are presented regarding their mutual relationships as this aspect could not be studied.

Sample G1 is from the Woodville granite pluton near George; G5 is from a quartz prophyry that is present as cobbles along the coast near Port Elizabeth (this might represent ballast from a wrecked 17 th. century Portugese ship, believed to be the Sacramento); G9 is a gneiss from Mapumulo in Zululand and IR 54, a Bushveld granite. The remaining samples represent the heavy mineral concentrates from various granites in the eastern Transvaal supplied by Dr. E. Oosthuyzen.

An ore microscopic investigation of the opaque oxides in a much larger suite of granites than that shown in Table 13 indicates the existence of an extremely large degree of variability in the nature of the oxides present. This variability is much greater than that shown by the opaque oxides of the basic igneous rocks and their microstructures indicate that at least some of the granites have undergone complex post-crystallisation histories. A detailed examination of their oxides should therefore ideally be carried out in conjunction with detailed petrographic studies. These would allow for the classification of the granites into various compositional types with distinctions being made on the basis of their possible mode of origin and subsequent metamorphic histories so that the nature of their opaque oxides can be better assessed. The data in the following section are included in order to present at least some information on their opaque oxides for comparative purposes, but it is stressed that a very much more detailed study is required before definite conclusions can be reached.

12.3 Nature and Occurrence of the Opaque Oxides.

The opaque oxides in granitic rocks are commonly present as small grains
that are preferentially associated with other hydrous mafic silicates such
as biotite, hornblende or chlorite. The grains are typically xenomorphic
and often very much smaller than their associated silicates. They usually
exhibit varying degrees of secondary alteration that can in part be related
to deuteric effects and in part to metamorphism.

Magnetite is present both as discrete grains and as tiny veinlets. The
grains are generally xenomorphic in outline, but at least one sample contains
euhedral magnetite octahedra that are optically homogeneous and exhibit
no alteration features. Magnetite was only noted in a small number of
samples and is Ti-poor, normally containing only a few sparsely distributed
ilmenite lamellae of varying sizes. Minor amounts of tiny transparent
spinel granules are occasionally developed along the margins of these lam-
ellae. The groundmass magnetite is optically homogeneous and free from
fine-grained exsolution products. These magnetite grains are commonly found
as discrete minerals and are not necessarily associated with ilmenite grains.
A minor amount of external granule ilmenite exsolution is also sometimes
evident in the clustering on several small ilmenite grains around the peri-
pheries of larger magnetites.

The magnetite generally exhibits varying degrees of martitization which takes
place directily along the octahedral planes. This process can normally be
ascribed to the effects of atmospheric weathering, but oxidative effects
during deuteric alteration are not discounted. The development of goethite
at the expense of the martite occurs in the more highly weathered samples.

Ilmenite is far more commonly encountered in the granites than magnetite and

generally displays varying degrees of alteration, mostly to sphene and hydrous silicates (Plate C (7)). The process is particularly noticeable in samples completely devoid of magnetite which has presumably been completely replaced. The ilmenite commonly contains variable amounts of hematite lamellae that are exsolved along (0001) in the usual manner.

Hemo-ilmenite grains characterised by intergrowths of approximately equal amounts of hematite and ilmenite, are present in several granites. The ilmenite grains contain large areas of apparently exsolved hematite that in turn contain a finer series of ilmenite lamellae and vice versa. Fine rutile exsolution lamellae are occasionally developed in the hematite-rich areas. Primary magnetite is not associated with the hemo-ilmenite and ilmeno-hematite grains that are indicative of crystallisation under relatively high oxygen fugacities.

An extremely interesting variation of the typical hemo-ilmenite microstructural type was noted in a sample of the Dimani granite that is associated with the Tugela Rand Mafic Intrusion. Portions of the oxide grains in this rock still retain the typical features of hemo-ilmenites, but other portions appear to have been partially reduced resulting in the conversion of the original hematite to magnetite (Plate C (7)). This reduction has caused the original ilmenite lamellae to segregate to form long continuous bands of ilmenite that separate the unreduced hematite from the magnetite. The magnetite is nowhere in direct contact with the relict hematite and is always separated from it by a veneer of ilmenite. The magnetite in turn shows incipient alteration to martite along its octahedral planes.

12.4 Reflectivity and Micro-Indentation Hardness Determinations.

The reflectivity and micro-indentation hardness for ilmenites from several granites are given in Table 14 for comparison with ilmenites from other rock types.

TABLE 14.

REFLECTIVITIES AND VICKER'S HARDNESS NUMBERS FOR ILMENITES FROM GRANITIC ROCKS.

Sample number	Reflectivity (546nm)		Micro-indentation hardness (VHN_{100})
	R_o (%)	R_e (%)	
G 1	19,8	17,1	N.D.
G 5	19,5	17,2	612-664
IR 54	19,3	16,7	599-664
7326	19,8	17,0	N.D.
7388	19,6	16,9	N.D.
7391	19,6	16,6	N.D.
2N51	19,6	16,9	N.D.
801A2	19,6	16,9	N.D.
801D2	19,6	16,8	N.D.

N.D = not determined - grains are too small, highly altered or full of inclusions to allow for meaningful determinations of micro-indentation hardness.

The reflectivities are within the range of values obtained for the basic igneous rocks while the VHN ranges are also similar. These features suggest that no great compositional differences exist between the ilmenites from these two groups of rocks.

12.5 Chemical Compositions of Ilmenites from Granitic Rocks.

The analyses of 10 typical coarse-grained ilmenites from granitic rocks are presented in Table 13. These ilmenites are characterised by slightly higher MnO contents that range up to a maximum of 6 per cent. This feature is con-

sistent with the published analyses of ilmenites from SiO_2-rich rocks. The lower MnO values overlap in part with the higher range of values exhibited by ilmenites from basic igneous rocks and diabases. The MnO content alone can thus not be used as a criterion for distinguishing between ilmenites from these two group of rocks.

12.6 Conclusions.

1). Iron-titanium oxides are sparingly present in granitic rocks and encompass a range of types ranging from discrete Ti-poor magnetite and ilmenite through to hemo-ilmenites.

2). The opaque oxides, in particular ilmenite, commonly exhibit extensive alteration to sphene and hydrous silicates. Rutile is also sometimes developed.

3). The granitic ilmenites are in some cases characterised by slightly higher MnO contents than ilmenite from basic igneous rocks, but this does not represent a safe criterion for distinguishing between these two types.

4). The reflectivities and micro-indentation hardness of these granitic ilmenites fall within the same range as that of ilmenites from basic igneous rocks and cannot be used as a means of distinguishing between ilmenites from granitic and basic igneous rocks.

5). The Ti-poor nature of the titanomagnetites can be ascribed to their having crystallised at lower temperatures as suggested by Buddington and Lindsley (1964) and also to the depletion of SiO_2-rich magmas in TiO_2 and Fe.

6). The presence of hemo-ilmenite grains in certain granites indicate cryst- allisation under higher oxygen fugacities as would be expected from H_2O- rich granitic magmas.

7). The extreme variability in the nature of the iron-titanium oxides and their degree of oxidation in granitic rocks indicate that a very much more detailed study of many different types of granite is urgently required.

13. THE CO-EXISTING IRON-TITANIUM OXIDES IN PEGMATITES.

13.1 Introduction.

Iron-titanium oxides are occasionally found as accessory phases in certain pegmatites, but are apparently absent from the majority. Puffer (1972, 1975) investigated the occurrence of these oxides in pegmatites and noted that large euhedral octahedra of Ti-poor magnetite containing sparse ilmenite lamellae represent the dominant phase in many North American pegmatites. He also noted that hemo-ilmenites and ilmeno-hematites are also frequently developed.

Puffer (1975) reported that the Ti-poor magnetites exhibit a very narrow compositional range and contain only minor amounts of other cations. The hemo-ilmenites, in contrast, exhibit a wide range of intermediate compositions between the hematite and ilmenite end members. The ilmenite-rich members also contain notable amounts of MnO and he reported a maximum value of 5,6 per cent. Virtually no other published information is available on the iron-titanium oxides in pegmatites.

Puffer (1975) suggested that the Fe-Ti bearing pegmatites may have been formed from iron-rich vapours derived by re-equilibration of hydrous ferromagnesian silicates in response to metamorphism in deep-seated environments. He concluded that the oxide minerals had crystallised at temperatures between 600° and $700^{\circ}C$ under conditions of high water pressure. He also noted that oxidation and recrystallisation commonly continued down to temperatures near $500^{\circ}C$. His data indicated that the hematite-bearing pegmatites crystallised under very much higher oxygen fugacities than the hemo-ilmenite-bearing types.

13.2 Samples Investigated.

Grains of opaque oxides from a variety of pegmatites developed in the region

between the confluence of the Swakop and Khan Rivers in South West Africa were kindly supplied by Dr. R.E. Jacob of Rhodes University. A large quantity of heavy mineral concentrates prepared from pegmatite samples collected in the N.W. Cape was also placed at the author's disposal by Mr. C.T. Logan of NIM, but these were found to be largely devoid of iron-titanium oxides.

The relationships between the opaque oxides and their hosts were not examined since the majority of samples were in the form of mineral separates. The identity of certain phases was confirmed by x-ray diffraction. Only one sample (REJ 287) was found suitable for analysis and the microprobe analysis of this grain is presented in Table 13. The remaining samples were too highly exsolved to obtain any useful analysis by means of the microprobe.

13.3 Nature of the Oxides Present.

The samples investigated consist predominantly of ilmeno-hematite grains in which small, but variable amounts of ilmenite lamellae or discs are developed along the basal planes of the hematite hosts. Small, but variable, amounts of exsolved rutile are also present as thin plates oriented parallel to $(22\bar{4}3)$ of the hematite (Ramdohr, 1956, 1969). The nature of the oxides present in the samples examined are summarised in Table 15.

The magnetites examined are all optically homogeneous and free from intergrown phases. This magnetite exhibits varying degrees of oxidation to martite which takes place directly along their octahedral planes. The ilmeno-hematite grains could not be analysed by microprobe on account of their complex exsolved nature. The analysis of the hemo-ilmenite was made on an area relatively free from hematite lamellae and is comparable with the analyses presented by Puffer (1975) (Table 13, A and B),

TABLE 15.

NATURE OF THE OXIDE PHASES PRESENT IN TEN PEGMATITES.

Sample number	Oxide present
REJ 197	Ilmeno-hematite with rutile intergrowths.
REJ 234	Ilmeno-hematite with rutile intergrowths.
REJ 287	Ilmenite with exsolved hematite.
REJ 454	Ilmeno-hematite with rutile intergrowths.
REJ 459	Optically homogeneous magnetite.
REJ 470	Ilmeno-hematite with rutile intergrowths.
REJ 471	Ilmeno-hematite with rutile intergrowths.
REJ 490	Ilmeno-hematite with rutile intergrowths.
REJ 711	Optically homogeneous magnetite, strongly martitized.
R 1[+]	Martite + rutile.

[+] Sample from the N.W. Cape ex. C.T. Logan, National Institute for Metallurgy.

13.4 Conclusions.

1). Insufficient data are available on the iron-titanium oxides in pegmatites to draw definite conclusions, but the dominant phases are generally ilmeno-hematites and hemo-ilmenites. Ti-poor magnetite is also present, but no magnetite containing ilmenite lamellae was noted.

14. THE ILMENITES IN SOME EASTERN CAPE BEACH SANDS.

14.1 Introduction.

The beach sands along the South African coast contain variable amounts of ilmenite that have been derived by the weathering and erosion of rocks in the hinterland. These ilmenites occasionly become concentrated in the coastal dune sands to such an extent that they become economically significant as in the case of the deposits currently being exploited near

Richard's Bay. The South African ilmenite deposits of this type have been recently reviewed by Hammerbeck (1976).

The beach sand ilmenites were investigated with a view to determining their properties in the hope that these might yield information on their provenance. The ilmenites in the beach sands represent both primary-cycle grains released by the weathering of igneous (and metamorphic) rocks and secondary cycle grains released from the sediments in which they had become incorporated during an earlier cycle of deposition.

14.2 Samples Investigated.

Natural heavy mineral concentrates were collected from present-day beaches at various localities along the Eastern Cape coast as indicated in Table 16 and figure 1.

TABLE 16.

LOCALITY OF BEACH SAND SAMPLES.

Sample Number	Locality
BS 1	Jeffrey's Bay
BS 2	Maitland River Mouth
BS 3	Swartkops River Mouth
BS 4	East of Fish River Mouth
BS 5	Morgan's Bay, Transkei Coast
BS 6	Nahoon, East London
BS 7	Boknes Beach
BS 8	Bushman's River Mouth
BS 9	Kasouga
BS 10	Port Alfred

FIGURE I.

BEACH SAND LOCALITIES
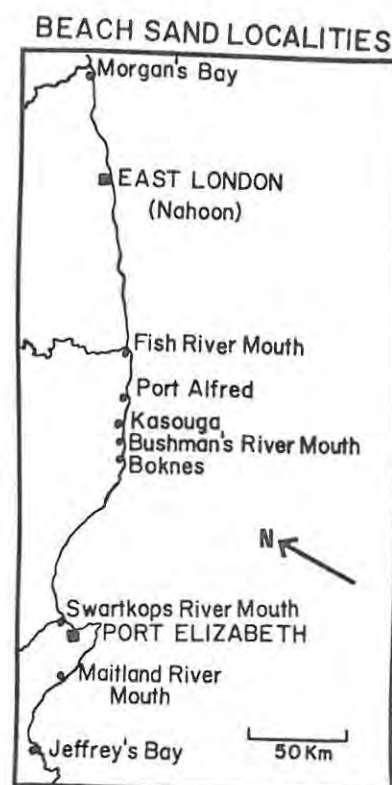
The ilmenites exhibit variable degrees of alteration and only the ilmenites that were separated at a current strength of 0,2 amps on the electromagnetic separator set with 25° forwards and sideways tilts were examined. Higher current strengths resulted in the separation of increasing amounts of garnet which could only be removed from the ilmenite concentrates with difficulty.

14.3 Nature of the Opaque Oxides Present in the Beach Sands.

Titaniferous magnetite is present in only minor amounts and generally displays advanced oxidation to martite. Ilmenite is the dominant opaque oxide while small, but variable amounts of rutile, leucoxene and zircon are also present. Garnet represents the dominant heavy silicate mineral in the sands and a variety of types was noted, but not studied.

The ilmenite grains are sub-rounded to well-rounded and are generally free from silicate inclusions. They generally exhibit incipient alteration to leucoxene which commences around their grain boundaries and along fractures (Plate C (8)). The alteration is progressive in nature and moves inwards in an irregular manner and involves the oxidation and removal of iron from the ilmenite as discussed in Part 1, section 6.5. This process eventually results in the conversion of the original ilmenite into a mixture of amorphous and finely crystalline TiO_2-rich products, largely anatase and rutile.

14.4 Reflectivity and Micro-Indentation Hardness.

The reflectivities and micro-indentation hardnesses of 10 grains in each polished section were determined for comparison with the values determined for ilmenites of known origin. The results obtained are presented in Table 17. The range of values obtained is comparable with that obtained for the ilmenites from Karroo dolerites and other gabbroic types. The reflectivity values of certain grains are slighly low and this might be due to the effects

of incipient alteration and leaching of iron from the ilmenite.

TABLE 17.

BEACH SAND ILMENITES: REFLECTIVITIES AND MICRO-INDENTATION HARDNESS VALUES.

Sample number	Reflectivity at 546 nm R_o (%)		Micro-indentation Hardness (VHN$_{100}$)
	Range	Average	
BS 1	19,1-19,7	19,5	559-604
BS 2	18,8-19,2	18,9	553-608
BS 3	19,3-19,9	19,6	577-628
BS 4	19,2-19,6	19,3	582-632
BS 5	19,3-19,9	19,6	583-651
BS 6	19,3-19,6	19,5	572-632
BS 7	19,0-19,8	19,3	587-640
BS 8	19,4-19,6	19,5	574-632
BS 9	19,3-19,7	19,5	560-606
BS 10	19,2-19,5	19,2	569-629

14.5 Chemical Composition.

The bulk chemical compositions of the purified ilmenite concentrates are presented in Table 18.   These analyses are characterised by the presence of relatively large, but variable, amounts of Fe_2O_3 due to the slightly oxid-ised and altered nature of the majority of grains in each sample.   Both MgO and MnO values are low and show relatively little variation between the samples from different localities. No titaniferous magnetite is present in the analysed ilmenite concentrates.

The overall minor element content of the ilmenite concentrates places them within the range typical of ilmenites from basic igneous rocks.   The possibility of the preferential leaching of Mg and/or Mn from the ilmenite

TABLE 18

ANALYSES OF ILMENITE CONCENTRATES FROM EASTERN CAPE BEACH SANDS

	BS1	BS2	BS3	BS4	BS5	BS6	BS7	BS8	BS9	BS10	A	B	C
TiO_2	49,53	50,26	50,68	49,54	49,76	50,47	51,08	51,29	50,97	49,77	46,00	49,7	50,0
FeO	35,23	37,51	38,45	40,36	39,27	39,92	40,43	40,30	38,25	37,71	33,87	36,6	38,0
MgO	0,21	0,37	0,30	0,57	0,36	0,33	0,22	0,33	0,32	0,23	0,76	-	-
MnO	0,50	0,43	0,42	0,48	0,40	0,39	0,42	0,46	0,40	0,44	0,85	-	-
CaO	0,04	0,04	0,06	0,10	0,03	0,05	0,06	0,04	0,04	0,04	-	-	-
Fe_2O_3	13,88	11,14	9,70	8,36	9,91	7,96	7,14	7,04	9,62	11,18	13,12	11,1	13,1
Cr_2O_3	0,08	0,10	0,06	0,04	0,04	0,04	0,11	0,02	0,04	0,03	0,00	0,19	0,05
TOTAL:	99,47	99,85	99,67	99,45	99,77	99,16	99,46	99,48	99,64	99,40	94,60	97,59	101,15

NORMATIVE COMPOSITION (MOLE PER CENT)

	BS1	BS2	BS3	BS4	BS5	BS6	BS7	BS8	BS9	BS10
$FeTiO_3$	69,35	74,61	77,02	83,77	79,85	81,68	82,33	81,93	76,35	75,90
$MgTiO_3$	0,71	1,29	1,01	2,09	1,31	1,17	0,73	1,17	1,15	0,87
$MnTiO_3$	0,99	0,86	0,86	1,05	0,88	0,73	0,88	0,87	0,86	0,87
R_2O_3	12,43	10,14	8,90	7,74	9,05	7,33	6,72	6,41	8,60	10,10
TiO_2	16,52	13,10	12,21	5,35	8,91	9,09	9,34	9,62	13,04	12,26
TOTAL:	100,00	100.00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

N.B. The excess TiO_2 is due to the leaching of Fe from the ilmenites during alteration (leucoxene formation) while the high Fe_2O_3 contents are due to oxidation. The mineral formulae cannot be calculated in the normal manner due to their altered nature.

A = ilmenite concentrate from the west coast in the Vanrhynsdorp District (Coetzee et al., 1957).

B = ilmenite concentrate from Morgan's Bay (Hammerbeck (1976)

C = ilmenite concentrate from Richard's Bay (Hammerbeck (1976)

structure should, however, not be overlooked as a reason for the uniformly low values obtained for these components in the analyses. Low Cr_2O_3 values are attributed to the presence of minor amounts of Cr in the ilmenite crystal structure , since no chromite was noted in the analysed concentrates.

14.6 Conclusions.

1). The ilmenite concentrates prepared from beach sands along the Eastern Cape coast exhibit only minor compositional variations that are related largely to their degree of oxidation and secondary oxidation.

2). The chemical compositions of these ilmenite concentrates are similar to those shown by ilmenites from basic igneous rocks. Caution must, however, be exercised in ascribing a basic igneous rock origin for the bulk of these ilmenites since the effect of leaching on the Mg and Mn contents of these ilmenites is not known. The abundantly developed Karroo dolerites of the Eastern Cape hinterland would provide suitable source rocks for much of this ilmenite, but a certain amount will also be of the second-cycle type derived from older sediments.

3). The reflectivities and micro-indentation hardnesses of ilmenite grains randomly selected in the polished sections fall within the ranges of values obtained for ilmenites from a wide range of basic and granitic igneous rocks.

4). The beach sand ilmenites are more altered than their counterparts in unweathered igneous rocks as reflected in their higher Fe_2O_3 contents. Their TiO_2 contents are, however, not significantly higher and indicate that little iron leaching has occurred in the grains showing incipient alteration.

15. <u>CONCLUDING REMARKS</u>.

15.1 <u>Titaniferous Magnetite</u>.

The titaniferous magnetites from a wide variety of basic and granitic igneous rocks characteristically display varying degrees of alteration that can be ascribed to deuteric and in some cases, metamorphic alteration. This feature indicates that the accessory titaniferous magnetite in many igneous rocks does not represent a stable phase with respect to the entrapped late-stage volatiles. This results in its partial oxidation and replacement, with the degree of alteration being related to the relative abundance of both titaniferous magnetite and late stage fluids.

It is interesting to note that evidence of late-stage deuteric alteration of the titaniferous magnetite generally becomes less evident as the amount of oxides present in a particular rock increases (see Part 3 of this thesis). This can be ascribed to the increased amount of oxides present, in relation to the volatiles present , and which exert a strong buffering effect on oxygen fugacities.

The late-stage alteration of titaniferous magnetite requires additional study, particularly with respect to the development of the skeletal subgraphic and vermicular ilmenite grains. The author has commenced a more detailed study of this phenomenon in Karroo dolerites and basalts with particular reference to the associated sulphides.

The titaniferous magnetites in the various rock types examined display all the various microstructures discussed in Part 1, sections 4 and 5 and their development is interpreted in essentially the same way. The overall TiO_2 contents of the titaniferous magnetites also decrease with increasing SiO_2 contents of their host rocks from basic through to granitic rock types as

described by Buddington et al. (1955, 1963).

15.2 <u>Ilmenite</u>.

Ilmenite is often the dominant phase in a wide range of igneous rocks ranging from basic through to granitic types. This ilmenite is characterised by a fairly limited compositional range in which the MgO content is rarely higher than 6 per cent or the MnO content higher than 10 per cent. The majority of ilmenites are, however, generally much closer to the theoretical ilmenite end-member composition. This feature, combined with the degree of $MgTiO_3$, $MnTiO_3$ and Fe_2O_3 substitution that can theoretically take place, imply that the use of relatively insensitive parameters such as reflectivity measurements, micro-indentation hardness and unit cell dimensions or d-spacings cannot be used to determine the composition or origin of ilmenites in this compositional range.

The ilmenites from kimberlites are chemically distinct and are characterised by relatively high MgO, Fe_2O_3 and Cr_2O_3 contents. The effect of these components in solid solution in the ilmenite is to decrease the unit cell dimensions and reflectivities, and to increase their micro-indentation hardness. These parameters can thus be used to distinguish the kimberlite ilmenites from those of the usual range of igneous rocks. They cannot be used as indirect methods for determining the compositions of these ilmenites, however, since the $MgTiO_3$, Fe_2O_3 and Cr_2O_3 contents are highly variable and show no direct relationship between themselves. The trace element variation in the ilmenites from both kimberlitic and non-kimberlitic sources should be studied since this might yield parameters which can be used to characterise the ilmenites from particular rock types.

The ilmenites in a wide range of igneous rocks also exhibit varying degrees of deuteric alteration, but this is not as marked as in the case of the

co-existing titaniferous magnetite. The alteration to sphene appears to be a common occurrence, but the reactions involved have not been investigated in detail and warrant further study.

The compositions of the major ilmenite groups studied are summarised in figure 2 together with the same data for the coarse grained ilmenites from the titaniferous iron ores described in Part 3.
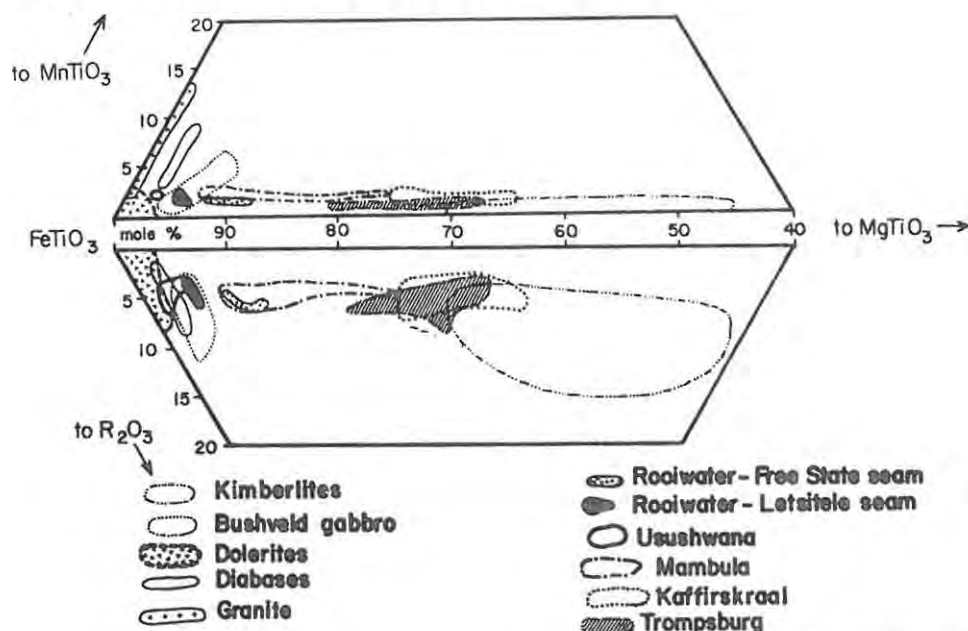
FIGURE 2: Variation in chemical composition of the ilmenites described in Parts 2 and 3 of this thesis. The data are presented in terms of the molecular percentages of normative $FeTiO_3$, $MgTiO_3$, $MnTiO_3$ and R_2O_3 (essentially Fe_2O_3).

The compositional differences between the ilmenites from the different igneous rock types can be clearly seen in the $FeTiO_3$–$MgTiO_3$–$MnTiO_3$ field. There is generally only minor overlap while the kimberlite ilmenites are distinctly different. The ilmenites from the titaniferous iron ores effectively bridge the compositional gap between the kimberlite ilmenites and those from basic igneous rocks. These analyses illustrate the presence of complete solid solution series between $MgTiO_3$–$FeTiO_3$ and $MnTiO_3$–$FeTiO_3$ over the compositional ranges shown, and highlight the limited extent of $MgTiO_3$–$MnTiO_3$ solid solutions in naturally occurring ilmenites. It can be concluded that Mg-rich ilmenites exhibit increasing Fe-enrichment with fractional crystallization while Fe-rich ilmenites exhibit Mn-enrichment.

The kimberlite ilmenites typically show high Fe_2O_3 contents, but considerable overlap occurs in the values shown by the other ilmenites. The $FeTiO_3$–$MgTiO_3$–R_2O_3 diagram illustrates the presence of a complete solid solution series between ilmenite and hematite over the compositional range shown.

A COMPARATIVE MINERALOGICAL STUDY OF SOME TITANIFEROUS IRON ORES FROM THE ROOIWATER, MAMBULA, USUSHWANA, KAFFIRSKRAAL AND TROMPSBURG IGNEOUS COMPLEXES

1. INTRODUCTION

The iron-titanium oxides contain appreciable quantities of Fe and Ti as well as lesser amounts of V. They are important potential sources of these commodities and they are present in significant concentrations in many mafic igneous rocks. In addition, they are concentrated in discrete, well-defined, and easily mineable layers in certain stratiform basic intrusions. The numerous titaniferous magnetite seams of the Bushveld Igneous Complex constitute the largest reserves of this type of ore in the world. A number of smaller, but less well-studied South African basic intrusions also contain large deposits of a similar nature. In particular, ore-rich concentrations that have potential economic significance are developed within the gabbroic rocks of the Rooiwater, Mambula, Usushwana, Kaffirskraal and Trompsburg Igneous Complexes.

The titaniferous iron ores of layered basic intrusions are essentially monomineralic rocks that are analogous to the dunites, pyroxenites, chromitites and anothosites that are commonly developed in igneous complexes of this nature. The origin of these ore-rich layers is consequently related to the various processes operating during fractional crystallisation of the igneous complex concerned.

The iron-titanium oxides in the ore-rich horizons exhibit microstructural relationships that are similar to those developed in these minerals when they are present as accessory phases in gabbroic rocks. The theoretical considerations discussed in Part 1 regarding their microstructural development are thus equally applicable. The relative abundance of the iron-titanium oxides in these ores, however, focuses on their mutual intergranular relationships and compositional variations.

2. THE ECONOMIC SIGNIFICANCE OF TITANIFEROUS IRON ORES

The development of economically viable processes for the recovery of Fe, TiO_2 and V_2O_5 from vanadium-bearing titaniferous iron ores has been the subject of intensive research during the last 150 years. It is only recently, however, that progress has been made in this direction. It is appropriate to re-evaluate the potential of these deposits since they are not only capable of supplying a large portion of the world's TiO_2 and V_2O_5 requirements, but can also make a substantial contribution to iron and steel production.

The vanadium-bearing titaniferous iron ores of stratiform basic intrusions typically contain 48-60% Fe, 10-25% TiO_2 and 0,2-2,5% V_2O_5 (Tables 1 and 2) and can be regarded as low- to medium-grade ores. They cannot normally be economically utilised unless more than one saleable product is recovered because of the high production costs involved. They are of metallurgical interest, however, since extremely large tonnages are present in a readily recoverable form in certain basic intrusions.

Titaniferous iron ores cannot be utilised for large-scale iron production in conventional blast furnaces since the Ti present necessitates extremely high operating temperatures and also forms infusible products that interfere with furnace operation. Numerous unsuccessful attempts were made to smelt or beneficiate these ores during the latter part of the last century (Rossi, 1890) and similar investigations have been carried out sporadically since then (Elliot, 1959 ; Rose, 1969). Recent developments have, however, resulted in the limited exploitation of these resources in various parts of the world.

The nature and behavior of these ores was not understood until Singewald (1913a,b) published the results of an ore microscopic investigation of titaniferous iron ores in the United States. He noted that they consist of magnetite together with lesser amounts of granular ilmenite and gangue minerals. The magnetite typically contains abundant microscopic lamellar- and granular-ilmenite intergrowths that are the major cause of unsuccessful benefication. Mineralogical investigations during the following 75 years have added many details to Singewald's descriptions, but his conclusions that Ti-free magnetite cannot be produced from these ores by conventional ore-dressing techniques remains valid.

The development of the electric arc furnace made the smelting of these

ores technically possible, but has not resulted in their widespread utilisation for iron production because of the high energy consumption required. The many significant advances made in the utilisation of these ores during the first two-thirds of this century have been summarised by Rose (1969).

The bulk of the world's TiO_2 production is used in pigment manufacture for which rutile is the most suitable raw material. The high cost and the rapid depletion of the world's rutile reserves has, however, led to an increased interest in alternative TiO_2 sources (Roskill, 1971 ; Sinha, 1973). Ilmenite (48-53 % TiO_2) is the next most abundant titanium mineral and it is widely used for pigment manufacture, although its high Fe content makes it unsuitable for use via the chloride process. In recent years intensive research has been carried out into the production of synthetic rutile or other high titanium products from ilmenite (Becher, et al., 1965 ; Walker, 1967 ; Marshall and Finch, 1967 ; O'Brien and Marshall, 1968 ; Gaskin, 1969 ; Judd and Palmer, 1973 ; Mackey, 1974 ; Rolfe, 1973). Numerous processes have been patented and the subject has been extensively reviewed by Hartly (1965) , Henn and Barclay (1970) and Kothari (1974). The South African titaniferous ore deposits have been reviewed by Hammerbeck (1976).

The titaniferous iron ores contain less TiO_2 than ilmenite, but they also warrant attention since the higher production costs can be offset by the recovery of iron and possibly V_2O_5. Many of the processes for upgrading the TiO_2 content of ilmenite can also be modified to suit these ores. MacMillan, Heindl and Conley (1952) have described a soda sinter process for the recovery of TiO_2, Na_3VO_4 and iron as well as other by-products from vanadium-bearing titaniferous iron ores containing between 18 and 22 % TiO_2. The electric arc smelting of similar ores has been investigated by Holmes and Banning (1964) who produced pig iron and high titania slags from ores containing between 1,63 and 22,5 % TiO_2. Elger and Stickney (1971) , Oden et al. (1975) and Elger et al. (1974) have produced synthetic rutile from high titania slags.

Research carried out at the National Institute for Metallurgy (NIM) on titaniferous iron ores from the Tete district in Mocambique containing 51,5 % Fe, 19,7 % TiO_2 and 0,5 % V_2O_5 has shown the technical feasibility of recovering pig iron as well as TiO_2 and V_2O_5 (McRae et al. , 1973 ;

Faure et al., 1973 ; Yom Tov et al., 1973 ; Faure et al., 1974 ; McRae, 1974). Cost estimates of this process indicate that the recovery of both TiO_2 and V_2O_5 is necessary (Wilson, 1973). No TiO_2 is currently recovered from South African titaniferous magnetites, but their cost of treatment might be lower than that of the Tete District, especially if the pig iron is converted to steel.

South Africa is already the major interational producer of V_2O_5, but the world market is fast approaching saturation (Roskill, 1975) so that V_2O_5 recovery from additional sources will be of little interest unless new markets can be developed. Vanadium pentoxide is presently recovered in slag form from Bushveld Main Seam ores mined near Roossenekal in the eastern Transvaal. It is also produced from similar ores to the north and west of Pretoria by the sodium metavanadate process. The South African vanadium resources have been reviewed by Luyt (1976) and an account of vanadium mineralogy and recovery has been given by Rose (1973).

3. TITANIFEROUS MAGNETITE SEAMS IN STRATIFORM BASIC INTRUSIONS

3.1 Introduction

The presence of well defined layering in many large, differentiated basic intrusions has been reported from numerous localities and this subject has been reviewed by Wager (1967) and Wager and Brown (1968). Monomineralic layers consisting of more than 90 per cent plagioclase, pyroxene or olivine are commonly present in these intrusions. Economically interesting layers of titaniferous magnetite or chromite may also be developed. These ore-rich layers are characteristically thin (0,1–10m) when compared to the overall thickness of the intrusions in which they occur, but they nevertheless often exhibit a remarkable lateral continuity. For example, the main titaniferous magnetite seam in the Bushveld Igneous Complex varies between 1 and 2,8m in thickness, but has been traced along strike for approximately 120 km in the eastern Transvaal and for 200 km in the western Transvaal (Willemse, 1969b). Less extensive titaniferous magnetite-rich seams of a similar nature are also present in the basic rocks of the Rooiwater, Mambula, Usushwana, Kaffirskraal and Trompsburg Igneous Complexes.

3.2 Factors Influencing the Formation of Titaniferous Magnetite Seams

The formation of monomineralic layers within stratiform basic intrusions has been the subject of considerable debate in the geological literature

and a comprehensive review of this topic is beyond the scope of this
thesis. Only certain aspects that have a direct bearing on the nature
and origin of the titaniferous magnetite-rich layers are considered
here and readers are directed to the book of Wager and Brown (1968) for
addition information.

The general consensus is that these rocks are formed by magmatic
sedimentation processes that resulted in the accumulation of precipitated
crystals in layers on the magma chamber floor (Wadsworth, 1973). These
layers may have formed by a simple process of crystal settling or by a
variety of other mechanisms including a convective overturn process
(Hess, 1960), crystallisation from a stagnant sheet of magma near the
floor of the intrusion (Jackson, 1961), convection and turbidity currents
(Wager, 1967), the effects of contamination by a salic melt formed from
the roof rocks (Irvine, 1974, 1975b), or by the influx of additional
unfractionated magma (Irvine, 1977). The settled minerals are known as
cumulus crystals and crystallisation of the intercumulus liquid can
follow various paths, each of which results in the formation of a rock
with a characteristic texture as described by Wager et al. (1960).

Wager and Brown (1968) commented on the presence of large titaniferous
magnetite concentrations in many stratiform basic intrusions, particularly
amongst the later crystallisation products. This feature can be accounted
for by iron enrichment of the residual liquid having taken place during
fractional crystallisation and it is necessary to consider the factors
that may have controlled this process.

Numerous analogies can be drawn between the occurrence of chromite-rich
and titaniferous magnetite-rich layers in stratiform basic intrusions
which suggest that essentially similar mechanisms must have operated during
their formation. The chromitites have been more extensively studied than
the titaniferous magnetite-rich layers because of their greater economic
importance. The many similarities between them, however, indicate that
at least some of the conclusions reached on the formation of chromite-
rich layers should also be applicable to the titaniferous magnetite seams.

Chromite always appears to crystallise early during the cooling history
of stratiform basic intrusions and results in the accumulation of chromite-
rich layers near their bases. After a certain crystallisation period the
chromite precipitation ceases and an essentially chromite-free zone is

formed. Titaniferous magnetite precipitation commences towards the later crystallisation stages of the igneous complex and distinct layers are also formed where concentrations of this mineral are sufficiently high. This pattern of initial chromite crystallisation followed by later titanomagnetite precipitation is a common feature of basaltic magma crystallisation (Evans and Moore, 1968).

Irvine (1967) postulated that the disappearance of chromite is due to a liquid-spinel-pyroxene reaction that produces a slightly chromiferous pyroxene at the expense of the spinel phase. Titaniferous magnetite is able to crystallise as the spinel phase when the iron and titanium concentrations in the residual liquid rise to a sufficiently high level during the later stages of crystallisation.

Oxygen fugacity plays an important role during the crystallisation of a basaltic magma since it influences the oxidation state of the iron present and so determines the nature of the iron-bearing phases that will be precipitated. Following the work of Kennedy (1948), Osborn (1959, 1962) suggested that changes in oxygen fugacity during the fractional crystallisation of a basaltic magma might be an important factor in determining the distribution of iron oxide and silica in the residual fractions. Osborn (1959) showed experimentally that the fractional crystallisation of a simplified basaltic liquid under conditions of low oxygen fugacity produced an iron-enriched residual liquid. No iron-enrichment of the residual liquid occurred when crystallisation was carried out under conditions where the oxygen fugacity was maintained or increased. Roeder and Osborn (1966) carried out similar experiments on mixtures that more closely approximated natual basalt in composition. They also observed an iron enrichment trend in the residual liquid under conditions of low oxygen fugacity. No iron enrichment resulted when fractional crystallisation was carried out under higher oxygen fugacities.

Studies of phase relationships in basaltic and other related systems by Muan and Osborn (1956), Presnall (1966) and Hamilton and Anderson (1967) also show that oxygen fugacity exerts a strong influence on the composition of the residual liquid produced during fractional crystallisation. Kuno (1965) also noted that the degree of iron enrichment in magmas is largely determined by the quantity of magnetite that separates from the magma and at what stage this separation takes place.

The formation of magnetite is controlled by oxygen fugacity and Hynlman (197?) concluded that iron would be largely present as Fe^{2+} in magmas under conditions of low oxygen fugacity. Mg^{2+} rather than Fe^{2+} would, however, be preferentially incorporated into the early-formed mafic silicates during the early stages of crystallisation. This would result in the bulk of the Fe^{2+} remaining in the magma and its concentration would increase during the course of fractional crystallisation. Portion of the Fe^{2+} would become oxidised to Fe^{3+} under conditions of higher oxygen fugacity, so that magnetite would precipitate along with the magnesian silicates. This process results in a relatively even removal of iron from the liquid during crystallisation so that iron-enrichment of the residual liquid cannot occur.

The available data suggest that the formation of an iron-enriched residual liquid is necessary before titaniferous magnetite can be precipitated in sufficient quantities to form monomineralic layers. Even if this stage of iron enrichment is reached, it is evident that abundant titaniferous magnetite precipitation cannot occur unless the oxygen fugacity is increased to a level at which substantial oxidation of Fe^{2+} to Fe^{3+} can take place, i.e. the precipitation of titaniferous magnetite must be triggered by an increase in the oxygen fugacity of the magma. If partial oxidation of Fe^{2+} to Fe^{3+} does not take place at this late stage, the iron enrichment will result in the ferrous iron being incorporated into other mafic silicates such as iron-rich clinopyroxene or fayalitic olivine. Ulmer (1969) and Cameron and Desborough (1969) have also shown that oxygen fugacity is important in controlling the precipitation and chemical characteristics of chrome spinels. Molyneux (1970a, b) also noted the possible effect of oxygen fugacity in controlling titaniferous magnetite precipitation in the Bushveld Igneous Complex.

Experimental investigations by Hill and Roeder (1974) into the crystallisation of spinel as a function of oxygen fugacity in natural basaltic liquids support the earlier observations of Osborn (1959) and Roeder and Osborn (1966). Hill and Roeder (1974) concluded that the lower the oxygen fugacities are during fractional crystallisation, the greater will be the iron enrichment in the residual liquid and the lower the temperature at which the iron-rich phases will crystallise. Under higher oxygen fugacities ferric oxide is produced which causes the early precipitation of spinel and rhombohedral phases so that iron enrichment

of the residual liquid is not attained.

Irvine (1974, 1975b) proposed that the chromite-rich layers of stratiform basic intrusions are precipitated on occasions when extensive contamination of the basic parental magma by granitic liquid, melted from the salic roof rocks, occurs. He also suggested that this hypothesis might be extended to include the formation of titaniferous magnetite-rich layers. He mentioned that precipitation of the titaniferous magnetite layers may have resulted from a sudden oxidation of the magma and noted that this contamination mechanism provides a convenient method for suddenly introducing oxygen into the system at this stage. The influx of fresh, undifferentiated magma into the system might produce similar results (Irvine, 1977).

A study by Irvine (1975a) of the phase relationships indicates that the salic contamination of subalkaline basaltic magma would tend to enhance the crystallisation of Ca-poor pyroxene relative to both olivine and plagioclase. This feature is in accordance with the abundant development of orthopyroxene cumulates associated with chromite layers in many stratiform basic instrusions. In the Bushveld and many other complexes, however, the titaniferous magnetite-rich layers are often interlayered with anorthosites and troctolites. Irvine (1975a) has shown that abundant plagioclase can be precipitated by mixing contaminated basic liquid that has crystallised sufficient pyroxene with relatively fresh liquid. Fractional crystallisation of this liquid of intermediate composition would then yield abundant plagioclase precipitates to form anorthositic layers. By analogy, these findings of Irvine may have a direct bearing on the formation of titaniferous magnetite layers in stratiform basic intrusions.

3.3 Grain-Boundary Relationships in Titaniferous Magnetite Cumulates

The constituent grains in many of the monomineralic layers in stratiform basic intrusions are often unzoned and characteristically exhibit a fair degree of polygonalisation showing the development of triple junctions with interfacial angles approximating 120°. These features are normally associated with granoblastic metamorphic rocks that have formed under conditions of medium to high grade metamorphism and their presence in primary igneous rocks has not received much attention.

Hess (1939) concluded that these textures were formed by the enlargement

of settled crystals by some form of diffusion controlled growth that occurred at the same temperature as that at which the crystals were originally formed. Diffusion of suitable ions from the overlying magma reservoir into the intercumulus liquid is necessary to ensure the continued growth of the original crystals, while the unwanted ions diffuse back into the magma reservoir. This process can only operate near the top of the accumulated crystal pile where diffusion can take place freely while the intercumulus liquid would be gradually eliminated by continued growth of the settled crystals.

Wager et al. (1960) introduced the term "adcumulus growth" to describe the enlargement of the cumulus crystals by material of the same composition, the resulting rock being termed an adcumulate. Adcumulus growth can take place only when the free diffusion of ions between the magma and inter-cumulus liquid is possible. Additional growth of the original crystals tends to force out the intercumulus liquid thus reducing pore-space. In cases where the diffusion of ions between the overlying magma reservoir and the intercumulus liquid is prevented, crystallisation of the intercumulus phase would continue resulting in the development of different textural types (Wager et al., 1960).

Voll (1960) examined the grain boundary relationships in monomineralic layers from various basic layered intrusions and concluded that many of their features were not produced solely by contemporaneous growth into pores. He noted in many cases, particularly in the chromitites, that grain boundary curvatures at triple junctions are indicative of solid state adjustment. Voll (1960) concluded that these textures are formed, at least in part, by the sintering together of crystals under the influence of interfacial tension.

Weedon (1965) reported the presence of equilibrium grain boundary relationships in layered ultrabasic rocks and suggested that they may have formed via a mechanism similar to that proposed by Voll (1960). Vernon (1970) also noted the textural similarity between single phase adcumulates from igneous rocks and metamorphic granulites, both of which consist largely of polygonal grains with smoothly curved interfaces. In a discussion of Voll's mechanism, Vernon (1970) added that the interstitial liquid would be gradually expelled during sintering, initially through pore networks and later by a solid-state diffusion

process. The mineral grains would thus grow together under the influence of interfacial free energy to produce a space-filling aggregate of polygonal grains having interfacial angles of approximately 120°. This process involves the movement of interfaces by diffusion and should be possible provided that enough heat is available. Vernon (1970) noted that these factors might operate if cooling of the intrusion is slow enough and that this mechanism obviates the delicate diffusion balance and connection with the overlying magma reservoir required by the Hess model.

Powders are consolidated into dense polycrystalline aggregates during sintering by heating at temperatures below their melting points. The process has been reviewed by Coble and Burke (1963) and when applied to oxide and metal powders, results in the formation of foam-like microtextures in which the polygonalised constituent grains have boundaries that meet in triple junctions having interfacial angles that approximate 120°. These intergranular relationships are indicative of equilibrium conditions. The subject of grain boundaries and their relationships has been reviewed by Harker and Parker (1945) and Smith (1948, 1964).

Stanton (1964) synthesised various sulphide aggregates showing similar grain boundary relationships by sintering the required constituents in vacuo at temperatures well below their melting points. Grain growth took place in the solid state and the resulting polygonal texture was produced by the attainment of grain boundary equilibrium.

The available data on the sintering of oxides and sulphides suggest that this process might play a mineralogically important role in the development of the grain boundary relationships observed in essentially monomineralic titaniferous magnetite layers. In support of this view, Stanton (1965) stated that the iron-titanium oxides should also conform to normal principles governing the shape of polycrystalline aggregates. He also noted that iron-titanium oxide aggregates from the Skaergaard Intrusion consist of approximately straight-sided polyhedra having well defined triple junction points.

Cameron (1969) examined post-cumulus changes in rocks associated with chromitites in the eastern Bushveld. He noted that at least half or

more of the final crystalline products consist of material precipitated during the postcumulas stage. A partial, or greater, equilibration between cumulus crystals and liquid appears to have taken place and Cameron (1969) concluded that the resulting textures were produced by a process of re-crystallisation supplemented by adcumulus growth. Subsequent work by Cameron (1975) also indicated that a certain amount of post-cumulus and subsolidus equilibration has taken place in the cumulate rocks of the eastern Bushveld.

The mechanisms involved in the formation of the characteristic grain relationships exhibited by monomineralic titaniferous magnetite layers in stratiform basic intrusions are not well understood and require further study. Vernon (1970) concluded that these textures might be accounted for by the partial post-cumulus enlargement of settled crystals by adcumulus growth according to the Hess mechanism, followed by grain boundary adjustment during slow cooling. The available data suggest that this combination of processes might well account for the development of the grain boundary relationships exhibited by these ores.

3.4 The Mineralogical and Chemical Compositions of Titaniferous Iron Ores

Titaniferous iron ores have been described from numerous areas and their mineralogical associations are well known. The early reports of Singewald (1913a,b), Warren (1918), Ramdohr (1926) and Osborne (1928) outlined most of the important features of these ores with the result that subsequent studies have merely served to add the finer descriptive details. They also provided explanations that were in keeping with the theoretical developments current at the time as outlined in Part 1 of this thesis.

Titaniferous iron ores can be classified into a wide variety of types as suggested by Lister (1966), each of which can be ascribed to a different mode of origin. The South African examples investigated during this study can be classified as concordant deposits that are located within gabbroic intrusions. Only information concerning deposits of a similar nature is discussed here. Readers requiring additional information are referred to publications on Indian deposits by Dunn and Dey (1937) and Roy (1954); on North American deposits by Lister (1966) and Anderson (1968b); on Scandinavian deposits by Gjelsvik

(1957) Vaasjoki and Heikkinen (1962), Duchesne (1970, 1972) and Gierth and Krause (1973) ; and on the Bushveld Igneous Complex by Schwellmus and Willemse (1943) Coertze (1966) Willemse (1969b) and Molyneux (1970a,b).

The vanadium-bearing titaniferous iron ores of gabbroic intrusions are composed essentially of variable amounts of titaniferous magnetite and granular ilmenite together with variable amounts of silicate impurities, normally plagioclase, pyroxene or olivine. The proportions of these gangue minerals vary widely in the different deposits and only rocks containing more than 60 per cent by volume of iron-titanium oxides will be referred to as "ore" in this thesis.

The proportions of coarse-grained granular ilmenite vary considerably with respect to the amount of titaniferous magnetite present in the different deposits. The magnetite itself characteristically displays the development of a wide range of titanium-and aluminium-bearing micro-intergrowths. The larger ilmenite grains commonly contain minor crystallographically oriented hematite or magnetite intergrowths.

In contrast to the large number of published microscopic descriptions of various titaniferous iron ores, there is an extreme paucity of complete chemical data. Numerous complete analyses of individual co-existing ilmenite and magnetite grains or concentrates, and details of total iron and TiO_2, are, however, available for these ores from many areas. Comparisions based on bulk chemistry and minor element variations are therefore not easily made in view of the lack of published data. Selected analyses of essentially pure titaniferous iron ores and mineral concentrates from various localities are presented in Table 1 for comparison with analyses of some typical South African ores (Table 2).

On the basis of the available analyses it can be concluded that the chemical compositions of titaniferous iron ores from gabbroic rocks (largely stratiform basic intrusions) will lie within the following limits:

TABLE 1

ANALYSES OF TYPICAL TITANIFEROUS IRON ORES OF GABBROIC ASSOCIATION

Reference Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
No. of Analyses	1	1	1	1	1	1	1	4	3	3	3	3	1	1
SiO_2	1,10	0,57	9,76	1,00	2,44	1,63	11,8	N.R.	N.R.	N.R.	N.R.	N.R.	0,54	0,46
TiO_2	13,06	13,84	16,84	10,20	16,40	18,20	18,8	25,24	23,47	23,74	24,30	25,80	27,50	23,40
Al_2O_3	1,02	2,83	N.R.	0,75	0,56	2,70	7,5	0,45	0,28	0,06	0,25	0,23	1,18	1,31
Cr_2O_3	N.R	N.R	N.R	N.R	N.R	0,70	N.R	0,32	0,10	0,06	0,04	0,06	0,38	0,03
Fe_2O_3	71,90	72,17	42,88	60,68	66,03	26,80	57,5	N.R	N.R	N.R	N.R	N.R	28,90	32,80
FeO	9,00	8,07	24,22	20,01	11,93	45,0	−	N.R	N.R	N.R	N.R	N.R	39,50	42,10
MgO	0,26	0,20	0,94	0,59	0,34	3,00	0,5	1,76	1,28	0,99	0,81	0,66	0,19	0,34
MnO	0,50	0,14	0,52	0,13	0,13	0,41	N.R	0,41	0,39	0,27	0,54	0,52	0,98	0,39
V_2O_5	1,90	0,59	2,20	1,93	0,59	1,07	0,5	0,50	0,41	0,18	0,14	0,23	N.R	N.R.
TOTAL :	98,74	98,41	97,36	95,29	98,42	99,51	96,6	—	—	—	—	—	99,17	100,83
TOTAL Fe :	57,28	56,75	48,82	57,99	55,45	53,72	40,22	51,7	53,5	54,8	52,0	52,8	50,84	55,66

Source of analyses: N.R. = not reported

1) Dublabera, Singhbhum, India. (Dunn and Dey, 1937).
2) Kumhardubi, Mayurbhanj, India. (Dunn and Dey, 1937).
3) Dublabera, Singhbhum, India. (Dunn and Dey, 1937).
4) Dublabera, Singhbhum, India. (Dunn and Dey, 1937).
5) Khariadih, Singhbhum, India. (Dunn and Dey, 1937).
6) Söira Ulvön ore (Mogensen, 1946).
7) Tahawus ore (MacMillan et al., 1950).

8) Duluth gabbro N. (Lister, 1966).
9) Duluth gabbro S. (Lister, 1966).
10) Ellen Lake (Lister, 1966).
11) Pusey Mine (Lister, 1966).
12) Seine Bay (Lister, 1966).
13) 74 Fa, Dufek (Himmelberg and Ford, 1977).
14) 171 Fa, Dufek (Himmelberg and Ford, 1977).

TABLE 2

ANALYSES OF SOUTH AFRICAN VANADIUM-BEARING TITANIFEROUS IRON ORES

	BUSHVELD IGNEOUS COMPLEX				ROOIWATER IGNEOUS COMPLEX			Mambula Complex Average	Usushwana Complex Average	Kaffirs-kraal Complex Average	Trompsburg Complex Average
	Main Seam °	Main Seam +	Middle Seams +	Upper Seams +	Lower Seam x	Upper Seam x	Magnetite Lens x	x	x	x	x
No. of Analyses	"Thousands"	5	3	5	7	5	1	16	12	5	18
SiO_2	1,22	1,76	1,59	3,59	2,85	1,66	2,09	6,72	1,80	1,38	2,55
TiO_2	13,05	12,63	16,56	18,20	14,69	22,08	12,23	12,33	14,04	12,98	16,36
Al_2O_3	3,02	3,35	3,36	2,84	2,04	3,72	6,12	7,79	1,54	2,41	4,55
Cr_2O_3	0,29	0,42	0,07	0,02	0,75	<0,05	<0,05	<0,05	<0,05	<0,05	0,30
Fe_2O_3	N.R.	69,16	64,09	59,86	66,13	44,89	55,11	43,62	60,60	64,19	35,09
FeO	N.R.	7,76	10,82	10,09	11,51	25,65	22,97	24,76	21,36	15,92	35,11
MgO	0,75	1,04	0,75	0,70	0,56	1,75	1,78	3,14	0,31	2,20	4,43
MnO	N.R.	0,21	0,25	0,37	0,19	0,30	0,19	0,27	0,23	0,26	0,39
V_2O_5	1,53	1,22	0,53	0,24	1,35	0,81	0,86	0,68	0,31	0,81	0,70
TOTAL :	-	97,55	98,02	95,91	100,07	100,86	101,35	99,31	100,19	100,15	99,48
TOTAL Fe :	56,70	54,40	53,23	49,71	55,20	51,34	56,40	49,68	58,99	57,27	51,83

° Analyses from Luyt (1976).

+ Analyses from Schwellnus and Willemse (1943).

x New Analyses (this thesis).

N.R. Not reported

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$$TiO_2 \quad 10-25\% \qquad MnO \quad 0,1 - 1,0\%$$

$$Al_2O_3 \quad 1-7\% \qquad MgO \quad 0,2 - 4,0\%$$

$$Cr_2O_3 \quad 0-1,5\% \qquad V_2O_5 \quad 0,2 - 2,5\%$$

$$Fe \text{ (total)} \quad 48 - 60\%$$

The SiO_2 values reported in the various analyses largely reflect the presence of minor silicate impurities. In part, some of the reported MgO and Al_2O_3 will also be due to the presence of silicates. The variations in Fe_2O_3 and FeO can be ascribed to oxidation that might, in part, occur during deuteric alteration and which normally occurs during weathering.

Schwellnus and Willemse (1943), Willemse (1969b) and Molyneux (1970a,b, 1972) have shown that the V_2O_5 contents of the titaniferous iron ores decrease progressively upwards in the Bushveld complex, while the TiO_2 content increases (Table 2). Similar compositional trends were reported for the accessory titaniferous magnetites in the Skaergaard Complex (Vincent and Phillips, 1954) and the Dufek Intrusion (Himmelberg and Ford, 1977). This V_2O_5 depletion and corresponding TiO_2 increase appears to be a characteristic feature of the progessive crystallisation of titaniferous magnetites and similar trends have been reported from a teschenite sill (Wilkinson, 1957), alkali basalts (Prevot and Mergoil, 1973), and certain zones within the Somerset Dam Layered Intrusion (Mathison, 1975). These authors also report decreases in MgO and Al_2O_3 contents with progressive differentiation.

3.5 Genesis of the Titaniferous Magnetite-rich Layers

The formation of essentially pure titaniferous magnetite layers within stratiform basic intrusions is the result of a complex interplay of factors related to fractional crystallisation and magmatic sedimentation processes. The common occurence of several titaniferous magnetite enriched zones and separate ore-rich layers within the same complex indicates that the correct physico-chemical conditions for large-scale titanomagnetite precipitation were reached on more than one occasion during crystallisation.

Bateman (1951) and Lister (1966) reviewed the possible mechanisms by which titaniferous iron ore deposits might be formed. Bateman (1951) stressed that the well defined seams in stratiform basic intrusions are formed by the late-stage gravitative accumulation of an iron oxide liquid. He suggested that this liquid might crystallise in place under quiescent conditions to form the seam or be forced into the surrounding rocks to form discordant deposits. Lister (1966) concluded that the titaniferous iron ores are formed by various combinations of the following three processes:

1) the accumulation of a Fe-Ti-rich liquid,

2) injection of a Fe-Ti-rich liquid and

3) injection of a Fe-Ti-rich basic pegmatite

The phase relationships and minor element variations in the titaniferous iron ore seams of stratiform basic intrusions also reflect the differentiation trends exhibited by titaniferous magnetites from a wide variety of igneous rocks. This indicates that their formation can be related to normal magmatic crystallisation processes and that they are an integral part of their host rocks. The nature of the individual ore-rich seams and their relationships towards their surrounding rocks are also consistent with their having formed by various "magmatic sedimentation processes" as reviewed by Wadsworth (1973).

In accordance with the available data it is proposed that the formation of titaniferous magnetite-rich layers in stratiform basic intrusions and the development of their characteristic textural features should be divided into several well-defined stages as follows:

1. The formation of an iron enriched residual liquid towards the closing stages of crystallisation of a stratiform basic intrusion. This iron enrichment is probably controlled by fractional crystallisation under low oxygen fugacities during the earlier stages of precipitation.

2. The precipitation of titaniferous magnetite in sufficient quantities to form a concentrated layer. Partial oxidation of the iron enriched liquid appears to be the simplest mechanism that accounts for this phenomenon. The quantity of titaniferous magnetite produced and the rate at which it is precipitated in relation to other silicates will also be controlled by the oxygen fugacity. The relative proportions of titaniferous magnetite and silicates crystallising

from the magma at this stage will be an important factor in determining whether monomineralic titaniferous magnetite layers or merely titaniferous magnetite-bearing silicate rocks are produced.

3. The formation of a titaniferous magnetite cumulate layer (at the top of the crystal pile) on the magma chamber floor. This layer of crystals and intercumulus liquid may form either by simple crystal settling or by one or other of the magmatic sedimentation processes invoked to account for the formation of layered igneous rocks. When silicates are precipitated together with the titaniferous magnetite, certain magmatic processes such as differential settling or current action might be responsible for the concentration of titaniferous magnetite into well-defined layers.

4. Adcumulus growth of the precipitated titaniferous magnetite crystals. This process will take place by the Hess mechanism for as long as a free diffusion of ions between the intercumulus liquid and the overlying magma reservoir is maintained. Adcumulus growth will become progressively less important as this diffusion becomes restricted due to a reduction in pore-space caused by crystal growth or by the burial of the titaniferous magnetite layer beneath a thick pile of accumulating crystals. Some of the intercumulus liquid will be expelled by pore-space reduction during adcumulus growth.

5. Grain-boundary adjustment towards or after completion of adcumulus growth. Once diffusion of ions between the intercumulus liquid and the overlying magma reservior has effectively ceased, the remaining trapped intercumulus liquid will crystallise to form post-cumulus phases as cooling progresses. At this time, however, and before crystallisation of the intercumulus liquids commence, the sintering mechanism of Voll might become operative resulting in the adjustment of the opaque oxide grain boundaries under the influence of surface energy. The reduction in pore space during this process will cause the continued expulsion of intercumulus liquid until an essentially monomineralic rock is produced. The final product will be a space-filling aggregate of polygonal titaniferous magnetite grains having interfacial angles approximating 120°.

6. Subsolidus changes in the titanomagnetite caused by cooling of the

igneous mass. As cooling takes place from the elevated temperatures of titanomagnetite precipitation, various solid-state exsolution and oxidation/exsolution processes are initiated. The microstructures produced in the originally homogeneous titanomagnetite reflect not only the composition of the initial phase and the rate of cooling, but also the influence of oxygen fugacity in determining the nature of the phases produced as discussed in Part 1. Solid state ionic diffusion decreases with a lowering of temperatures and it is thought to effectively cease at approximately 300°C in the iro--. titanium oxides. Grain boundary adjustment would likewise be operative at high temperatures, but the process would become progressively slower as temperatures decrease. The microstructural developments in the co-existing iron-titanium oxides will be essentially the same as that outlined in Part 1 for iron-titanium oxides from slowly cooled basic igneous rocks.

7. Any thermal metamorphic event would reactivate these solid-state processes, resulting in a modification of the primary igneous microstructures. The nature and appearance of the new microstructures would depend largely on the temperature and duration, and any applied stress, as well as the oxygen fugacity and cooling rate, during the metamorphic event.

4. SCOPE OF THE PRESENT INVESTIGATION

The bulk of the mineralogical investigations embodied in this part of the thesis were undertaken in the Mineralogy Division of the National Institute for Metallurgy (NIM) whilst the author was in the employ of that Institute. The data presented here also form the subject of a separate NIM report that will be issued in due course (Reynolds, 1978, in preparation).

This study represents the logical evolution of an interest in iron-titanium oxides as accessory phases in a variety of igneous rocks, into a study of their development as ore-rich concentrations in basic intrusions. These deposits might have considerable economic value in the future. This investigation into the South African vanadium-bearing titaniferous iron ores was initiated in view of the research orientation at NIM regarding the application of mineralogical studies to problems in extractive metallurgy. Considerable data are currently available on

the titaniferous iron ores of the Bushveld igneous complex, with the
result that the present investigation was directed mainly at the
deposits in the Rooiwater, Mambula, Usushwana, Kaffirskraal and Trompsburg
Igneous Complexes since virtually no published information exists on them.

The principal purpose of this study was to characterise the nature of each
of these deposits by means of chemical analyses and to determine whether
any potential exists for their economic exploitation. The mineralogical
investigation was carried out in order to determine the nature of ·l .
phases and intergrowths present in the ores in order that their response
to beneficiation could be assessed. A large amount of the data
collected during this study is, however, of a more academic interest and
forms the basis of this section. Considerable differences were found
to exist between the various deposits, and an attempt has been made to
interpret the accumulated data within the framework of the phase
relationships and microstructural developments outlined in Part 1 of this
thesis.

Field trips were made to the Rooiwater, Mambula, Usushwana and Kaffirskraal
Igneous Complexes for the collection of material used in the laboratory
studies. The field work was restricted to the collection of
representative iron-ores and associated rock types. Sample localities
were determined by means of published maps and the earlier descriptions.
Mapping and other field studies were not undertaken since they were
beyond the scope of this project and are also beyond the terms of
reference of mineralogical investigations carried out at NIM. Mr. R.
Fouche, of General Mining, kindly gave permission for borehole core
samples from the Trompsburg Igneous Complex to be used in this study.

The present mineralogical investigation was confined to an examination
of the coexisting iron-titanium oxide phases, their mutual relationships
and microstructural developments. The co-existing silicates were not
studied in detail since they are only present as relatively minor phases
in the bulk of the ores examined and rarely exceed 5 per cent by volume.
Any study of the co-existing silicates would also have been further
complicated by the weathered nature of many of the samples collected
from surface exposures. The original silicates in these ores are
commonly decomposed to clay minerals and other alteration products. In
addition to the weathering effects, the silicate minerals in the

Rooiwater and Usushwana Complexes have been extensively altered to chlorite, while the Trompsburg olivines have been largely serpentinised.

The bulk chemical analyses of the titaniferous iron ores were restricted to the determination of the nine most abundant oxides, in view of the large number of samples analysed and the costs involved. Minor amounts of CaO, Na_2O, and K_2O are also probably present in the analysed ores and had they been determined their values would reflect the presence of minor silicate impurities. Trace element studies, particularly of Ni, Cu, Co, Zn, Zr and Nb would have provided some of the valuable additional data required to elucidate the crystallisation history of these ores. Investigations of this nature were, unfortunately, also beyond the scope of this study.

Quantitative electron microprobe analyses were confined to the large co-existing ilmenite grains in each chemically analysed sample and the larger-sized ilmenite intergrowths developed in the Rooiwater and Kaffirskraal titaniferous magnetites. Analyses of the co-existing titaniferous magnetites were not undertaken in view of the large number of analyses required for the ilmenites and the costs involved. The complex and extremely fine-scale intergrown nature of the exsolved titaniferous magnetites investigated and the consequent difficulties involved in obtaining good, reliable analyses under these conditions also contributed to this decision. Compositional data obtained for the groundmass areas of these titaniferous magnetites would also have been of limited value in view of the complex cooling histories reflected by their microstructures as discussed in Part 1 of this thesis.

5. METHODS OF INVESTIGATION

1) Representative suites of samples were collected from each complex for detailed laboratory investigations.

2) The ores were sawn into slabs for examination under a binocular microscope in order that their macroscopic features could be observed.

3) Polished, and thin sections of suitable material were prepared for microscopic examination under both incident and transmitted light.

4) Mineral identifications were made by optical inspection and x-ray powder diffraction techniques, while the identity of certain phases was confirmed by qualitative electron microprobe analyses.

5) Representative samples were crushed to less than 200 mesh and were submitted to the Analytical Chemistry Division of NIM for analysis. TiO_2, SiO_2, Al_2O_3, Cr_2O_3, Fe_2O_3 (as total Fe) and MnO were determined by x-ray fluorescence while FeO, MgO and V_2O_5 were determined by wet chemical methods.

6) Quantitative electron microprobe analyses were made of the co-existing ilmenite grains using an A.R.L. microprobe under the supervision of Mr.E.A.Viljoen of the Mineralogy Division. The standards and operating conditions are discussed in Part 2 of this thesis.

7) Laboratory-scale benefication tests involving crushing, screening, heavy liquid-and electromagnetic-separation techniques were carried out on selected samples.

DESCRIPTIONS OF INDIVIDUAL DEPOSITS

6. ## THE TITANIFEROUS IRON ORES OF THE BUSHVELD IGNEOUS COMPLEX

Only a brief summary of the main characteristics is given here and readers are directed to papers by Wagner (1928) , Hall (1932) , Schwellnus and Willemse (1943) , Hiemstra and Liebenberg (1964) , Coertze (1966) , Willemse (1969 a,b) , Hammerbeck (1970) , Molyneux (1970 a,b) (1972) , von Gruenewaldt (1973) and Buchanan (1976) for further information. Molyneux (1970a) reported the presence of 21 titaniferous magnetite seams in the eastern Bushveld ranging in thickness from 0,12m to 10m. Numerous titaniferous magnetite plugs are also present, but, with the exception of that at Kennedy's Vale, they are generally too small for exploitation.

The economically important Main Seam ores (Table 2) are composed of large, closely packed, multi-phase titaniferous magnetite grains with minor, but very much smaller, interstitial ilmenite grains. This ilmenite accounts for only a small portion of the TiO_2 reported in the ore and the bulk of it is present as microscopic, crystallographically oriented, ilmenite and ulvospinel intergrowths that cannot be separated by mechanical means. Minor exsolved pleonaste is also present. Molyneux (1970a, 1972) reported

the increase in lamellar ilmenite in the titaniferous magnetite towards the upper seams of the complex.

The Upper Group of seams are mineralogically similar to the Main Seam, but contain a higher percentage of silicates. They are characterised by a low V_2O_5 content (0,24%) and do not represent potential vanadium ores. Their high TiO_2 content (18,2%) suggests that they might be suitable for high-TiO_2 slag production.

The Bushveld ores are extensively weathered in surface exposures and have been largely altered to titaniferous maghemites. The more highly weathered samples exhibit extensive martitisation and the concomitant development of secondary goethite that is present along cracks and forms botryoidal coatings on exposed surfaces. The original ulvospinel has been largely converted to ilmenite while the different sized ilmenite grains and intergrowths show varying degrees of alteration to leucoxene.

The total ore reserves for the Main Seam to a depth of 30m have been calculated at 1 030 million tons by Von Gruenewaldt (1977). Luyt (1976) has summarised the vanadium potential of the complex and reports proven reserves of 232 million tons with a V_2O_5 content of between 1,5 and 2,0%. Potential reserves are probably very much greater.

7. **THE TITANIFEROUS IRON ORES OF THE ROOIWATER IGNEOUS COMPLEX**

7.1 **Introduction**

The Rooiwater Igneous Complex consists of an elongated mass of metamorphosed gabbroic rocks that strike parallel to the northern margin of the Murchison Range schist belt in the north eastern Transvaal. The complex has been briefly described by Hall (1912) and van Eeden et al. (1939) and consists of a variety of rocks types ranging from coarse, hornblende-rich pegmatites, through both quartz-free and quartz-bearing gabbros to diabases. The complex is intrusive into the Murchison Range schists and has itself been intruded and partly engulfed by the Basement Granite. The gabbros are altered and have been extensively saussuritized and uralitized. Large amounts of titaniferous magnetite and apatite are present in certain zones while two parallel titaniferous magnetite seams are also developed. The seams are each approximately

8m thick and can be traced over a strike distance of more than 16 km in the eastern portion of the complex. No published age determination of the Rooiwater rocks are available, but the geological relationships suggest that they are probably more than $3,0 \times 10^9$ years old.

The titaniferous magnetite seams dip very steeply and are almost vertical in many areas. Exposures are generally poor in the area investigated, the presence of the ore-rich seams being indicated by abundant rounded residual pebbles of iron-ore rubble. The titaniferous magnetite seams are shown to terminate near the western margin of the area mapped by van Eeden et al. (1939), but the presence of a seam immediately south of Letsitele station indicates their reappearance westwards. It is conceivable that the titaniferous magnetite seams outcrop westwards for a greater distance and the abundance of magnetite surface rubble suggests that additional narrower seams are also present in the area.

7.2 Sample Localities

Samples were collected from exposures immediately south of Letsitele station on the main road to Lydenburg, on the farm Free State 763 in the Gravelotte District, and from a magnetite lens to the north of Rubbervale station. The sample localities are shown on the accompanying geological map (Map 1). The samples from the three areas differ appreciably and are referred to as the "magnetite lens", "Letsitele" and "Free State" samples.

THE ROOIWATER IGNEOUS COMPLEX

Younger Cover (undifferentiated)

Archean Schists (undifferentiated)

A G 3 Granite

A G 2 Granite

Rooiwater Granite

Rooiwater Igneous Complex

Main Roads

Sample Localities

Ⓐ Letsitele

Ⓑ Magnetite Lens

Ⓒ Free State

(AFTER THE 1:1 000 000 GEOLOGICAL MAP OF SOUTH AFRICA 1970 EDITION)
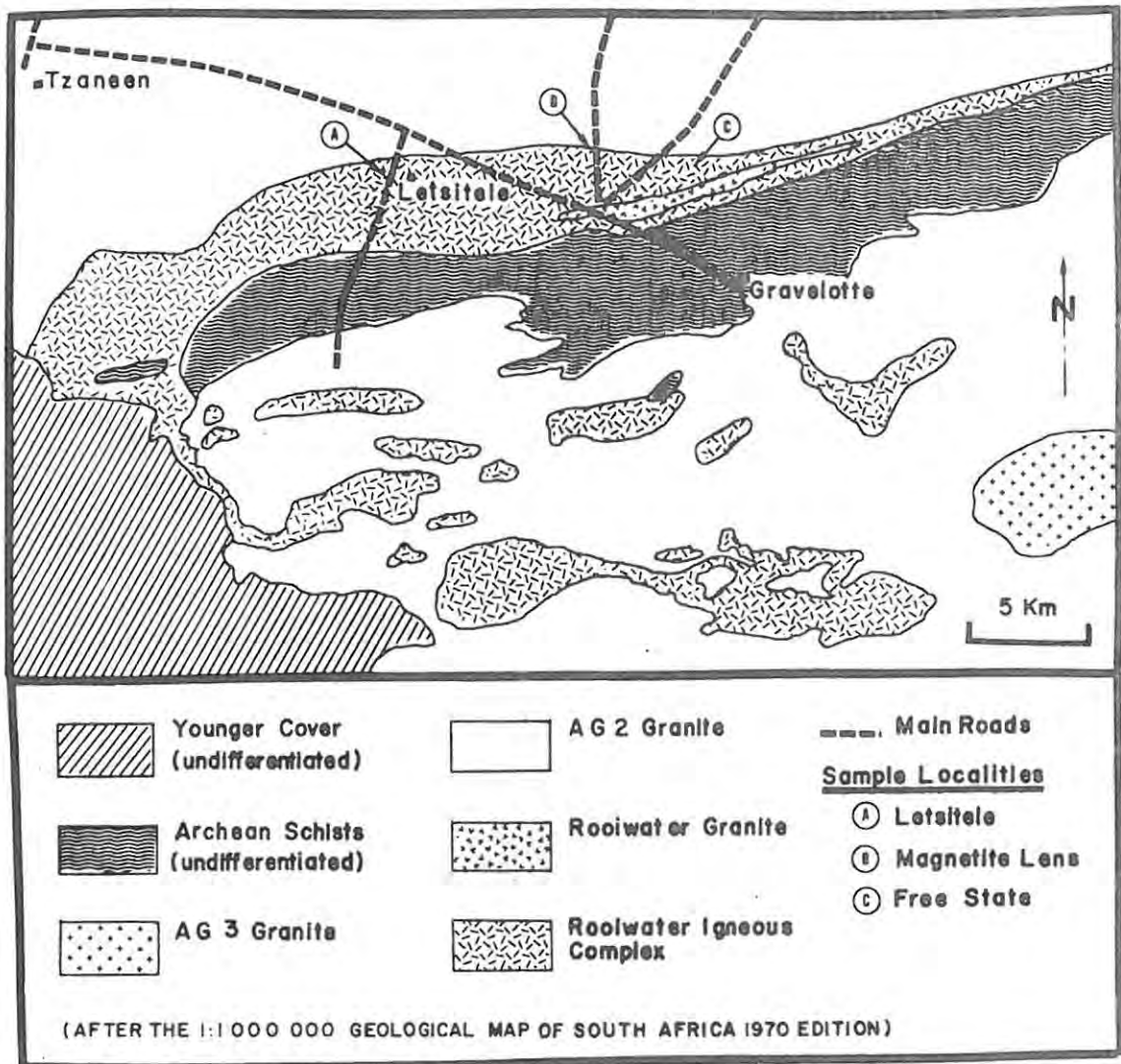
MAP 1   Sample localities in the Rooiwater igneous complex.

7.3 Description of the Ores

The two major titaniferous magnetite seams are present as massive, steeply dipping layers, each approximately 8m thick.   The ores are well jointed and relatively pure, containing only minor amounts of chloritic impurities that appear more abundant towards the top and bottom of each seam.   Minor, but variable amounts of apatite are also present.

The ores from surface exposures are moderately to highly weathered and show the development of variable amounts of secondary hematite (martite) and goethite.   They vary from black to reddish-brown in colour and are weakly to moderately magnetic.   These properties are largely dependent on their

degree of weathering, oxidation and hydration. They exhibit all gradations from relatively fresh through to completely decomposed material.

The Rooiwater titaniferous iron ores exhibit a grain size of between 2 and 4 mm and are characterised by the presence of abundant granular ilmenite. They exhibit varing degrees of recrystallisation and their exsolution processes have continued to a much greater extent than is usually encountered in ores of this nature. Their primary microstructures have been modified and their present appearance is due to the effects of a later thermal metamorphic event. The titaniferous magnetite seams are located at varying distances from the intrusive granite contact so that they have been metamorphosed to varying degrees in different areas of the complex. The ores from the three areas differ both texturally and chemically from each other and are described separately in sections 7.3.1 to 7.3.3.

7.3.1 The magnetite lens samples

Samples RW 1-8 were collected from the area to the north of Rubbervale station and marked as a "magnetite lens" on the map of van Eeden et al. (1939). This lens lies very close to the contact between the granite and the Rooiwater rocks and is isolated from the two eastern titaniferous magnetite seams by a slight southerly bulge of the intrusive granite. Direct correlation of this exposure with either of the titaniferous magnetite seams to the east is not possible on either chemical or textural grounds.

The titaniferous iron ore is present as a compact, fine-grained and well jointed rock that is composed of more than 95 per cent opaque oxides. The grain size varies between 0,5 and 1,0mm and is much finer than the other Rooiwater ores.

The ores exhibit a high degree of polygonalisation and are composed of numerous small polygonal ilmenite grains that are located interstitially between slightly larger and more abundant magnetite grains as illustrated in Plate 1 (A-E). Smaller, very much more rounded, ilmenite grains are also occasionally present and are sometimes completely enclosed by the magnetite (Plate 1(C)).

Small, elongated, lath-shaped ilmenite grains that resemble exsolution
lamellae are sparingly present in the magnetite and are often connected to
the larger interstitial ilmenite grains as illustrated in Plate 1 (A-C).
These lath-like grains are sometimes more irregular in shape and appear
to coalesce with one another to form larger grains as shown in plate 1 (D).

The larger ilmenite grains commonly contain numerous small magnetite
lamellae that are oriented parallel to their (0001) planes. These
lamellae are generally less than a micrometre in width, but may occasionally
be thicker, and are up to 40 micrometres in length. They are confined to
the central portions of the larger ilmenite grains and are absent from the
marginal areas as illustrated in Plate 1 (E and F). This lamellar
magnetite commonly shows oxidation to martite in the more weathered
samples.

Small, but variable amounts of transparent spinel are present as irregularly
shaped grains that vary between 0,05 and 0,10mm in size. Qualitative
electron microprobe analyses indicate that the spinel consists largely of
Mg, Fe and Al with only minor Mn, Ti and Cr and is close to pleonaste in
composition. The pleonaste grains are located interstitially between the
larger magnetite and ilmenite grains as illustrated in plate 1 (A-E).

Micrometre-sized lamellae of an iron-rich spinel that is close to magnetite
in composition are oriented along the (100) planes of the larger pleonaste
grains. The pleonaste shows incipient alteration to chlorite and other
clay minerals in the more highly weathered samples.

The pleonaste grains are generally located along the boundaries between
the opaque oxides and often occur together with slightly smaller euhedral
to subhedral apatite, and lath-shaped chlorite grains. These three
minerals commonly contain small rounded inclusions of ilmenite, and more
rarely, magnetite.

The magnetite that forms the dominant phase in the "magnetite lens"
samples is generally optically homogeneous and free from fine-grained
intergrowths other than those already mentioned, even at the highest
magnificiation (approximately 2000X, oil immersion). This magnetite
shows varying degrees of oxidation to martite that commences at grain
boundaries and moves inwards along the octahedral planes of the magnetite

PLATE 1

Rooiwater Titaniferous Iron Ores

All photomicrographs taken in incident light using oil immersion objectives.

A) Magnetite lens : Typical sample containing abundant polygonal ilmenite (dark grey) distributed interstitially between larger grains of magnetite showing extensive martitization (lighter grey and mottled). Small amounts of chlorite, transparent spinel and apatite are present (black).

B) Magnetite lens: Portion of the same field in (A) under higher magnification showing the martitization (light) of magnetite (medium grey) and the nature of the ilmenite grains (dark grey). Small numbers of ilmenite lamellae are also present. Spinel and chlorite are black.

C) Magnetite lens: Relict ilmenite lamellae in a large magnetite grain near centre of field. Incipient martitization (light) is developed along fractures and grain boundaries.

D) Magnetite lens: Similar to (C), but the relict ilmenite lamellae exhibit more irregular shapes.

E) Magnetite lens: Completely recrystallised ore consisting of polygonal ilmenite grains (dark grey) and magnetite showing incipient martitization. Spinel grains are sub-hedral (black).

F) Magnetite lens: Grain boundary relationships between co-existing ilmenite grains. Note the sparse magnetite lamellae in the top right-hand and bottom left-hand grains.

G) Free State seam: Relict microstructures in titaniferous magnetite core (dark grey) containing exsolved transparent spinel (black). Outer portions of the magnetite are now martite (light) revealing the presence of abundant ilmenite trellis lamellae. Small ilmenite grains towards top left-hand corner (dark grey).

H) Free State seam: Martitized titaniferous magnetite with well defined ilmenite trellis networks (dark) showing considerable variation in size. Numbers of short, stumpy spinel intergrowths are also present (black). Note the large ilmenite grain on the left-hand side (dark grey).

PLATE 1

2,0 mm
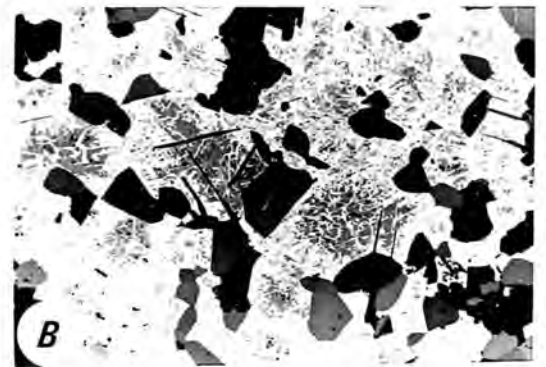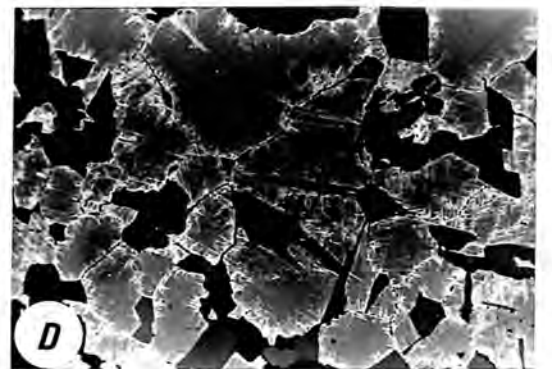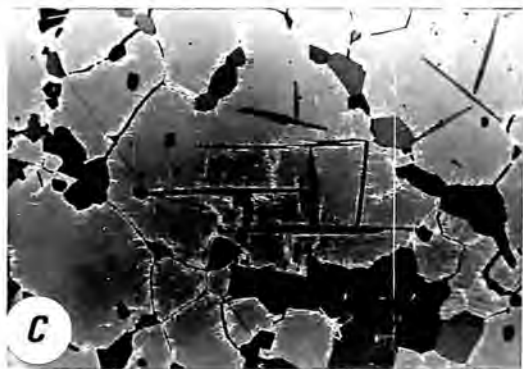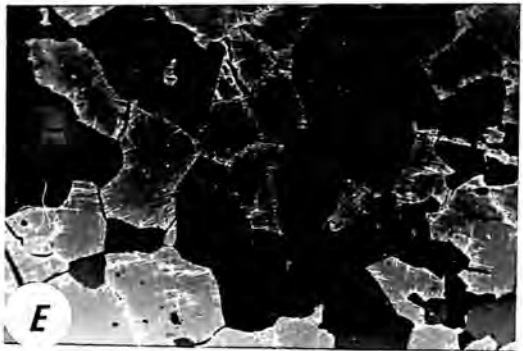
1,0 mm

1,0 mm

1,0 mm
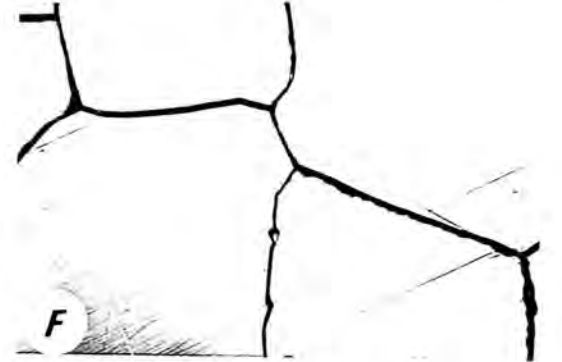
0,25 mm
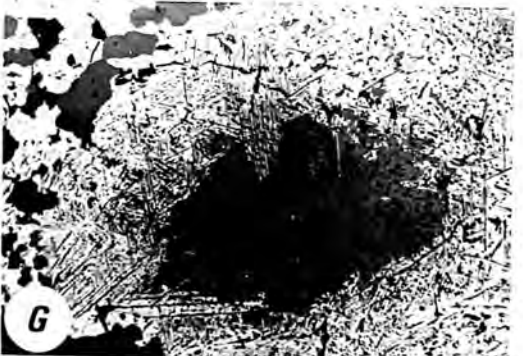
0,5 mm

0,25 mm

as illustrated in Plate 1 (A-E). The martitization takes place directly without the formation of intermediate maghemite.

These ores have been extensively recrystallised and exhibit none of the usual microstructural features typical of titaniferous magnetites from slowly cooled basic rocks. The degree of recrystallisation and polyonalization varies slightly between the samples examined resulting in minor microstructural differences. Occasional irregular and lath-shaped ilmenite grains are present in some samples (Plate 1 (A-D)), while they are virtually absent from others (Plate 1 (E)). The samples that do not contain the irregular and lath-shaped ilmenite grains exhibit an overall granoblastic polygonal texture with straight to slightly curved grain boundaries that meet in well defined triple points. The ilmenite grains exhibit a close approximation to equilibrium conditions (Plate 1 (F)). The spinel and apatite are also generally more euhedral in the more highly recrystallised samples.

7.3.2 The Free State samples

Samples RW 9-25 were collected from a thick titaniferous magnetite seam on the farm Free State 763 and from iron-ore rubble in the same area that might have been derived from other narrower and more poorly exposed seams. Field relationships are somewhat obscure, but this material appears to represent the northernmost seam mapped by van Eeden et al. (1939) and is the lowermost major titaniferous magnetite seam exposed in that part of the complex.

The titaniferous magnetite seam in this area is a massive, well jointed and steeply dipping body approximately 7m thick. Its central portion consists almost entirely of iron-titanium oxides, but it becomes increasingly chlorite-rich towards its upper and lower contacts. The chlorite is present in variable amounts reaching a maximum of about 15 per cent and is located interstitially between the larger opaque oxides. The chloritic material exhibits a preferred orientation and is commonly segregated into narrow bands that alternate with bands of more massive, silicate-poor ore. The chlorite-bearing ores consequently display a sheared and slightly schistose appearance.

The massive, chlorite-poor ores have a grain size that varies between 2 and 3mm, but the chlorite-rich zones display a wider range of grain sizes.

The opaque oxide grains in the chlorite-rich areas are generally smaller
than 1mm in size and are commonly fractured and slightly sheared.   The
residual titaniferous iron ore rubble in the surrounding area is
generally of the chlorite-poor, massive type and is similar to material
from the massive portion of the 7m thick seam.

The Free State samples exhibit a much greater textural variation than the
ores from the magnetite lens and are generally much coarser grained.
There is also a marked variation in microstructural development, not only
between adjacent samples, but also over very short distances, down to the
scale of a microscope field as illustrated in Plates 1 (G), (H) and 2
(A-F).

The ores are composed of large,multi-phase titaniferous magnetite grains
and smaller, polygonal ilmenite grains.   Minor, but variable, amounts of
chlorite, pleonaste, and apatite are also present and are generally
located along the grain boundaries between the very much larger opaque
oxides.   A wide range of microstructures are developed in the titaniferous
magnetites and they differ from those normally encountered in these minerals
from plutonic basic intrusions.   They have been modified by variable amounts
and illustrate successive stages in the continued exsolution and
recrystallisation of these minerals beyond that which occurs during their
normal slow cooling.   The modification of the primary microstructures is
an essentially continuous process and all possible gradations between the
different textural types are present, often over a distance of only several
millimetres.   The microstructures are divided into four types for
descriptive purposes and are dealt with in sections 7.3.2.1 to 7.3.2.4.

7.3.2.1 Relict microstructures

Microstructures displaying only incipient modification are preserved
locally and indicate the possible nature of the primary titaniferous
magnetite microintergrowths.   They are confined to small areas near the
centres of large titaniferous magnetite grains that exhibit greater degrees
of modification towards their margins as illustrated in Plate 1 (G).

The relict microstructures consist of well-developed trellis networks
of fine ilmenite lamellae that are oriented parallel to the octahedral
planes of their magnetite hosts.   The lamellae are generally between 2
and 4 micrometres wide and are up to 30 micrometres long.   Larger and
more sparsely distributed ilmenite lamellae are also occasionally present

but in insufficient numbers to form trellis networks.

A portion of the smaller ilmenite lamellae have the appearance of typical oxidation/exsolution lamellae, but others are slightly broader than usual in relation to their length as illustrated in Plate 2 (A-C). These lamellae often coalesce with their neighbours, especially at places where they intersect and form larger, more irregularly-shaped grains. They exhibit complex morphologies and commonly pinch and swell along their lengths. The lamellae sometimes vary in thickness over a short distance, but this might be due, in part, to orientation effects that arise when the magnetite octahedral planes intersect the polished section surface at small angles.

Short, stumpy, crystallographically oriented pleonaste laths are also present along the cubic planes of the magnetite hosts as illustrated in Plates 1 (G,H) and 2 (A). They are also wider in respect to their length than usual and commonly coalesce to form larger, more irregularly-shaped grains. The spinels are generally between 1 and 3 micrometres wide and are up to 15 micrometres long. The pleonaste laths are often developed along only one of the magnetite cubic planes and form a linear or "sandwich" pattern instead of their normal grid-like arrangement. The relationships between the pleonaste laths and ilmenite lamellae are complex as shown in Plate 2 (A). The spinel grains cut across the ilmenite lamellae in some areas, but in others, often within the same microscope field, they are themselves cut by transgressive ilmenite lamellae.

The magnetite between the ilmenite lamellae is optically homogeneous and free from inclusions other than spinel, even at the highest magnification (approx. 2000X oil immersion). Oxidation of the homogeneous magnetite to martite takes place directly along its octahedral planes and progresses inwards from grain boundaries and fractures. The crystallographic orientation of the tiny pleonaste lamellae becomes disrupted during martitization and they are not as abundant in the oxidised areas (Plate 1 (G)). The pleonaste intergrowths in the martitized areas are also more equant than lath-shaped, but the size, shape and orientation of the ilmenite lamellae remains unaltered.
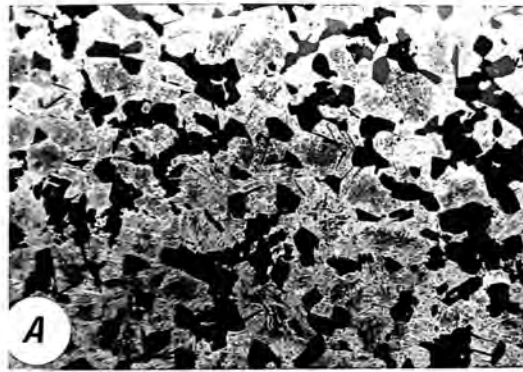
PLATE 2

Rooiwater Titaniferous Iron Ores

All photomicrographs taken in incident light using oil immersion objectives.

A) Free State seam :   Slightly modified ilmenite trellis network
(dark grey) in martitized titaniferous
magnetite (light). Transparent spinel
exsolution bodies (black) are oriented
parallel to (100) of their host. Small
triangular areas of unoxidised magnetite
(grey) are present between the ilmenite
lamellae.

B) Free State seam :   Similar to (A) but with ilmenite lamellae
(dark grey) showing greater modification.
Transparent spinel absent.

C) Free State seam :   Slightly modified ilmenite lamellae
developed on a coarse scale. The
differences in colour intensity of the
3 sets is due to reflection pleochroism.
Incipient martitization of the magnetite
is also noticeable. Transparent spinel
grains (black) have become more equant and
show evidence of segregation into elongated
granular clusters.

D) Free State seam: Moderately modified ilmenite lamellae (dark)
showing characteristic thickening, coalescence
and blunt terminations in martitized magnetite matrix.

E) Free State seam :   Highly modified microstructure consisting of a
large central grain of titaniferous magnetite
containing abundant lamellar ilmenite and
surrounded by granular aggregates of magnetite,
ilmenite (dark) and chlorite (black).

F) Free State seam :   Similar to (E) showing the typical granular
appearance of the highly modified microstructures.

G) Letsitele seam :   Irregular ilmenite (grey) and spinel (black) set
in a matrix of martitized magnetite. Note the
morphology of the lamellar ilmenite.

H) Letsitele seam :   Typical appearance of the symplectite-like ilmenite
intergrowths showing variable size ranges and
orientation in at least 3 crystallographically
controlled directions.

PLATE 2

0,015 mm

0,08 mm
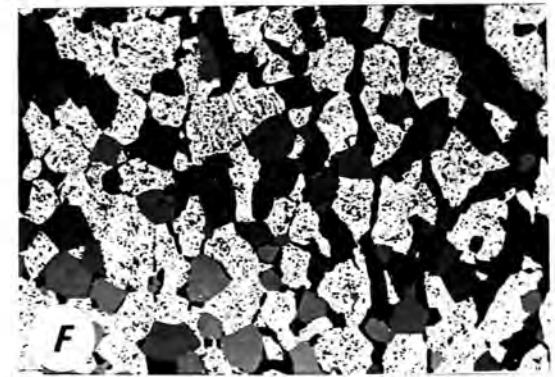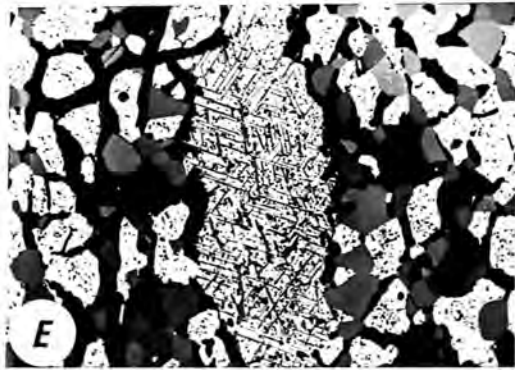
1,0 mm
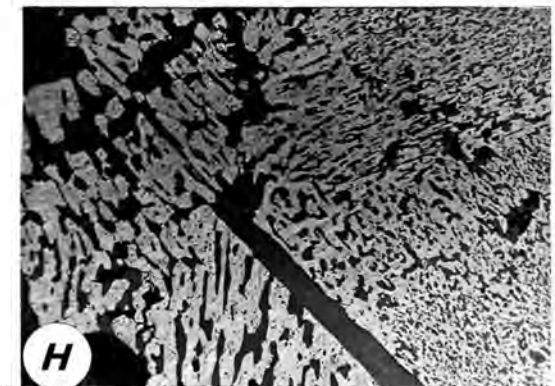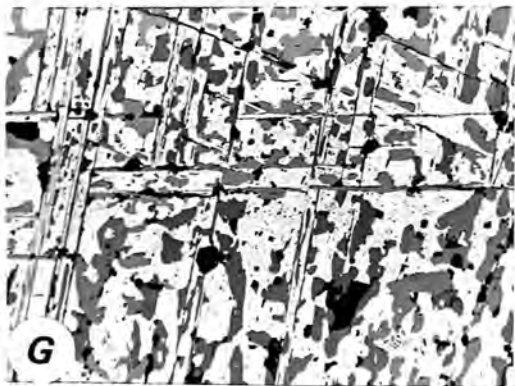
0,15 mm

7.3.2.2 Slightly modified microstructures

These microstructures are characterised by well developed lamellar ilmenite trellis networks in the titaniferous magnetites that vary considerably in size over short distances, even on the scale of the width of a microscope field as illustrated in Plate 1 (H). The lamellae show evidence of coarsening and are typically thicker than usual in relation to their length. They are up to 10 micrometres wide, but are generally less than 50 micrometres long and have coalesced in places to form larger, irregularly-shaped grains.

The pleonaste is not present as lamellae, but forms larger, more equidimensional grains. A small amount of the pleonaste replaces portions of the ilmenite lamellae, particularly at the intersection of two differently oriented lamellae as illustrated in Plate 1 (H). The magnetite forming the groundmass in which the ilmenite and pleonaste are developed is optically homogeneous and free from other finer-grained inclusions.

7.3.2.3 Moderately modified microstructures

These microintergrowths are the most widely developed types in the titaniferous magnetites from the seam in this area. The ilmenite lamellae are very much larger than those in the other two microstructural types and are also oriented along the octahedral planes of their hosts. They vary between 0,01 and 0,02mm in width and 0,1 to 0,8mm in length and form well defined, but wider spaced trellis networks. They are generally very much thicker than normal in relation to their length and terminate abruptly without tapering. Their thickness is variable and they rarely exhibit straight grain boundaries (Plate 2 (D)).

Numerous micrometre-sized, rounded ilmenite and sub-angular pleonaste grains are present in the optically homogeneous magnetite between the closer-spaced ilmenite lamellae. The areas between the coarser-and wider-spaced lamellae contain finer, originally lamellar microintergrowths, that have been considerably disrupted. These ilmenite lamellae are no longer as continuous and well defined as before, but thicken, coalesce, and pinch out. In the more extreme cases, the ilmenite lamellae are virtually absent and have been replaced by numbers of irregularly-shaped ilmenite grains that vary between 0,01 and 0,2mm in size. These grains are typically present in clusters or form stringers with similar-sized pleonaste grains within their magnetite hosts. Stringers of these

grains are also present along the titaniferous magnetite grain boundaries.

The small ilmenite grains exhibit a moderate degree of polygonalization at places where they are in contact with other ilmenite grains in the clusters. Their interfacial angles tend towards 120°, but complete equilibrium is rarely attained. The isolated grains exhibit more rounded or elongated morphologies when surrounded by magnetite, but have relatively straight interfaces with their neighborouring pleonaste grains.

The pleonaste microintergrowths have also lost their former lath-like habit and are more equant or irregularly shaped. They exhibit a variable distribution, being relatively abundant in the areas of fine ilmenite trellis networks, but less common in the areas between the larger, wider-spaced ilmenite lamellae. The pleonaste grains in these areas appear to have segrated to form larger-sized grains that are associated with the ilmenite clusters and stringers. A lesser amount of pleonaste is present as smaller grains that are located along the interfaces between the intergrown ilmenites and their magnetite hosts.

7.3.2.4 Highly modified microstructures

These microstructures are developed only in samples that contain more than 10 per cent chlorite and are characterised by the appearance of numerous small rounded to polygonal ilmenite grains. These ilmenites vary between 0,02 and 0,1mm in size and are generally separated from each other and similarly sized, but more irregularly shaped magnetite grains, by a thin veneer of chlorite as illustrated in Plate 2 (E and F). The small magnetite grains contain numerous small, equant pleonaste grains, but granular or lamellar ilmenite is generally absent. Occasional, very much larger, elongated magnetite grains containing modified ilmenite lamellar intergrowths are also present amongst the smaller grains as illustrated in Plate 2 (E). The margins of these larger grains are highly irregular and some dissolution of the magnetite has occurred so that the ilmenite lamellae extend beyond the magnetite grain boundaries into the chlorite. Minor amounts of very fine-grained sphene are occasionally intergrown with the chlorite in these areas. The ore has a brecciated appearance and a preferred orientation has developed in the chlorite-rich areas. The larger magnetite grains appear to be the remains of pre-existing large titaniferous magnetites that were fractured to yield the numerous small, irregularly shaped grains.

7.3.2.5 Coarse grained ilmenite

The ores from the Free State area contain between 10 and 15 per cent of coarse granular ilmenite irrespective of the type of microstructure developed. The grains vary between 1 and 2mm in size and are located interstitially between the larger titaniferous magnetite grains. They generally exhibit irregular grain boundaries and numbers of small pleonaste grains are typically located along their interfaces with titaniferous magnetite as illustrated in Plate 1 (G) and (H).

The large ilmenite grains are normally surrounded by a narrow zone of ilmenite-free magnetite, and are occasionally connected to some of the larger ilmenite lamellae. Small polygonal ilmenite grains displaying different crystallographic orientations are occasionally present in clusters around the peripheries of the larger ilmenite grains.

Small numbers of magnetite platelets are characteristically present along the basal planes of these ilmenites. They are normally less than a micrometre wide and are between 10 and 20 micrometres long. They have the appearance of exsolution lamellae and are confined to the central portions of the larger ilmenite grains. These magnetite lamellae are generally martitized in the more highly weathered ores.

The large ilmenite grains occasionally display a poorly developed lamellar twinning that is present in two directions. Micrometre-sized tabular magnetite bodies are developed at places where the two sets of twin lamellae intersect. The crystallographically oriented magnetite lamellae described above are deflected across twin boundaries and display a different orientation.

7.3.3 The Letsitele samples

Samples RW 26-42 were collected from exposures approximately 300m south of Letsitele station on the main road to Lydenburg. This is the stratigraphically highest major seam in that part of the complex and is more than 5m thick, although the upper and lower contacts are not exposed. A 0,3m thick seam (RW 26-28) is present approximately 10m below the +5m thick seam while titaniferous iron ore rubble (RW 43) is present 150m further to the south of the main outcrop and probably indicates the presence of another narrow seam.

The Letsitele ores are characterised by the presence of abundant coarse granular ilmenite. These ilmenite grains vary between 1 and 2mm in size and are located interstitially between titaniferous magnetite grains that are generally 2 to 3 times larger. The ores exhibit a high degree of polygonalization and the opaque oxide grain boundaries are gently curved with interfacial angles that approximate 120°.

The ilmenite and titaniferous magnetite grains are generally in direct contact with each other, but a thin chloritic veneer is developed between them in certain areas of the seam.

The granular ilmenite content varies between 15 and 20 per cent, but may locally reach as high as 30 per cent. The larger ilmenite grains occasionally show the development of lamellar twinning and contain small numbers of crystallographically oriented magnetite platelets.

The titaniferous magnetites exhibit microstructures that differ from those developed in the areas already described. The bulk of the grains contain complex myrmekite-like intergrowths of small, rounded, elongated ilmenite grains set in a groundmass of optically homogeneous magnetite as illustrated in Plates 2 (G-H) and 3 (A-H). They display a considerable size range, even over very short distances, as illustrated in these plates. They vary between several micrometres and 0,05mm in size and exhibit a variety of external morphologies that range from roughly lamellar through flame-like forms, to more rounded shapes.

The ilmenite intergrowths are also crystallographically oriented parallel to the octahedral planes of their titaniferous magnetite hosts, even though they are more irregularly shaped than the usual lamellae. Groups of similarly oriented intergrowths are commonly optically continuous over large areas up to 1mm across. These sets of optically continuous grains have a three-fold axis of symmetry with respect to each other and are oriented at approximately 120° to one another. This orientation corresponds to the octahedral planes of their hosts and the effect can be clearly seen by rotating the microscope stage under crossed nicols. The groups of optically continuous grains commonly exhibit a preferred orientation parallel to the plane in which they are located as illustrated in Plate 2 (H).

PLATE 3

Rooiwater Titaniferous Iron Ores

All photomicrographs taken in incident light using oil immersion objectives.

A) Letsitele seam : Typical appearance of myrmekite-like intergrowths
of ilmenite (dark) in martite (light). Note the
transgressive veinlet of optically homogeneous
magnetite, cutting diagonally across the left-
hand side of the photomicrograph.

B) Letsitele seam : Similar to (A), but showing the development of a
mesh-like array of ilmenite grains towards the
top right-hand corner.

C) Letsitele seam : Similar to (A), but showing the development of
stringers of small polygonal ilmenite (grey)
and spinel (black) grains.

D-H) Letsitele seam : A series of photomicrographs illustrating the
progressive breakdown and spheroidization of
originally lamellar ilmenite intergrowths. The
ilmenite exhibits various shades of grey due to
the slight reflection pleochroism characteristic
of this mineral. Small rounded grains of
transparent spinel (black) are also present.

PLATE 3
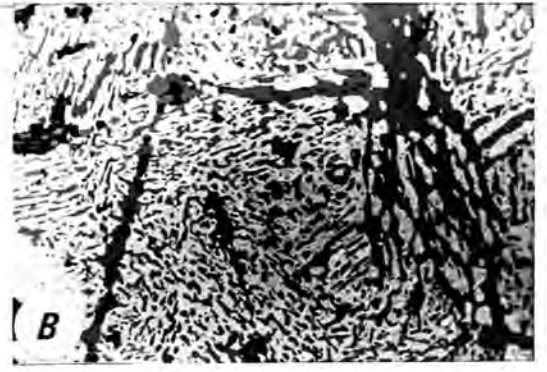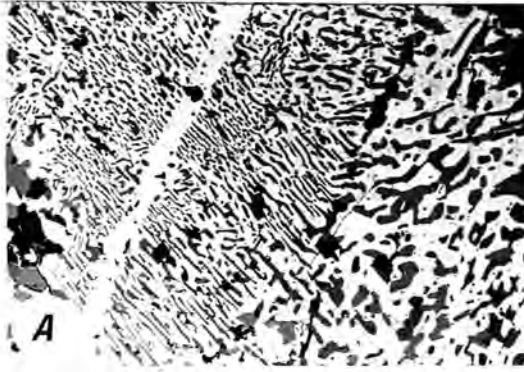
0,15 mm
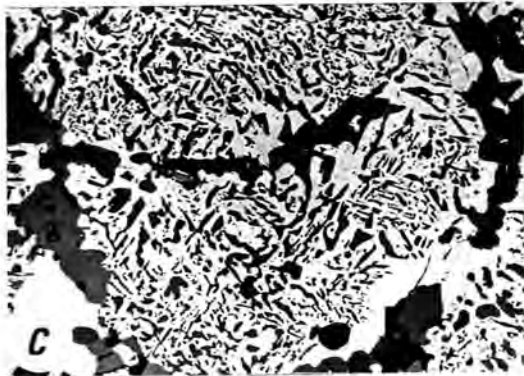
0,15 mm   0,07 mm

0,07mm

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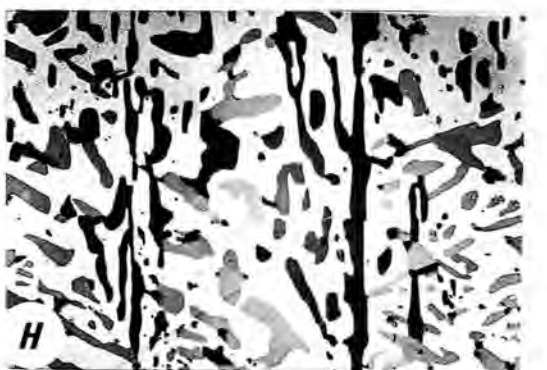
Relict ilmenite lamellae are rare and when present they commonly display
all stages of transformation into more rounded grains as illustrated in
Plate 2 (G). The lamellae retain their original orientation along the
magnetite octahedral planes, but become progressively shorter and wider
until they have broken down completely and have been transformed into rounded
grains. The progressive nature of this process is illustrated in Plates
3 (D) through to 4 (C).

The larger ilmenite intergrowths are commonly surrounded by a narrow
zone of ilmenite-free magnetite as illustrated in Plate 3 (C). They
appear to have formed from the coalescence of numbers of smaller grains
in certain areas and display evidence of polygonalization. The larger
grains are also more widely spaced than the smaller ones and are commonly
arranged in stringers along grain boundaries or gently curved zones within
their titaniferous magnetite hosts. In contrast, these grains occasionally
form mesh-like bodies composed of numerous polygonal ilmenite grains that
enclose areas of magnetite as illustrated in Plate 3 (B).

The appearance of the finer ilmenite intergrowths are illustrated in Plate
4 (D). The grains illustrated are all in optical contimuity and many of
them are connected at the level shown in the photomicrograph. They exhibit
an overall preferred orientation, but are much more irregularly shaped than
the usual lamellar intergrowths that they have been derived from. They
exhibit all intermediate stages in a continuous breakdown and spheriodization
process that ultimately results in larger, and more rounded forms such as
those illustrated in Plate 4 (C).

Small, irregular shaped pleonaste grains are randomly distributed within
the titaniferous magnetite and are present in stringers along the opaque
oxide grain boundaries. They also vary between several micrometres and
0,5mm in size and are commonly associated with the ilmenite intergrowths
as illustrated in Plates 2 (G and H) and 3 (A-D). There is a sympathetic
relationship between the size of the pleonaste intergrowths and the size
of their associated ilmenite grains. The larger pleonaste grains also
appear to have grown at the expense of numbers of smaller grains and show
evidence of polygonalization.

The magnetite between the ilmenite and pleonaste grains is optically
homogeneous and free from other very fine-grained intergrowths. It

PLATE 4

Rooiwater Titaniferous Iron Ores

All photomicrographs taken in incident light using oil immersion objectives.

A-C) Letsitele seam : Continuation from plate 3 (H) showing the final stages of progressive spheriodization of original ilmenite lamellae. Note the presence of well-defined martite lamellae (light) in Plate 4 (C).

D) Letsitele seam : The detailed appearance of the finer-grained ilmenite intergrowths (dark) showing their morphologies and mutual relationships.

E) Rooiwater meta-gabbros : A cluster of hemo-ilmenite grains showing irregular outlines. Minor titaniferous magnetite is present (small, slightly lighter grains).

F) Rooiwater meta-gabbros : A corroded ilmenite grain (light) showing the development of sphene around its periphery.

G) Rooiwater meta-gabbros : Triangular pattern of ilmenite grains (white) set in a silicate (hornblende) matrix that possibly represent the ilmenite "skeleton" of a pre-existing titaniferous magnetite grain.

H) Rooiwater meta-gabbros : Similar to (G), but showing numbers of small ilmenite rodlets in the silicate matrix adjacent to a larger ilmenite grain (white).

PLATE 4

A

B

0,07 mm

C

0,07 mm

D

0,015 mm

E

1,0 mm

F

0,07 mm

G

H
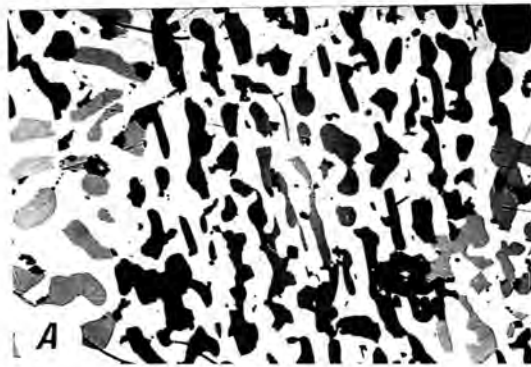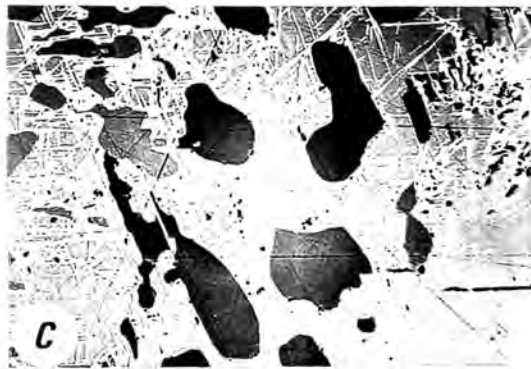
0,07 mm

oxidises directly to martite along its octahedral planes without the
formation of intermediate maghemite as allustrated in Plate 4 (C).
Narrow transgressive veinlets of later, inclusion-free, magnetite
occasionally cut across the samples as illustrated in Plate 3 (A).

7.3.4 Weathering of the Rooiwater titaniferous iron ores

The ores typically exhibit varying degrees of secondary oxidation and
hydration due to near-surface weathering processes that have resulted
in the formation of abundant martite, goehite, secondary hematite,
leucoxene and minor amounts of lepidocrocite.   The degree of alteration
is highly variable and irregularly distributed throughout the ore, being
related to the proximity of grain boundaries, fractures, joints, exposed
surfaces and other permeable features.   All possible gradations between
relatively fresh and completely decomposed materials are found in the
Rooiwater ores.

The weathering process is progressive and commences with the oxidation
of the titaniferois magnetite.   Martite oxidation lamellae are formed
along grain boundaries and fractures and migrate into the titaniferous
magnetite grains along their octahedral planes as illustrated in Plates
1 (C-E).   These lamellae increase in size as oxidation proceeds and
penetrate further into the magnetite.   They ultimately coalesce to form
large continuous areas of martite that commonly contain small triangular
"islands" of unoxidised magnetite.   The partially oxidised titaniferous
magnetites generally have unaltered cores and are surrounded by martite
zones of varying width as illustrated in Plates 1 (A), (B) and (G).

The martite formation takes place directly without the production of
intermediate titaniferous maghemite.   The larger-sized microstructures
are preserved in the martized areas, but the finer ones, particularly
the small pleonaste lamellae, become disrupted during the martitization
process.   The martite becomes hydrated and is in turn altered to
goethite as weathering proceeds.

Volume-changes associated with the titaniferous magnetite oxidation
commonly result in fracturing of the ores and goethite becomes
precipitated along the fractures to form transgressive veinlets.   The
goethite veinlets commonly display delicately banded, oolloform
textures and show the local development of secondary hematite.   Botryoidal
goethite coatings are also commonly developed along open joints and on
exposed surfaces.

The pleonaste grains are variably altered to fine reddish-brown aggregates of chlorite and clay minerals in the more highly weathered samples. The ilmenite shows varying degrees of alteration to leucoxene at grain boundaries and along fractures. This alteration proceeds into the grains in an irregular manner and results in the formation of amorphous TiO_2 products and poorly-crystalline anatase.

7.4 Ilmenite and Apatite in the Rooiwater Basic Rocks

van Eeden et al. (1939) reported the presence of appreciable apatite and magnetite concentrations in certain zones in the Rooiwater Igneous Complex. The metagabbros in the vicinity of the titaniferous magnetite seams were investigated and contain variable amounts of opaque oxides and apatite, the highest concentrations being noted in samples collected immediately south of the magnetite lens.

The metagabbros immediately south of the magnetite lens are composed of hornblende, andesine and opalescent blue, rutilated-quartz together with accessory ilmenite, titaniferous magnetite and apatite. The ilmenite is generally very much more abundant that the titaniferous magnetite and is present as large, irregularly-shaped grains that vary between 1 and 2mm in size. The ilmenite is generally present in amounts between 5 and 10 per cent, but may locally reach 15 to 20 per cent.

The ilmenite grains commonly exhibit corroded, cuspate outlines and are often surrounded by narrow reaction rims of chlorite and sphene or hornblende (Plates 4 (E and F)) hematite, and more rarely, magnetite. Narrow platelets are oriented along their basal planes and are more abundant than the magnetite bodies in the granular ilmenites of the ores. These ilmenites also occasionally exhibit lamellar twinning.

Numerous very much smaller, rod-shaped ilmenite grains that are generally arranged in an intersecting triangular pattern are often present in the silicates in the vicinity of the larger ilmenite grains. They are often set in a fine-grained matrix of sphene and chlorite and represent the ilmenite "skeletons" of completely altered exsolved titaniferous magnetite grains. These ilmenite networks are more rarely enclosed in hornblende and also exhibit slightly corroded embayed outlines (Plates 4 (G and H)).

Titaniferous magnetite is generally present in only minor amounts and

is largely altered to sphene and chlorite aggregates. The unaltered grains exhibit a fine, well developed ilmenite trellis network similar to that described in section 7.3.2.2. The surviving titaniferous magnetite grains are generally completely martitized, most probably as a result of near-surface weathering processes.

Apatite is present in the metagabbros as small hexagonal prisms and locally reaches concentrations of up to 4 per cent. The grains range in size from 0,1 to 0,5mm and are present in the silicate matrix as well as being associated with ilmenite. Euhedral apatite inclusions are commonly present in the larger ilmenite grains (Plate 5 (A)). The apatite was not analysed, but is most probably the normal fluorapatite that is associated with basic igneous rocks and should be similar to the apatites in the Skaergaard complex (Brown and Peckett, 1977).

The metagabbros decompose on weathering to produce a deep clay-rich soil that contains abundant ilmenite. This ilmenite is identical to that occurring in the underlying rocks, but is generally more highly altered. The alteration commences around the periphery of the grains and moves inwards along fractures and other permeable features and results in the formation of anatase and other poorly crystalline TiO_2-rich products that are known collectively as leucoxene. Large amounts of ilmenite are present in the Rooiwater soils, particularly in the vicinity of ilmenite-rich zones. In contrast, the titaniferous magnetite content of the soil is low, reflecting in part the low magnetite content of the metagabbros and its more rapid decomposition under weathering conditions.

7.5 Sulphides in the Rooiwater Ores

Pyrite, chalcopyrite and pyrrhotite are present in very minor amounts in the Rooiwater ores. They are almost always in the form of small, rounded, droplet-like grains that are completely enclosed by the larger, coarse grained ilmenites. The droplets vary in size from several micrometres up to 0,03mm, but are usually less than 10 micrometres across. The pyrite grains occasionally exhibit euhedral outlines and are also generally larger than the other sulphides (Plate 5 (B)).

The sulphides are only rarely present in the titaniferous magnetite groundmass where they are generally associated with smaller ilmenite grains or lamellae. Sulphides are notably absent from the martitized areas, having been oxidised and hydrated to form goethite. Goethite

pseudomorphs of sulphide grains are sometimes recognisable and their apparent paucity might be a result of their destruction during weathering.

7.6 The Chemical Composition of the Rooiwater Ores

The chemical compositions of typical Rooiwater ores are given in Table 3 together with several analyses from the literature. The Free State and Letsitele samples can be readily distinguished between on the basis of their TiO_2 and V_2O_5 contents. The variation in bulk chemical composition of the titaniferous magnetite ores with increasing height in the Free State and Letsitele seams is illustrated graphically in Figure 1.

The Free State samples were collected from the lowermost seam in the complex and are characterised by moderate TiO_2 (14,4–15,1%), and relatively high V_2O_5 values (1,3–1,4 %). They also contain a significant amount of Cr_2O_3 that reaches an anomalously high value of 1,39% approximately 2 metres above the base of the seam. No chromite is present in the samples and it is concluded that the Cr_2O_3 is in solid solution in the titaniferous magnetite and possibly in one of the intergrown phases.

The composition of sample RW 17 differs slightly from the other Free State analyses, in that it shows lower V_2O_5 and Cr_2O_3 values and higher Al_2O_3 and SiO_2 contents. These chemical differences also suggest that this sample is derived from a minor, poorly exposed seam that is stratigraphically higher than the thick Free State seam in this area.

The Letsitele samples correspond to the southernmost seam of van Eeden et al. (1939), and represent material from the uppermost thick seam in the complex. They are characterised by high TiO_2 (20,8–24,6%) and low V_2O_5 contents (0,76, 0,86%). They also differ from the Free State samples in that they contain virtually no Cr_2O_3 (less than 0,05%). They also exhibit marginally higher MnO and lower MgO contents.

The majority of samples from both areas contain only minor silicate impurities as reflected by the low SiO_2 values reported in the analyses. The variation in SiO_2 and Al_2O_3 can be correlated directly with variations in the amounts of silicate and pleonaste in the samples. Portion of the MgO is also present in the silicate impurities (largely chlorite) as shown by sample RW 17. This contains 7,46 % SiO_2, 6,37 % Al_2O_3, 1,75 % MgO, but the removal of the bulk of the silicates during benefication has reduced these values to 1,67 % SiO_2, 1,66 % Al_2O_3 and 0,32 % MgO (Table 7).

TABLE 3

ANALYSES OF ROOIWATER TITANIFEROUS IRON ORES

	FREE STATE SAMPLES								LETSITELE SAMPLES					MT. LENS	♣	+	♣	x
	RW 17	RW 18	RW 19	RW 20	RW 22	RW 23	RW 24	RW 25	RW 27	RW 32	RW 33	RW 37	RW 40	RW 2	Ke 53	R26	R11	M22
SiO_2	7,42	1,78	2,92	1,53	3,18	4,67	3,60	2,26	2,66	2,21	1,09	1,72	0,64	2,09	1,25	2,47	2,02	0,36
TiO_2	15,20	14,62	14,93	14,42	14,66	14,48	14,64	15,14	20,83	21,52	22,30	21,20	24,57	12,23	18,40	16,00	13,00	14,84
Al_2O_3	6,37	2,68	2,34	2,90	2,13	1,37	1,64	1,23	3,83	4,08	3,71	3,93	3,07	6,12	2,72	3,14	4,31	3,25
Cr_2O_3	0,22	0,80	1,19	1,39	0,51	0,46	0,47	0,45	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	trace	0,02	0,33	0,08
Fe_2O_3	54,06	66,05	61,82	65,34	63,23	66,02	66,45	74,00	48,37	52,00	50,50	36,60	35,20	55,11	66,70	69,47	73,78	43,37
FeO	13,76	11,09	14,00	11,59	14,78	11,71	11,83	5,58	22,50	17,06	20,57	33,92	34,20	22,97	8,77	5,75	2,59	35,92
MnO	0,17	0,21	0,18	0,19	0,20	0,22	0,18	0,14	0,32	0,27	0,30	0,28	0,32	0,19	0,23	0,23	0,15	0,26
MgO	1,75	0,60	0,86	0,42	0,67	0,41	0,67	0,27	1,68	2,34	1,12	2,00	1,62	1,78	1,07	0,67	0,78	1,53
V_2O_5	1.08	1,41	1,37	1,32	1,32	1,33	1,32	1,35	0,80	0,84	0,80	0,86	0,76	0,86	0,82	0,70	1,30	0,80
TOTAL :	100,03	99,24	99,61	99,10	100,68	100,67	100,80	100,42	100,99	100,32	100,39	100,51	100,38	101,35	99,96	98,45	98,26	100,41
TOTAL Fe :	48,51	54,82	54,12	54,70	55,71	55,28	55,67	56,10	51,32	49,63	51,31	51,96	51,20	56,40	53,47	53,06	53,61	58,25

♣ Analysis of ore from the southernmost seam of the Rooiwater complex (van Eeden et al., 1939).

+ Analysis of ore from the middle group of seams, Bushveld Igneous Complex (Schwellnus and Willemse, 1943).

♣ Analysis of ore from the lower group of seams, Bushveld Igneous Complex (Schwellnus and Willemse, 1943).

y Analysis of ore from seam 11, Bushveld Igneous Complex (Molyneux, 1970a, 1972).
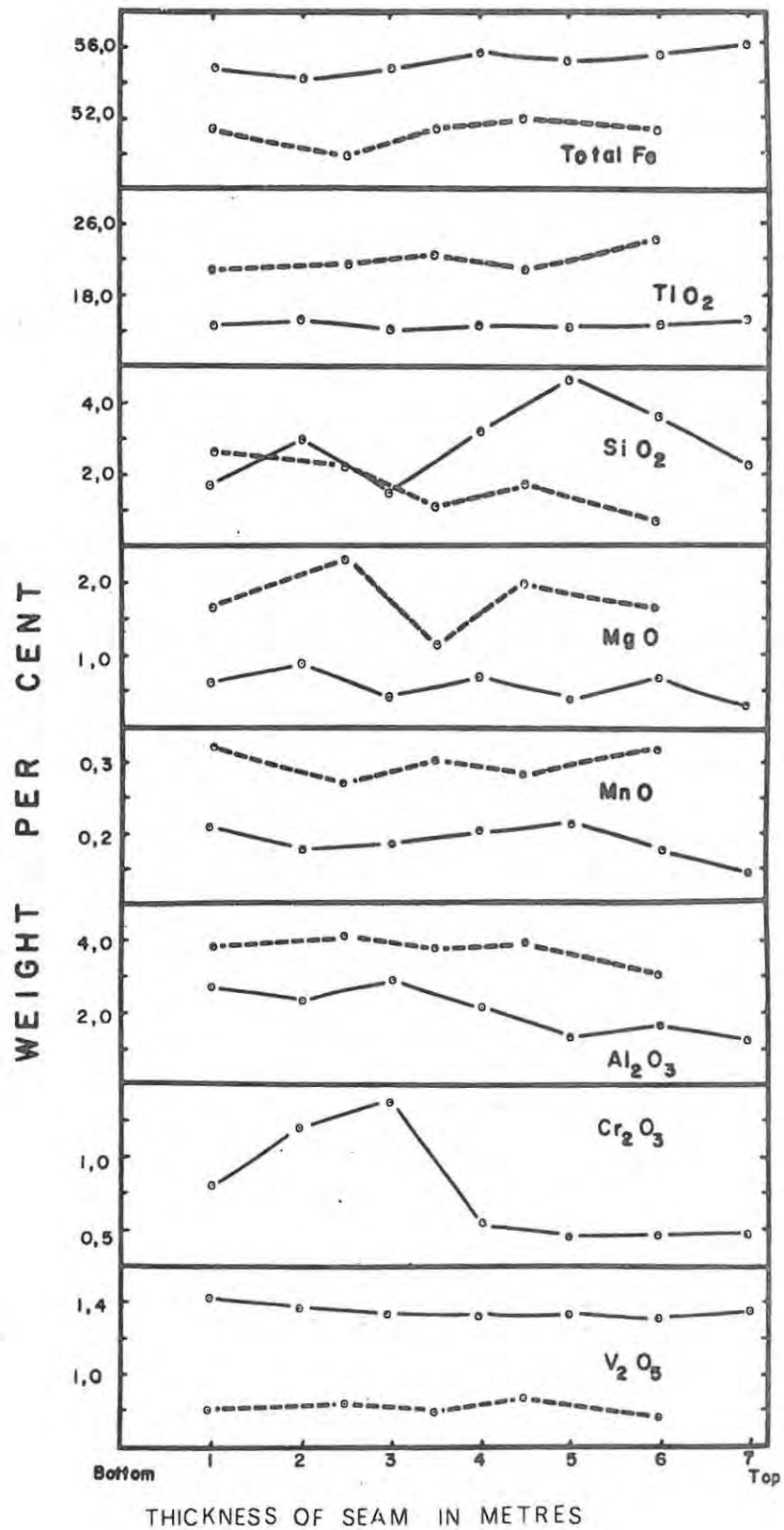
Figure 1: Variation in chemical composition of the Rooiwater titanifer-
ous iron ores with height in the Free State (solid lines) and
Letsitele (dashed lines) seams.

The more highly metamorphosed magnetite lens samples cannot be correlated directly with either the Free State or Letsitele samples on the basis of chemical composition. They do, however, show certain affinities with the Letsitele ores in having low (0,86 %) V_2O_5 contents. Their TiO_2 values are, however, very much lower. It is possible that this material is derived from a minor seam that has not been sampled elsewhere, rather than from one of the two major seams.

The wide variation in FeO/Fe_2O_3 ratios reflected in the analyses is largely a result of oxidation during weathering. The Free State samples are in general more highly oxidised than the Letsitele ores and calculations show there is insufficient FeO to combine with the TiO_2 to form ilmenite in certain cases. This indicates that at least part of the Fe^{2+} in the ilmenite must have been oxidised to Fe^{3+} and further illustrates the highly weathered and oxidised nature of these ores. The effects of possible oxidation during metamorphism or deuteric alteration have been masked by the weathering effects.

The Free State ores are chemically similar to ores from the economically important, Main Seam of the Bushveld Complex, although they contain on average 0,1-0,2 % less V_2O_5. The Letsitele ores are chemically more closely related to the ores of the middle group of seams of the Bushveld Complex.

7.7 The Composition of Coexisting Ilmenites from the Rooiwater Complex

Electron microprobe analyses of the large ilmenite grains present in the Rooiwater ores are presented in Table 4 together with analyses of ilmenites from three associated Rooiwater basic rocks. Quantitative electron microprobe analyses of the smaller co-existing ilmenite grains within the magnetite and larger-sized lamellae in the titaniferous magnetites are presented in Tables 5 and 6 respectively. The variation in composition of these ilmenites with height in the Free State and Letsitele seams is shown graphically in Figure 2.

It is possible to distinguish between the ilmenites from the different seams on the basis of their MgO contents. The Free State samples have relatively high MgO contents (2,01-2,91 %) while those from the Letsitele seam are lower (0,90-1,48 %). The magnetite lens ilmenite has a very high MgO content of 4,35 %. The higher MgO values shown by the Free

TABLE 4

ROOIWATER COMPLEX : MICROPROBE ANALYSES OF COARSE GRAINED ILMENITES

	FREE STATE SAMPLES								LETSITELE SAMPLES					MT. LENS	ROOIWATER BASIC ROCKS			BUSHVELD ILMENITES	
Oxide	RW 17	RW 18	RW 19	RW 20	RW 22	RW 23	RW 24	RW 25	RW 27	RW 32	RW 33	RW 39	RW 40	RW 2	RW 6	RW 16	RW 41	M 23	M3
TiO_2	50,82	50,33	50,16	50,40	49,51	52,18	51,22	51,23	50,95	50,35	50,85	50,24	51,18	50,59	51,13	51,11	50,88	52,1	52,2
FeO	43,32	41,93	41,76	42,40	41,75	43,99	43,04	43,01	41,55	39,93	41,34	40,40	40,19	36,83	43,49	43,03	43,14	40,1	28,8
MgO	0,90	1,21	1,48	1,23	1,22	1,18	1,26	1,21	2,01	2,57	2,05	2,31	2,91	4,35	0,81	0,66	0,70	4,2	6,3
MnO	0,75	0,82	0,74	0,69	0,80	0,83	0,81	0,82	0,72	0,71	0,72	0,69	0,69	0,85	1,06	1,79	1,39	N.R.	N.R.
$+Fe_2O_3$	3,91	5,27	5,03	4,39	5,38	3,51	4,63	3,91	4,55	5,51	5,27	6,07	5,83	6,07	3,03	3,51	3,43	3,5	11,3
Al_2O_3	0,12	0,12	0,12	0,12	0,12	0,12	0,12	0,12	0,12	0,12	0,13	0,12	0,12	0,12	0,12	0,12	0,12	0,5	1,1
Cr_2O_3	0,19	0,21	0,24	0,23	0,19	0,21	0,21	0,20	0,17	0,17	0,17	0,18	0,18	0,17	0,17	0,18	0,17	N.R.	N.R.
TOTAL:	100,01	99,89	99,53	99,46	98,97	102,02	101,29	100,50	100,07	99,36	100,53	100,01	101,10	98,98	99,81	100,40	99,83	100,4	99,7

NUMBER OF IONS OF THE BASIS OF 6 OXYGENS.

Al^{3+}	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006
Cr^{3+}	0,006	0,006	0,012	0,012	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006
Fe^{3+}	0,145	0,198	0,188	0,163	0,201	0,120	0,172	0,144	0,167	0,204	0,196	0,228	0,217	0,226	0,114	0,132	0,127
Ti^{4+}	1,922	1,895	1,897	1,910	1,893	1,934	1,908	1,922	1,910	1,892	1,896	1,880	1,885	1,881	1,937	1,928	1,930
Fe^{2+}	1,822	1,757	1,755	1,785	1,768	1,812	1,783	1,796	1,731	1,670	1,714	1,680	1,644	1,525	1,831	1,805	1,818
Mg	0,066	0,090	0,112	0,094	0,092	0,086	0,092	0,090	0,150	0,192	0,152	0,170	0,212	0,320	0,061	0,048	0,052
Mn	0,033	0,048	0,030	0,030	0,034	0,036	0,033	0,036	0,030	0,030	0,030	0,030	0,030	0,036	0,045	0,075	0,061
TOTAL :	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000

NORMATIVE COMPOSITION (MOLE PER CENT)

$FeTiO_3$	91,09	87,82	87,76	89,26	88,40	90,66	89,14	89,81	86,53	83,48	85,69	84,01	82,20	76,23	91,52	90,21	90,91
$MgTiO_3$	3,32	4,51	5,59	4,69	4,58	4,30	4,61	4,50	7,49	9,61	7,60	8,52	10,59	16,05	3,03	2,41	2,58
$MnTiO_3$	1,66	2,41	1,51	1,51	1,68	1,78	1,64	1,80	1,50	1,50	1,49	1,49	1,47	1,78	2,27	3,77	3,03
R_2O_3	3,93	5,26	5,14	4,54	5,34	3,26	4,61	3,90	4,49	5,41	5,22	5,98	5,74	5,94	3,18	3,61	3,48
TOTAL :	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

$+Fe_2O_3$ calculated assuming ilmenite stoichiometry.

M23 Analysis of coarse-grained ilmenite from Seam 11, Bushveld Igneous Complex (Molyneux, 1970a, 1972).

M 3 Analysis of coarse-grained ilmenite from the Main Seam, Bushveld Igneous Complex (Molyneux, 1970a, 1972).

N.R. not reported.
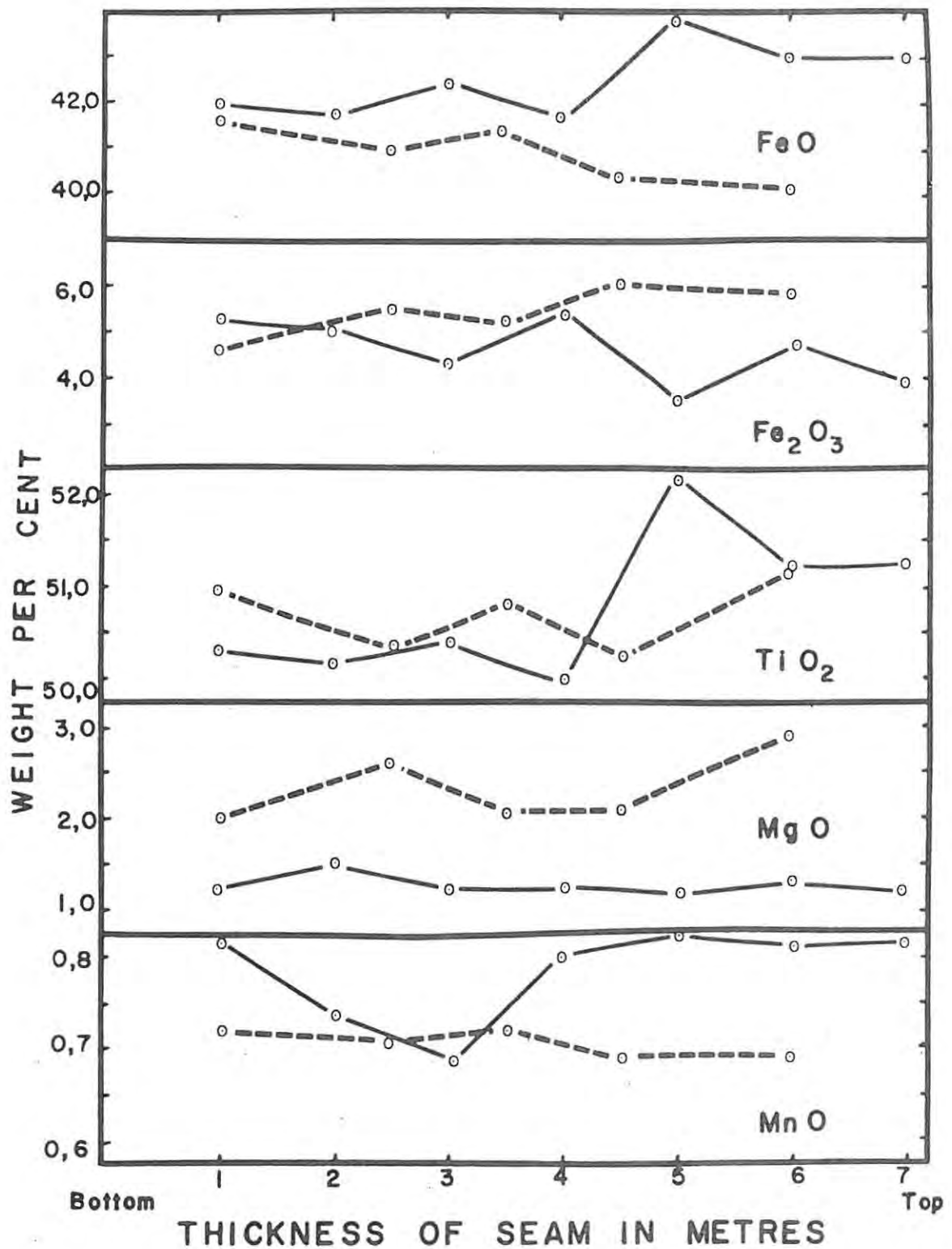
Figure 2: Variation in composition of the co-existing coarse grained ilmenites with height in the Free State (solid lines) and Letsitele (dashed lines) seams.

TABLE 5

ROOIWATER COMPLEX   :   MICROPROBE ANALYSES OF SMALL ILMENITE GRANULES IN TITANIFEROUS MAGNETITE

	FREE STATE SAMPLES								LETSITELE SAMPLES					MT. LENS
Oxide	RW 17	RW 18	RW 19	RW 20	RW 22	RW 23	RW 24	RW 25	RW 27	RW 32	RW 33	RW 39	RW 40	RW 2
TiO_2	50,94	50,94	50,35	50,45	50,64	51,42	51,48	51,51	51,49	50,73	50,62	50,30	51,29	50,14
FeO	43,51	42,91	41,77	42,57	42,62	43,44	43,41	43,77	42,06	40,01	41,77	40,48	41,65	36,22
MgO	0,90	1,19	1,52	1,13	1,20	1,13	1,16	0,97	2,00	2,76	1,75	2,29	2,10	4,51
MnO	0,71	0,78	0,75	0,70	0,81	0,82	0,80	0,88	0,68	0,75	0,71	0,68	0,71	0,86
$+Fe_2O_3$	3,11	2,24	4,31	3,27	3,67	3,51	3,59	2,71	4,07	7,10	5,19	5,27	4,39	9,75
Al_2O_3	0,12	0,12	0,12	0,12	0,12	0,13	0,12	0,13	0,12	0,12	0,12	0,12	0,12	0,13
Cr_2O_3	0,20	0,24	0,24	0,29	0,20	0,23	0,24	0,20	0,17	0,18	0,17	0,18	0,18	0,19
TOTAL :	99,49	98,42	99,06	98,53	99,26	100,68	100,80	100,17	100,59	101,65	100,33	99,32	100,44	101,80

NUMBER OF IONS ON THE BASIS OF 6 OXYGENS.

Al^{3+}	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006
Cr^{3+}	0,006	0,012	0,012	0,012	0,006	0,006	0,012	0,006	0,006	0,006	0,006	0,006	0,006	0,006
Fe^{3+}	0,114	0,086	0,164	0,122	0,140	0,132	0,138	0,104	0,148	0,258	0,198	0,198	0,166	0,352
Ti^{4+}	1,937	1,948	1,909	1,930	1,924	1,928	1,922	1,942	1,920	1,865	1,895	1,895	1,911	1,818
Fe^{2+}	1,837	1,822	1,761	1,813	1,800	1,811	1,803	1,834	1,744	1,633	1,736	1,694	1,726	1,459
Mg	0,067	0,092	0,115	0,086	0,091	0,084	0,086	0,072	0,149	0,200	0,129	0,171	0,155	0,324
Mn	0,033	0,034	0,033	0,031	0,033	0,033	0,033	0,036	0,027	0,032	0,030	0,030	0,030	0,035
TOTAL :	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000

NORMATIVE COMPOSITION (MOLE PER CENT).

$FeTiO_3$	91,91	91,14	88,03	90,67	89,98	90,43	90,15	91,72	87,19	81,68	86,85	84,66	86,31	72,94
$MgTiO_3$	3,39	4,58	5,76	4,28	4,55	4,19	4,33	3,61	7,45	9,97	6,43	8,57	7,74	16,21
$MnTiO_3$	1,51	1,68	1,67	1,53	1,67	1,64	1,64	1,81	1,34	1,61	1,49	1,50	1,49	1,74
R_2O_3	3,19	2,60	4,54	3,52	3,80	3,74	3,88	2,86	4,02	6,74	5,23	5,27	4,46	9,11
TOTAL :	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

$+Fe_2O_3$ calculated assuming ilmenite stoichiometry.

TABLE 6

ROOIWATER COMPLEX : MICROPROBE ANALYSES OF LARGE ILMENITE LAMELLAE OR MODIFIED LAMELLAE IN TITANIFEROUS MAGNETITES

Oxide	FREE STATE SAMPLES								LETSITELE SAMPLES					MT. LETES
	RW 17	RW 18	RW 19	RW 20	RW 22	RW 23	RW 24	RW 25	RW 27	RW 32	RW 33	RW 39	RW 40	RW 2
TiO_2	50,94	50,11	50,31	50,53	50,27	51,67	52,05	50,79	49,89	49,60	50,80	50,59	51,83	50,29
FeO	43,57	41,78	42,14	42,37	42,08	43,39	43,97	43,08	40,99	38,84	41,43	40,26	40,04	35,66
MgO	0,87	1,31	1,28	1,28	1,30	1,25	1,11	0,97	1,79	2,83	1,96	2,52	3,32	4,89
MnO	0,73	0,80	0,76	0,70	0,79	0,84	0,80	0,88	0,70	0,68	0,71	0,71	0,71	0,88
+Fe_2O_3	2,87	4,16	4,55	3,43	4,23	3,03	2,08	2,95	5,30	7,26	5,34	5,27	3,43	8,14
Al_2O_3	0,12	0,12	0,13	0,12	0,12	0,14	0,12	0,12	0,12	0,12	0,13	0,13	0,12	0,13
Cr_2O_3	0,20	0,25	0,26	0,38	0,21	0,25	0,21	0,22	0,17	0,18	0,17	0,18	0,17	0,17
TOTAL :	99,30	98,53	99,43	98,81	99,00	100,57	100,34	99,01	98,96	99,51	100,54	99,66	99,62	100,16

NUMBER OF IONS ON THE BASIS OF 6 OXYGENS.

	RW 17	RW 18	RW 19	RW 20	RW 22	RW 23	RW 24	RW 25	RW 27	RW 32	RW 33	RW 39	RW 40	RW 2
Al^{3+}	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006
Cr^{3+}	0,006	0,012	0,012	0,018	0,006	0,012	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006
Fe^{3+}	0,110	0,156	0,170	0,128	0,158	0,113	0,078	0,110	0,200	0,270	0,196	0,198	0,124	0,298
Ti^{4+}	1,939	1,913	1,906	1,924	1,915	1,934	1,955	1,939	1,894	1,859	1,896	1,895	1,932	1,845
Fe^{2+}	1,842	1,775	1,773	1,797	1,785	1,806	1,838	1,830	1,730	1,620	1,720	1,676	1,658	1,455
Mg	0,067	0,098	0,097	0,097	0,097	0,093	0,084	0,073	0,134	0,209	0,146	0,189	0,244	0,355
Mn	0,030	0,040	0,036	0,030	0,033	0,036	0,033	0,036	0,030	0,030	0,030	0,030	0,030	0,035
TOTAL :	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000

NORMATIVE COMPOSITION (MOLE PER CENT)

	RW 17	RW 18	RW 19	RW 20	RW 22	RW 23	RW 24	RW 25	RW 27	RW 32	RW 33	RW 39	RW 40	RW 2
$FeTiO_3$	92,10	89,13	88,65	89,80	89,19	90,29	91,89	91,46	86,49	80,98	85,99	83,83	82,89	72,73
$MgTiO_3$	3,34	4,90	4,84	4,87	4,88	4,63	4,20	3,66	6,68	10,48	7,30	9,43	12,20	17,74
$MnTiO_3$	1,52	1,99	1,82	1,52	1,67	1,79	1,65	1,83	1,52	1,50	1,49	1,50	1,49	1,76
R_2O_3	3,04	3,98	4,69	3,81	4,26	3,29	2,26	3,05	5,31	7,04	5,22	5,24	3,42	7,77
TOTAL :	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

+Fe_2O_3 calculated assuming ilmenite stoichiometry.

State ilmenites are also reflected in the corresponding bulk ore analyses
that also show higher MgO contents than those from the Letsitele area.
The MgO contents of ilmenites from the Rooiwater basic rocks are generally
lower than those from the titaniferous magnetite seams.

The MnO values for the Free State, magnetite lens and Letsitele samples
are all very similar, but they are distinctly higher in the ilmenites
from the associated basic rocks.

Recalculation of the analyses, assuming stoichiometry, indicates the
presence of several per cent excess FeO in all the samples. This excess
FeO has been recalculated as Fe_2O_3 in Table 4, and is probably present
in solid solution in the ilmenite. The presence of minor magnetite
lamellae in these ilmenites also indicates that they contain excess iron.

The Free State ilmenites also contain slightly greater amounts of Cr_2O_3
(0,19-0,24 %) than the ilmenites from the Letsitele area. The analyses
of samples RW 19 and RW 20 exhibit high Cr_2O_3 values and correlate with
the bulk ore analyses from this portion of this seam that also show
higher Cr_2O_3 contents.

Only minor compositional differences exist between the large co-existing
ilmenite grains and the larger rounded ilmenite grains and lamellae that
are present in the associated titaniferous magnetites. This suggests
that extensive re-equilibration may have taken place between these phases
at relatively low subsolidus temperatures.

7.8 Beneficiation

The various Rooiwater ores are amenable to beneficiation and can be
upgraded to produce raw materials that would be suitable for the recovery
of both high- TiO_2 and $-V_2O_5$ products as well as iron. The ores contain
variable amounts of recoverable granular ilmenite, while the minor silicate
impurities can be removed from the ore by crushing followed by magnetic
separation.

7.8.1 The magnetite lens samples

These samples are the most amenable to beneficiation, but ore reserves
are unfortunately limited. Their V_2O_5 contents are too low (0,86 %) for
consideration as potential vanadium ores, but they contain approximately
20 per cent of recoverable coarse-grained ilmenite. This ilmenite has

a grain-size of approximately 0,15 mm, and can be liberated by crushing
to a grain size of less than 200 mesh. The ilmenite can then be
recovered by simple magnetic separation while the minor silicate impurities
can be removed by electromagnetic separation or possibly by some other
gravatitational separation process.

The vanadium is preferentially incorporated into the magnetite crystal
structure so that the effect of removing approximately 20 per cent of
ilmenite from the ore is to increase the V_2O_5 content of the magnetic
fraction by a similar amount. Microscopic examination has shown that
the bulk of the ilmenite is present in a recoverable form as large
polygonal grains and that only between 3 and 5 per cent is present as
fine-grained intergrowths that cannot be separated by mechanical means.

Two samples (RW 2 and RW 8) were crushed to less than 200 mesh and the
fraction with a grain size between 200 and 400 mesh was subjected to
magnetic and electromagnetic separations. A magnetite-rich magnetic
fraction was obtained by the use of a strong permanent magnet while an
ilmenite-rich fraction was obtained by use of a Frantz isodynamic
separator. Chemical analyses of the magnetic fractions are presented
in Table 7. This treatment reduced their TiO_2 contents from approximately
12,3 % to 3,03 and 4,67 % respectively. The reduction in volume caused
by the removal of ilmenite also increased the overall V_2O_5 contents of the
magnetic fractions to 1,03 and 0,94 % respectively. The beneficiation
process also slightly reduced the SiO_2, Al_2O_3, MnO and MgO contents due
to the removal of silicate impurities and coarse-grained ilmenite.

The ilmenite concentrates were not analysed chemically, but microscopic
examination indicates that they are approximately 98 per cent pure. Their
compositions should be similar to that indicated by the electron microprobe
analysis of an ilmenite from the magnetite lens shown in Table 4 (RW 2).

TABLE 7
Analyses of Beneficiated Magnetic Fractions

Oxide	untreated		beneficiated		
	RW 2	RW 17	RW 2	RW 8	RW 17
SiO_2	2,09	7,42	0,90	1,06	1,67
TiO_2	12,23	15,20	3,03	4,67	10,08
Al_2O_3	6,12	6,37	2,32	1,89	1,66
Cr_2O_3	0,05	0,22	0,05	0,05	0,?7
Fe_2O_3	55,11	54,06	71,34	78,95	74,95
FeO	22,97	13,76	20,92	11,75	8,88
MnO	0,19	0,17	0,05	0,05	0,12
MgO	1,78	1,75	0,87	0,63	0,32
V_2O_5	0,86	1,08	1,03	0,94	1,42
Total :	99,31	100,03	99,71	99,99	99,37

7.8.2 The Free State samples

These samples are chemically very similar to the commercially exploited ores of the Main Seam of the Bushveld Igneous Complex. They contain up to 1,42 % V_2O_5 and represent potential vanadium ores. Approximately half their TiO_2 content is also in the form of recoverable coarse grained ilmenite.

Beneficiation can be achieved by crushing to less than 200 mesh followed by magnetic and electromagnetic separations. These yield a low-titanium, vanadium-bearing magnetic fraction and an ilmenite concentrate. The minor silicate impurities are removed in the non-magnetic fractions.

Several samples were treated in this manner and relatively clean ilmenite concentrates amounting to approximately 10 % by mass of the feed were produced. The removal of the coarse-grained ilmenite resulted in an overall decrease in the TiO_2 contents of the magnetite while the V_2O_5 contents were increased by approximately 15 %. An analysis of the magnetic fraction produced from the most impure sample, (RW 17) is presented in Table 7. The V_2O_5 content was increased from 1,08 to 1,42 % while the TiO_2 content was reduced from 15,20 to 10,08 % by this treatment. This TiO_2 is present as very fine-grained ilmenite intergrowths that cannot be separated by mechanical means.

The majority of samples from this area contain less silicate impurities, but are otherwise mineralogically similar. Microscopic examinations of separates prepared from various samples indicate that similar concentrates were obtained during beneficiation tests. The ilmenite concentrates were not analysed chemically, but their overall composition is expected to be similar to those obtained by electron microprobe analyses in Table 4 (samples RW 17 - RW 25).

7.8.3 The Letsitele samples

These samples contain very large amounts of TiO_2 (21 to 25 %), but exhibit lower V_2O_5 contents (0,76 to 0,86 %). The samples are characterised by the presence of between 20 and 25 per cent by mass of potentially recoverable coarse-grained ilmenite. These ores are chemically similar to the middle group of seams of the Bushveld Igneous Complex, but contain more TiO_2.

Beneficiation can be achieved by crushing to less than 200 mesh followed by magnetic and electromagnetic separation to yield a low-titanium, vanadium-bearing magnetic fraction and an ilmenite concentrate. The minor silicate impurities are removed in the less-magnetic fractions.

Beneficiation tests indicate that an ilmenite concentrate of up to 20 per cent by mass of the sample can be obtained. The magnetic concentrates were not analysed chemically, but microscopic examinations indicate that their TiO_2 contents would be reduced by between 12 and 15 per cent. This implies that the V_2O_5 contents of the magnetic fractions would also be increased to between 1,0 and 1,1 %. The composition of the ilmenite concentrates should be similar to that indicated by the electron microprobe analyses presented in Table 4 (RW 27 - RW 40).

Although it is possible to produce ilmenite concentrates from these samples, their high TiO_2 contents suggest that they might be suitable for the pyrometallurgical production of high-titania slag products together with iron.

7.8.4 The Rooiwater basic rocks

The zones of ilmenite and apatite-rich Rooiwater basic rocks locally carry up to 20 per cent ilmenite and represent potential ores that warrant further investigation. The coarse-grained ilmenite can be

readily recovered by crushing followed by electromagnetic separation and any concentrate produced in this manner would have a composition similar to that shown by the electron microprobe analyses presented in Table 4 for samples RW 6, 16 and 41.

Minor apatite is present in amounts of up to 4 per cent in these metagabbros and has a sufficiently coarse grain size to be recoverable by crushing followed by some form of heavy-medium concentration. It could thus present a valuable by-product.

7.9 Discussion

The vanadium-bearing, titaniferous iron ores of the Rooiwater Complex are chemically similar to ores of this nature from other stratiform basic intrusions, but differ in that they contain substantial quantities of coarse-grained ilmenite. The development of abundant ilmenite of this type in the Rooiwater ores is problematical since these rock types usually contain only minor amounts of granular ilmenite. The microstructures developed in the Rooiwater titaniferous magnetites are also markedly different from those present in similar minerals from slowly cooled, unmetamorphosed basic intrusions (e.g. Bushveld and Skaergaard Complexes).

The investigated Rooiwater titaniferous magnetite seams all lie within the metamorphic aureole of the granite that has engulfed the complex, but are located at variable distances from the contact and have been metamorphosed to varying degrees. The Rooiwater Complex and Murchison Schist Belt rocks have also undergone widespread regional metamorphism. In addition to the thermal metamorphic effects of the nearby intrusive granite. (Hall, 1912; van Eeden et al., 1939). The Rooiwater Complex and Murchison Range rocks are now present as small remnants in the surrounding Basement Granite and Saager and Köppel (1976) have drawn analogies between them and the more intensively studied Archean rocks of the Barberton area. They also noted that the Murchison Range represents a strongly metamorphosed greenstone belt. These metamorphic episodes have been largely responsible for the modifications that developed in the Rooiwater titaniferous magnetite ores.

The most commom morphology exhibited by an exsolving phase is plate-or

disc-shaped (Brett, 1964 ; Yund and McCallister, 1970). Nabarro (1940) has shown that a plate is the most stable shape for an exsolved phase in an isotropic medium while a sphere is least stable. These observations are in general agreement with the morphologies of exsolution bodies in iron-titanium oxides from unmetamorphosed, slowly cooled, basic rocks in which the exsolved phases are invariably lamellar, plate-like or disc-shaped. The microstructures exhibited by the Rooiwater ores, particularly those from the magnetite lens and Letsitele areas, depart markedly from this relationship and show the development of more complex morphologies.

A coherent interface is generally no longer present between exsolution bodies and their host (Champness and Lorimer, 1976) once exsolution bodies have grown to a microscopically visible size, and they can be regarded simply as inclusions within their hosts. The interface between an inclusion and its host is a true grain boundary and its morphology is governed by the same factors that determine grain shapes in polycrystalline aggregates (Vernon, 1976) (section 3.3). Vernon (1976) has demonstrated that inclusions in minerals also exhibit a tendency to minimise their grain boundary energies and that their ideal equilibrium form will be a sphere when both the host and inclusion are isotropic. Approximately spheroidal or ellipsoidal shapes will result when the two phases are not markedly anisotropic, provided that growth has occurred in the absence of a stress field. When two or more inclusions are in contact within a host, their mutual grain-boundary relationships are also controlled by interfacial tension and polygonal equilibrium boundaries are preferentially developed between them.

Brett (1964) and Yund and McCallister (1970) have noted that plate-like exsolution bodies represent the stable morphology only up to a certain stage during the exsolution process. Once this stage has been reached it becomes necessary to reduce the high surface energy of the plate-like bodies and there is a tendency for then to break down in the solid state to form spheroidal bodies. Numbers of smaller grains may coalesce to form larger ones during this spheroidisation process.

Lamellar-type intergrowths of ilmenite and ulvospinel or both are commonly present in titaniferous magnetites from slowly cooled igneous rocks, but they do not generally show evidence of spheroidisation (author's observation). These lamellar bodies exhibit energetically unfavourable morphologies, but they cannot readjust to a more stable form since the

ionic mobility is too low to allow any large-scale rearrangement during
low-temperature stages of exsolution and the intergrowths are preserved
in a metastable state. A subsequent rise in temperature would result in
an increase in the ionic mobility and the exsolution process would either
continue until the supersaturation at that particular temperature was
eliminated or else resorption of the lamellae would occur depending
on the sub-solvus phase relationships.

The effects of an increase in temperature on an exsolved titaniferous
magnetite would depend not only on the temperature attained, but also
on the oxygen fugacity. In the case of a titaniferous magnetite heated
to above the ulvospinel solvus under suitably buffered fO_2 conditions,
the previously exsolved ulvospinel would dissolve together with any
exsolved pleonaste. Ilmenite is only sparingly soluble in magnetite
so that only minor dissolution of any intergrown ilmenite would occur.
At temperatures below the ulvospinel solvus, less dissolution of
ulvospinel and pleonaste would occur while the ilmenite would remain
virtually insoluble. Since the ilmenite cannot dissolve in magnetite
to any appreciable extent during heating under suitably buffered oxygen
fugacities, the resulting increased ionic mobility might instead lead to
the breakdown and spheroidization of the energentically unfavourable
ilmenite lamellae. Subsequent slow cooling of the titaniferous magnetite
will result in renewed exsolution, the nature of the phases produced being
dependent on the oxygen fugacity and cooling rate as discussed in Part 1
as well as the composition of the host minerals.

The wide variety of microstructures exhibited by the Rooiwater titaniferous
magnetites reflect successive stages in the breakdown and spheroidization
of the original microstructures. These processes appear to have been
controlled largely by the temperatures and oxygen fugacities prevailing
during the metamorphism of these ores as well as their post-metamorphic
cooling history. The differences in microstructural development between
the ores from the different areas examined can be related to differences
in the grades of matamorphism that were reached in different parts of the
complex. Differences in bulk chemistry between the Free State and
Letsitele ores might also have played an important part in controlling
their microstructural development.

In addition to these various intragranular relationships, the individual

large titaniferous magnetite and ilmenite grains exhibit a high degree of polygonalization. The presence of similar textures in unmetamorphosed titaniferous iron ores has been discussed in section 3.3, but the metamorphism would also have provided suitable conditions for additional grain boundary migration.

The nature of grain boundary relationships in metamorphic rocks has been studied by Voll (1960), Stanton (1964), Kretz (1966) and Vernon(1968, 1970, 1976). These authors all noted that these textures are also characterised by the formation of essentially polygonal grain boundaries in which interfacial angles approximating 120° are developed between relatively isotropic minerals. Similar relationships exist between the coarser opaque oxides in the Rooiwater ores, but it is not possible to determine to what extent the original grain boundary relationships have been modified. The presence of abundant granular ilmenite in certain samples together with the recrystallised nature of the more highly modified ores indicates that considerable grain boundary migration has taken place during metamorphism.

The nature of the pre-metamorphic Rooiwater microstructures is not known, but small areas containing relicts of an earlier microstructure are present in certain Free State samples. The majority of titaniferous magnetite seams from unmetamorphosed layered basic instrusions are composed largely of multi-phase titaniferous magnetite grains showing the development of intergrown ulvospinel and variable amounts of lamellar ilmenite. Coarse-grained intergranular ilmenite is generally present in only minor amounts in ores of this type. e. g. the Bushveld, (Schwellnus and Willemse, 1943; Molyneux, 1970a, b; 1972), Kaffirskraal and Trompsburg Igneous Complexes (this report). By analogy, the original titaniferous magnetite microstructures developed in the Rooiwater ores may have been similar, but probably contained greater amounts of lamellar ilmenite.

No ulvospinel or ulvospinel-type microintergrowths were noted in the samples examined and it is not known whether this phase was originally present. Ulvospinel is soluble in magnetite so that any ulvospinel originally present would have been resorbed during a metamorphically induced temperature rise, provided that the oxygen fugacity remained low enough. The absence of ulvospinel indicates that the oxygen fugacities were too high for its existance as a stable phase in the microintergrowths and any present during this stage would have been oxidised to ilmenite.

The oxygen fugacities were also not high enough to cause oxidation of
the titaniferous magnetite and the presence of magnetite lamellae in
the coarse-grained co-existing ilmenites provides further evidence for
the existence of intermediate oxygen fugacities during the period of
microstructural development.   These lamellae are generally interpreted
as being formed by the solid-state reduction of originally exsolved
hematite lamellae in the ilmenite rather than by exsolution (Buddington
et al., 1963 ; Buddington and Lindsley, 1964).   This suggests that,
although the oxygen fugacities were too low for hematite stability, they
were also too high for ulvospinel development.   In general, the large
amounts of titaniferous magnetite and other oxides in the ores would
have buffered the oxygen fugacities to within closely controlled values
in the seams during metamorphism so that widespread fluctuations would
not be expected, except perhaps locally.

The Free State ores are the least metamorphosed of the Rooiwater samples
and contain small areas that resemble relatively unmodfied primary
microintergrowths.   These areas are confined to the cores of large
titaniferous magnetite grains and possibly represent relict microstructures
that have survived because of their isolated positions and distances from
grain boundaries.   Should these represent true relicts of the original
Rooiwater microstructures, then the ores would have had an overall primary
appearance similar to that of the Usushwana titaniferous iron ores (this
report).   This would indicate that they crystallised under conditions of
relatively high oxygen fugacity.   Should ulvospinel have been present in
the original Rooiwater titaniferous magnetite microintergrowths, these
textures could conceivably have formed during an early stage of
metamorphism by the oxidation/exsolution of ilmenite, derived from the
original ulvospinel that was either present in solid solution or as an
exsolved phase.

The least-modified Free State microstructures indicate that the breakdown
and spheroidisation of the pre-existing ilmenite lamellae had commenced
under the influence of increased temperature.   This is evident in a
thickening of the lamellae while curved, irregular surfaces are commonly
developed along their boundaries so that the regular nature of the original
trellis network becomes disrupted.   Many of the larger ilmenite lamellae
have grown at the expense of smaller ones and they often exhibit a
thickening at their mutual intersections.   Any ilmenite produced by the

oxidation of either dissolved or exsolved ulvospinel during this stage
would have segregated towards the ilmenite bodies already present and have
contributed to their growth.

The numerous small ilmenite grains developed around the peripheries of
the titaniferous magnetites represent externally exsolved material
(external granule exsolution). A portion of this ilmenite would also
have contributed to the growth of favourably situated intergranular
ilmenite grains. This growth would also result in grain-boundary migration
between the ilmenite and the magnetite grains leading to the development
of larger amounts of coarse-grained ilmenite.

The behaviour of the exsolved pleonaste during metamorphism differs from
that of the Fe-Ti oxides since the various spinel solid solution solvi
close at higher temperatures (approximately 800-1000°C as discussed in
Part 1). Only a small portion would consequently be dissolved at the
lower metamorphic temperatures and exsolved pleonaste plates and lamellae
would readjust to more stable morphologies. This results in the formation
of more equant pleonaste grains by a solid state diffusion process.

On slow cooling after the metamorphic thermal peak the small amount of
redissolved pleonaste would again exsolve. This material would initially
contribute to the growth of existing pleonaste grains, but at lower
temperatures and lower ionic mobilities, the diffusion would take place
over shorter distances giving rise to the smaller and more widely spaced
lamellae present in the Free State titaniferous magnetites.

The Letsitele ores exhibit higher degrees of modification than those from
the Free State seam and are characterised by the large-scale spheroidization
of ilmenite intergrowths. Their generally rounded forms indicate that
widespread recrystallisation of their magnetite hosts has, however, not
yet occurred.

It is uncertain what percentage of the coarse-grained ilmenite in the
Letsitele ores represents a primary precipitate. It is unlikely that
more than approximately 6 per cent of coarse-grained ilmenite was
originally present by analogy with other unmetamorphosed titaniferous
iron ores. This implies that the original grains not only increased
in size, but that new grains were also formed during metamorphism by

the external diffusion of ilmenite from the marginal areas of neighbouring titaniferous magnetites. Considerable grain boundary migration also took place during the growth of these ilmenites.

The higher temperatures apparently reached by these ores would have been more favourable for annealing and they exhibit a particularly well-developed polygonal texture. The titaniferous magnetite grains are slightly larger that the co-existing interstitial coarse-grained ilmenites and the samples have a uniform grain size. Grain boundaries are relatively straight or slightly curved, and their interfacial angles approximate 120°. These features indicate a close attainment of equilibrium between the larger-sized opaque oxides, but although extensive spheroidisation of their intergrowths has occurred, complete equilibrium was not reached and their hosts did not recrystallise.

The magnetite lens ores are located approximately 100m from the intrusive granite and have been metamorphosed to a greater extent than those from the other areas. As a result, they display the greatest degree of microtextural modification and have been almost completely recrystallised. The higher temperatures reached during metamorphism apparently resulted in the almost complete spheroidisation of the contained ilmenite and pleonaste phases. External granule exsolution would have proceeded under these conditions of very much higher ionic mobility while the ilmenite and pleonaste spheroids would have coalesced to form larger grains. Polygonalization of these spheroids would then have occurred under the influence of interfacial free energy and the magnetite matrix would ultimately have recrystallised to form equilibrium grain-boundary relationships with the enclosed phases as envisaged by Brett (1964). This would then result in a much finer-grained, highly polygonalized texture that would in turn become progressively coarser-grained as the annealing process continued.

The magnetite lens samples appear to have reached this stage, but the process was halted before coarser textures could be developed. The ores contain only occasional modified relict lamellae and rounded grains which indicate that equilibrium was very nearly attained.

The textural differences between the ores from different areas reflects variations in metamorphic grade. It is unlikely that equilibrium

conditions were ever completely attained since the ores from each
locality contain certain relict textures that are characteristic of an
earlier stage of development. Large-scale textural variations are
present between different samples from the same area and are even
noticeable within the same grain. In general, the outer portions of
the titaniferous magnetite grains are more modified than their interiors
which appear to have been isolated from the metamorphic changes.

The overall effect of increasing metamorphic grade has resulted in an
increase in the relative amount of coarse-grained, intergranular ilmenite
in the ores in addition to the modification of the primary microstructures.
The higher metamorphic grades led to the ultimate recrystallisation of the
ores resulting in the development of polycrystalline ilmenite and
intergrowth-free magnetite aggregates. The process is essentially
continuous and the ores from the three areas clearly illustrate successive
stages in its development.

In contrast to is occurrence in the ore-rich seams, titaniferous magnetite
is generally present in lesser amounts than ilmenite in the associated
Rooiwater basic rocks and is, in some cases, virtually absent. This
titaniferous magnetite shows extensive resorption and alteration to
sphene and chlorite. Hornblende may also develop at the expense of the
titaniferous magnetite in the more highly altered specimens, while the
co-existing ilmenite also shows signs of resorption. Buddington et al.
(1963) noted the progressive disappearance of titaniferous magnetite and
partial resorption of ilmenite is regionally metamorphosed gabbros and
concluded that this was a result of a metamorphic reaction leading to
the formation of hornblende. These authors also noted the formation of
sphene at the expense of titaniferous magnetite during regional
metamorphism.

The Rooiwater ores exhibit the same minor element variation trends as the
Bushveld ores. The Free State ores are the lowermost preserved
titaniferous magnetites in this part of the Rooiwater Complex and contain
greater amounts of V_2O_5 and Cr_2O_3 than the Letsitele ores that are
stratigraphically higher up in the basic sequence. This decrease in
V_2O_5 and Cr_2O_3 content upwards in the complex is similar to the trend
shown by the Bushveld titaniferous magnetites in which there is a marked
decrease in V_2O_5 content upwards in the sequence (Molyneux, 1970 a,b,1972).

Similar relationships were found in the Skaergaard Complex (Vincent and Phillips, 1954) and in the Dufek Intrusion (Himmelberg and Ford, 1977).

The lowermost Rooiwater seam contains moderate amounts of TiO_2 while the uppermost seam contains substantially more. MnO shows a similar, but less marked variation. Both these trends are again similar to those exhibited by the Bushveld ores and the titaniferous magnetites of the Skaergaard and Dufek Intrusions.

The MgO increases slightly in the uppermost seam of the Rooiwater Complex relative to the lowermost one which is in contrast to the Bushveld trend. Portion of the MgO reflected in the analyses is present in chlorite so that the higher values can be ascribed to a slightly higher chlorite content in the upper seam, rather than to the MgO content of the titaniferous magnetite.

The economically important result of the Rooiwater metamorphism is the development of abundant coarse-grained ilmenite in the ores. The amount of ilmenite formed is related to the grade of metamorphism reached, the prevailing oxygen fugacities, the original TiO_2 content of the ore and the subsequent cooling history, so that variable concentrations are developed in different seams in different areas. A large proportion of this ilmenite is recoverable by standard ore-dressing techniques and possibilities exist for the beneficiation of the Rooiwater ores. Very little is known about the titaniferous iron-ores in other parts of the Rooiwater Complex and this preliminary study indicates that a thorough geological investigation is necessary.

Numerous titaniferous magnetite seams are present in the Bushveld Complex (up to 26) which suggests that several thinner seams that are not well exposed remain to be discovered in the Rooiwater Complex. In particular, any seams that are lower down in the sequence of basic rocks than the Free State Seam would be expected to contain higher V_2O_5 contents and would be of economic interest.

7.10 Genesis of the Rooiwater Ores

The overall similarity in minor element chemistry and distribution between the Rooiwater ores and those of the Bushveld Complex suggest an essentially similar mode of origin. Willemse (1969) and Molyneux (1970 a,b, 1972),

regarded the Bushveld titaniferous magnetites as igneous cululates, but acknowledged that the original textures have been modified by post-cumulus growth and other factors. The formation of titaniferous magnetite seams and associated silicates in the Bushveld Complex was reviewed by von Gruenewaldt (1973) who noted that periodic increases in oxygen fugacity would enhance the crystallisation of titanomagnetite. He concluded that the concentration of titaniferous magnetite into layers was probably assisted by it having a faster settling velocity than other precipitating silicates. The possible mechanisms whereby rocks of this nature can be formed are discussed further in section 3.

The world-wide occurrence of titaniferous magnetite layers or titaniferous magnetite-rich silicate layers in certain stratiform basic intrusions supports the view that the formation of these rock types is controlled by the late-stage iron-enrichment of a strongly fractionated basic magma. van Eeden et al. (1939) considered that the Rooiwater titaniferous magnetite ores are "pegmatitic" intrusions into, and probable partial replacements of the original gabbro. They recognised three stages in the formation of these ores:

i) the emplacement of titanomagnetite from which the ilmenite lamellae exsolved. Various ilmenite and magnetite intergrowths were also formed at this stage -

ii) Emplacement of the later granular ilmenite that partially replaces and veins the original titanomagnetite and

iii) the emplacement of later ilmenite-free magnetite.

van Eeden et al. (1939) did not recognise the microstructural and textural differences that exist between the Rooiwater titaniferous magnetites and similar ores from unmetamorphosed stratiform basic intrusions, nor did they recognise the textural variations between ores from different parts of the complex. In the author's opinion, these ores are typical of magmatic titaniferous magnetite layers developed in stratiform basic intrusions that have been texturally modified during subsequent metamorphism. The genesis of the Rooiwater ores can be considered to have taken place as follows:-

1) The two major titaniferous magnetite seams, and possibly several other thinner layers, were formed as cumulus rocks by normal crystallisation and differentiation processes during the solidification

of the Rooiwater rocks. The minor elements, V and Cr, were enriched in the earlier-formed lower seam relative to the later-formed upper seam in which Mn and Ti were enriched.

2) The titaniferous magnetite-rich layers were formed by the accumulation of an initially homogeneous spinellid phase containing Fe, Ti, V, Mn, Al, Cr and Mg together with minor co-precipitated silicates and possibly ilmenite. Factors such as post-cumulus growth, removal of intergranular fluids by filter-pressing and annealing may also have played an important role in the formation of the ore-rich layers.

3) During cooling, exsolution of a titanium-rich phase would have been initiated resulting in the development of ilmenite exsolution lamellae and external granules. Further cooling would have resulted in the exsolution of pleonaste and other Ti-rich phases. The nature of the Ti-rich phases would have been controlled by the prevailing oxygen fugacities and a number of possibilities exist. Either octahedrally oriented ilmenite oxidation/exsolution lamellae would have been formed under high oxygen fugacities or cubically oriented ulvospinel bodies would have formed under low oxygen fugacities. Various combinations of ilmenite and ulvospinel would have developed under intermediate oxygen fugacities. The exact nature of the primary microstructures is not known. Annealing processes would also have been important in the development of grain-boundary relationships.

4) The exsolution processes would have effectively ceased once temperatures dropped low enough to prevent ionic diffusion taking place and the titaniferous magnetites would have exhibited microstructures that are typical in unmetamorphosed rocks of this nature.

5) The Rooiwater Complex was engulfed and metamorphosed by granitic intrusions at a later stage and the associated elevated temperatures resulted in a modification of the original microstructures. A variety of textural types were produced that reflect variations in the metamorphic grade reached in different areas. The ores exhibit successive stages in the breakdown and spheroidization of original lamellar microintergrowths and the polygonalization of their constituent opaque oxides. Continued oxidation/exsolution resulted

in the growth of coarse-grained intergranular ilmenite while complete recrystallisation of the ores occurred in areas of higher-grade metamorphism.

6) Minor microstructural modifications and small amounts of further exsolution would have occurred during the post-metamorphic cooling.

7) Oxidation and hydration of the ores in the zone of surface weathering has resulted in their partial martitization and the development of abundant secondary goethite and hematite.

7.11 Conclusions

1. The presence of the Rooiwater titaniferous iron ores in discrete layers towards the upper parts of a large gabbroic intrusion is in accord with their development by normal crystallisation-differentiation processes that are operative in stratiform basic intrusions.

2. The Rooiwater titaniferous magnetites are chemically similar to ores of this nature that are typically developed in layered gabboic complexes. Their minor element variation with increasing height in the Complex is also in accord with the normal differentiation trends exhibited by titaniferous magnetites during fractional crystallisation.

3. The ores are characterised by an unusual abundance of coarse-grained ilmenite, while the titaniferous magnetites display a wide range of microstructures that are not normally developed in ores of this type. These unusual mineralogical relationships and microstructural developments reflect changes that were brought about in the ores during metamorphism.

4. The metamorphic event was initiated by the intrusion of a nearby granite that also engulfed large portions of the Rooiwater Complex. The ores examined are located at various distances from the contact and consequently exhibit varying degrees of metamorphism. The highest grade reached is represented by the magnetite lens samples that were collected from very close to the granite contact. The least modified ores are represented by the Free State samples that were collected at a greater distance from the contact. The Letsitele ores appear to

have been metamorphosed under intermediate conditions.

5. The metagabbros immediately south of the magnetite lens consist of andesine, hornblende and rutilated-quartz and are typical of amphibolites formed under conditions of medium grade metamorphism (Winkler, 1976). The metagabbros from the Free State and Letsitele areas are extensively saussuritized and uralitised, reflecting lower grade metamorphic conditions.

6. The increased temperature conditions during metamorphism resulted in the breakdown and spheroidisation of the original lamellar ilmenite and pleonaste microintergrowths. Extensive external granule exsolution processes were also operative and resulted in the formation of abundant intergranular ilmenite. Complete recrystallisation of the ores occurred under the highest grade of metamorphic conditions reached resulting in the formation of polycrystalline aggregates of polygonal ilmenite and intergrowth-free, Ti-poor magnetite.

7. The nature of the modified microstructures produced in the titaniferous magnetites was dependent on the initial composition of their host grains, the nature of the primary microstructures developed, the temperature and duration of the metamorphic heating event, the subsequent cooling rate and the prevailing oxygen fugacities during all stages of the process.

8. The compositions of the coarse-grained ilmenite grains and the larger-sized granular-and lamellar-ilmenite intergrowths developed in their co-existing titaniferous magnetites are similar. This suggests that considerable solid-state re-equilibration tool place between these phases during the metamorphic event.

9. The Rooiwater ores are essentially pure and contain only minor silicate impurities that can be readily removed by coventional ore dressing techniques. The abundant coarse-grained ilmenite can be largely liberated by crushing to less than 200 mesh and can be concentrated by electromagnetic separation techniques.

10. The ores of the lowermost seam are chemically similar to the economically important iron ores of the Main Seam of the Bushveld Igneous Complex and represent potential vanadium ores. Their vanadium content can be

further upgraded to approximately 1,5 % by beneficiation involving separation of the co-existing coarse-grained ilmenite.

11. The ores of the uppermost seam exhibit high TiO_2 values of up to 24,5 % and might represent suitable raw material for high-titania slag production. They contain between 15 and 20 % by mass of coarse-grained ilmenite (locally reaching up to 30 %) that is largely recoverable by conventional ore dressing techniques and can be regarded as potential ilmenite ores.

12. In spite of its large size (strike length of over 90 km), the Rooiwater Complex has not been investigated in any detail. Comprehensive geological studies and detailed mapping are necessary to determine the nature of the Complex, the number and extent of the titaniferous magnetite seams present, and the distribution of the different textural types of ore.

13. The Rooiwater Complex represents an interesting area for research into the behaviour of stratiform basic intrusions during regional metamorphism. In particular, the co-existing iron-titanium oxides are sensitive indicators of both the oxygen fugacities and temperatures reached during metamorphism and this aspect requires further study. A detailed study of the differences in behaviour between the co-existing iron-titanium oxides in the metagabbros and those in the ore-rich horizons is also indicated.

14. The Rooiwater Complex represents one of the most attractive areas for further investigation by anyone interested in the production of one or more of the following commodities :
ilmenite, high-titania slag, V_2O_5, iron or steel.

8. THE TITANIFEROUS IRON ORES OF THE USUSHWANA COMPLEX

8.1 Introduction

The Usushwana Igneous Complex is situated along the South African-Swaziland border in the area north and east of Piet Retief. It consists of a large mass of gabbroic rocks that were intruded along the contact between the Basement Granite-Gneiss and the overlying Pongola rocks. The Complex does not generally show any well-defined igneous layering apart from the titaniferous magnetite seams and is capped by a granophyric zone.

The occurrence of titaniferous magnetite ores in the Complex near Piet Retief has been known since the last century, but no detailed descriptions have been published. No published maps exist of the area in which the titaniferous magnetite seams occur, although the area immediately to the south was mapped and described by Humphrey and Krige (1931). The Usushwana rocks in Swaziland were described by Winter (1965) and Hunter (1970). The Complex is Archean in age and has been dated at 2784 ∓ 30 million years by Davies et al. (1970).

The titaniferous iron ores from this area have been briefly described by Wagner (1928) who stated that "the magnetic iron ore is found at several places on the farms Belfast No.74, Derby No.54, and Ishlelo No.7, north of Piet Retief. It occurs in disseminated veins or lenses near the upper boundary of the gabbro, which, together with the overlying granophyre, forms an intrusion in the rocks of the Pongola series. The outcrops occupy a line running approximately NW-SE, its two extremities being distant 7 and 15 miles respectively from Piet Retief".

Wagner (1928) noted the presence of nine seams that vary in length from several hundred metres up to slightly less than two kilometers. The seams range from approximately a metre up to 15 metres in thickness and they dip towards the east or north-east at approximately 30 degrees on Ishlelo. Winter (1965) and Hunter (1970) also reported the presence of a number of titaniferous magnetite-rich layers in the Swaziland portion of the Complex. Numberous layers of titaniferous magnetite are present along the south western flank of the complex in that area and a particularly well defined layer crops out over a strike length of 2,4 km. These titaniferous magnetite layers pinch and swell, reaching maximum thickness of 1,5 m and contain between 0,2 and 0,3 per cent V_2O_5.

THE USUSHWANA IGNEOUS COMPLEX
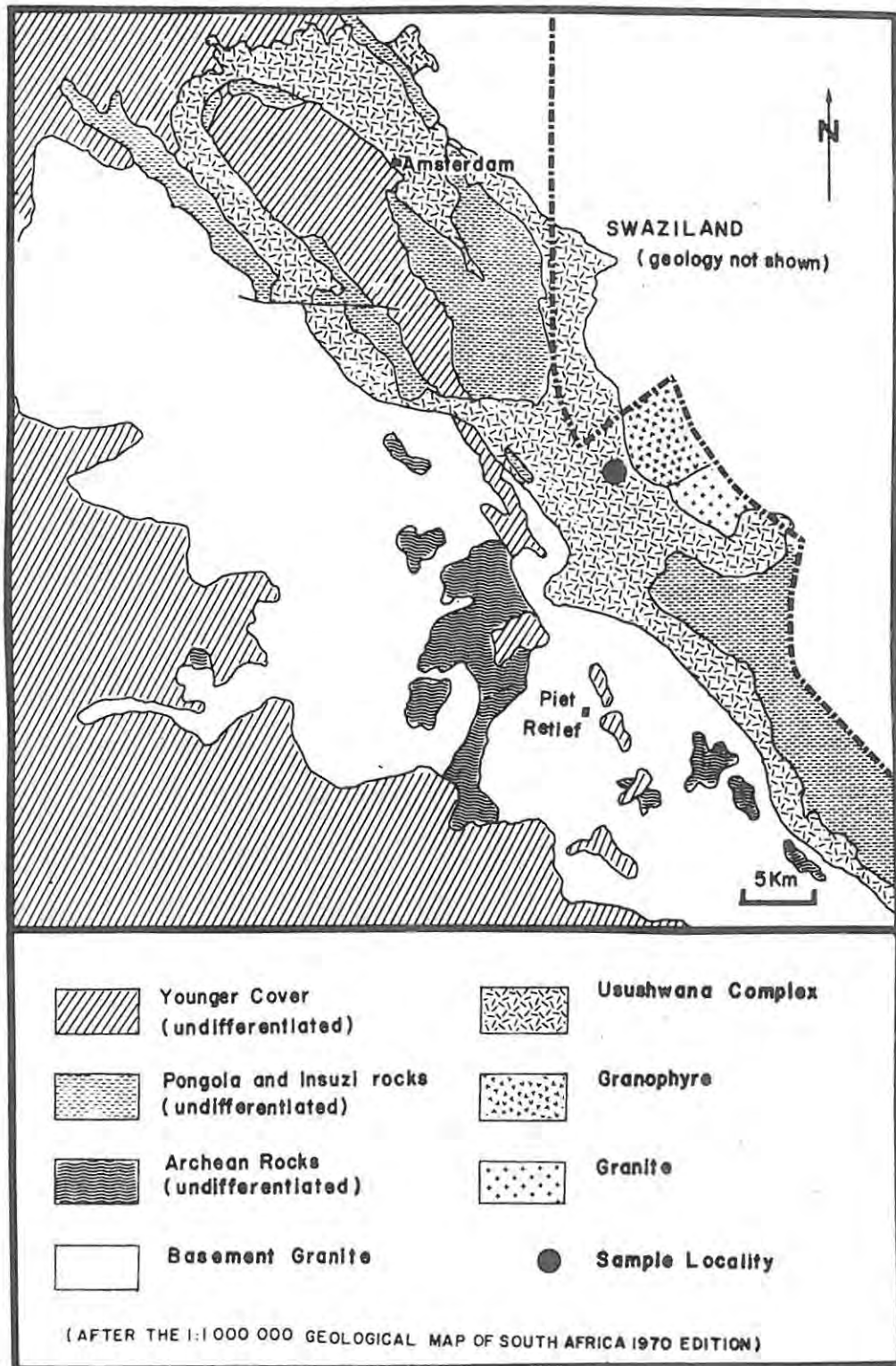
MAP 2 : The Usushwana Igneous Complex.

8.2 <u>Sample Locality</u>

The general geology of the area as well as the sample locality is shown
in the accompanying map (Map 2). The southern part of the area in which
the ores are present is afforested and was not investigated. The
country becomes more open towards the north, but outcrops are generally
poor, the presence of the ore-rich seams being indicated by titaniferous
magnetite rubble. A titaniferous magnetite seam approximately 10 m
thick, herein termed the Main Seam, forms a prominent scarp on the farm
Ishelo No.7, while a narrow and, less-pure seam, is exposed in a stream
section below the main outcrop.

Samples IR 240-251 were collected at approximately 1 m intervals across
the 10 m thick seam while samples IR 252-253 were collected from the
thinner seam. Ore-rich gabbros were also collected 50 and 100 m above
the thick seam.

8.3 <u>Description of the Ores</u>

The 10m thick titaniferous magnetite seam on Ishlelo No.7 dips eastwards
at approximately 25 degrees and is an essentially monomineralic rock
consisting of titaniferous magnetite with only minor silicate impurities.
The lower contact of the seam is not sharply defined, but grades into a
titaniferous magnetite-bearing gabbro due to a progressive increase in
the amount of silicates present. The footwall rocks are highly
weathered and decomposed so that their original nature could not be
accertained.

A highly weathered titaniferous magnetite seam approximately half a metre
thick is present 2 metres below the main seam while the intervening rock
contains large, but variable amounts of titaniferous magnetite. A
further titaniferous magnetite-rich zone is present about 4 metres below
the Main Seam.

Weathering processes have exposed the upper surface of the thick seam
over a fairly wide area to form an ore-pavement similar to those
developed by the Main Magnetite Seam of the Bushveld Complex in the
eastern Transvaal between Magnet Heights and Roossenekal. The upper
contact of the titaniferous magnetite seam and the overlying gabbroic
rocks is not exposed in the area investigated and its nature could not
be determined. The fairly even nature of the exposed surface of the

seam suggests that the transition from an essentially monomineralic titaniferous magnetite rock to a silicate-rich type might be fairly sharp.

The Usushwana ores are generally highly weathered and exhibit the extensive development of secondary oxidation and hydration products. The ores vary from reddish-brown to purple in colour and are generally only weakly magnetic as a result of their highly weathered state. The more highly weathered samples are commonly traversed by irregular goethite veinlets, and are soft and friable with the result that they can be readily disaggregated into their constituent grains. The silicates associated with the titaniferous magnetite-rich zones have been largely altered to fine-grained, chloritic aggregates.

The Main Seam is a massive, dense rock that exhibits a well developed set of closely spaced horizontal and vertical joints and breaks up readily into small rectangular blocks. On a smaller scale, the samples have a highly fractured appearance and are traversed by numerous small irregular fractures as illustrated in Plate 5 (C) and (D). These fractures are not always related to the cleavage directions of the titaniferous magnetite and in many cases they are continuous for several centimetres, cutting across both titaniferous magnetite and matrix. Some of these fractures might in part be related to volume changes that occur during oxidation and subsequent hydration of the magnetite.

The ore is composed of small polygonal titaniferous magnetite grains that are generally separated from each other by a narrow veneer of chloritic material as illustrated in Plates 5 (C-H) and 6 (A-B). The chlorite is in the form of finely crystalline aggregates and is commonly iron-stained, containing variable amounts of goethite and secondary hematite. Extensive alteration of the titaniferous magnetite has taken place at grain boundaries and along fractures where it is in contact with the chlorite resulting in the formation of sphene. This sphene is present as aggregates of fine wedge-shaped crystals that show alteration to leucoxene-like products having yellowish internal reflections in the more weathered samples, (Plate 6 (C) and (D)). Minor amounts of gibbsite are also present in the weathered samples together with secondary TiO_2-rich ilmenite alteration products (leucoxene).

PLATE 5

Photomicrographs taken in incident light using oil immersion objectives.
C & D taken using low power, dry, incident-light objectives.

ROOIWATER TITANIFEROUS IRON ORES

A. Rooiwater basic rocks: Basal sections of two euhedral apatite crystals (black) enclosed by ilmenite (light grey).

B. Letsitele Seam: Euhedral pyrite (white) and transparent spinel (black) crystals present within titaniferous magnetite containing partially spheroidized ilmenite intergrowths (dark grey).

USUSHWANA TITANIFEROUS IRON ORES

C. The typical appearance of the Usushwana ores consisting of an aggregate of polygonal titaniferous magnetite grains separated from each other by a thin chlorite veneer. Note the uniform size and fractured nature of the grains.

D. Similar to (C), but showing the presence of a titaniferous magnetite grain that is very much larger than the surrounding grains.

E. Elongated ilmenite grains (dark grey) located along the boundaries between titaniferous magnetite grains. Note the fractured nature of the titaniferous magnetite and the presence of intergranular chlorite (black).

F. Similar to (E), but showing partial martitization of the magnetite (light) in areas adjacent to fractures and grain boundaries. Notice the cores of unoxidised magnetite (darker grey) in the areas away from the fractures.

G. Similar to (F), but illustrating the corroded nature of the titaniferous magnetite along the fractures and grain boundaries.

H. A large multi-phase titaniferous magnetite grain traversed by chlorite-filled fractures (dark grey). Martitization of the magnetite has occurred adjacent to the fractures (light) leaving "islands" of darker, unoxidised magnetite.

PLATE 5
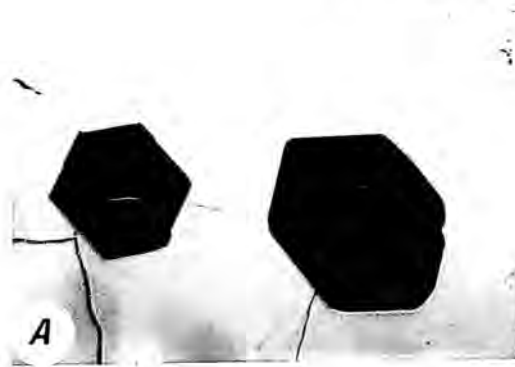
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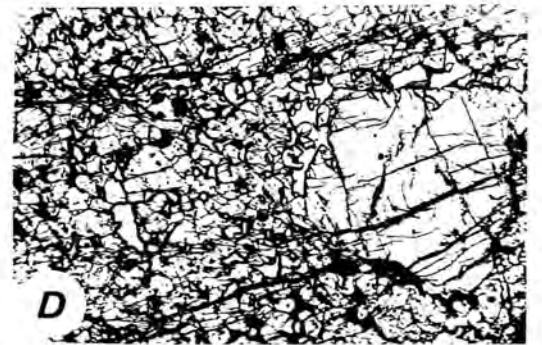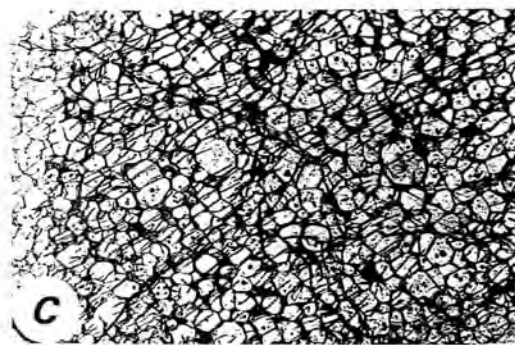
10,0 mm
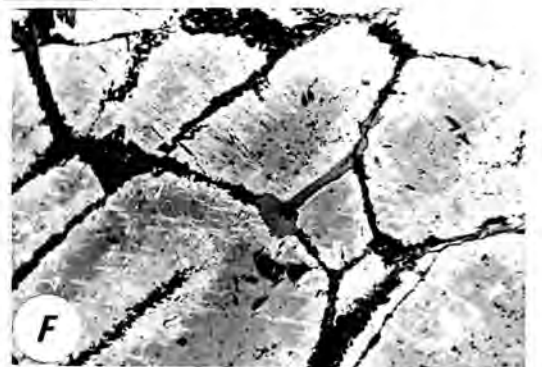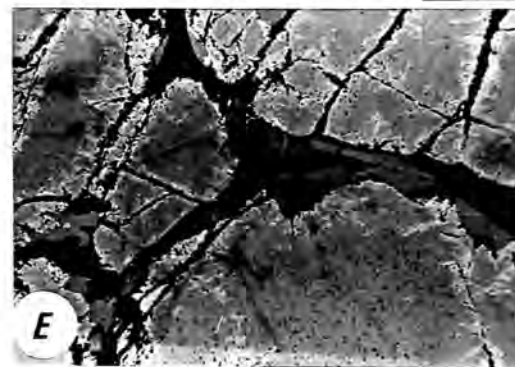
0,15 mm

0,15 mm

Minor, but variable amounts of relatively coarse grained ilmenite are present and are located interstitially between the larger titaniferous magnetite grains (Plates 5 (E-G)). Grain boundaries that are not obscured by the presence of chlorite and other alteration products appear slightly curved and they exhibit a tendency to form triple junctions with interfacial angles approximating 120°.

The Usushwana ores are characterised by complex mineralogical relationships and exhibit a wide range of microstructural development. These features are described more fully in the following sections.

8.3.1 The titaniferous magnetite

Titaniferous magnetite is the dominant opaque phase in the Usushwana ores and it is characterised by the presence of abundant intergrown titanium-rich phases. The titaniferous magnetites have a remarkably uniform grain-size of approximately 1mm, although very much larger grains up to 10mm across may occasionally be present as illustrated in Plate 5 (D).

Grain boundaries between neighbouring titaniferous magnetites tend to be rather straight, but where they are in contact with intergranular ilmenite they are more irregular. The titaniferous magnetite-chlorite grain boundaries are highly irregular and the magnetite has a corroded appearance as illustrated in Plates 5 (E-G) and 6 (A-D).

The titaniferous magnetite margins are characteristically fractured and corroded, while the grains themselves are occasionally completely traversed by irregular fractures. No large-scale displacement of the fragments is apparent and the individual pieces have only been pulled apart very slightly. Extensive alteration of the opaque oxides has occurred in these fractured areas resulting in the formation of finely crystalline sphene. A narrow selvage of sphene is also often present between the titaniferous magnetite and chlorite aggregates. The titaniferous magnetite grains are more rounded in outline at places where the chlorite is more abundantly developed as illustrated in Plates 5 (E-G) and 6 (A-D).

The magnetite-rich parts of the multi-phase titaniferous magnetite grains are preferentially altered to sphene, while the ilmenite intergrowths are less affected. This produces a serrated appearance around the margins of

PLATE 6

All photomicrographs taken in incident light using oil immersion objectives.

USUSHWANA TITANIFEROUS IRON ORES

A. A typical rounded titaniferous magnetite grain (centre) surrounded by chlorite (black). Note the numerous fractures in the grains.

B. Typical Usushwana titaniferous iron ores exhibiting incipient martitization (light). Note the presence of a transgressive veinlet of delicately banded goethite.

C. A highly corroded titaniferous magnetite grain showing the development of wedge-shaped sphene crystals (light) around its margins. The intergranular chlorite is black.

D. Similar to (C), but showing the sphene crystals under higher magnification. The bright internal reflections in the sphene are largely due to secondary alteration to leucoxene.

E. Usushwana basic rocks : A multi-phase titaniferous magnetite grain showing extensive alteration to fine grained sphene and chlorite aggregates. Notice the presence of unaltered ilmenite lamellae in the altered portions of the host grain.

F. Usushwana basic rocks : A corroded titaniferous magnetite grain (light) surrounded by abundant secondary sphene (dark grey).

G. Coarse intergranular ilmenite (dark grey) surrounded by martitized multi-phase titaniferous magnetite and containing small magnetite platelets (light) oriented parallel to (0001).

H. Similar to (G), but showing two large, elongated ilmenite grains located within a titaniferous magnetite grain.

PLATE 6

0,15mm

0,07mm

0,015mm
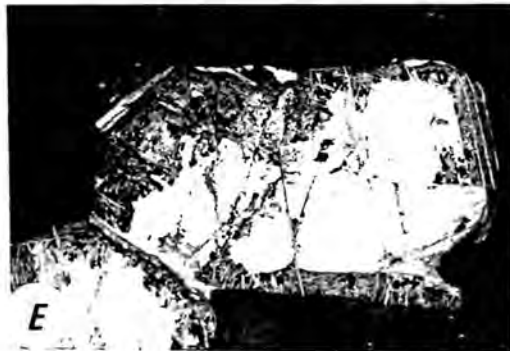
0,15mm
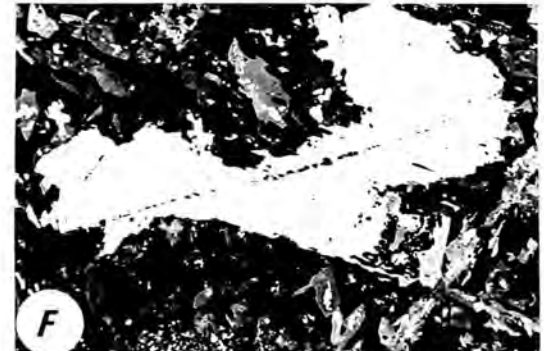
0,07mm

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the titaniferous magnetites containing abundant broad lamellar ilmenite
since the lamellae project beyond the new limits of their hosts into the
surrounding chlorite- and sphene- rich areas.   This relationship is more
clearly observed in the gabbros from above the Main Magnetite Seam in which
the titaniferous magnetites have been extensively altered to fine-grained
aggregates of turbid sphene (Plate 6 (E and F).   The original
crystallographically oriented broad ilmenite lamellae are still present in
these grains and show only incipient alteration to sphene.

Narrow, irregular veinlets of optically homogeneous, intergrowth-free
magnetite are occasionally present in the samples.   These veinlets
exhibit a transgressive relationship to the titaniferous magnetite, but
are not evident in the chloritic matrix.   This magnetite alters directly
to martite and also appears more susceptible to the oxidation process since
it often exhibits incipient martitization even when the surrounding
titaniferous magnetite shows no sign of oxidation.

The Usushwana titaniferous magnetites contain complex ilmenite intergrowths
of various types as well as an exsolved spinel phase.   These relationships
are described further in sections 8.3.2 and 8.3.3.

8.3.2 Ilmenite in the Usushwana ores

Six distinct types of ilmenite, each characterised by differences in grain
size and morphology are present as individual grains and intergrown phases
in the Usushwana ores.   These intergrowths were developed at different
stages during cooling of the complex and represent various stages in an
essentially continuous oxidation/exsolution process.   The various
microintergrowths are discussed separately for descriptive purposes although
a complete gradation exists between the various types.

8.3.2.1 Coarse intergranular ilmenite

Large, elongated, irregularly shaped, ilmenite grains are located
interstitially between the larger titaniferous magnetite grains as
illustrated in Plate 5 (E-G).   These ilmenites are generally in the form
of single crystals, although aggregates of several irregularly shaped grains
may occasionally be present.   They range between 0,1 and 0,4mm in length
and are located along the grain boundaries between the larger titaniferous
magnetites.   They are also occasionally present as inclusions within the
titaniferous magnetite.   The intergranular ilmenite content varies between

3 and 7 volume per cent, but their distribution is extremely variable.
There is a slight increase in their abundance with increasing height
in the seam.

Very small magnetite platelets are sparingly present in the central
portions of the larger ilmenite grains as illustrated in Plate 6·(G-H).
They are oriented along the basal planes of the ilmenite and, although
they are generally less than a micrometre thick, they are up to 15
micrometres in length.   They are uniformly thick and have characteristi-
cally sharp terminations.   These magnetite platelets are martitised
in the more highly weathered samples, but exhibit various stages of
martitization in the less-weathered ores.   The martitization proceeds
directly along the octahedral planes of these magnetite bodies as in
the case of the larger titaniferous magnetite grains.

Small, rounded- to oval-shaped titaniferous magnetite inclusions up to
0,02mm in size, are also occasionally present in these ilmenites and
appear to be accidental inclusions.   They are texturally similar to the
surrounding larger titaniferous magnetite grains.

The intergranular ilmenites show virtually no signs of polygonalization,
but are rather elongated, and are characterised by highly irregular
grain boundaries.   Their location is almost always controlled by the
titaniferous magnetite grain boundaries.   They are also occasionally
connected to broad, sparingly present ilmenite lamellae that are oriented
along the octahedral planes of their titaniferous magnetite hosts.

8.3.2.2 Broad ilmenite lamellae

Broad ilmenite lamellae up to 0,5mm in length and between 0,01 and 0,02mm
in width are sparingly present as intergrowths within the titaniferous
magnetites.   They are oriented along the octahedral planes of their hosts
and occasionally extend to the margins of the titaniferous magnetite grains
where they become broader as illustrated in Plate 7 (B).

These lamellae commonly extend slightly beyond the present boundary of
their titaniferous magnetite hosts into the regions of sphene and chlorite
development.   They are also occasionally connected to the coarse inter-
granular ilmenite grains and are often optically continuous with them.

These lamellae are erratically distributed, within the titaniferous magnetites, but become progressively more common in the ores towards the top of the main seam. They are developed along all the octahedral planes of the titaniferous magnetites, but are too sparsely distributed to form typical trellis patterns and are more often present as sandwich lamellae.

8.3.2.3 Fine intergranular ilmenite

A second type of intergranular ilmenite is preferentially developed along the numerous irregular cracks and fractures that traverse the titaniferous magnetites rather than along their original grain boundaries. These grains are generally rather equant in shape, although some are slightly elongated. They range from 0,04 to 0,01mm in size and have an average diameter of approximately 0,02mm.

The fine granular ilmenites are generally aligned in stringers along the fractures and are intimately mixed with chlorite and sphene as illustrated in Plate 7 (A). They also occasionally form granular aggregates, but do not exhibit the development of polygonal grain boundaries. Stringers of these grains are also occasionally developed along the periphery of the titaniferous magnetite grains at places where they are in contact with chlorite.

These ilmenite grains are often connected to the ends of fine ilmenite lamellae that extend beyond the present margins of the titaniferous magnetite grains into the chlorite and sphene-rich areas. These grains are optically continuous with the lamellae in some cases, but in others they are not.

8.3.2.4 Fine ilmenite lamellae

The Usushwana titaniferous magnetites are characterised by the widespread development of fine ilmenite trellis lamellae. They vary in width from 1 to 3 micrometres, but are up to 0,06mm in length and are generally uniformly thick with gently tapering ends. They are oriented along the octahedral planes of the host titaniferous magnetites and form a well defined, intersecting, triangular, trellis pattern as illustrated in Plates 7 (C and D).

The titaniferous magnetite between closely spaced ilmenite lamellae is

PLATE 7
All photomicrographs taken in incident light using oil immersion objectives.

USUSHANA TITANIFEROUS IRON ORES

A. Fine intergranular ilmenite grains (dark grey) and lath-shaped chlorite grains (black) developed around the margins of a fracture in martitised titaniferous magnetite.

B. A corroded titaniferous magnetite grain containing several broad ilmenite lamellae (dark grey) and surrounded by chlorite (black).

C. An extremely well developed trellis network of fine ilmenite lamellae (dark grey) developed along the octahedral planes of a titaniferous magnetite grain.

D. Similar to (C), but showing small numbers of very fine ilmenite internal granules (dark grey) that are developed in the areas between the ilmenite lamellae.

E. Ilmenite trellis lamellae (dark grey) with abundant very fine-grained ilmenite internal granules (dark grey) developed in the areas between the lamellae.

F. Portion of a titaniferous magnetite grain illustrating the abrupt transition from an area of extensive irregular ilmenite internal granule development (left hand side) into an area of ilmenite trellis development.

G. Similar to (F), but under higher magnification showing the abrupt transition between the two morphological types of ilmenite (dark grey).

H. Fine ilmenite lamellae (dark grey) showing evidence of thickening and coalescence.

PLATE 7

A

0,15 mm

B

0,25mm

C

D

0,015 mm

E

F

0,015mm

G

H
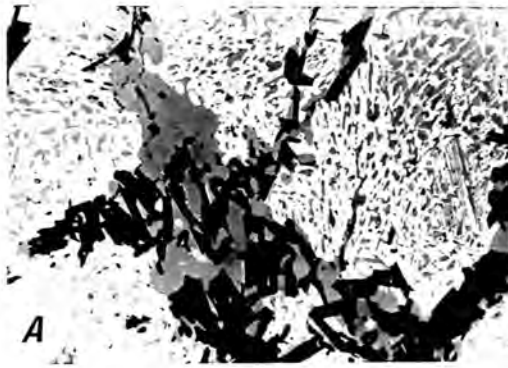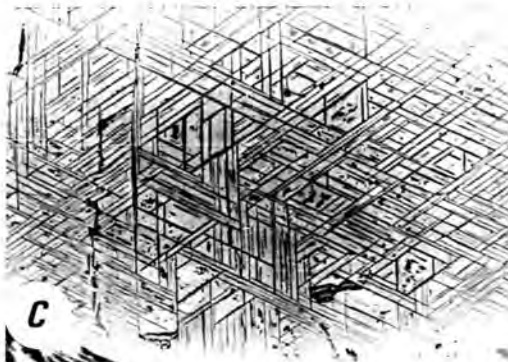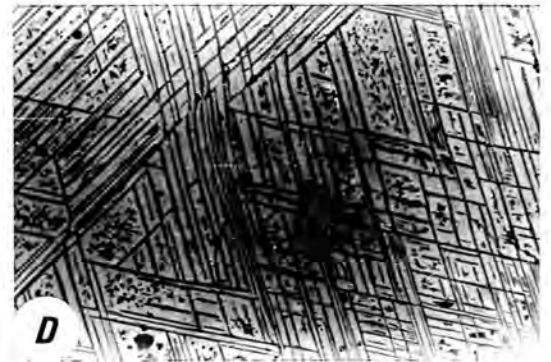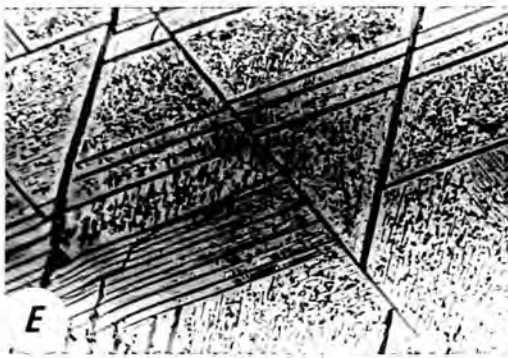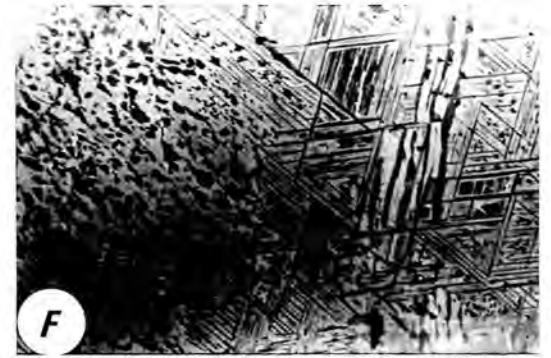
0,015 mm

usually free from other intergrowths and is optically homogeneous as
illustrated in Plate 7 (C). The ilmenite lamellae often enclose areas
of titaniferous magnetite containing very small, irregularly shaped
ilmenite grains in places where they are coarser and more widely spaced
as illustrated in Plate 7 (E).

The well defined trellis network occasionally changes abruptly into a
zone consiting of an apparently disordered array of irregular, elongated
ilmenite granules as illustrated in Plate 7 (F) and (G). The
relationships between the ilmenite trellis networks and these more
irregular areas is described further in section 8.3.2.5. More rarely,
the ilmenite lamellae show signs of breaking down into more irregular
shapes and coalesce with their neighbours as illustrated in Plate 7 (H).

The fine ilmenite lamellae generally taper slightly towards their mutual
intersections and are evenly distributed throughout their hosts, being
present right up their margins. They do not decrease in size or abundance
towards the titaniferous magnetite grain margins and commonly extend
slightly beyond the present boundaries of their hosts, particularly in
areas where fractures containing chlorite and sphene are developed. These
lamellae are sometimes connected to the fine intergranular ilmenite that
is present in the chlorite-rich areas.

These lamellae are occasionally developed on a slightly coarser scale
and are slightly spinelliferous. Small numbers of micrometre-sized
rounded, transparent spinel grains are located along the ilmenite/
titaniferous magnetite interfaces, in these intergrowths, particularly
where the lamellae are larger and more widely spaced.

8.3.2.5 Very fine intragranular ilmenite

Numerous very small, irregularly shaped ilmenite grains ranging from
sub-micrometre sizes up to more than 5 micrometres are present in
restricted zones within the Usushwana titaniferous magnetites. The
fine trellis microstructures occasionally change character abruptly
over the width of a microscope field to form numerous irregularly
shaped ilmenite grains in certain areas as illustrated in Plate 7 (F and G).
They are also sometimes slightly elongated along the octahedral planes of
their hosts as shown in Plate 8 (A). These granular zones exhibit
ill-defined boundaries and are areally small in comparison with the typical

trellis networks. They are irregularly distributed throughout the titaniferous magnetite and are present at all levels within the seam. They are more commonly developed at grain boundaries and in the vicinity of fractures than in the central parts of titaniferous magnetite grains.

The orientation of these grains is crystallographically controlled and they are often optically continuous with neighbouring ilmenite lamellae. Three sets of grains are present in lamellae-free areas, each set consisting of a cluster of optically continuous grains. Each set extinguishes in turn on rotating the microscope stage between crossed nicols and the sets are oriented at approximately 120° with respect to each other. This indicates that they are also oriented along the octahedral directions of their titaniferous magnetite hosts.

The fine ilmenite granules occasionally coalesce to form slightly larger, but also irregularly-shaped, ilmenite grains. They are typically surrounded by a narrow zone of intergrowth-free magnetite and commonly contain small rounded inclusions of optically homogeneous magnetite (Plate 8 (B)).

A similar, but finer, type of irregular granular ilmenite, generally less than 3 micrometres in size, is present in the areas between the coarser and more widely spaced ilmenite lamellae (Plates 7 (E) and (A)). These grains are not crystallographically oriented, but their extremely fine grain size makes determinations of this nature difficult. ·

8.3.2.6 Ilmenite derived from the oxidation of ulvospinel
No typical exsolved ulvospinel microstructures were noted in the samples examined. A microtexture consisting of very fine-grained, elongated ilmenite bodies forming an approximately cubic pattern in titaniferous magnetite is present in the sample from the lowermost part of the Main Seam as illustrated in Plate 8 (C). This texture appears to represent secondary ilmenite derived from the oxidation of exsolved ulvospinel in which coarsening of the original oxidised intergrowths has occurred. This textural type is rare and was only noted in the lowermost part of the Main Seam.

8.3.3 Transparent Spinel Intergrowths
A transparent, aluminium-rich spinel, probably pleonaste, is present as

a minor intergrown phase in the titaniferous magnetite. It is probably
close to pleonaste in composition and is present as extremely small grains
that are sparsely distributed throughout the titaniferous magnetites.
Minor amounts are associated with the larger ilmenite lamellae where it is
present as small rounded grains between 1 and 5 micrometres in size, that
are arranged along the ilmenite/titaniferous magnetite interfaces.

The bulk of the pleonaste is present as micrometre-to sub-micrometre
sized, rounded grains that are intergrown with the magnetite in the
areas between the ilmenite lamellae. It is less frequently present as
fine lamallae that are oriented along the cubic planes of the host
titaniferous magnetites. These lamallae are less than a micrometre wide,
but are up to 5 micrometres long. They become disrupted and destroyed
during the martitization process and are not generally present in the
martitized portions of the titaniferous magnetite grains.

8.3.4 Weathering of the Usushwana ores

The Usushwana ores typically exhibit varying degrees of secondary
oxidation and hydration due to near surface weathering processes. This
has resulted in the formation of abundant martite, goethite and secondary
hematite together with lesser amounts of leucoxene and titaniferous
maghemite. The degree of alteration is highly variable and irregularly
distributed throughout the ore, being related to the proximity of grain
boundaries, fractures, joints, exposed surfaces and other permeable
features. The ores are generally highly weathered, but all gradations
between completely decomposed and only moderately oxidised samples are
present.

The weathering process is progressive and commences with the oxidation
of the titaniferous magnetite. Martite oxidation lamellae are formed
along grain boundaries and fractures and migrate into the titaniferous
magnetite grains along their octahedral planes as illustrated in Plates
5 (E-H) and 6 (A-D). These lamellae increase in size as oxidation
proceeds and penetrate further into the magnetite. They ultimately
coalesce to form large continuous areas of martite that commonly contain
small triangular "islands" of unoxidised magnetite. The partially
oxidised titaniferous magnetites usually exhibit unaltered cores and are
surrounded by martite zones of varying width (Plate 5 (E-H).

The martite formation normally takes place directly, but small amounts of titaniferous maghemite are developed locally between the martite and unoxidised areas. The titaniferous maghemite formation also commences along fractures and grain boundaries, but migrates into the titaniferous magnetite in a more diffuse and irregular manner. Where developed, the titaniferous maghemite is generally present as a narrow, diffuse zone that separates the magnetite from the martite. The inversion of titaniferous maghemite to martite takes place in an irregular fashion and boundaries between these phases are not well defined. The martite becomes hydrated and is in turn altered to geothite as weathering proceeds.

Volume changes associated with the oxidation processes commonly result in fracturing of the ores and goethite becomes precipitated along the fractures to form transgressive veinlets. The geothite veinlets commonly display delicately banded, colloform textures as illustrated in Plate 6 (B). The veinlets commonly show the development of secondary hematite and botryoidal goethite coatings are commonly developed along open joints and on exposed surfaces.

The pleonaste grains are generally decomposed and have been removed from the more highly weathered samples while the ilmenites show varing degrees of alteration to amorphous TiO_2-rich products and poorly-crystalline anatase (leucoxene). Minor amounts of secondary rutile are also developed locally. The ilmenite alteration also commences along grain boundaries and fractures and migrates into the grains in an irregular manner.

The chloritic matrix becomes stained with secondary iron hydroxides and shows alteration to clay minerals. Minor gibbsite is present as a secondary alteration product and the sphene shows varying degrees of alteration to leucoxene-like aggregates having yellowish internal reflections.

8.4 Chemical Composition of the Usushwana Ores

The Usushwana ores were not all analysed as typical whole rock specimens due to their highly weathered nature. The presence of abundant secondary geothite and other oxidised and hydrated products would have resulted in low totals since combined water was not determined.

Titaniferous magnetite concentrates containing lower percentages of

oxidised material were prepared for analysis. Several samples of untreated ore were, however, analysed in order to furnish information on the bulk chemistry of the ores and for use as a check on the effectiveness of the sample preparation procedures. The analyses of typical untreated, weathered ores from the Usushwana complex are given in Table 8.

TABLE 8

Bulk analyses of Usushwana titaniferous iron ores

Sample Element	IR 243	IR 246	IR 249	IR 250	UF 177[*]	UF 191[*]	R 7[+]
SiO_2	3,63	3,73	3,85	3,24	7,05	8,77	5,12
TiO_2	13,30	13,08	12,27	13,32	15,64	13,16	15,17
AlO_2	3,77	2,79	3,33	3,03	3,66	4,01	3,99
Cr_2O_3	0,12	0,08	0,04	0,05	0,02	0,01	0,02
Fe_2O_3	62,72	67,40	64,98	49,66	39,56	39,60	56,69
FeO	15,38	12,10	13,88	29,64	29,14	28,78	11,50
MnO	0,36	0,35	0,38	0,43	0,26	0,56	0,40
MgO	0,42	0,93	0,97	0,75	0,82	0,08	0,80
V_2O_5	0,29	0,29	0,28	0,29	0,22	0,05	0,40
TOTAL :	99,99	100,75	99,98	100,41	96,37	95,02	94,09

[*] Analyses of titaniferous magnetite from the Usushwana complex (Winter, 1965)

[+] Analysis of titaniferous magnetite from the upper group of seam of the Bushveld Igneous Complex (Schwellnus and Willemse, 1943).

The high purity of the Usushwana ores is reflected in the relatively low SiO_2 values shown in the analyses. These SiO_2 values, together with a portion of the Al_2O_3 and MgO, are due largely to the presence of small amounts of chloritic material in the ore.

The TiO_2 values are in the normal range for rocks of this type and can be largely accounted for by the granular and intergrown ilmenite. The secondary sphene and ilmenite alteration products would account for the remaining TiO_2. The V_2O_5 contents of the ores are extremely low and the Usushwana titaniferous magnetites cannot be regarded as potential vanadium ores.

The high Fe_2O_3 values reflect the highly oxidised nature of the ores which has resulted from near surface weathering processes. The possible effects of late-stage deuteric oxidation have been obscured by the weathering process.

The Usushwana ores are chemically similar to the titaniferous iron ores of the Upper Seam of the Bushveld Complex, but contain less TiO_2. Analyses of two Usushwana titaniferous magnetites from Swaziland (Winter, 1965) are given for comparison and it can be seen that they also exhibit very low V_2O_5 contents. These two samples (UF 177 and 191) contain greater amounts of SiO_2 and Al_2O_3 which indicate a higher content of silicate impurities.

8.5 Chemical Analyses of Usushwana Titaniferous Magnetite.

Titaniferous magnetite concentrates were prepared by disaggregating samples using gentle pressure in a ceramic mortar. The disaggregated samples were then stirred vigorously in water for 15 minutes using a mechanical stirrer. The samples were allowed to stand for one minute after which the material in suspension was decanted. This process was continued until no red colouration of the water was apparent and no fine material remained in suspension after stirring.

The suspended solids in the decanted wash water were sedimented by centrifugation and the phases present identified by x-ray diffraction. This material consisted largely of chlorite, together with smaller amounts of poorly-crystalline goethite and hematite as well as minor ilmenite and magnetite.

The titaniferous magnetite concentrate was prepared by repeated magnetic separations under acetone using a powerful permanent magnet. A non-magnetic residue was generally present in small, but variable amounts and consisted largely of secondary hematite containing fine ilmenite lamellae, goethite, chlorite and ilmenite. X-ray diffraction investigations indicated the presence of poorly crystalline hematite and goethite together with ilmenite and some chlorite. Analyses of the titaniferous magnetite concentrates are given in Table 9 and are also presented graphically in figure 3.

TABLE 9

ANALYSES OF USUSHWANA TITANIFEROUS MAGNETITES

	IR 240	IR 241	IR 242	IR 243	IR 244	IR 245	IR 246	IR 247	IR 248	IR 249	IR 250	IR 251	IR 252	M 600+
SiO_2	1,12	0,87	1,39	1,63	1,92	2,44	1,24	1,41	2,48	2,62	3,04	1,48	2,29	1,18
TiO_2	14,10	14,35	14,51	14,61	13,80	13,88	13,59	14,31	14,06	13,61	13,73	14,01	16,67	18,92
Al_2O_3	1,43	1,22	1,45	1,14	1,92	1,81	1,15	1,50	1,54	1,79	1,75	1,72	1,07	2,31
Cr_2O_3	< 0,05	< 0,05	< 0,05	0,13	< 0,05	< 0,05	0,10	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	0,10	0,03
Fe_2O_3	52,77	53,97	62,30	62,08	63,93	56,08	71,74	58,75	66,32	66,90	51,80	60,59	44,75	42,07
FeO	30,58	28,46	20,10	18,54	18,77	25,11	12,09	22,57	15,26	13,76	29,82	21,30	33,36	33,50
MnO	0,30	0,28	0,20	0,22	0,22	0,23	0,22	0,25	0,19	0,23	0,23	0,23	0,32	0,27
MgO	0,37	0,32	0,36	0,38	0,32	0,36	0,27	0,31	0,30	0,31	0,21	0,20	0,54	0,71
V_2O_5	0,26	0,27	0,31	0,35	0,30	0,30	0,29	0,30	0,32	0,30	0,35	0,31	0,23	0,23
TOTAL :	100,93	99,74	100,62	99,08	101,18	100,21	100,69	99,40	100,47	99,52	100,93	99,84	99,33	99,22
TOTAL Fe:	60,77	59,87	59,20	51,83	59,30	58,74	59,57	58,63	58,25	57,49	59,41	58,93	57,23	55,46

+ Sample of titaniferous magnetite from the upper seam of the Bushveld Complex (Molyneux, 1970a, 1972).
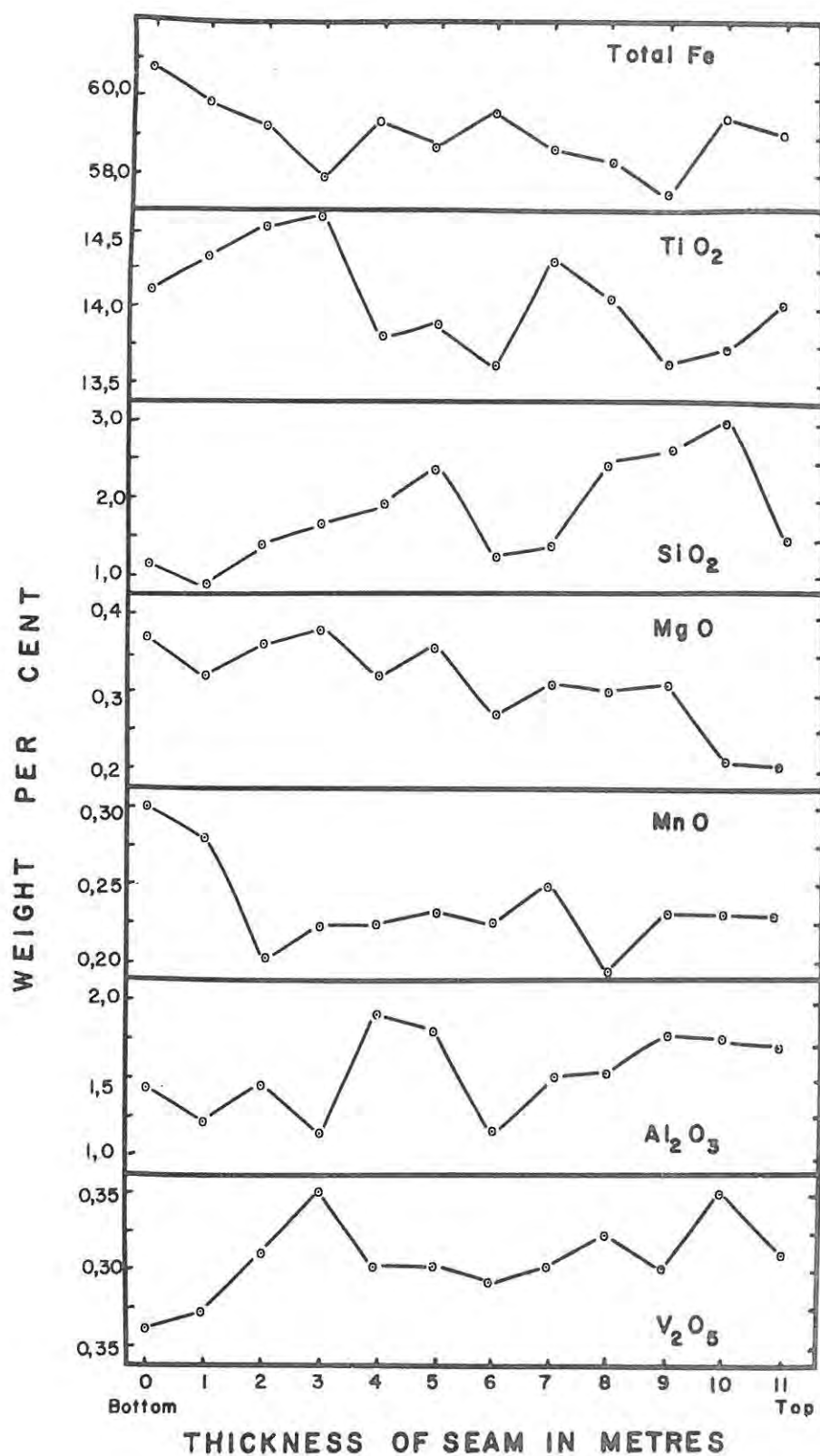
FIGURE 3 : Variation in chemical composition of the multi-phase
titaniferous magnetites with height in the Usushwana
main seam.

The beneficiation process removed only a portion of the chlorite impurities, a minor amount of ilmenite and some completely altered titaniferous magnetite grains. The analyses of the separated titaniferous magnetites do not differ substantially from the analyses of untreated ores apart from lower SiO_2, Al_2O_3 and MgO values. In particular, the slightly higher TiO_2 values in the separated samples are not understood, since a portion of the coarse-grained ilmenite was lost during the beneficiation process. This loss would have been expected to balance the increase in TiO_2 in the samples after the removal of up to 6 per cent by mass of chloritic impurities. The V_2O_5 content of the ores is only marginally improved by the beneficiation process.

The overall Fe_2O_3 content of the titaniferous magnetite concentrate is lower than that of the untreated ore since the magnetic grains generally have cores or small areas of unoxidised magnetite. In some cases the magnetic character of the oxidised grains is due to the presence of maghemite.

The low FeO contents of the samples reflect their highly oxidised nature. Mineralogical calculations indicate that once all the TiO_2 has been combined with FeO to form ilmenite only minor amounts of FeO remain which can be assigned to magnetite. In the extreme case (e.g. IR 246) there is even insufficient FeO to form ilmenite with all of the TiO_2 present and this indicates that some oxidation of Fe^{2+} to Fe^{3+} must also have occurred in the ilmenite.

The titaniferous magnetites from different levels within the Main Seam are all compositionally similar. Sample IR 252 represents a titaniferous magnetite concentrate from a narrow, silicate-rich seam about 50m below the Main Seam and is characterised by a slightly higher TiO_2 content. The SiO_2 values obtained for these samples are largely due to the presence of minor chloritic impurities that were not removed during the separation process. Analyses of titaniferous magnetites commonly show the presence of somewhat less than 0,5 per cent SiO_2 in which the Si is probably present in solid solution in the magnetite. (Vincent and Phillips, 1954). The Al_2O_3 values are also lower than in the untreated ores and are in part due mainly to the presence of the chloritic impurities. The remaining Al_2O_3 can be accounted for by the transparent spinel lamellae in the titaniferous magnetite. The low Al_2O_3 content of

the titaniferous magnetite is reflected by the very small size and paucity of spinel exsolution lamellae.

Both MgO and MnO exhibit low values in the titaniferous magnetite and there is no significant variation between different levels in the main seam. The V_2O_5 values are marginally higher in the titaniferous magnetite concentrates that in the ore as a whole, but are nevertheless too low to warrant recovery.

8.6 Analyses of Co-existing Ilmenites from the Usushwana Complex

Electron microprobe analyses of co-existing coarse grained intergranular ilmenites from the Usushwana Complex are given in Table 10 and are also expressed graphically in figure 4. The ilmenites exhibit higher values for both MnO and MgO than thei co-existing titaniferous magnetites. This indicates the preferential incorporation of these elements into the rhombohedral rather than cubic phase during crystallisation. The two analysed ilmenites from the stratigraphically higher gabbros (IR 255-256) show higher MnO values than the ilmenites from the main seam, but have similar MgO contents.

Recalculation of the analyses assuming stoichiometry indicates the presence of small amounts of excess Fe in the ilmenite. This Fe is probably in the form of Fe_2O_3 in solid solution in the ilmenite.

8.7 Beneficiation

The Usushwana titaniferous iron ores from the main seam contain less than 6 per cent of silicate impurities, and as such, require only limited beneficiation. Their TiO_2 contents are probably too low for high-titania slag production while their V_2O_5 contents are also very low and would not warrant recovery.

It is possible to produce an ilmenite concentrate from the Usushwana ores by crushing to a grain-size of less than 350 mesh, followed by electromagnetic separation. The amount of ilmenite with a sufficiently large grain-size for recovery is, however, limited and it is unlikely that an ilmenite concentrate consisting of more than 3 per cent by mass of the total ore can be prepared in this way. Comparison of analyses of the beneficiated titaniferous magnetites in Table 9 with those of the corresponding untreated ores in Table 8 indicates that little can be

TABLE 10

USUSHWANA COMPLEX : MICROPROBE ANALYSES OF COARSE GRAINED ILMENITES

Oxide	IR 240	IR 241	IR 242	IR 243	IR 244	IR 245	IR 246	IR 247	IR 248	IR 249	IR 250	IR 251	SILICATE-RICH SEAM IR 252	USUSHWANA BASIC ROCKS IR 255	IR 256	BUSHVELD COMPLEX M 600
TiO_2	50,52	50,18	50,01	49,53	51,55	50,13	50,59	50,95	49,88	50,72	50,16	51,29	50,68	49,74	51,30	51,9
FeO	43,12	42,99	43,32	42,56	44,34	43,00	43,43	43,51	42,85	43,60	43,19	44,05	43,32	41,36	42,68	38,4
MgO	0,65	0,55	0,59	0,60	0,61	0,62	0,63	0,63	0,60	0,61	0,60	0,64	0,65	0,65	0,64	3,4
MnO	1,15	1,14	0,84	0,89	0,90	0,91	0,87	0,89	0,91	0,90	0,92	0,92	1,04	2,17	2,30	N.R.
$+Fe_2O_3$	3,59	4,95	5,75	5,43	2,63	4,55	3,67	5,43	4,07	4,23	5,19	4,87	5,99	6,31	2,75	5,8
Al_2O_3	0,24	0,12	0,12	0,12	0,13	0,12	0,14	0,13	0,15	0,12	0,13	0,13	0,13	0,13	0,13	0,3
Cr_2O_3	0,17	0,18	0,19	0,23	0,18	0,17	0,17	0,17	0,17	0,16	0,17	0,18	0,18	0,17	0,17	N.R.
TOTAL :	99,44	100,11	100,82	99,36	100,34	99,50	99,50	101,71	98,63	100,34	100,36	102,08	101,99	100,53	100,01	99,80

NUMBER OF IONS ON THE BASIS OF 6 OXYGENS

	IR 240	IR 241	IR 242	IR 243	IR 244	IR 245	IR 246	IR 247	IR 248	IR 249	IR 250	IR 251	IR 252	IR 255	IR 256	
Al^{3+}	0,012	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	
Cr^{3+}	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	
Fe^{3+}	0,134	0,188	0,216	0,208	0,096	0,170	0,140	0,202	0,154	0,156	0,200	0,178	0,226	0,240	0,102	
Ti^{4+}	1,924	1,900	1,886	1,890	1,946	1,909	1,924	1,893	1,917	1,916	1,894	1,905	1,881	1,874	1,943	
Fe^{2+}	1,826	1,810	1,805	1,805	1,862	1,823	1,839	1,799	1,831	1,832	1,810	1,819	1,789	1,733	1,798	
Mg	0,049	0,042	0,045	0,046	0,045	0,046	0,049	0,047	0,046	0,045	0,045	0,047	0,047	0,048	0,048	
Mn	0,049	0,048	0,036	0,039	0,039	0,040	0,036	0,047	0,040	0,039	0,039	0,039	0,045	0,093	0,097	
TOTAL :	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	

NORMATIVE COMPOSITION (MOLE PER CENT)

	IR 240	IR 241	IR 242	IR 243	IR 244	IR 245	IR 246	IR 247	IR 248	IR 249	IR 250	IR 251	IR 252	IR 255	IR 256	
$FeTiO_3$	91,32	90,47	90,27	90,24	93,01	91,17	91,95	89,92	91,55	91,56	90,50	90,95	89,47	86,62	89,86	
$MgTiO_3$	2,44	2,12	2,25	2,29	2,28	2,28	2,43	2,37	2,30	2,26	2,26	2,37	2,37	2,41	2,42	
$MnTiO_3$	2,44	2,42	1,80	1,98	1,98	1,98	1,82	2,37	2,00	1,96	1,96	1,93	2,23	4,66	4,84	
R_2O_3	3,80	4,99	5,68	5,49	2,73	4,57	3,80	5,34	4,15	4,22	5,28	4,75	5,93	6,31	2,88	
TOTAL :	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	

$+Fe_2O_3$ calculated assuming ilmenite stoichiometry.

M600 coarse-grained ilmenite from Seam 21, Bushveld Complex (Molyneux, 1970a, 1972).

N.R. not reported.
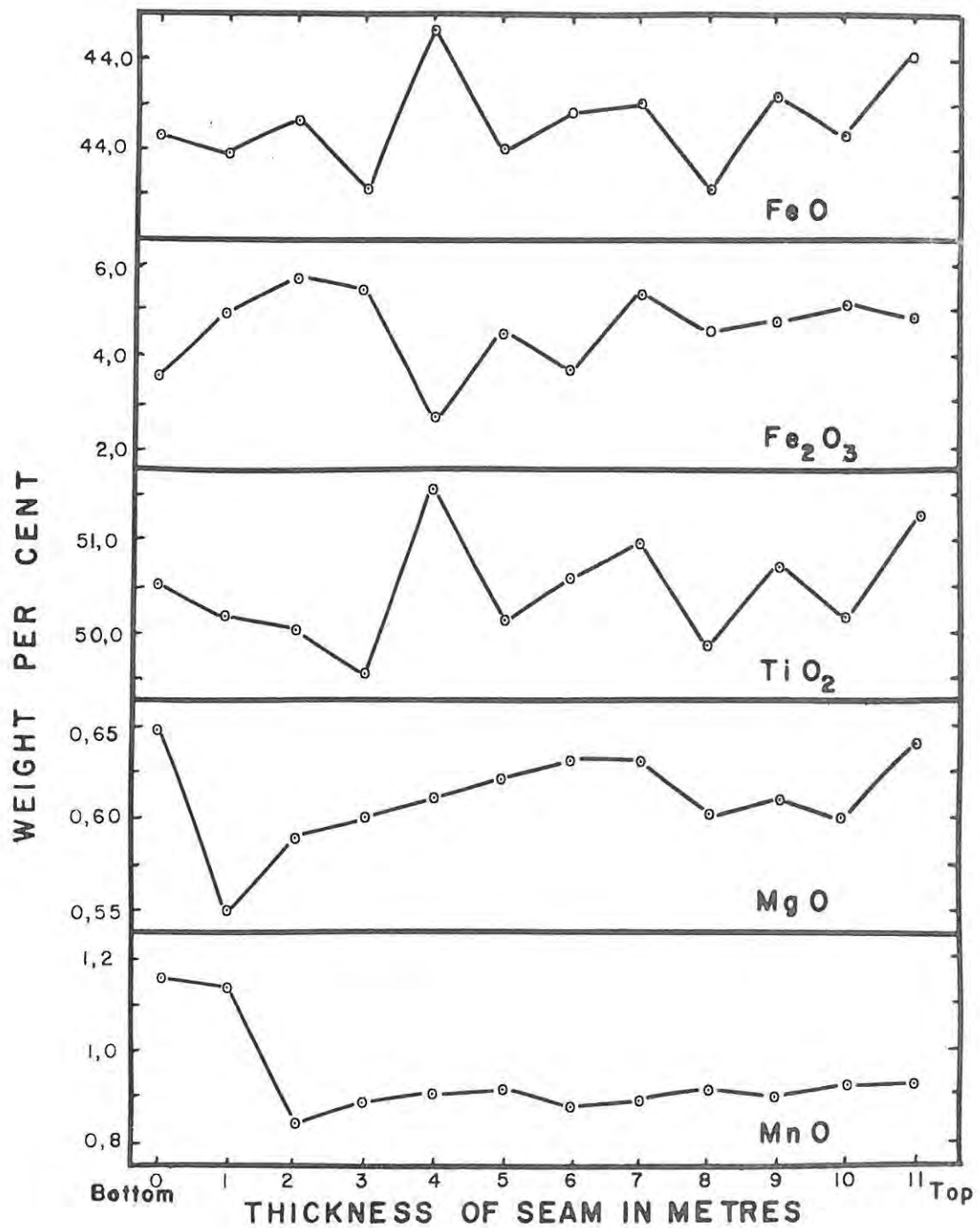
FIGURE 4 : Variation in composition of the co-existing coarse grained ilmenite with height in the Usushwana main seam.

achieved by beneficiation, apart from the removal of a portion of the silicates.

The removal of the small amount of chlorite and coarse grained ilmenite results in a marginal increase in V_2O_5 in the magnetic fraction, but this increase in insufficient to warrent treatment. The bulk of the TiO_2 is present in the form of numerous fine-grained ilmenite intergrowths that are too fine-grained to be liberated to any extent by conventional mechanical separation processes. Any magnetite concentrate produced during beneficiation would have a TiO_2 content of at least 10 per cent.

8.8 Discussion

The Usushwana titaniferous iron ores can be distinguished both chemically and texturally from the ores of the other complexes investigated. They are chemically similar to the upper magnetite seam of the Bushveld Complex (seam 21) and might also be texturally similar since Molyneux (1970 a) reports an increase in the proportion of lamellar ilmenite in this seam.

The microstructures and mineral associations present in the Usushwana ores reflect a complex post-crystallisation history. In particular, the fractured nature of the titaniferous magnetite grains and the associated secondary sphene and chlorite development is problematical. These alteration features could have developed either during late magmatic processes (deuteric alteration) or are possibly the result of a later low-grade metamorphic event.

Humphrey and Krige (1931) reported the extensive uralitization of pyroxene and saussuritization of plagioclase in the Usushwana rocks in the area immediately to the south of the ore deposits. They also mention that the gabbros further to the north (i.e. the area of present interest) are similarly altered. Winter (1965) also reported the widespread alteration of pyroxene to amphibole in the Swaziland portion of the Usushwana Complex. The gabbroic rocks associated with the titaniferous magnetites (this study) show variable degrees of pyroxene amphilbolitization. The alteration of the Usushwana gabbros has not been investigated in detail, but their features are consistant with low grade metamorphism.

The formation of sphene and other secondary minerals at the expense of titaniferous magnetites has been reported in the literature, but has not

been investigated in detail. Ramdohr (1956) stated that sphene is
present as an alteration product of ilmenite in metamorphic rocks formed
above 400°C and is also formed as a hydrothermal alteration product in
certain basic rocks. A review of the literature also indicates that
sphene can be developed at the expense of titaniferous magnetite, both
under late-stage magmatic conditions and during metamorphism.

Campbell et al. (1932) reported that the titaniferous iron oxides in a
basic sill had been partially replaced by "granules of brown crystalline
sphene". They noted that the sphene alteration is most pronounced in
rocks that show evidence of "calcification" and is associated with
chloritization. Cornwall (1951) reported that the magnetite and ilmenite
in thick Keweenawan basaltic lava flows are moderately to intensely
veined and irregularly replaced by chlorite, sphene and hematite. He
concluded that this alteration was the result of volatile activity in
the cooling magma. Wilkinson (1957) reported that the titanomagnetites
in a teschenite sill often exhibit internal deuteric alteration to sphene
and leucoxene.

Baragar (1960) noted the presence of turbid, ophitic masses of granular
sphene containing triangularly, or rectangularly arranged ilmenite
lamellae in gabbros. He concluded that they were altered titaniferous
magnetite grains containing exsolved ilmenite. He suggested that the
alteration was presumably facilitated by the presence of exsolved
ulvospinel since it weakened the resistance of the magnetite to
replacement and provided the titanium necessary for sphene formation.

Desborough (1963) described the alteration of magnetite-ulvospinel to
sphene aggregates in differentiated basic rocks and noted that the ilmenite
commonly remained unaffected during this process. He reported that the
replacement of magnetite-ulvospinel by sphene apparently occurred without
a volume change resulting in the preservation of the delicate ilmenite
lamellae within the sphene aggregates. He noted that all stages of the
replacement process could be observed within the same specimen and that
the co-existing olivine also showed alteration to chlorite. The
associated plagioclase is only slightly saussuritized while the augite is
rarely altered.

Desborough (1963) reviewed the literature on sphene formation associated

with the alteration of titanomagnetite and noted that this phenomenon
might be more common than previously recognised. He investigated the
alteration of magnetite-ulvospinel intergrowths to turbid sphene in
altered differentiated basic rocks and suggested that it was caused by
fluids derived from the basic magma. These fluids were reported to be
in the temperature range of higher-temperature hydrothermal solutions
and were active during the later-stages of crystallisation.

Jensen (1966) reported the alteration of both titanomagnetite and ilmenite
to turbid sphene in dolerite dykes. He concluded that the alteration was
due to the action of highly penetrative hypergene solutions expelled from
the residual molten parts of the magma.

Davidson and Wyllie (1968) reported the dissolution of magnetite and the
presence of skeletal ilmenite grains that were intimately associated with
hydrous mafic minerals in a granophryric diabase. They concluded that
this ilmenite was originally present as lamellae in the magnetite that
had been dissolved by the action of later solutions. These solutions
were also responsible for the formation of the secondary hydrous mafic
minerals which crystallised at high temperatures, possibly above the
magnetite-ulvospinel solvus.

Willense (1969b) and Molyneux (1970 a,b) reported minor late magmatic stage
replacement of Bushveld titaniferous magnetites by sphene and other gangue
minerals. According to Willense (1969b) chlorite, biotite, amphibole,
sulphides and, possibly sphene, are formed at the expense of titaniferous
magnetite by late stage volatile activity during cooling. Hubicka-
Ptasinska and Jasienska (1971) reported that the alteration of
titanomagnetite to sphene takes place via the formation of intermediate
titanomaghemite and involves the diffusion of Ca^{2+}, Si^{4+}, and Ti^{4+} cations
from the surrounding minerals while Fe^{3+} is removed from the titaniferous
magnetite.

Elsdon (1972) noted that the titanomagnetites in the Kap Edvard Holm Basic
Intrusion sometimes show considerable late-stage alteration to chlorite
intergrown with an unidentified, extremely fine-grained, dark brown
material (possibly sphene?).

Sphene can also form from titaniferous magnetite and ilmenite during

regional metamorphism (Ramdohr, 1956). Buddington et al. (1955,1963)
reported its formation at the expense of these minerals in regionally
metamorphosed gneisses. Wilcox and Poldervaart (1958) reported the
development of granular sphene rims round titaniferous magnetite in
metadolerites and noted that sphene commonly takes the place of magnetite
in some amphibolites. Ruckmick and Noble (1959) also reported the common
occurrence of sub-hedral to euhedral sphene in intimate association with
magnetite in a saussuritized metagabbro. Desborough (1963) noted that
the iron-titanium oxides in diabases and related rock types would a' 'c be
converted to sphene under regional metamorphic conditions.

According to the experimental data of Schuiling and Vink (1967), the
sphene stability field lies within the temperature range encountered both
during the subsolidus cooling of basic rocks and during low grade
metamorphism (less than 500°C). Hunt and Kerrick (1977) also noted that
sphene can be formed from ilmenite during metamorphism, but comment on
the lack of published experimental data on the possible mechanisms
involved.

The exact mechanism by which sphene, chlorite and other hydrous silicates
can be formed from titaniferous magnetite is uncertain, but the foregoing
literature review suggests that it involves the presence of a solution or
at least of some volatiles. The process is also operative at elevated
temperatures both during the late stages of magmatic crystallisation or a
subsequent metamorphic event. The reactions involving the formation of
sphene from ilmenite or ulvospinel can be represented schematically as
follows:

$$3\ FeTiO_3 + 3\ CaO + 3\ SiO_2 + 2\ O_2 \longrightarrow 3\ CaTiSiO_5 + 2\ Fe_3O_4$$

ilmenite   (from plagioclase)   sphene + magnetite component

OR,

$$3\ Fe_2TiO_4 + 3\ CaO + 3\ SiO_2 + O_2 \longrightarrow 3\ CaTiSiO_5 + Fe_3O_4$$

ulvospinel   (from plagioclase)   sphene + magnetite component
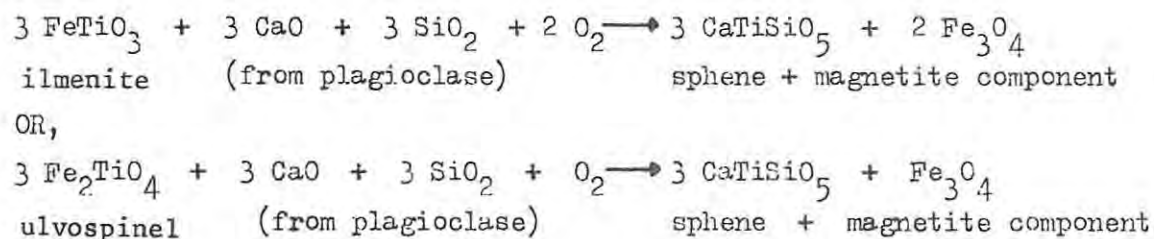
No experimental data are available on the formation of sphene from
titaniferous magnetite, but Fe and Ti ions would become liberated during
its dissolution, while the Ca and Si ions required to form sphene can be
obtained from either the original interprecipitate liquid, plagioclase or
Ca-rich pyroxene. The presence of a fluid phase at elevated temperatures

would facilitate the ionic mobility and possible introduction of oxygen.
A portion of the Fe liberated during reaction might be incorporated
into secondary chlorite or hornblende while any excess might have
contributed to the formation of occasional transgressive magnetite
veinlets in the manner envisaged by Davidson and Wyllie (1968).
Transgressive magnetite veinlets apparently originating at the site of
abundant sphene development were, however, not noted in this study.

The nature of the fracturing of the titaniferous magnetite grains
suggests that it was caused by some process other than tectonic stress
since this would have resulted in the complete brecciation of the grains.
The fractures would then have been continuous both across individual and
neighbouring grains while displacement of fragments would also have
occurred.   A well defined, preferred orientation would have developed
in the more extreme cases of deformation.

The fracturing occurred at temperatures that were too low for any marked
annealing or healing of the fractures to have taken place.   There is
no evidence of post-fracturing grain-boundary migration or any other
form of re-adjustment having taken place between the individual fragments
and their neighbours.   The presence of small irregularly-shaped ilmenite
grains along the margins of fractures suggests that, although the
temperatures were sufficiently high for the small-scale oxidation/
exsolution of ilmenite, they were not high enough for grain boundary
migration.

Many of these small ilmenite grains are connected to fine ilmenite
lamellae that project beyond the margins of the corroded titaniferous
magnetites.   This suggests that they might represent a second generation
of lower-temperature "external granule" ilmenite oxidation/exsolution
bodies that have developed on a much finer scale due to the decreased
ionic mobilities at lower temperatures.   The fracturing would have
generated fresh nucleation sites along the newly formed grain boundaries
and this type of exsolution would also have been facilitated by reducing
the distances over which diffusion would be necessary.   It is also
possible that a portion of this ilmenite might have been formed from the
Ti and Fe ions released during titaniferous magnetite dissolution when
there was insufficient Ca present to form sphene.   The projecting ends
of the ilmenite lamellae would have provided suitable nucleation sites

for growth of this ilmenite.

The marginal fracturing of the titaniferous magnetite grains may have occurred during the alteration process which commenced at grain boundaries and along pre-existing cracks. Dissolution would cause the formation of slight embayments and it is possible that slight volume changes associated with the sphene- and chlorite-formation were sufficient to cause fracturing of the titaniferous magnetite. This would produce fresh surfaces that would in turn be available for reaction and would become coated with a thin veneer of chlorite and sphene to produce the typical Usushwana textures. This is contrary to the views of Desborough (1963) who suggested that no volume changes are involved during this process.

The alteration is generally only incipient in the Main Seam, but increases slightly where there is an increase in chlortic material. The degree of alteration is more extensive in the chlorite-rich ores underlying the main seam while the disseminated titaniferous magnetite in the overlying gabbros has been almost completely altered to turbid sphene containing relict ilmenite lamellae. The pyroxenes in the altered gabbros have narrow outer rims of green hornblende that may have incorporated some of the Fe released during the alteration of the associated titaniferous magnetite.

The alteration of titaniferous magnetite to sphene may have, in part, been due to the action of late-stage magmatic fluids. The widespread alteration of the Usushwana basic rocks reported by Humphrey and Krige (1931), Winter (1965), Hunter (1970) and the ubiquitous development of chlorite in the ores examined during this study, suggest, however, that the bulk of the sphene was developed during a subsequent low grade metamorphic event. The temperatures reached during this event must have been low enough to prevent any marked recrystallization of the ores, but were high enough to allow the observed reactions to take place. The second generation of fine-grained external granule ilmenite may have been formed, at least in part, during cooling after the thermal peak of the metamorphic event.

The temperature conditions reached during this metamorphic episode were not high enough to allow for the widespread modification of the pre-existing titaniferous magnetite microstructures in the Usushwana ores. The well

defined ilmenite trellis networks occasionally show evidence of
breakdown, but the resulting spheroidization is only of an incipient
nature. The abundant fine ilmenite granules most probably formed
during subsolidus cooling under conditions of high oxygen fugacity
as envisaged by Buddington and Lindsley (1964) (internal granule
exsolution).

The well developed, fine ilmenite trellis microintergrowths together
with their enclosed fine ilmenite grains (internal granules) are
indicative of relatively high oxygen fugacities during cooling at
temperatures below the magnetite–ulvospinel solvus. The general lack
of relict ulvospinel textures, except in the lowermost part of the
thick seam, provides additional evidence for higher oxygen fugacities
during this stage of cooling. This is in contrast to relationships
in the Skaergaard complex in which there is a decrease in oxygen fugacity
with falling temperature (Williams, 1971).

The co-existing coarse-grained ilmenite grains are only present in minor
amounts and their morphologies suggest that they are early-stage, external
granule exsolution products, rather than co-precipitated grains.

The presence of oriented magnetite lamellae in this ilmenite is also
problematical. The microstructural evidence suggests that relatively
high oxygen fugacities existed during the cooling of the Usushwana ores so
that any iron-rich ilmenite might have been expected to exsolve hematite
rather than magnetite. Providing that the oxygen fugacities were buffered
to low enough values during cooling, reduction of Fe_2O_3, both in solid
solution and in the exsolution lamellae would occur to form magnetite.
This magnetite would then be present as "exsolution lamellae" in the
ilmenite according to the mechanism of Buddington et al. (1963) and
Buddington and Lindsley (1964). The reduction of ilmenite to ulvospinel
requires exceptionally strong reducing conditions, so that even though the
oxygen fugacities were low enough to reduce hematite, they would not have
been low enough to have influenced the the other microstructures. Ilmenite
would have remained as the stable phase in the titaniferous magnetites.

8.9 Genesis of the Usushwana Ores
The nature of the Usushwana titaniferous magnetites and their occurrence

in well defined layers towards the upper parts of a large basic intrusion
is consistent with their having formed during the normal crystallisation
processes that are operative in large fractionated basic intrusions that
show late-stage iron enrichment.   The microstructures developed in the
Usushwana ores suggest the following sequence of formation:-

1)   The formation of cumulate layers consisting essentially of a
      homogeneous high temperature, iron-rich, spinellid phase containing
      moderate amounts of Ti and minor amounts of Mg, Mn, Al and V.   A
      little plagioclase and pyroxene may have co-precipitated with the
      spinel in the relatively pure seams, while larger amounts of these
      mineral co-precipitated in the silicate-rich seams.   Factors such as
      post-cumulus growth, removal of intergranular fluids by filter pressing
      and annealing may also have played an important role in the development
      of the ore-rich horizons.

2)   At the commencement of cooling, exsolution of a titanium-rich oxide
      phase was initiated resulting in the formation of several per cent
      by mass of intergranular ilmenite and possibly the sparsely distributed
      broad ilmenite lamellae.   This ilmenite represents less than 5 per cent
      of the total mass of the ore and is probably true exsolved ilmenite
      (Anderson, 1968b).   The nucleation and growth of these phases
      occurred along grain boundary imperfections with the discrete grains
      developing externally and the lamellae growing into the magnetites
      parallel to their octahedral planes.   This corresponds to the
      "external granule" exsolution products described by Buddington and
      Lindsley (1964) and this process would have ceased once temperatures
      fell to below approximately 750°C (Buddington and Lindsley, 1964 ;
      Anderson, 1968b).   Grain-boundary adjustment would have taken place
      under the influence of interfacial free energy during this stage due
      to the higher ionic mobility at elevated temperatures.   This annealing
      process would have contributed to the development of polygonal grains
      with interfacial angles approximating 120°.

3)   As cooling continued to lower temperatures, the processes in stage 2
      would have become progressively less important as the ionic mobility
      decreased.   Once the amount of exsolved ilmenite had risen above
      approximately 5 per cent by mass of the titaniferous magnetite, any
      additional ilmenite must have formed by a contemporaneous oxidation/

exsolution process (Anderson, 1968b). This process operates under conditions of relatively high oxygen fugacity and can take place at temperatures both above and below the magnetite ulvospinel solvus to produce similar textures. These conditions led to the widespread formation of fine ilmenite trellis lamellae along the octahedral planes of the magnetite. This corresponds to the contemporaneous oxidation/exsolution trellis intergrowths recognised by Buddington and Lindsley (1964) and would have continued at temperatures down to approximately 500°C.

The titaniferous magnetites also contain some Al-rich spinel in solid solution. Exsolution of this in the form of pleonaste would occur towards the end of stage 2 (below approximately 900°). Dislocations and other grain-boundary imperfactions along the interfaces between the sparsely distributed, broad ilmenite lamellae would have provided suitable sites for the heterogeneous nucleation and growth of this phase resulting in the formation of numerous small grains. Minor external granule exsolution may also have occurred at this stage. Further cooling would have increased the pleonaste supersaturation in the magnetite in areas away from the earlier-formed grains. These conditions led to the subsequent nucleation and growth of the sparsely developed fine pleonaste lamellae that are oriented parallel to the cubic planes of their magnetite hosts.

Iron-rich ilmenite can only hold between 6 and 9 per cent Fe_2O_3 in solid solution at low temperatures and exsolution commences at temperatures below 800°C (Lindsley and Lindh, 1974). The magnetite lamellae now present in the intergranular ilmenite may have developed as hematite lamellae during this stage, but were subsequently reduced to magnetite, or else they may have formed by a complex reduction/exsolution process. In the latter case, the oxygen fugacities must have had intermediate values such that they were not only too high for ulvospinel stability, but were also too low for the existance of hematite.

4) Exsolution and oxidation/exsolution would continue during further cooling, but diffusion rates would decrease with lower ionic mobility and growth of the exsolved phases would become more sluggish. Grain boundary migration and readjustment would also have effectively ceased

once the temperatures reached "several hundred degrees" (Buddington and Lindsley, 1964). Iron-titanium oxide supersaturations would have increased in the magnetite areas between the ilmenite lamellae during this period, but ionic mobility would have been too low to allow for the migration of this material to the pre-existing lamellae. The oxygen fugacities also appear to have remained fairly high during this stage (lack of ulvospinel). These conditions led to the nucleation and growth of the small rounded to irregular-shaped, micrometre-sized, ilmenite grains in the areas between the ilmenite lamellae. They also formed by contemporaneous oxidation/exsolution and correspond to the internal granule exsolution textures described by Buddington and Lindsley (1964). These textures require high oxygen fugacities for their formation and their presence in narrow zones bordering fractures indicates the presence, at least locally, of high oxygen fugacities in the interstitial fluids during this stage.

Minor late-stage deuteric alteration may have occurred during this stage and also possibly towards the end of stage 3. Minor late-stage alteration of pyroxene to amphibole and chlorite may have occurred while minor sphene developed at the expense of titaniferous magnetite.

5) Alteration of the opaque oxides and silicates occurred during a later low grade metamorphic episode resulting in the formation of sphene and abundant chlorite. The temperatures reached were not high enough to cause any marked modification of the existing microstructures and were probably in the range of the lower part of stage 3 and upper part of stage 4. Provided that the oxygen fugacity remained high enough to prevent any reduction of ilmenite to ulvospinel, no modification of the microstructure would have occurred beyond a possible continuation of low temperature exsolution during subsequent cooling. Ionic mobilities would have been too low under these conditions for any large scale diffusion and recrystallisation. It is possible that the fine-grained external ilmenite grains present in the fractures were formed during renewed oxidation/exsolution during cooling through the higher temperature stages after the metamorphic thermal peak. The oxygen fugacities were buffered by the abundant oxide assemblage in the ores during the metamorphism so that, although they prevented the formation of ulvospinel, they may have been low enough to allow the reduction of hematite in solid solution in the intergranular ilmenite. This

resulted in the formation of oriented magnetite lamellae in the ilmenite.

6) The extensive oxidation and hydration of the ores resulted from weathering under near-surface conditions and is continuing at the present time.

8.10 Conclusions

1. The occurrence of the Usushwana titaniferous iron ores in discrete layers towards the upper parts of a large gabbroic intrusion is in accord with their having developed by the normal crystallisation-differentiation processes that are operative in stratiform basic intrusions.

2. The Usushwana titaniferous magnetites are chemically similar to ores of this nature that are typically developed in layered gabbroic complexes.

3. The ores are characterised by the development of abundant ilmenite trellis networks and internal granules in the titaniferous magnetites that are indicative of subsolidus cooling under conditions of high oxygen fugacity.

4. The ores appear to have undergone low grade metamorphism that has resulted in the development of abundant sphene and chlorite at the expense of the original opaque oxides and silicates. Extensive fracturing of the marginal areas of the titaniferous magnetite grains also occurred during this period.

5. The metamorphic temperatures were not high enough to cause widespread modification of the pre-existing microstructures and only incipient spheroidization of the lamellar intergrowths occurred.

6. The Usushwana ores are essentially pure and contain only minor chloritic impurities that can be readily removed by conventional ore-dressing techniques. They contain only minor coarse grained ilmenite that can be recovered by crushing to less than 350 mesh followed by electromagnetic separation.

7. The ores of the Main Seam are chemically similar to the titaniferous

iron ores of the Upper Seam (No. 21) of the Bushveld Igneous Complex. Their vanadium content is extremely low and cannot be more than marginally upgraded by beneficiation procedures with the result that they cannot be regarded as potential ores of this element.

8. The TiO_2 content of the ores is also fairly low with the result that they do not represent potential raw materials for high-titania slag production. The bulk of their TiO_2 content is present as extremely fine-grained microintergrowths that cannot be separated from the magnetite by conventional ore-dressing techniques.

9. The South African portion of the Usushwana Complex has not been studied in detail. Comprehensive geological studies and detailed mapping are necessary to determine the nature of the complex, the number and extent of the titaniferous magnetite seams present and their V_2O_5 contents.

10. The iron-titanium oxides of the Usushwana Complex exhibit micro-structures that are indicative of crystallisation and subsolidus cooling under conditions of high oxygen fugacity. These features are rarely developed to this extent in rocks of this type and warrant further investigation.

11. These ores are characterised by the widespread development of sphene and chlorite at the expense of titaniferous magnetite. Little is currently known about the mechanisms involved in this process and the Usushwana ores represent ideal materials for an investigation into sphene development.

12. The Usushwana ores do not appear to have any economic potential at present in view of their chemical composition and limited ore reserves of approximately 5 million tons at or near the surface (Wagner, 1928). The location of the deposit very near to the main railway line to Richards Bay may, however, have a strong bearing on the future economic significance of this deposit.

9.8 THE TITANIFEROUS IRON ORES OF THE MAMBULA COMPLEX

9.1 Introduction

The Mambula Igneous Complex is located at the confluence of the Tugela
and Mambula rivers in Zululand and covers an area of approximately 25
square kilometres. It is roughly square in plan and is composed of a
variety of basic igneous rocks. The petrology of the complex has been
described by du Toit (1918, 1931), and it has also been mentioned briefly
by Wagner (1928) and Lambert (1962).

The Complex is largely gabbroic in nature and consists of a medium grained
gabbro, with or without orthopyroxene, but devoid of olivine (du Toit, 1918;
1931). Norites, pyroxenites and coarse grained anorthosites are also
present, while a well defined ingeous layering is developed in places.
The complex is intrusive into the metamorphosed Tugela formations and
du Toit (1918, 1931) inferred the presence of a nearby intrusive granite
on the basis of numerous transgressive pegmatitic dykes and veins. A
number of titaniferous magnetite-rich seams composed of varying
proportions of polygonal magnetite and ilmenite grains ranging from 0,3-
1,2mm in size are present in the gabbro. du Toit also noted the presence
of ilmenite lamellae oriented in three directions and intersecting at
angles of about 120° in the magnetite.

du Toit (1931) and Lambert (1962) concluded that a genetic relationship
exists between the mafic Mambula Complex and a wide range of mafic to
ultramafic rock types that are exposed in the Tugela Valley. Matthews
(1972) noted that these isolated and deformed masses of intrusive ultra-
basic rocks are located within a belt of metamorphosed rocks (the Tugela
Gneissic Amphibolite Complex). They have been highly metamorphosed,
migmititized and extensively recrystallised. Their original nature is
uncertain, but Matthews (1972) concluded that they were largely derived
from rocks of basaltic, and possibly andesitic, composition. This mafic
to ultramafic association is characteristic of the intermediate layer of
an ophiolite suite and he proposed that the Tugela Gneissic Amphibolite
Complex represents an extensive segment of transformed oceanic crust.
He concluded that the Tugela rocks are an obducted ophiolit suit and that
they represent a nappe structure that is underlain by a major tectonic
slide.

Cain (1975) reviewed the regional geology of the area and concluded that,

although, various mafic and ultramafic rock types of the Tugels valley
might be members of an obducted ophiolite suit, the bulk of the rocks
represent a thick sequence of metasedimentary material. He noted that
many of the mafic to ultramafic intrusive bodies have relatively
unaltered cores (magnetite-gabbros and norite in the case of the Mambula
Complex) that grade outwards into massive hornblende gneisses, ortho-
amphibolites and uncommon dioritic gneisses which all display palimpsest
igneous textures. According to Cain (1975) the Mambula Complex is
located in a zone of metamorphic rocks of the almandine-amphibolite
facies. Cain (1975) estimated that the age of the ophiolite suite and
associated mafic and ultramafic intrusive rocks is in the region of 2400
million years and noted that the whole region was involved in the wide-
spread Natal-Namaqua metamorphic episode that is dated at between 900 and
1000 million years.

9.2 Sample Localities

Numerous seams of titaniferous magnetite and titaniferous magnetite-rich
gabbro are present within the Mambula Complex and an attempt was made to
sample each seam. A detailed field examination of the geological
relationships both within the Complex and between the different ore-rich
seams was beyond the terms of reference of this investigation and was not
undertaken.

Samples were collected from exposures along a gravel road that traverses
the Complex in a roughly north-south direction on the western side of the
Tugela river. The traverse was commenced at the southern margin of the
Complex and 15 individual ore-rich seams of titaniferous magnetite-rich
gabbros were sampled. Nine seams were sampled on the south side of the
Mambula river (samples MB 1-48) while 6 were sampled on the north side
(samples MB 49-68). Samples MB 69-72 were collected from a thick massive
titaniferous magnetite seam that crops out on the western bank of the Tugela
river. The relationship between this seam and the others examined is
uncertain. Titaniferous magnetite-rich seams are also present in the small
portion of the Complex on the eastern side of the Tugela river, but they
were not sampled.

The Mambula Complex has been deformed by folding and faulting and it was
not possible to correlate individual seams during the time available for
sample collection. There appears to be a duplication of several of the
seams sampled in the traverse and in all, probably no more than 6

substantial titaniferous magnetite seams are exposed. The structure of the Complex suggests that four of the seams on the south side of the Mambula river are also present on the north side. The location of samples is indicated in the accompanying sketch map (map 3) that has been compiled from uncorrected aerial photographs.

SKETCH MAP OF THE MAMBULA IGNEOUS COMPLEX
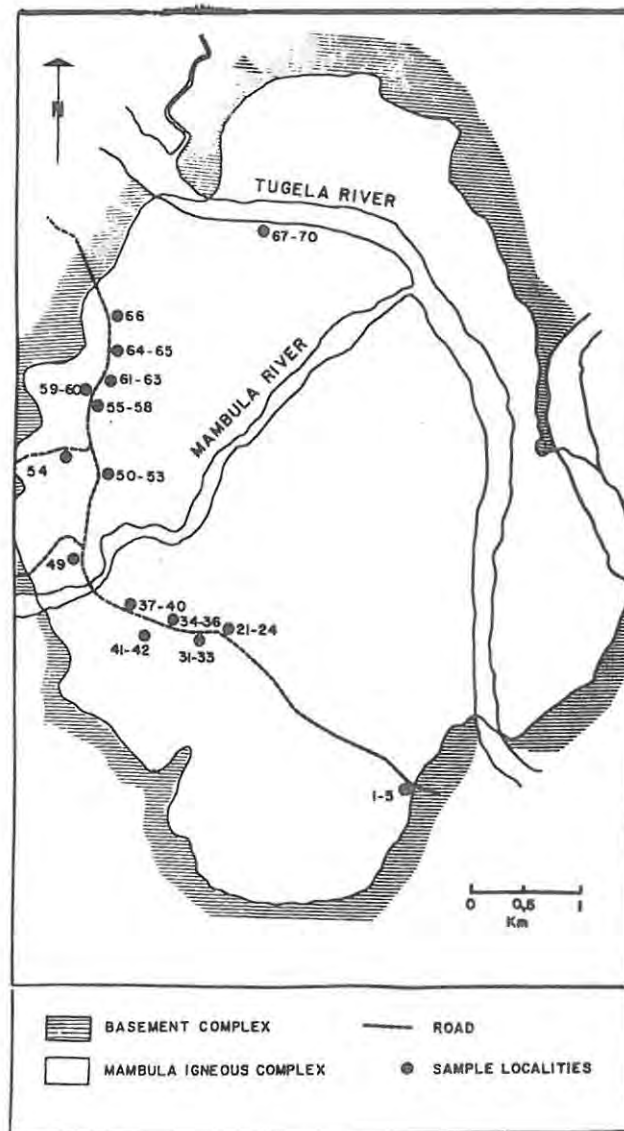
MAP 3. Sketch map of the Mambula complex showing sample localities.

9.3 Description of the Ores

A detailed report on the magnetic iron ores of the Mambula Complex was given by du Toit (1918) and, although his investigation was confined largely to field and thin section studies, it serves as an excellent intruduction to a more detailed study of the opaque constituents.

The Mambula titaniferous magnetite seams outcrop to varying degrees, but they are generally not well exposed. Their true thickness or relationships with the surrounding gabbros could consequently not be determined in many cases. The presence of certain titaniferous magnetite seams is indicated merely by abundance of titaniferous magnetite rubble on the surface. The individual seams vary from less than a metre up to 5m in thickness, but are only rarely pure and commonly contain between 10 and 30 per cent silicate impurities. The co-existing silicates are largely plagioclase and pyroxene but smaller and variable amounts of hornblende and olivine are also present. The seams are only rarely massive and commonly exhibit a distinct layering due to variations in the amount of silicates present in certain zones. An example of this layering is illustrated in Plate 8 (D).

The weathered surfaces of the ore-rich seams are covered by a thin coating of secondary iron oxides and hydroxides. The decomposed silicates have been largely removed producing a rusty, pitted appearance with the result that variations in silicate and oxide contents, as well as any mineralogical layering, is clearly seen. The surface weathering crust is generally less than 10mm thick below which the ores are remarkably fresh and only show incipient oxidation. The titaniferous magnetite-rich ores are also strongly magnetic due to their relatively minor degree of oxidation. In contrast, the thick (up to 5m), massive titaniferous magnetite seam that crops out on the west bank of the Tugela river is extensively weathered and it was not possible to collect fresh material from surface exposures.

Massive titaniferous magnetite seams that are relatively free from silicate impurities rarely developed in the Mambula Complex, and only the thick seam that crops out on the western bank of the Tugela river would fit this description. Narrow layers of massive titaniferous magnetite, typically less than 10cm in thickness, are commonly present between silicate-rich portions of the other seams. All gradations between massive and silicate-rich ores are found, often within the same seam. The tabular plagioclase

grains exhibit a slight preferred orientation parallel to the layering
in some of the silicate-rich portions of the titaniferous magnetite seams,
but this feature is rarely well-developed.

According to du Toit (1918) at least four of the ore-rich seams are up to
4,5m thick while a number are slighly thinner.   Several narrower,
lenticular, ore-rich layers several centimetres thick and up to a metre in
length were noted in a stream section at places within the otherwise
unlayered gabbro.

The Mambula titaniferous iron ores are characterised by the presence of
abundant granular ilmenite that generally exhibits polygonal outlines.
The grain size of the ores generally ranges between 0,5 and 2mm, but the
silicate impurities are very often much larger than their co-existing
iron-titanium oxides.   The ores show evidence of recrystallisation and
have a well developed, granoblastic polygonal texture.   The opaque
oxides generally exhibit a high degree of polygonalization and have
interfacial angles that approximate 120°.   In contrast, the silicate
impurities are generally sub-rounded, and show the development of narrow,
well-defined reaction rims or coronas as illustrated in Plate 8 (D and E).

Grain boundaries between oxides tend to be rather straight or slightly
curved and irregular boundaries are rare.   In general, ilmenite/ilmenite
and magnetite/magnetite grain interfaces are fairly straight while those
between ilmenite and magnetite are slightly curved, the ilmenite grains
being concave.   Highly irregular boundaries are present between
titaniferous magnetite and olivine-rimmed hypersthene, while the
boundaries between the oxides and other silicates generally exhibit
signs of embayment.

A much greater degree of exsolution has taken place in the titaniferous
magnetites than is usual in rocks of this type.   This has resulted in
the modification of their primary microstructures and their present
appearance is presumably related to the occurrence of a thermal metamorphic
event since their primary crystallisation.   The Mambula Complex is located
in an area of medium grade metamorphism (Cain, 1975) and evidence of this
is also reflected in the iron ore microstructures.

The Mambula titaniferous iron ores are all microscopically similar, but

microstructural variations exist in the ores from different localities.
In particular, differences are noticeable in the fine-scale microstructures
developed in the titaniferous magnetites from the seams lying to the south
of the Mambula river and those present to the north. The major
difference is that the titaniferous magnetites from the southern portion
of the Complex are generally optically homogeneous and exhibit brownish-
pink colours in the areas between the various coarser, intergrown phases
whereas the titaniferous magnetites from the northern part of the Complex
generally show the development of very fine grained microstructures related
to the formation of ulvospinel. In addition, the coarse ilmenite grains
from near the southern margin of the Complex show the development of
abundant stress-twinning lamellae. These lamellae are rare in ores from
other parts of the Complex.

The Mambula ores are characterised by complex mineralogical relationships
and exhibit a wide range of microstructure development. These features
are discussed separately in the following sections.

9.3.1 The associated silicates

The Mambula ores characteristically contain between 10 and 30 per cent
silicate impurities. Labradorite is the most common impurity and is
typically present as large tabular grains between 3 and 8mm in size that
are often several times larger than the associated opaque oxides. The
plagioclase is often sub-rounded and a narrow reaction rim of fine fibrous
hornblende between 0,2 and 0,5mm in width is usually developed around the
plagioclase where it is in contact with the opaque oxides.

The pyroxene grains are also characteristically larger than their
associated opaque oxides, but appear to be slightly smaller than the
co-existing plagioclase. Both bronzite and augite are present and are
also commonly rimmed by a narrow zone, or corona, of hornblende. A
narrow reaction rim of iron-rich olivine or a mixture of olivine and
hornblende is present in places where the bronzite is present in contact with
the opaque oxides. The pyroxenes generally contain oriented inclusions
of small rod-or plate-like rutile and possibly ilmenite and /or hematite
grains that produce a typical schiller texture.

The reaction rims are normally only present between the silicates and
opaque oxides and are not developed along the contacts between silicate

PLATE 8

USUSHWANA TITANIFEROUS IRON ORES

All photomicrographs taken in incident light using oil immersion objectives.

A. Internal ilmenite granules (dark grey) developed in areas between ilmenite lamellae and showing their typical morphologies.

B. The typical appearance of ilmenite granules (dark grey) that are developed in the titaniferous magnetite in areas devoid of ilmenite lamellae.

C. Probable modified ulvospinel-type microstructures (dark grey) in martitized titaniferous magnetite from the base of the Main Seam.

MAMBULA TITANIFEROUS IRON ORES

D. A polished slab of massive ore from the Mambula Complex viewed in reflected light showing the opaque oxides (light) and a narrow silicate-rich layer (dark, rounded grains with reaction rims).

E. Portion of a polished section surface of silicate-rich ore viewed in incident light showing relatively large silicate grains (dark grey) with well defined reaction rims. The silicates are separated from each other by polygonal aggregates of titaniferous magnetite and ilmenite (light).

F. The typical appearance of silicate-poor ore showing a polygonal titaniferous magnetite grain (centre of photograph) containing abundant crystallographically oriented transparent spinel intergrowths (black). The magnetite is surrounded by large ilmenite grains (dark grey).

G. The typical polygonal texture exhibited by clusters of titaniferous magnetite grains containing transparent spinel microintergrowths (black) in the silicate-poor ores.

PLATE 8
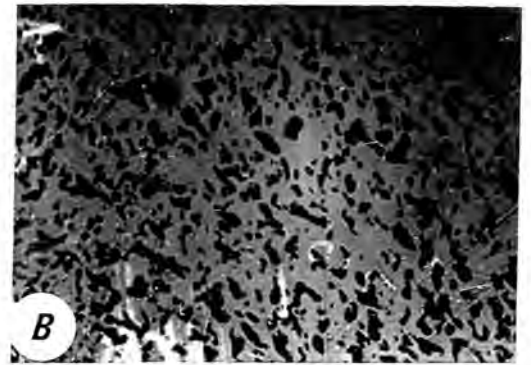
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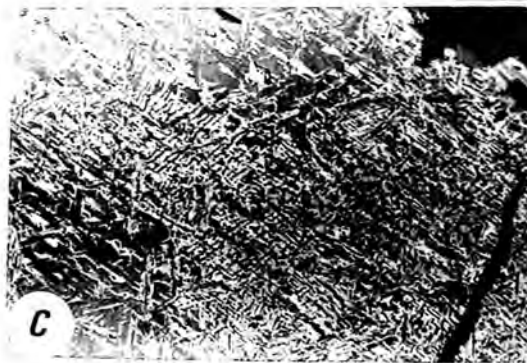
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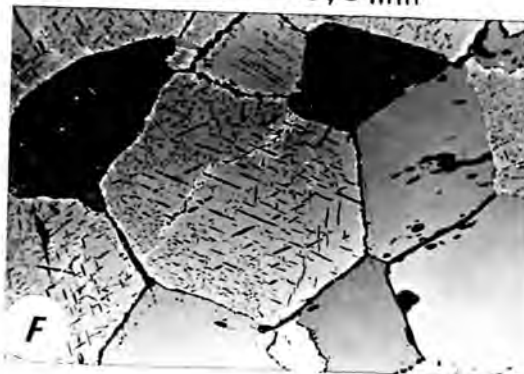
1,0 mm

grains. The individual silicate grains, even in the silicate-rich
samples, are, however generally separated from each other by opaque
oxides and consequently appear as isolated grains irregularly
distributed in a fine grained, opaque oxide matrix as illustrated in
Plate 8 (D and E).

Considerable solution of the opaque oxides has taken place along their
contacts with the silicates so that grain boundaries are highly irregular
and embayed as illustrated in Plate 8 (E). These features, together
with the well developed reaction rims, are indicative of extensive post-
crystallisation reaction between the opaque oxides and silicates,
probably during the metamorphic episode.

9.3.2 The titaniferous magnetite

Titaniferous magnetite is the dominant opaque phase in these ores and is
generally present as small, polygonal grains that vary in size between
0,7 and 1,5mm. On a large scale, the grain boundaries between the
titaniferous magnetites and other opaque oxides are generally straight-
to slightly-curved and exhibit a tendency to meet in well defined triple
junctions with interfacial angles approximating 120° as illustrated in
Plates 8 (F and G). The boundaries between ilmenite and titaniferous
magnetite are often highly irregular on a smaller scale of 10 to 15
micrometres due to the presence of numbers of small, transparent spinel
grains that are located along the mineral interfaces. The grain
boundaries are highly irregular, embayed, and show signs of corrosion
in areas where the titaniferous magnetite is in contact with silicates,
while the grains themselves are less polygonal and more irregularly shaped.

The titaniferous magnetite grains exhibit a distinct pinkish-brown colour
that suggests relatively high TiO_2 contents. They also contain a complex
series of ilmenite and spinel microintergrowths in addition to inclusions
of various silicates and sulphides.

The titaniferous magnetite and associated ilmenite grains in certain
samples are fractured and both minerals are occasionally traversed by
small irregular veinlets of magnetite up to 0,05mm wide. This magnetite
appears optically homogeneous even under the highest magnifications
(approx. 2000 x, oil immersion) and is free from inclusions. These
veinlets are also occasionally transgressive across silicates that are

enclosed within the fractured titaniferous magnetite grains.

Very fine, complex myrmekitic or symplectite-like intergrowths of magnetite and a silicate, possible orthopyroxene, are occasionally present within the olivine corona surrounding silicate impurities (Plate 9 (A)). The magnetite in these intergrowths exhibits elongated, skeleton-like, rounded forms in which the width of individual arms ranges from between 1 and 5 micrometres and are up to 0,04mm in length (Plate 9 (B)). Some martitization of this magnetite has occurred in the more weathered samples. These intergrowths appear to be confined to samples collected from south of the Mambula river.

Small numbers of very small magnetite platelets are present oriented along the basal planes of certain coarse grained ilmenites. These platelets are particularly abundant in stress-twinned ilmenite grains and commonly exhibit varying degrees of oxidation to martite.

The titaniferous magnetites generally exhibit incipient oxidation to martite. This oxidation takes place directly, commencing at grain boundaries, along fractures and cleavages and moves inwards along the octahedral planes of their hosts. This type of oxidation is also occasionally present around the margins of various sized ilmenite lamellae that are located well within the titaniferous magnetite grains are are some distance away from areas of grain boundary oxidation.

The Mambula titaniferous magnetites only rarely show the development of titaniferous maghemite as an intermediate oxidation product and it was only noted in any quantity in samples MB 68-72 from the highly oxidised seam exposed on the western bank of the Tugela river. This maghemite also shows alteration to martite, but the boundaries between maghemite and martite are diffuse and not clearly defined. The formation of maghemite appears to be confined to titaniferous magnetites containing extremely fine-grained, micrometre-sized intergrowths, and is absent from those grains containing magnetite that is optically homogeneous on a micrometre scale.

9.3.3 The ilmenite

Ilmenite is present in the Mambula ores in a wide variety of forms that include both discrete grains and complex microintergrowths with titaniferous magnetite. There is an almost continuous variation between

the different types, but for descriptive purposes it is convenient to distinguish seven types, each of which is characterised by differences in grain size and morphology. The various types are described in sections 9.3.3.1 to 9.3.3.7.

9.3.3.1 Coarse granular ilmenite

The bulk of the ilmenite in the Mambula ores is present as small polygonal grains that range in size between 0,5 and 1,2mm with an average of approximately 0,8mm. Larger grains up to 3mm in size are occasionally present. The amount of this ilmenite in individual samples is highly variable, but it generally accounts for between 15 and 25 per cent of the opaque oxides present and may locally reach as high as 30 per cent.

The large ilmenite grains are generally present as single polygonal crystals that are located interstitially between slightly larger titaniferous magnetite grains (Plate 9 (C)), or form small clusters of several grains enclosed by a number of titaniferous magnetite or silicate grains (Plates 9 (D-F)). The individual crystals in these granular clusters often exhibit different crystallographic orientations with respect to one another and there is a tendency for the development of well-defined triple junctions at their mutual grain boundaries as illustrated in Plate 9 (E).

Many of these ilmenite grains have spinelliferous outer rims containing numerous small, equant, transparent spinel grains that range in size from 2 to 10 micrometres. These spinels are generally located along the interfaces between the ilmenite and titaniferous magnetite grains, but are also occasionally completely enclosed by the ilmenite. These spinels form rows of inclusions that are arranged close to, and are concentric with, the outer margins of the host ilmenites. These spinelleferous ilmenite/titaniferous magnetite interfaces are highly irregular on a fine scale of 10 to 20 micrometres, particularly in places where large numbers of spinel grains are present (Plate 9 (G)). These textures are occasionally developed on a coarser scale as illustrated in Plates 9 (C,E,F)). The rows of spinel inclusions mark the positions of earlier ilmenite grain boundaries, and the more irregular outer ilmenite layer in contact with titaniferous magnetite has the appearance of later, or secondary overgrowths (Plates 9 C,E, and F).

The coarse granular ilmenites occasionally show the development of poly-synthetic stress twin lamellae that are commonly developed in two and sometimes three directions. These textures are particularly well developed in ore samples from near the southern margin of the Complex and examples are illustrated in Plates 9 (H) and 10 (A).

PLATE 9

MAMBULA TITANIFEROUS IRON ORES

All photomicrographs taken in incident light using oil immersion objectives.

A. A multi-phase titaniferous magnetite grain (light) separated from an orthopyroxene grain (black) by a rim of olivine containing a fine symplectite-like intergrowth of magnetite (light).

B. Similar to (A), but under higher magnification showing the nature of the magnetite/olivine symplectite-like intergrowth. The magnetite is light grey.

C. A polygonal ilmenite grain (centre of photomicrograph) surrounded by titaniferous magnetite grains exhibiting typical grain-boundary relationships. Note the stringer of transparent spinel inclusions (black) arranged parallel to the ilmenite grain boundary.

D. A cluster of large ilmenite grains exhibiting relatively straight or gently curved mutual grain-boundaries. More irregular interfaces are developed between the ilmenite and titaniferous magnetite grains.

E. Similar to (D), but showing the development of a typical triple junction between the central 3 ilmenite grains.

F. An ilmenite grain(dark grey, centre of photomicrograph) showing the development of a secondary ilmenite overgrowth along its lower boundary.

G. A typical spinelliferous ilmenite boundary developed between ilmenite (dark grey) and titaniferous magnetite (light grey) showing incipient martitization (white). Transparent spinel grains (black) are located along the highly irregular interface between the ilmenite and magnetite and are also present within the ilmenite where they mark the position of an earlier interface.

H. A stress-twinned polygonal ilmenite grain (centre of the photomicrograph) showing polysynthetic twin lamellae and a complex pattern of deformation. (partially crossed nicols).

PLATE 9

A

0,15 mm

B

0,015 mm

C

D

1,0 mm

E

F

1,0 mm

G

0,015 mm

H
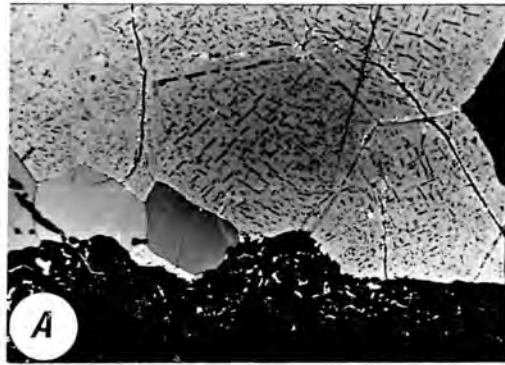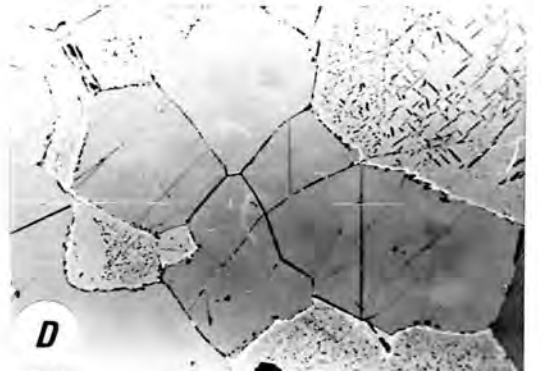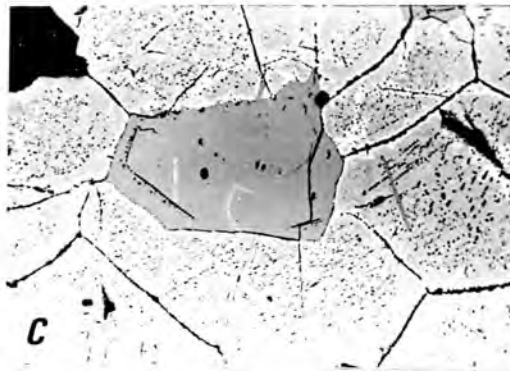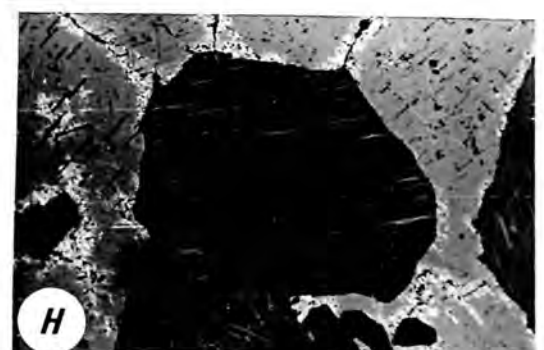
1,0 mm

Small, plate-like bodies of magnetite up to several micrometres in size are commonly developed in the ilmenite at the points of intersection of twin lamellae (Plate 10 (B)). These platelets are crystallographically oriented parallel to the basal planes of the ilmenite hosts and marked deflections in their orientations occur across the twin composition planes reflecting differences in the orientations of their hosts (Plate 10(C)). The magnetite platelets characteristically exhibit varying stages of oxidation to martite that takes place directly along their octahedral planes. This magnetite appears more susceptible to oxidation since partially oxidised platelets are sometimes found in ilmenite grains that are surrounded by titaniferous magnetite that shows no sign of oxidation.

Small, crystallographically oriented, magnetite platelets are also sparingly present along the basal planes of untwinned granular ilmenites from the ore-rich samples (Plate 10 (D)). In contrast, the ilmenites from associated silicate-rich, gabboic rocks commonly exhibit numbers of small hematite exsolution lenses that are developed along their basal planes. Small numbers of micrometre-sized spinel grains are occasionally developed along the interface between the magnetite lamellae and their host ilmenites (Plate 10 (E)). Small spinel lamellae are also occasionally developed (Plate 10 (F)).

9.3.3.2 Fine granular ilmenite
Small, elongated or irregularly-shaped ilmenite grains are commonly present as rows or stringers along the interfaces between neighbouring titaniferous magnetite grains as illustrated in Plate 10 (G). These grains range in size from 0,02 to 0,10mm and commonly have numbers of very much smaller, transparent, spinel grains arranged around their borders. In some cases, the spinel grains are of a similar size to the ilmenite grains and are arranged in the rows and stringers with them.

The fine granular ilmenites are also occasionally connected to large broad ilmenite lamellae that cut across the titaniferous magnetite grains and are characteristically surrounded by numerous small spinel grains. These ilmenite inclusions are generally surrounded by a narrow zone of titaniferous magnetite up to 0,02mm wide that is free of other ilmenite intergrowths.

9.3.3.3 Broad ilmenite lamellae
Broad ilmenite lamellae, usually between 7 and 20 micrometres wide and up to 0,3mm long are sparsely developed along the octahedral directions

PLATE 10

MAMBULA TITANIFEROUS IRON ORES

All photomicrographs taken in incident light using oil immersion objectives.

A. Stress-twinned ilmenite grains showing polysynthetic twinning (crossed nicols).

B. Stress-twinned ilmenite showing the development of martitized magnetite platelets (light grey) at the intersection of twin lamellae (medium-grey).

C. Ilmenite containing abundant martitized magnetite platelets (white). Notice the difference in orientation of the magnetite platelets in the darker coloured twin lamella that cuts diagonally across the photograph.

D. Typical appearance of magnetite lamellae (light) in ilmenite showing their characteristic uniform thickness and sharp terminations.

E. Similar to (D), but the lamellae contain minute rounded transparent spinel grains (black) arranged along their boundaries. Appreciable transparent spinel (black) is present in the central magnetite lamella .

F. The typical form of transparent spinel lamellae (black) oriented parallel to (0001) of their ilmenite host.

G. Narrow stringers of small ilmenite grains located along the interfaces between titaniferous magnetite grains (centre portion of photograph).

H. Sparsely developed broad ilmenite lamellae (dark grey) extending from the grain boundaries into their titaniferous magnetite hosts.

PLATE 10

A

1,0 mm

B

0,015 mm

C

D

0,015mm

E

F

0,015 mm

G

H
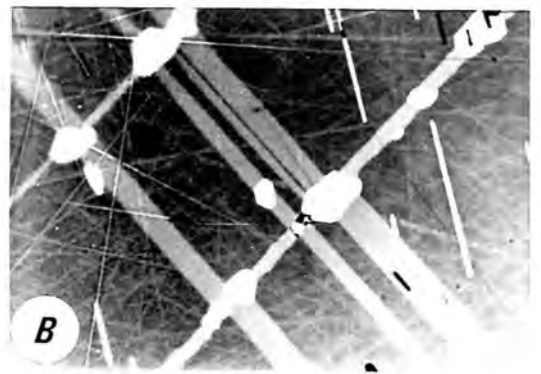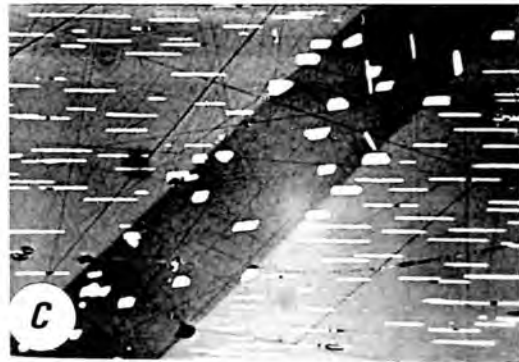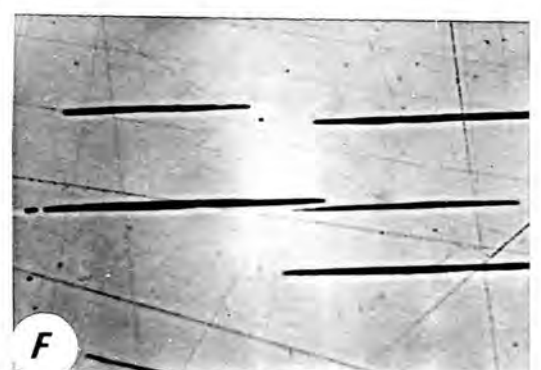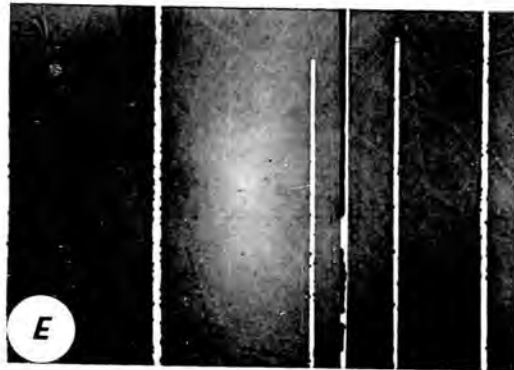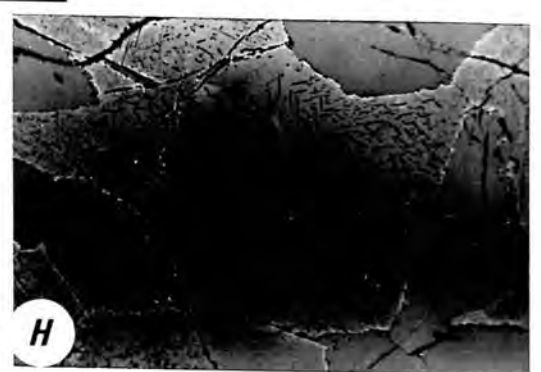
1,0 mm

of the titaniferous magnetites as illustrated in Plates 10 (H) and 11(A).
Several of these lamellae are generally present in most titaniferous
magnetite grains, but they are rarely developed to the extent where they
form a typical trellis network. In certain grains these lamellae are
preferentially developed along a particular octahedral plane of the host
and produce a sandwich texture as illustrated in Plate(11 A).

The broad ilmenite lamellae are typically spinelliferous and large numbers
of very small, transparent spinel grains are arranged along the interfaces
between them and their host titaniferous magnetites. Portion of the
spinel grains are located within the ilmenite lamellae, but even these are
situated near the margins of the lamellae. The titaniferous magnetite
in the immediate vicinity of the ilmenite lamellae is generally devoid of
other finer-grained ilmenite microintergrowths for a distance of up to
0,02mm from the lamellae.

The lamellae often exhibit a slight thickening towards the outer margins
of their titaniferous magnetite hosts in areas where they extend to the
grain boundary as illustrated in Plate 11 (A). These lamellae reach their
thickest development at the grain boundary and in a few extreme cases, they
extend as a small rounded bulge beyond the limits of the host grain into
the intergranular area. These small rounded grains are often developed
in the marginal areas of neighbouring titaniferous magnetites as illustrated
in Plates 10 (H) and 11 (A).

The broad lamellae that are totally enclosed by titaniferous magnetite are
generally thicker in relation to their length than is usual in intergrowths
of this type. They hav= an overall lens-like shape, but tend to terminate
abruptly and have sharp, cut off, ends rather than gently tapering ones.

Incipient martitization of their titaniferous magnetite hosts is commonly
evident around the periphery of these broad lamellae, particularly in
grains where the lamellae extend to the mineral boundaries.

9.3.3.4 Fine ilmenite lamellae
A second series of finer ilmenite lamellae are present in the Mambula
titaniferous magnetites and are particularly abundant in the samples
collected from south of the Mambula river. They range from 1 to 2
micrometres in width and are up to 0,025mm in length. They are also

oriented along the octahedral planes of their hosts and exhibit blunt
terminations. Numbers of small spinel grains are generally located
along their margins and, in some cases, there is an apparent replacement
of these ilmenite lamellae by spinel (Plate 11 (B-D)).

The lamellae in the samples from south of the Mambula river are set in a
groundmass of titaniferous magnetite that is generally devoid of
intergrown phases other than spinel. In the samples from the north of the
Mambula river the magnetites generally contain finer intergrown titanium-
bearing phases. These intergrowths are characteristically absent from
a narrow rim surrounding each lamella.

The fine lamellae are more abundant than the broader ones, but they are
only rarely developed in sufficient numbers to form a distinct trellis
network. Lamellae intermediate in size between the broad and fine types
are very rare.

9.3.3.5 Very fine ilmenite lamellae

The very fine ilmenite lamellae are generally less than a micrometre wide
and are of variable length ranging up to 0,02mm. They are relatively rare
in titaniferous magnetites collected from south of the Mambula river, but
are more common in samples from the northern side. They are oriented along
the octahedral planes of their magnetite hosts and occupy the areas between
the fine ilmenite lamellae (Plate 11 (E and F). They are characteristically
absent from narrow zones several micrometres wide surrounding other ilmenite
intergrowths.

These lamellae are occasionally more irregular in shape, and are present
along only one of the octahedral planes forming a distinct lineated pattern
resembling a less robustly developed ulvospinel texture as illustrated in
Plate 11 (G). The size of these lamellae is at the limit of optical
resolution and their relationships are not clear. They are often
associated with similar-sized spinel rodlets that are oriented along the
cubic planes of their hosts.

9.3.3.6 Very fine rounded ilmenite

Very small, rounded ilmenite grains, generally less than two micrometres
in size, are occasionally present in aggregates arranged around the periphery
of spinel lamellae in certain of the titaniferous magnetites (Plate 11 (E)).

PLATE 11

MAMBULA TITANIFEROUS IRON ORES

All photomicrographs taken in incident light using oil immersion objectives.

A. Titaniferous magnetite grains containing several sparsely distributed
    broad ilmenite lamellae (dark grey). Notice the increase in width
    of these lamellae towards the grain boundaries and the development of
    small rounded grains at their broadest points.

B. Fine ilmenite lamellae (dark grey) and transparent spinel lamellae
    (black) in titaniferous magnetite. Note the apparent replacement of
    the ilmenite by the spinel.

C. Fine ilmenite lamellae (dark grey) exhibiting a distinct thickening
    and the development of sharp terminations in titaniferous magnetite.
    Some intergrown transparent spinel (black is also present.

D. Fine ilmenite lamellae (dark grey) with small rounded transparent spinel
    grains (black) located along their margins. Other crystallographically
    oriented spinels show up as rows of black lines.

E. Very fine spinelliferous ilmenite lamellae (dark grey) oriented parallel
    to (111) of their titaniferous magnetite hosts. Larger transparent
    spinel bodies (black) are also present.

F. Similar to (E), but with a much greater degree of very fine ilmenite
    trellis development. The transparent spinel is black while the
    titaniferous magnetite host is light grey.

G. Extremely fine ilmenite lamellae (dark grey) derived from ulvospinel
    and tiny transparent spinel laths (black) intergrown with titaniferous
    magnetite.

H. Titaniferous magnetite containing number of rounded transparent spinel
    grains (black) surrounded by clusters of very fine rounded ilmenite
    grains (dark grey).

PLATE II

A

1,0 mm

B

0,015 mm

C

D

0,015 mm

E

F

0,015 mm

G

H
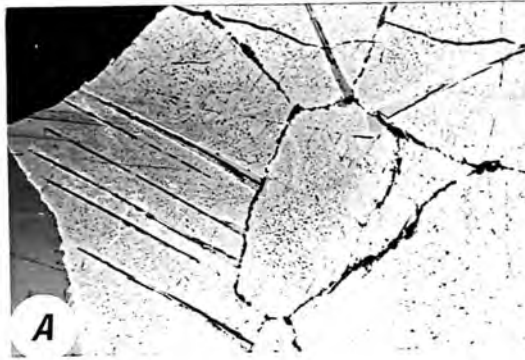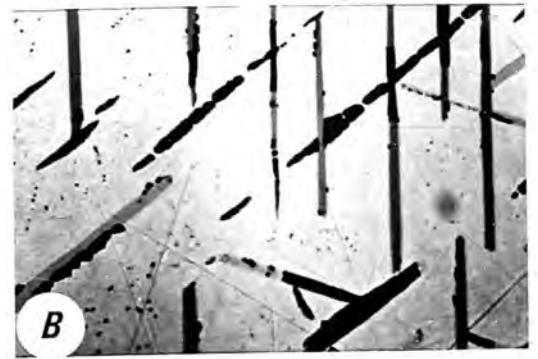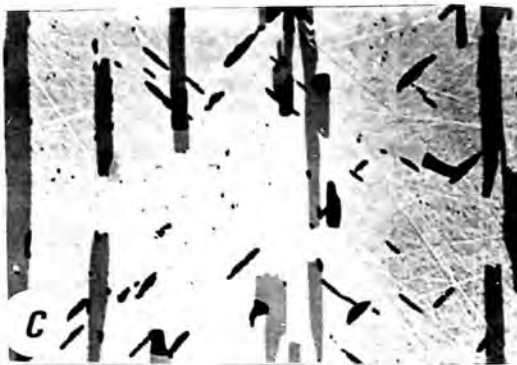
0,015 mm

These grains are preferentially developed in the titaniferous magnetites collected from north of the Mambula river and are characteristically present in grains containing numerous, very fine-grained intergrowths.

9.3.3.7 Ilmenite derived from ulvospinel

Sets of extremely fine, micrometre sized, ilmenite lamellae are developed along the cubic planes of their titaniferous magnetite hosts and have the typical appearance of an ulvospinel cloth texture. This material is generally only present in the titaniferous magnetites from north of the Mambula river and represents oxidised ulvospinel. It is present in the areas between the various other larger-sized, intergrown phases.

9.3.4 The transparent spinel

The Mambula titaniferous iron ores are highly aluminous and are characterised by the presence of abundant dark green, transparent spinel. It is present both as discrete grains, and as various exsolution bodies within the titaniferous magnetites. Qualitative electron microprobe analyses indicate that the larger grains are composed essentially of Mg and Al with smaller amounts of Fe and Ti. They are most probably very close to pleonaste in composition and are typical of the transparent spinels developed in titaniferous magnetites.

Large euhedral to subhedral spinel grains varying from 0,5 to 1,2mm in size are present in the oxide-rich ores. They are located interstitially between the opaque oxides and exhibit complex grain boundary relationships as illustrated in Plate 12 (A). The boundaries are, in part, straight and well-defined, but in others they are more irregular and the spinel locally appears to replace both ilmenite and titaniferous magnetite. The areas surrounding these grains commonly contain numbers of smaller, often highly irregular spinel grains that are sometimes connected to the larger grains as illustrated in Plate 12 (A).

The larger spinel grains commonly contain fine lamellae of an opaque, iron-rich spinel, probably magnetite, that are oriented along their cubic planes. These magnetite lamellae are typically absent from the smaller spinel grains. The spinel grains are also commonly fractured and incipient alteration is evident along these zones.

Smaller, equant spinel grains, generally between 2 and 10 micrometres in

size are located along the interfaces between titaniferous magnetites and coarse grained ilmenites as described in section 9.3.3.1. A series of generally smaller, equant spinel grains are also present along the margins of both the broad and fine ilmenite lamellae as described in sections 9.3.3.3 and 9.3.3.4. The spinel lamellae are generally developed along all the cubic planes of their hosts as illustrated in Plate 12 (B). They may, however, occasionally exhibit preferential development along only one of the cubic planes and this leads to the formation of a characteristic lineated or sandwich texture as illustrated in Plate 12 (C and D). A second set of very much finer spinel lamellae is commonly present in the areas between the larger lamellae.

Lamellar and lensoid spinel grains are ubiquitiously developed along the cubic planes of the titaniferous magnetites as illustrated in Plates 8 (F and G) ; 9 (A,C,D,F) and 10 (G-H). These bodies are extremely variable in size and range from sub-micrometre-sized bodies to large lamellae over 0,1mm in size. These spinel intergrowths also typically exhibit a wide range in size within individual titaniferous magnetite grains. They are generally largest in the central portions of their hosts, but become progressively smaller towards the titaniferous magnetite margins, until they disappear, being absent from the outer 5 to 15 micrometres of their hosts as illustrated in the above mentioned plates.

The larger spinel lamellae are generally slightly curved and are lens-shaped as illustrated in Plates 12 (B and C). The spinel lamellae are sometimes arranged in a definite en echelon fashion as illustrated in Plate 12 (B). This feature is particularly noticeable in areas where the lamellae have developed slightly curved, and more lenticular forms. These lamellae are generally cut by broad ilmenite lamellae (Plates 12 (B and E)) and are also surrounded by a 5 to 10 micrometre wide zone of homogeneous, inclusion free, magnetite. The areas between the larger spinel lamellae are generally occupied by a second set of extremely small spinel grains that are also oriented along the cubic planes of the titaniferous magnetite as illustrated in Plate 12 (B). These spinels are generally equant or lath-shaped and range between 0,5 and 1,5 micrometres in size. Similar sized, but more needle-shaped spinel grains are also present in the ulvospinel-type and very fine lamellar ilmenite intergrowths as illustrated in Plate 11 (G).

PLATE 12

MAMBULA TITANIFEROUS IRON ORES

All photomicrographs taken in incident light using oil immersion objectives.

A. A large pleonaste grain (dark grey) containing minute lamellae of an exsolved iron rich spinel (light). The surrounding grains are titaniferous magnetites.

B. A well developed set of transparent spinel lamellae (black) oriented parallel to the cubic planes of the titaniferous magnetite host. A broad ilmenite lamellae (dark grey) cuts diagonally across the photomicrograph.

C. Typical appearance of spinel lamellae (black) in the Mambula titaniferous magnetites. Note the "sandwich" texture developed by these lamellae in the lower central grain.

D. Transparent spinel lamellae (black) preferentially developed along only one of the cube planes of the titaniferous magnetite host to produce a lineated pattern.

E. Large ilmenite lamellae (dark grey) disrupting a transparent spinel body (black).

F. Transparent spinel grains (black) associated with an ilmenite lamella (dark grey). Other spinel bodies showing markedly rounded to lensoid forms (black) are also present.

G. Transparent spinel lamellae (black) present in rounded lensoid forms in the titaniferous magnetite.

H. Similar to (G), but the original large spinel lamellae show evidence of breaking down into numbers of smaller grains.

PLATE 12

1,0 mm

0,2 mm

1,0 mm

0,015 mm

0,015 mm

Distinct differences exist between the morphologies of the spinel bodies
developed in the Mambula ores and those present in aluminous titaniferous
magnetites from unmetamorphosed basic intrusions.   The larger spinel
bodies, in particular, are not developed in the form of characteristic
narrow lamellae, but exhibit varying degrees of coarsening and breakdown
resulting in more rounded forms.   The degree of modification of these
microstructures also varies between different areas of the complex.

The transparent spinel intergrowths from the southern side of the Mambula
river exhibit only minor modifications and are still distinctly lamellar.
They are, however, often slightly curved and show the development of
slightly lensoid forms (Plate 12 (B and C)). They also occasionally
break up into a number of short stumpy laths that are aligned along
their length as illustrated in Plates 11 (D) and 12 (G).   The spinel
microintergrowths in the titaniferous magnetites from the northern side
of the Mambula river exhibit greater degrees of modification.   The
original lamellae are commonly broken up into numbers of short stumpy
laths as illustrated in Plate 12 (F), while the bodies themselves are
definitely more lensoid and have, in many cases, developed into quite
well-rounded bodies as illustrated in Plates 11 (H) and 12 (G).   The
smaller spinel intergrowths also exhibit lensoid forms in the more highly
modified samples while the spinels associated with the ilmenite lamellae
coalesce to form larger grains (Plate 12 (H).

9.3.5 Sulphides in the Mambula ores

A variety of sulphides are present in trace amounts in the Mambula ores.
They are generally in the form of small rounded inclusions that are less
than 20 micrometres across and are usually present in ilmenite.   Slightly
larger grains are occasionally developed in the titaniferous magnetite
where they are commonly associated with the larger spinel grains.
Pyrrhotite, occasionally containing pentlandite exsolution lamellae, is
the most common sulphide while lesser amounts of pyrite are also present.
Slightly larger pyrite grains are located interstitially between the oxide
grains in certain samples and often show alteration to goethite.   Minor
chalcopyrite is also present as small rounded inclusions in the ilmenite.

9.3.6 Weathering of the Mambula ores

The Mambula titaniferous iron ore surface exposures are characteristically
surrounded by a thin crust of highly decomposed weathering products below

which the ores often show only incipient alteration. The weathering
crust varies in thickness, but generally consists of an outer centimetre
of highly decomposed material followed by a narrow transition zone below
which is the relatively unaltered titaniferous magnetite. In contrast,
the seam exposed on the western bank of the Tugela river shows extensive
and deep weathering.

The titaniferous magnetite has been completely oxidised to martite in
the more highly weathered portions and this in turn shows extensive
alteration to goethite. The upper surfaces of the ores are commonly
coated by a thin layer of botryoidal goethite while the ore is veined
by narrow, irregular, goethite veinlets. The finer-grained ilmenite
grains show almost complete alteration to leucoxene while the larger
grains exhibit incipient alteration around their margins and along
fractures.

Oxidation of the titaniferous magnetite generally takes place directly
without the formation of intermediate titaniferous maghemite. It
commences at grain boundaries and moves inwards into the grains along
their octahedral planes. Extensive martitization disrupts the fine
microstructures and the original fine microintergrowths are not generally
well preserved in the weathered samples.

9.4 Chemical Analyses of Mambula Titaniferous Iron Ores

The chemical compositions of typical Mambula titaniferous iron ores are
given in Table 11. The analyses have not been expressed graphically
since the vertical separation and sequence of the seams is uncertain.

The relatively high SiO_2 values obtained for some of the samples is due to
the variable amounts of silicate impurities present. The low totals in
some samples, particularly those with high SiO_2 values, reflect the
incompleteness of the analyses and can be ascribed to the presence of Na_2O
and CaO that are largely present in the plagioclase.

The samples are characteristically highly aluminous as reflected by the
abundance of transparent spinel that is developed both as discrete grains
and microintergrowths. Some of the Al_2O_3 is present in the co-existing
plagioclase in certain samples. The ores also exhibit relatively low
TiO_2 contents, (with the exception of sampl MB 12), even when allowance
is made for the presence of several per cent of silicate impurities in
many of the samples.

TABLE 11

ANALYSES OF MAMBULA TITANIFEROUS IRON ORES

	SAMPLES FROM SOUTH OF MAMBULA RIVER									SAMPLES FROM NORTH OF MAMBULA RIVER						TUGULA RIVER	ℵ
	MB 6	MB 12	MB 28	MB 33	MB 36	MB 39	MB 42	MB 44	MB 46	MB 49	MB 52	MB 55	MB 60	MB 62	MB 65	MB 70	R 24
SiO_2	2,44	1,49	19,10	9,11	13,89	12,22	3,85	6,43	3,31	1,60	4,80	8,33	5,63	8,26	4,07	2,06	0,83
TiO_2	13,82	16,30	9,41	11,59	10,50	10,66	12,91	12,50	14,34	13,50	13,19	12,71	11,46	10,91	11,45	11,35	14,85
Al_2O_3	6,85	5,63	10,08	7,95	8,49	7,80	6,38	8,24	6,46	7,03	8,32	8,19	8,49	8,39	7,84	7,22	4,10
Cr_2O_3	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	0,05	<0,05	<0,05	<0,05	<0,05	<0,05	Tr.
Fe_2O_3	43,11	62,58	29,74	39,77	34,79	35,66	50,80	40,88	59,73	45,76	44,92	37,54	45,94	38,96	45,59	64,45	67,23
FeO	29,86	12,80	22,00	26,38	25,60	25,05	22,76	28,14	12,04	29,03	25,01	27,26	24,24	26,73	27,39	11,19	9,19
MnO	0,33	0,32	0,27	0,27	0,24	0,24	0,25	0,24	0,30	0,28	0,25	0,27	0,28	0,24	0,25	0,25	0,20
MgO	2,22	0,53	4,99	3,52	4,69	4,71	1,61	3,05	2,93	2,11	2,81	3,72	3,19	4,24	2,76	2,26	0,66
V_2O_5	0,75	0,54	0,53	0,60	0,54	0,63	0,78	0,71	0,64	0,82	0,82	0,75	0,67	0,60	0,68	0,63	0,50
TOTAL :	99,38	100,19	96,12	99,19	98,74	96,97	99,34	100,19	99,75	100,13	100,17	98,77	99,90	98,33	100,03	99,41	97,56
TOTAL Fe :	53,36	53,72	37,95	48,32	44,23	44,41	53,22	50,46	51,13	54,57	50,85	47,44	50,97	48,02	53,18	53,77	54,16

Tr = trace.

ℵ R24 : Analysis of titaniferous iron ore from the Middle Group of seams of the Bushveld Complex (Schwellnus and Willemse, 1943).

The V_2O_5 values are also generally low and vary between 0,5 and 0,8
per cent. In general there appears to be a decrease in V_2O_5 contents
in ores that are stratigraphically higher in the sequence. The Cr_2O_3
values are also low, being below the detection limit of 0,05 per cent.

The samples collected on the traverse to the south of the Mambula complex
generally contain slightly more silicate impurities that the seams from
the north side. A certain degree of correlation can however, be made
between the seams from the two areas on the basis of bulk chemistry as
follows:-

	MB 33	= MB 62
Increasing	MB 36	= MB 60
stratigraphic	MB 39	= MB 55
height	MB 42	= MB 52

The MgO contents are highly variable and are largely present in the
transparent spinel and orthopyroxene as well as in minor amounts in the
co-existing ilmenite. The distribution of this oxide is largely
governed by the amount of orthopyroxene in the ore. The MnO values are
uniformly low in all samples and do not exhibit any marked variation.

9.5 Analyses of Co-existing Ilmenites from the Mambula Complex

Electron microprobe analyses of the large co-existing granular ilmenites
from the ores and a sample from the associated gabbros are given in Table
12. Quantitative electron microprobe analyses of the fine grained
ilmenite lamellae and granules also indicate that their compositions are
similar to those of the large co-existing grains.

The ilmenites are characteristically magnesium-rich, although the amount
of MgO present varies considerably (1,7-6,6%). Direct correlation
between the amount of MgO present in the bulk ore analyses and its content
in the ilmenite is not possible because of the variable amounts of Mg-rich
orthopyroxene in the samples. The co-existing finer-grained ilmenites in
the samples containing MgO rich coarse-grained ilmenites are also
relatively MgO-rich. Several high MgO-ilmenites were re-analysed in a
batch of samples containing low MgO-ilmenites as a check on the analyses,
but essentially similar results were obtained. Analyses were also
repeated using different standards, but consistently high MgO values were
obtained.

TABLE 12

MAMBULA COMPLEX : MICROPROBE ANALYSES OF COARSE GRAINED ILMENITES

	SAMPLES COLLECTED SOUTH OF THE MAMBULA RIVER									SAMPLES COLLECTED NORTH OF THE MAMBULA RIVER						TUGELA RIVER	MAMBULA GABBRO	BUSHVELD COMPLEX	
Oxide	ME 5	MB 17	MB28	MB 33	MB36	MB 39	MB42	MB 44	MB 46	MB 49	MB 52	MB 55	MB 60	MB 62	MB 65	MB 70	MB 5	M 708	M 710
TiO_2	50,37	50,80	51,39	52,09	51,18	52,17	51,38	51,53	52,59	51,86	52,90	52,29	53,03	52,61	51,64	54,09	49,53	51,1	51,9
FeO	41,36	40,83	41,99	40,06	41,11	40,89	41,20	41,90	35,38	38,35	39,40	40,28	39,38	40,72	39,97	36,15	41,17	40,0	38,4
MgO	1,71	2,22	1,92	3,25	2,27	2,85	2,31	1,95	6,07	4,16	3,71	3,25	4,24	3,18	3,14	6,61	1,32	3,8	3,4
MnO	0,88	0,95	0,77	0,91	0,92	0,92	0,86	0,98	1,03	0,85	0,84	0,82	0,78	0,82	0,88	0,72	0,99	N.R.	N.R.
$*Fe_2O_3$	5,83	6,39	4,07	5,43	5,59	4,47	4,39	4,31	5,03	4,39	4,83	3,59	3,35	4,15	5,59	2,63	6,63	4,3	5,8
Al_2O_3	0,12	0,12	0,13	0,12	0,13	0,12	0,13	0,13	0,13	0,13	0,12	0,13	0,13	0,14	0,14	0,12	0,12	0,8	0,3
Cr_2O_3	0,17	0,17	0,17	0,17	0,17	0,17	0,17	0,17	0,16	0,17	0,17	0,17	0,17	0,17	0,17	0,18	0,18	N.R.	N.R
Total :	100,44	101,50	100,44	102,03	101,37	101,59	100,44	100,97	100,39	99,91	101,97	100,53	101,08	101,79	101,53	100,50	99,94	100,0	99,8

NUMBER OF IONS ON THE BASIS OF 6 OXYGENS

Al^{3+}	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006
Cr^{3+}	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006
Fe^{3+}	0,220	0,236	0,150	0,198	0,206	0,164	0,142	0,142	0,178	0,158	0,176	0,130	0,122	0,152	0,204	0,092	0,254
Ti^{4+}	1,884	1,876	1,919	1,895	1,891	1,912	1,923	1,923	1,905	1,915	1,906	1,929	1,933	1,918	1,892	1,948	1,867
Fe^{2+}	1,722	1,676	1,743	1,622	1,688	1,666	1,715	1,738	1,425	1,576	1,602	1,655	1,595	1,653	1,629	1,447	1,726
Mg	0,126	0,162	0,143	0,235	0,165	0,208	0,172	0,143	0,437	0,304	0,269	0,239	0,306	0,230	0,228	0,472	0,099
Mn	0,036	0,038	0,033	0,038	0,038	0,038	0,036	0,042	0,043	0,035	0,035	0,035	0,032	0,035	0,035	0,029	0,042
TOTAL :	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000

NORMATIVE COMPOSITION (MOLE PER CENT)

$FeTiO_3$	86,10	83,78	87,17	81,11	84,36	83,31	85,40	86,50	71,20	78,76	80,12	82,74	79,88	82,65	81,41	72,37	86,30
$MgTiO_3$	6,28	8,11	7,16	11,77	8,26	10,40	8,49	7,12	21,85	15,19	13,45	11,95	15,31	11,52	11,42	23,60	4,97
$MnTiO_3$	1,79	1,92	1,64	1,89	1,92	1,90	1,79	2,08	2,17	1,77	1,75	1,77	1,60	1,75	1,76	1,44	2,11
R_2O_3	5,83	6,19	4,03	5,23	5,46	4,39	4,32	4,30	4,78	4,28	4,68	3,54	3,21	4,08	5,41	2,59	6,62
TOTAL :	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

* Fe_2O_3 calculated assuming ilmenite stoichiometry.

M 708 Analysis of ilmenite in a magnetite gabbro, Bushveld Complex (Molyneux, 1970a, 1972).

M 710 Analysis of ilmenite from Seam 21, Bushveld Complex (Molyneux, 1970a, 1972).

N.R. Not reported.

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The MnO contents show only a minor variation between 0,8 and 1,0 per cent. The very much higher MnO content in the ilmenites compared with the bulk analyses of the ore indicates that the MnO is preferentially incorporated into the rhombohedral, rather than spinel phases during crystallisation.

Both Al_2O_3 and Cr_2O_3 are present in very minor, but constant amounts. The excess FeO in the analyses was recalculated as Fe_2O_3 assuming stoichiometry. The small amounts of excess Fe_2O_3 shown (2,63-6,39%) is reflected in the small number of hematite (now largely magnetite) exsolution lamellae present in the Mambula ilmenites.

9.6 Beneficiation

The presence of between 10 and 30 per cent silicate impurities in the majority of Mambula ores would necessitate beneficiation. A high degree of liberation of the major constituents is possible due to the relatively coarse grain size (2-5mm) of the silicate minerals and the generally polygonal shapes of the opaque oxides. Complete liberation of ore and gangue minerals can generally be achieved by crushing to less than 200 mesh. Titaniferous magnetite concentrates can be prepared by simple magnetic separation while ilmenite concentrates can be prepared by electromagnetic separation. The silicate impurities have lower specific gravities than the associated oxides and can be removed by gravity separation techniques. A portion of the hornblende and olivine might overlap slightly in magnetic susceptibility with the ilmenite, but the bulk of the silicates will be adequately separated during the electromagnetic separation of ilmenite.

The removal of the silicate impurities from the Mambula ores reduced their volume by between 10 and 30 per cent depending on their initial composition. This results in a decrease in SiO_2, Al_2O_3, MgO and CaO (largely present in silicates) and an increase in TiO_2 and V_2O_5 (present in the oxides) in the ore. More than half of the TiO_2 reflected in the analyses is present as coarse granular ilmenite while the bulk of the V_2O_5 is present in solid solution in the titaniferous magnetite. Separation of the 10-15% of coarse ilmenite from the titaniferous magnetite thus further reduces the TiO_2 content and increases the V_2O_5 content of the magnetite.

Microscopic examination of the concentrates indicates that a magnetic titaniferous magnetite concentrate with a grain size of less than 200

mesh will have a TiO_2 content of between 3 and 8 per cent depending on its initial composition and the nature of the microintergrowths present. Calculations based on the reduction in volume by the removal of silicates and coarse-grained ilmenite indicate that the V_2O_5 content of the titaniferous magnetite will be increased by between 20 and 40 per cent depending on the amount of volume reduction involved. The V_2O_5 contents of the most vanadium-rich samples (MB 42,49,52,55) would thus be increased to approximately 1 per cent while their TiO_2 contents would be reduced to between 5 and 8 per cent. This TiO_2 is present in the form of very fine, microintergrowths that cannot be separated by conventional ore-dressing techniques.

The compositions of the ilmenite concentrates can be obtained from the electron microprobe analyses of the corresponding ilmenites in Table 12. These ilmenites generally contain slightly higher MgO contents, but their low Cr_2O_3 contents render them suitable for use in TiO_2 pigment production. The effect of the higher MgO contents on their treatment would have to be investigated.

9.7 Discussion

The Mambula titaniferous iron ores can be distinguished chemically and texturally from the ores of the other complexes investigated. Their microstructures and mineralogical relationships indicate that they have been modified by variable amounts since their initial crystallisation and this presumably occurred during the widespread 900-1000 million year metamorphic event (Cain, 1975).

The abundance of coarse grained ilmenite together with the contrasting relative paucity of ilmenite microintergrowths in the titaniferous magnetite is problematical. This suggests that the oxidation/exsolution of Ti-rich phases to form external grains in the Mambula ores may have progressed to a much greater degree than is normal in unmetamorphosed or even slightly modified titaniferous magnetites. A comparison can be made in this respect between the relative amounts of granular and lamellar ilmenite in these ores and those of the Usushwana Complex as described in Section 8.

The Usushwana ores exhibit similar TiO_2 contents to the Mambula ores ($\pm$ 1 per cent), but on average contain only 5 per cent of coarse-grained ilmenite

together with a further 2-3 per cent of finer grained intergranular ilmenite. Approximately 8 per cent of the ilmenite (=4% TiO_2) is present in discrete grains while the remaining 10 per cent TiO_2 is present in the extensively developed ilmenite trellis lamellae. In contrast, the Mambula ores contain between 15 and 25 per cent coarse grained ilmenite (8-12% TiO_2) with the result that only between 2 and 6 per cent TiO_2 is present in solid solution and in the form of Ti-bearing intergrowths in the titaniferous magnetite. This lower TiO_2 content is reflected in the relative scarcity and poor development of ilmenite lamellae in the Mambula ores. The dark pinkish-brown colour of the magnetite might also indicate that a portion of the Ti has remained in solid solution and this will also have contributed to the weak lamellar development.

Further evidence of external granule exsolution and consequent lowering of the TiO_2 content is afforded by the stringers of small ilmenite grains that are located along the boundaries between titaniferous magnetites. In addition, any externally exsolved ilmenite would simply have formed overgrowths on the larger ilmenite grains at places where they were in contact with titaniferous magnetite, thus increasing their size. This is supported by the presence of spinelliferous rims that clearly outline the secondary overgrowths on many of the large ilmenite grains. These ilmenite grains may, in part, represent original co-precipitated material or might have been formed by an earlier phase of external granule exsolution during their primary cooling.

Homogeneous, single phase titaniferous magnetites from basaltic volcanic rocks invariably exhibit high TiO_2 contents that range between 11,5 and 27,6 per cent (Anderson and Wright, 1972 ; Akimoto and Katsura, 1959 ; Ade-Hall, 1964 ; Katsura and Kushiro, 1961, for example). These titanomagnetites represent primary unexsolved phases that have been preserved in a metastable state by rapid cooling. An analogy can be drawn between them and the composition of the original high-temperature spinels precipitated in the Mambula Complex. The 14 per cent TiO_2 reported in the ore analyses can be readily accomodated in the magnetite as a high temperature magnetite-ulvospinel solid solution and does not require the presence of discrete co-precipitated

ilmenite grains. The "overexsolved" nature of the Mambula titaniferous magnetites is supported by evidence from other weakly or unmetamorphosed igneous complexes that generally contain only minor coarse grained ilmenite in silicate-poor, ore-rich layers (Trompsburg, Kaffirskraal, Bushveld, Usushwana). These ores exhibit overall TiO_2 contents similar to those of homogeneous titaniferous magnetites from basic rocks and as far as the author is aware, no ores of this type have been reported to contain more than 30 per cent TiO_2.

In addition to being more sparsely distributed than usual, the various ilmenite lamellae show signs of modification and differ in appearance from those present in unmetamorphosed titaniferous magnetites. They are broader in relation to their length and have blunt terminations rather than gently tapering ones. These features are indicative of incipient breakdown of the lamellae, but the process did not develop enough to result in any marked spheroidization. This suggests that although temperatures were high enough for some ionic diffusion to occur, they were insufficient for spheroidization. These lamellae resemble those developed in the Free State seam of the Rooiwater Complex (section 7) that had been modified during metamorphism, but had not yet reached the spheroidization stage.

The presence of stress-twinned ilmenite grains in certain samples particularly from those near the southern margin of the complex, is indicative of tectonic deformation. Thin, plate-like bodies of magnetite are generally developed at the intersections of differently oriented twin lamellae and have probably formed by nucleation and subsequent growth at dislocations associated with the twinning. Chakravarty (1961) described similar twinning in sheared ilmenites from deformed quartz veins. Ramdohr (1969, p.969 and 970) has illustrated similar twinned ilmenite grains showing the development of magnetite platelets at the intersection of twin lamellae. He referred to this as "newly formed magnetite" and noted that it might have formed from hematite, but offered no explanation. Ramdohr (1969) reported that shearing takes place in ilmenites along twin planes parallel to (0001) and $(10\bar{1}1)$. Smith and Steele (1976) also reported that shock deformation of ilmenite produces multiple twinning

as shown by the abundant development of these structures in ilmenite
from lunar breccias. They reported that twinning in ilmenite
initially occurs on (0001) and that this is followed by twinning on
$(10\bar{1}1)$.

Cahn (1970) has described the formation of similar textures in annealed
deformed alloys. The nucleation of these grains takes place at the
intersection of deformed bands which represent regions of high
dislocation energy. The nuclei preferentially form in regions where
the local degree of deformation is the highest, in this case, the areas
of stress-twin lamellae intersection. This mechanism might, by analogy,
be equally applicable to the Mambula ilmenites in the areas that were
tectonically deformed. Recalculation of the microprobe analyses
assuming stoichiometry, indicates the presence of small amounts of
excess Fe that would account for the nucleation and growth of these
bodies at the newly formed dislocations. Their development as magnetite
instead of hematite indicates that oxygen fugacities must have been
relatively low during this process.

The presence of oriented magnetite bodies within the larger untwinned
ilmenite grains is also problematical as magnetite is reportedly not
markedly soluble in ilmenite even at elevated temperatures as discussed
in Part 1. Electron microprobe analyses show the presence of minor
amounts of excess Fe in the Mambula ilmenites, but unfortunately the
oxidation state of the iron cannot be determined by this method and
it is uncertain whether it is present in solid solution as magnetite
or hematite. In keeping with the currently available experimental
data discussed in Part 1 it is concluded that the magnetite bodies
represent original hematite lamellae or Fe_2O_3 in solution that have
been reduced, either during post-crystallisation cooling or subsequent
metamorphism. These magnetite bodies also change orientation across
twin boundaries which suggests that their formation (possibly as
hematite) might predate the deformational event.

Spinel exsolution bodies in unmetamorphosed titaniferous magnetites
normally form narrow lamellae oriented along the cubic directions of
their hosts. They are also often present as small rounded grains
located along the boundaries of ilmenite lamellae. In contrast, the

spinels in the Mambula titaniferous magnetites are more rounded and those in the ores from north of the Mambula river have a definite lensoid shape. The thickening and rounding of the lamellae is possible due to incipient spheroidization caused by higher ionic mobilities under the increased metamorphic temperatures.

Aluminous titaniferous magnetites from unmetamorphosed, slowly cooled basic igneous rocks do not normally exhibit the same marked size variation in exsolved spinel lamellae towards grain boundaries as developed in the Mambula ores. The highly aluminous titaniferous magnetites of the Trompsburg Complex, for example, contain a variety of abundant transparent spinel microintergrowths (this thesis), but textures resembling those in the Mambula Complex are not developed. Bowles (1977) has, in contrast, figured transparent spinel intergrowths in titaniferous magnetites from the Freetown Layered Complex that are similar to those developed in the Mambula ores. Bowles, (1976) mentioned that the opaque oxides in question are developed in a basic pegmatitic phase and he did not regard these samples as having been metamorphosed. The shapes of the ilmenite lamellae in his illustration, however, also suggest that they have undergone a certain degree of modification. The conditions involved in the formation of the basic pegmatite are uncertain and the spinel intergrowths developed in its titaniferous magnetites cannot be regarded as typical of this microstructural type.

The formation of the characteristic transparent spinel microintergrowths in the Mambula titaniferous magnetites must also be related to processes that were active during the metamorphism of these ores. The very fine spinel lamellae would most probably have been resorbed during the initial temperature increase and partial resorption of the larger lamellae might also have occurred depending on the temperature reached. The modifications to their normal lamellar forms would also have been initiated during this stage. A certain amount of the remaining insoluble spinel that was favourably located near the grain boundaries might conceivably have migrated out of the titaniferous magnetites to form external granules. This would have lowered the Mg and Al contents in the marginal areas of these grains and set up concentration gradients increasing towards the centre of the grains.

The marked decrease in the size of the transparent spinel lamellae

towards the titaniferous magnetite grain boundaries reflects a decrease in the amounts of Al and Mg towards the margins of these grains. This compositional zoning is unlikely to have resulted during primary crystallisation since the slow cooling conditions operating in basic plutons would favour the formation of unzoned grains.

The compositional variation may result partly from the loss of Mg and Al from the marginal areas during external granule exsolution processes that were operative during primary cooling. This mechanism depletes the marginal areas in Mg and Al and sets up a compositional gradient. The ionic diffusion rates were too slow for more than a minor reduction of this gradient with the result that nucleation and growth of the larger, more widely spaced lamellae occurred towards the centres of the grains once critical supersaturation levels were reached in these areas on cooling.

Continued cooling would result in the nucleation and growth of smaller, more closely spaced lamellae at progressively lower temperatures in the areas closer to the grain boundaries as the corresponding critical supersaturations were reached. The decreased ionic mobilities at progressively lower temperatures would also lead to the development of compositional gradients in the areas between the larger lamellae ultimately giving rise to another series of fine lamellae. These processes would produce titaniferous magnetite grains containing transparent spinel intergrowths that would show a gradual decrease in size towards the grain boundaries, depending on the nature of the original concentration gradient.

Heating during metamorphism would conceivably result in resorption of portion of the originally exsolved spinel and lead to the formation of more equilibrium grain boundary relationships (spheroidization) in the remaining lamellae. Continued external granule exsolution of the spinel might also occur from the marginal areas of the grains, particularly during subsequent cooling, forming an even greater concentration gradient. The exsolution processes would continue as before during slow cooling resulting in the further growth and coarsening of original lamellae, ultimately resulting in a greatly exaggerated microstructural development such as that exhibited by the Mambula ores. The minor amount of spinel remaining in solid solution would exsolve as a set of very fine lamellae parallel to the octahedral planes of their hosts under the lowest possible

temperature conditions.

The discrete co-existing spinel grains in the Mambula ores are also
problematical.   Investigations in synthetic and natural spinel systems
indicate widespread miscibility amongst the various end members above
800°C, as discussed in Part 1.   The temperature range for the
crystallisation of iron-titanium oxides in the basaltic Makaopuhi lava lake
is given at between 1070° and 980° C by Evans and Moore (1968).   Primary
crystallisation of the Mambula opaque oxides would have taken place under
essentially similar or possibly even higher, temperature conditions so that
the co-precipitation of two distinct spinels would have been unlikely.
The presence of numerous small spinel grains along grain boundaries and
the relative paucity of spinel from the outer portions of titaniferous
magnetites indicates the extensive external exsolution of this phase.
It is possible that the larger spinel grains have been formed by the
coalescence of numerous smaller, favourably located externally exsolved
spinels.

The presence of crystallographically oriented iron-rich spinel exsolution
lamellae in the larger intergranular transparent spinels suggests that
their original composition may have been more towards the hercynite
compositional side.   This also indicates that their temperature or
formation must have been high enough to allow for this degree of
miscibility.   The smaller spinel bodies, both granular and lamellar,
do not contain exsolved iron-rich spinel and may have formed at lower
temperatures.

The compositions of the various spinel grains and intergrowths were not
determined by electron microprobe, but it is conceivable that compositional
differences exist between them.   For example, Cameron and Glover (1973)
reported compositional differences between various spinel intergrowths
developed in titaniferous magnetites from basic pegmatites in the eastern
Bushveld Complex.

The development of narrow reaction rims between silicates and opaque
oxides, particularly the formation of biotite around titaniferous magnetite
in contact with plagioclase, in slowly cooled igneous rocks is a common
feature.   Reactions between co-existing femic silicates and opaque oxides
are, however, much rarer.   The Mambula ores are characterised by the

presence of a variety of well defined reaction rims around the various silicates, particularly where they are in contact with opaque oxides. This is indicative of considerable re-equilibration having taken place between co-existing phases during metamorphism, but the incomplete nature of the reaction rims indicates that equilibrium conditions were not attained.

The development of hornblende rims around titaniferous magnetites in metagabbros has been discussed by Buddington et al. (1955, 1963), but the formation of fayalitic olivine rims between bronzite and titaniferous magnetite is less well documentated and suggests a reaction of the type:-

$$2(Mg, Fe) \ SiO_3 + Fe_3O_4 \longrightarrow 2(Fe, Mg)_2 \ SiO_4 + O_2$$

For the reaction to occur, however, some exchange of MgO between the bronzite and other co-existing phase would be necessary.   Other re-equilibration reactions would also be proceeding concurrently and it is possible that some transparent spinel would be formed at this stage by reaction between liberated MgO and Al_2O_3 (from magnetite and/or plagioclase). Similarly, portion of the intergranular ilmenite may have been formed from the Ti released during these reactions.

The reaction: magnetite + $SiO_2 \longrightarrow$ fayalite is well-known from experimental and metamorphic petrology and takes place at elevated temperatures under conditions of low oxygen fugacity as indicated by the QFM buffer described in Part 1.   By analogy it can be inferred that the fayalitic reaction rims may have developed under similar conditions, although the Mg present in the bronzite and the Ti and Al in the magnetite would effect the stability relationships to some extent.   The oxygen fugacities required for this reaction to take place would be much lower than those required for the reduction of hematite to magnetite in the coarse ilmenite grains and would most probably be near to those of the QFM buffer described by Buddington and Lindsley (1964).

The complex magnetite/orthopyroxene symplectites present in the reaction rims surrounding titaniferous magnetites in certain samples are difficult to interpret.   Similar textures have been reported from the unmetamorphosed Carr Boyd Rocks Ultramafic Complex in Australia by Purvis et al. (1972), and from an amphibolite at Pikwe-Celebi by Wakefield (1976).   These authors

favour a late magmatic stage for the formation of these intergrowths
according to the reaction: olivine + $O_2 \longrightarrow$ orthopyroxene + magnetite
which is essentially the reverse of the reaction leading to the formation
of fayalitic olivine rims around the bronzite.   The intergrowths noted
in the Mambula ores are only developed locally and it is possible that a
minor fluctuation in oxygen fugacity led to their formation in certain
areas during metamorphism.   Bowles (1976) has commented on the variability
in oxygen fugacities over very short distances within a rock during
crystallisation and it seems likely that similar differences will exist,
at least locally, during metamorphism allowing for the developemnt of this
texture.

The Mambula titaniferous magnetites contain unusally large amounts of
Al_2O_3 and MgO which must reflect aspects of the composition and
differentiation of the Mambula magma at the time of crystallisation.
Carmichael et al. (1974) commented on the control exerted by pleonaste
in solid solution in titaniferous magnetites crystallising as a primary
phase in magmas of low silica activity.   They suggested that the pleonaste
is formed by a reaction of the type:-

$$Mg_2Al_2SiO_6 \longrightarrow MgAl_2O_4 \quad + \quad SiO_2$$

pyroxene component   pleonaste   glass

Wass (1973) noted that the available chemical data indicate that the spinel
phases (i.e. magnetite) in rocks with alkali basalt affinities contain
significantly more Al and Mg than those of tholeiitic types.   This suggests
that insufficient silica and alkalies were present to form plagioclase from
all the Al_2O_3 available at the time of crystallisation so that the excess
alumina was incorporated into the spinel phase.   The formation of
essentially monomineralic titaniferous magnetite layers in stratiform
basic intrusions has been discussed in section 3 and is normally associated
with late-stage iron enrichment of the basic magma.   A late-stage SiO_2
enrichment normally accompanies this high degree of fractionation so that
the apparent low SiO_2 - activity of the Mambula magma at this stage appears
anomalous.

The small size and strongly fractionated nature of the Mambula Complex
showing the development of at least 6 thick titaniferous magnetite seams is

also problematical. This suggests that the complex may have crystallised from an iron-enriched basic magma that might represent a fractionated liquid derived from the crystallisation of a larger basic intrusion at depth. A certain degree of correlation can be made between several of the titaniferous magnetite seams developed in the southern part of the Complex and others in the northern part on the basis of bulk chemical compositions. The major differences are largely due to variations in the proportions of silicates which are more abundant in the samples from near the southern margin of the Complex. This feature suggests that compositional variations might occur in the individual seams along strike and that they become progressively silicate-rich towards the margins of the Complex.

Spinelliferous ilmenite rims around large ilmenite grains where they are in contact with aluminium-bearing titaniferous magnetites are commonly developed in unmetamorphosed basic intrusions, but they are particularly noticeable in the Mambula ores. Numerous small transparent spinels are formed along the boundaries of the titaniferous magnetite grains, presumably as a result of nucleation at grain boundary imperfections followed by growth due to external exsolution. A certain amount of ilmenite external granule exsolution will also take place and will add to any neighbouring ilmenite to form a secondary overgrowth.

The presence of the spinel grains along the titaniferous magnetite/ ilmenite interface, however, interferes with the ilmenite grain boundary migration. Coble and Burke (1963) noted that a grain boundary has difficulty in migrating past an inclusion because in order to do so, an area of boundary equal to the cross-sectional area of the inclusion has to be reformed in the boundary on the far side of the inclusion. The inclusion impedes grain boundary movement since the surface energy of this area of boundary has to be provided by a decrease in the area of the rest of the boundary. The spinel impurities thus tend to remain along the ilmenite/titaniferous magnetite interfaces and varying degrees of complex grain-boundaries configuration arise due to the pinning of one member of the interface while continued growth of the next segment occurs. As a result, very irregular boundaries are produced instead of the expected gently curved ones. Sufficient energy has been available in certain cases and the grain boundary has migrated past the inclusions which then remain as a relict line demarkating the position of an earlier interface.

The very fine rounded ilmenite granules typically form clusters round the peripheries of the larger, lens-shaped spinel intergrowths as shown in Plates 11 (H) and 12 (G). The transparent lamellae in titaniferous magnetites from unmetamorphosed basic rocks that contain abundant exsolved ulvospinel are often surrounded by a rectangular framework of coarser-grained ulvospinel. By analogy, it is conceivable that similar textures were present in the Mambula ores and that oxidation of this ulvospinel to ilmenite occurred at some stage either before or during metamorphism. The spinel lamellae became modified during metamorphism and the original ulvospinel (or ilmenite) frameworks surrounding the spinels broke down to form the clusters of small ilmenite grains. The ionic mobilities were too low to allow for complete spheroidization of the spinel and rearrangement of the ilmenite to occur under the prevailing temperature conditions.

The primary microstructures are not preserved in the Mambula ores and their original nature is uncertain. The general lack of abundant lamellar-or modified lamellar-ilmenite intergrowths developed in the Mambula ores suggests that these microstructures were also not well-developed in the primary intergrowths. The presence of ulvospinel-type microstructures in certain titaniferous magnetites and the development of the very fine rounded ilmenite granules around modified spinel lamellae suggest the presence of abundant ulvospinel in the primary intergrowths. In view of this, it is suggested that the original titaniferous magnetite microstructures consisted of sparsely distributed ilmenite lamellae of various sizes and that the bulk of the TiO_2 was present in well defined ulvospinel cloth-textured intergrowths.

The original spinel microintergrowths were probably similar to those exhibited by the titaniferous magnetites of the Trompsburg Complex (this thesis). Variable amounts of coarse-grained, co-precipitated ilmenite may also have been present, probably becoming more abundant in the silicate-rich ores (by analogy with the Trompsburg ores). Minor amounts of fine granular ilmenite were derived from external exsolution processes.

Cain (1975) stated that the Mambula Complex is located in a zone of metamorphic rocks that generally belong to the almandine-amphibolite facies.

He also noted that the Complex is metamorphosed to a greater extent along
its margins than towards its interior. Winkler (1976) stated that the
possible temperature range reached during this degree of metamorphism varies
between approximately 525 and 700°C at low pressure. The temperature
range is reduced considerably with increasing pressure and coverges on
approximately 600°C. These figures thus provide a useful upper limit
to the temperatures reached during metamorphism and indicate that
extensive ionic diffusion and resultant modification of microstructure
was possible. The presence or absence of volatiles might also be
expected to influence the microstructures developed.

The original exsolved ulvospinel would have been largely redissolved
during heating up to temperatures near 600°C provided that the oxygen
fugacities remained low enough during this stage. The large amount of
titaniferous magnetite in the seams would have exerted a strong buffering
effect on the oxygen fugacity and these conditions may well have existed.
The presence of minor exsolved ulvospinel-type microintergrowths in
certain samples indicates that at least portion of the original exsolved
ulvospinel was resorbed and subsequently exsolved again.

The subsequent behavior of the titanium-bearing phases involves several
complex processes. The temperatures were not high enough to allow the
degree of ionic mobility required for extensive spheroidization, but were
nevertheless sufficiently high to allow for extensive external granule
exsolution, as suggested by the abundance of granular ilmenite and
paucity of intergrown Ti-rich phases. No data is currently available on
the mechanisms and solid state processes operative in titaniferous
magnetites during metamorphism with the result that it is difficult to
evaluate the significance of the Mambula microstructures.

Mildly oxidising conditions, either during heating or subsequent cooling
would have led to the formation of ilmenite from either exsolved or
dissolved ulvospinel. This ilmenite would have been insoluble and have
segregated to form typical trellis lamellae oriented paralled to (111).
The general paucity of these lamellae, however, suggests that other
processes might have been operative.

The temperatures necessary for the spheroidization of lamellar
intergrowths are not known, but they might be near to those developed

in the higher temperature range of medium grade metamorphism from analogy with the Rooiwater ores (this thesis). The metamorphic episode lasted over an extremely long period of time ($\overline{+}$ 100 million years) (Cain, 1975) and it is possible that a large portion of the ilmenite present as intergrowths was able to migrate out to form external granules over this period. This is supported by the presence of abundant fine grained granular ilmenite along titaniferous magnetite grain boundaries and the well defined secondary ilmenite overgrowths developed around the larger grains.

The secondary spinelliferous overgrowths on the larger ilmenites together with the external ilmenite and spinel granules indicate that considerable post-crystallisation growth of these phases has taken place. Grain boundary migration also occurred in order to accomodate these growing phases and led to the development of an overall granoblastic polygonal texture in the ores. The highly irregular, spinelliferous ilmenite grain boundaries between ilmenite and titaniferous magnetite were controlled by the pinning of spinel inclusions along their length.

The lamellar ilmenite and both lamellar- and granular-transparent spinels exhibit complex mutual relationships. The larger ilmenite lamellae commonly transgress the larger spinel lamellae that remain continuous on either side of the ilmenite and exhibit no thinning towards the ilmenite contact. These ilmenite lamellae appear to post-date the spinel lamellae. Other, often smaller, ilmenite lamellae are often transgressive across areas containing smaller spinel lamellae, but do not cut them. These spinel lamellae are present right up to the ilmenite contacts but do not continue on the other side. These ilmenite lamellae appear to predate the spinel lamellae.

Rounded to irregularly shaped spinel grains are commonly located along the interfaces between titaniferous magnetite and a variety of different sized ilmenite lamellae. This suggests that these grains nucleated and grew via the heterogeneous mechanism at sites of grain-boundary dislocations associated with the lamellar development. These spinels are also sometimes present as rows of inclusions within the lamellae and are oriented parallel to the lamellar grain boundaries. This indicates that a certain amount of coarsening of the ilmenite lamellae has occured since the formation of the spinel grains.

The transparent spinel appears to replace the ilmenite lamellae at places where the two types of lamellae intersect. This process also occurs, but less frequently, in the absence of lamellar intersections and usually takes place at the ends of the ilmenite lamellae. These relationships appear to be the result of the modifications that occurred during metamorphism. The ilmenite lamellae typically become shorter and wider during this process and it is possible that the associated spinel may have migrated into the "low pressure" areas in the titaniferous magnetite formerly occupied by the end of the ilmenite lamellae. This is n a true replacement process, but merely a volume for volume readjustment. The spinel grains located along the grain boundaries migrate and accumulate at the end of the shortening lamellae producing the replacement effect. The effect produced at lamellar-ilmenite and -spinel intersections is similar. (refer to Plate 11 (B-D)).

The modification of the primary microstructures during metamorphism is a complex process involving a number of variables including temperature, oxygen fugacity, the nature of the original microstructures and the rate of cooling. The evidence afforded by the magnetite bodies in the coarse-grained ilmenite and the fayalitic reaction rims indicates that, although oxygen fugacities were low during metamorphism, they were not low enough to allow for any large-scale existence of ulvospinel. The bulk of ulvospinel in solid solution was thus oxidised to ilmenite and contributed to the development of the various ilmenite oxidation/exsolution bodies. The "overexsolved" nature of the Mambula titaniferous magnetites has already been discussed, and is largely due to continued exsolution under mildly oxidising conditions with respect to ulvospinel during metamorphism. During the final stages of cooling, the oxygen fugacities were low enough at certain points within the complex to allow the formation of minor exsolved ulvospinel.

9.8 Genesis of the Mambula Ores

The world wide occurrence of titaniferous magnetite layers, or titaniferous magnetite-rich silicate layers, in the upper portions of layered basic intrusions supports the view that they are the products of normal crystallisation trends characterised by late-stage iron enrichment. The Mambula ores are very similar in many respects to other deposits of this nature, but differ to a small extent in minor element geochemistry. Their overall chemistry is, however, consistent with a magmatic origin and there

is a decrease in V_2O_5 content of the titaniferous magnetites
stratigraphically upwards in the sequence which is in agreement with
the trends displayed by the Bushveld, Skaergaard, Dufek, and Rooiwater
(this report) Complexes.

du Toit (1918) drew analogies between the titaniferous magnetite-rich
layers of the Mambula Complex and those of the Bushveld Complex and
suggested that they were formed in a similar manner.   He rejected the
idea of a gravitative concentration of the titaniferous magnetite and
drew analogies between · the behaviour of these ores and those of
pegmatites. du Toit (1918) concluded that the titaniferous magnetite
layers were formed by the injection from below of a fluid material
consisting almost wholly of iron and titanium oxides.   This material
was emplaced into the semi-solid gabbro, partly by actual intrusion,
and partly by a diffusion process.

A large amount of data has accumulated on layered basic intrusives since
du Toit's paper was published and in the author's opinion the Mambula
ores can be regarded as a high-alumina variant of the normal type of
titaniferous magnetites developed in these complexes during fractional
crystallisation.   The textural evidence also indicates that their
original mineralogical and microstructural relations have been modified
by metamorphism.

The genesis of the Mambula ores can be summarised as follows:-

1.   The various titaniferous magnetite seams were formed as cumulate
     rocks by normal fractional crystallisation processes during the
     solidification of the Mambula Complex.   The titaniferous magnetite-
     rich layers were formed during this process by the accumulation of
     an initially homogeneous spinellid phase containing Fe, Ti, Al, Mg,
     V and Mn together with minor, but variable amounts of co-precipitated
     silicates and possibly ilmenite.   Factors such as postcumulus growth,
     removal of intergranular fluids by filter pressing and annealing may
     also have played an important role in the development of the ore-rich
     layers.

2.   At the commencement of cooling, exsolution of a titanium-rich oxide
     phase was initiated resulting in the formation of several per cent

by mass of intergranular ilmenite and possibly some broad ilmenite lamellae. This probably represents true exsolved ilmenite and corresponds to the external granule exsolution described by Buddington and Lindsley (1964) and is in agreement with the data of Anderson (1968 b). This type of exsolution is thought to cease once temperatures drop below about 750°C. The nature and location of this ilmenite suggests that they nucleated at grain-boundary imperfections and grew into the titaniferous magnetite in a branching manner. Grain boundary adjustment would also have taken pla e under the annealing effects of the high temperature leading to the formation of polygonal grains having interfacial angles approximating 120°.

3. Once the temperature had dropped to below 1000°C, exsolution of the aluminous spinel would have commenced. Presumably at the highest temperatures nucleation would have occurred at grain boundary imperfections resulting in the formation of external granules and portion of the small grains located along the ilmenite lamellae. At lower temperatures and higher supersaturations, exsolution of the spinel lamellae would occur via the homogeneous nucleation and growth mechanism. This stage would thus overlap somewhat with lower temperature portions of stage two and would continue down to the temperatures at which exsolution effectively ceases.

4. Further cooling would result in the continued exsolution of titanium-rich phases, but the microstructures developed would depend larglely of the oxygen fugacity. The microstructures produced during cooling through this temperature range slightly below 750°C have been modified to varying extents during the subsequent metamorphism and their original nature is uncertain. The lack of abundant ilmenite trellis lamellae suggests that the original intergrowths may have consisted essentially of sparse, fine ilmenite lamellae and abundant ulvospinel forming a texture essentially similar to that displayed by the ores of the Trompsburg Complex (this report). Either hematite or magnetite exsolution lamellae would have been developed in the coarser-grained ilmenites, while abundant exsolved transparent spinel would also be present.

5. At a later stage the complex was involved in widespread regional metamorphism up to almandine-amphibolite facies which resulted in the

modification of the microstructures. Any hematite lamellae in the
larger ilmenite grains may also have been reduced to magnetite.
The temperatures reached were not high enough for complete resorp-
tion of the exsolved transparent spinel so that exsolution continued
and large evenly spaced lamellae showing slight tendency towards
spheroidization were formed. External granule exsolution of the
transparent spinel was favoured and much of the material favourably
located near grain boundaries migrated out to add to the external
grains. The resulting textures would thus show the development of
large spinel lamellae towards the centre of the grains that would
decrease in size and number towards the grain boundaries reflecting
the depletion in Al and Mg in this direction. The lamellae in the
titaniferous magnetites from north of the Mambula river are more
rounded and probably reflect incipient spheroidization under the
influence of slighter higher temperatures.

6. The behaviour of the titanium-bearing phases would depend essentially
   on oxygen fugacity, the nature of the original intergrowths and the
   temperatures and duration of heating. The conditions appear to have
   been mildly oxidising with respect to ulvospinel, resulting in the
   gradual oxidation/exsolution of fine ilmenite lamellae with much of
   this material ultimately being expelled externally from the
   titaniferous magnetite grains and contributing to the growth of the
   intergranular ilmenites. A certain amount of grain boundary
   adjustment would also have taken place during this stage while the
   re-equilbration of silicate and oxide phases would also have commenced,
   resulting in the development of well defined reaction rims.

7. Exsolution of the various phases would continue during cooling after
   the metamorphic thermal peak until the temperatures dropped below
   those at which ionic migration can effectively take place. With a
   decrease in temperature and resulting lower ionic mobilities, migration
   of the Al-rich and Mg-rich phase to the large lamellae would no longer
   be able to take place over such a large distance as before, and local
   areas of supersaturation would build up towards the centres of areas
   bounded by large lamellae. This would then result in the nucleation
   and growth of a second series of very much finer spinel lamellae.
   Some precipitation of transparent spinel would also occur around newly

formed ilmenite lamellae and grains.

8. The nature of the Ti-rich phases produced during the cooling episode are largely dependent on oxygen fugacity. The existence of fine ilmenite lamellae and small external granules illustrates that it was high enough for some oxidation of ulvospinel to occur. The samples from south of the Mambula river contain very fine-grained ilmenite lamellae in a trellis network indicating that conditions in at least part of the complex were oxidising with respect to ulvospinel down to the lowest temperatures. Other evidence for slightly oxidising conditions towards the closing stages is afforded by the local development of magnetite-orthopyroxene symplectites from original fayalitic olivine in this area. The samples from the north of the Mambula river commonly show ulvospinel-type intergrowths indicating that oxygen fugacities were lower in this area of the complex. Numbers of very small ilmenite grains nucleated and grew around the margins of larger spinel grains in the areas associated with ulvospinel development which suggests that the oxygen fugacities were buffered very close to the limiting value for ulvospinel oxidation, thus allowing for the precipitation of minor amounts of ilmenite.

9. Oxidation and hydration of the ores in the zone of surface weathering has resulted in their partial martitization and the development of secondary geothite, hematite and a variety of clay minerals.

9.10 Conclusions

1. The development of the Mambula titaniferous iron ores in discrete layers towards the upper parts of a gabbroic intrusion is in accord with their development by normal crystallisation-differentiation processes that are operative in large basic intrusions.

2. The ores are characterised by the presence of between 10 and 30 per cent silicate impurities that were co-precipitated with the opaque oxides.

3. The Mambula titaniferous iron ores are chemically similar to ores of this nature that are typically developed in layered gabbroic complexes. They are characterised by high Al_2O_3 contents and can be

regarded as a high-alumina variant of this type of ore.

4. The decrease in V_2O_5 contents of the ore with increasing stratigraphic height in the complex is in accord with the normal differentiation trends exhibited by titaniferous magnetites during fractional crystallisation. The variation in MgO and Al_2O_3 contents in the opaque oxides is obscured due to the presence of variable amounts of orthopyroxene and plagioclase in the ores. There appears to be a decrease in the amounts of these oxides upwards in the sequence when allowance is made for the impurities.

5. The ores are characterised by an abundance of coarse grained granular ilmenite and a relative paucity of intergrown Ti-bearing phases in their titaniferous magnetites.

6. The highly aluminous nature of the Mambula ores is reflected in the abundance of various-sized transparent spinel grains and the well-developed sets of spinel lamellae in the titaniferous magnetites.

7. The silicate impurities are characteristically surrounded by well defined reaction rims at places where they are in contact with opaque oxides. The titaniferous magnetite microstructures have also been modified and considerable solid state intergranular readjustment has taken place. These features reflect changes that were brought about in the ores during metamorphism.

8. The ores were metamorphosed under conditions reaching the almandine-amphibolite facies during the widespread Natal-Namaqua regional metamorphic episode between 900 and 1000 million years ago.

9. The increased temperature conditions during metamorphism allowed for the development of abundant coarse-grained intergranular ilmenite by external granule oxidation exsolution processes. External granules of transparent spinel originated in an analogous manner.

10. The Mambula ores contain variable amounts of silicate impurities (10-30 per cent) and require beneficiation. These impurities are characteristically coarse grained and can be largely separated by

crushing to less than 200 mesh followed by conventional magnetic, electromagnetic or gravity separation techniques.

11. The bulk of the coarse grained ilmenite can be recovered from the ore by crushing to less than 200 mesh followed by electromagnetic separation. This leaves a titaniferous magnetite concentrate containing between 3 and 8 per cent TiO_2 that can be separated from the silicate impurities. It is not possible to produce a magnetic fraction with lower TiO_2 contents since it is present in the form of extremely fine ilmenite and ulvospinel microintergrowths that cannot be liberated by mechanical separation procedures.

12. The highest V_2O_5 contents of approximately 0,8 per cent were recorded in the lowermost exposed seams and there is a gradual decrease in V_2O_5 upwards through the titaniferous magnetite layers with the lowest values of 0,5 per cent being recorded in the uppermost seams. These values are probably too low to warrant V_2O_5 recovery.

13. The V_2O_5 is preferentially incorporated into the titaniferous magnetite during crystallisation and it is possible to produce a magnetic concentrate containing approximately 1 per cent V_2O_5 from the lowermost seams by magnetic concentration. By analogy with other complexes, it is possible that additional titaniferous magnetite seams containing higher V_2O_5 values might be located at depth in the Complex.

14. The moderate TiO_2 ($\pm$ 13 per cent) and low V_2O_5 (0,5-0,8 per cent) contents of these ores makes them unsuitable for us as raw materials for the direct pyrometallurgical production of iron and steel, high titania-, or V_2O_5 -products. Possibilities, however, exist for the beneficiation of these ores that might yield useable products.

15. The Mambula Complex is rather small, but surface exposures indicate the presence of large tonnages of ore. Detailed exploration is necessary to determine whether additional higher V_2O_5 -bearing titaniferous magnetite seams are present at relatively shallow depths and for the calculation of ore reserves of the various types of ore.

16. Representative samples of Mambula ore should be investigated from
    an ore dressing point of view to determine the feasibility of
    commercial ilmenite production from the ore. The high $-V_2O_5$ $-$low
    TiO_2 magnetic concentrates should also be examined from a
    pyrometallurgical point of view to determine the feasibility of
    V_2O_5 $-$slag and iron production.

17. The Mambula Complex represents an attractive area for further
    investigation with respect to ilmenite production from a primary
    source. Possibilities exist for the recovery of V_2O_5 and iron,
    but the relatively small size of the deposit and the limited
    ore reserves will probably preclude its exploitation.

18. The Mambula Complex has not been investigated in any detail in
    spite of its relatively small size (approx. 25 square km).
    Comprehensive geological studies and mapping are necessary to
    determine the true nature of the complex, the number and extent
    of the titaniferous magnetite seams present and the distribution
    of the different ore types.

19. The Mambula Complex shows the development of a wide variety of
    cumulate rock types in addition to the numerous titaniferous
    magnetite seams and must rank as one of the world's smallest, highly
    fractionated basic Igneous Complexes. The Complex has undergone
    widespread regional metamorphism and should provide the basis for an
    interesting petrographic study.

20. The phase relationships between the co-existing silicates and oxide
    phases in the Mambula Complex and their behaviour during metamorphism
    require further study and should be investigated in detail.

10. THE TITANIFEROUS IRON ORES OF THE KAFFIRSKRAAL IGNEOUS COMPLEX
10.1 Introduction
The Kaffirskraal Igneous Complex is located approximately 16 km southeast
of Heidelberg on the main road to Vereeniging. It consists of a small,
pear-shaped mass of pyroxenitic rocks having dimensions of approximately
1,5 x 1 km. The Complex is intrusive into the Ventersdorp lavas in that
area and has been briefly described by Rogers (1921, 1922), and Nel and

Jansen (1957). A more detailed petrographic and mineralogical description
of the deposit has been given by Frick (1975) who concluded that it has
many features in common with zoned layered ultramafic complexes.

The Complex consists of a marginal zone of porphyritic norite and a
central layered zone of magnetite-clinopyroxenite within which is situated
a thick seam of titaniferous magnetite. The titaniferous magnetite rock
crops out in the central part of the Complex and is in the form of a sheet-
like body approximately 8m thick (Frick, 1975). The ore-rich layer
occupies a roughly circular area having a diameter of approximately 300m
and with a southerly extension some 50m wide and 300m in length.

10.2 Sample Localities

The titaniferous magnetite and associated pyroxenites are highly weathered
and do not outcrop well so that samples could only be collected from
surface rubble and old shallow prospecting pits. The form of the deposit
is shown in the accompanying geological map (Map 4).

10.3 Description of the Ores

The ore-rich layer forms a massive, well-jointed rock consisting
essentially of close-packed titaniferous magnetite grains together with
minor, but variable amounts of ilmenite and clinopyroxene. The ore is
composed almost entirely of opaque oxides in places, but in others up to
15 per cent of silicate impurities may be present.

THE KAFFIRSKRAAL COMPLEX

LEGEND

Ventersdorp lava

Kaffirkraal Complex (undifferentiated)

Titaniferous Magnetite

---- Road

0   200   400   600
Metres

(after Frick, 1975)
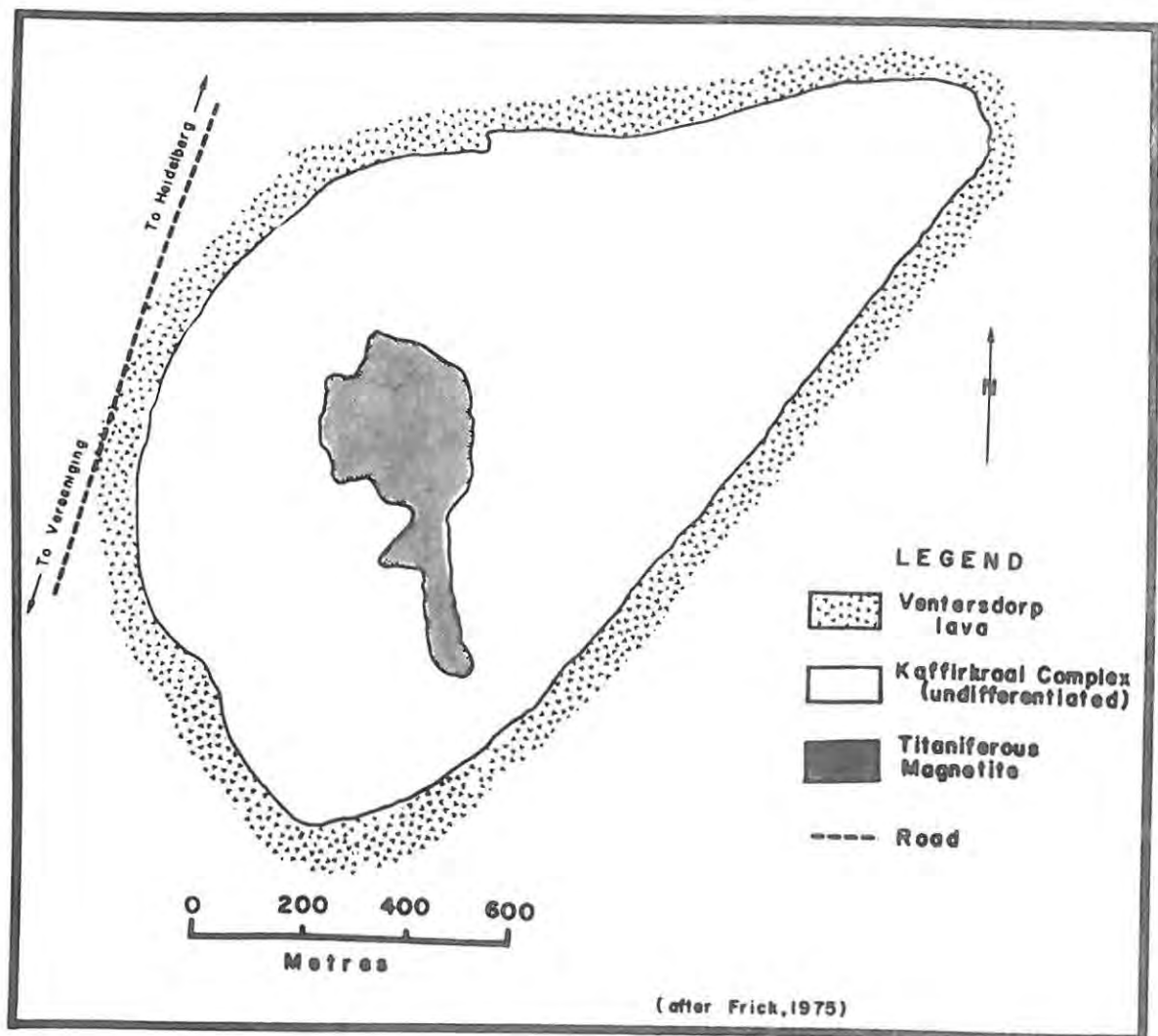
MAP 4 : The Kaffirskraal Igneous Complex

The titaniferous magnetite crystals vary between 1 and 2mm in size, having a mean diameter of approximately 1,5 mm. The clinopyroxene is generally present as larger, rounded plates up to 5mm across that poikilititcally enclose numbers of smaller, rounded titaniferous magnetite grains. The clinopyroxene decomposes to a variety of clay minerals on weathering and is removed from the rock imparting a coarse, pitted texture on surface exposures of silicate-rich material. The silicate-poor samples are denser and weathering produces a smoother, goethite coating on exposed surfaces.

The samples vary in colour from black to reddish-brown and are generally only weakly-to moderately-magnetic. These properties are largely dependent on the degree of weathering and reflect the highly oxidised nature of most of the samples examined. The weathering has resulted in extensive oxidation and hydration of the ores and they exhibit all gradations from relatively fresh through to completely decomposed material. The titaniferous magnetites typically show oxidation to titaniferous maghemite and martite while abundant secondary geohite is present, both as irregular veinlets and botryoidal coatings.

The Kaffirskraal ores have an overall polygonalized texture in which the titaniferous magnetites exhibit polygonal outlines and there is a tendency for grain boundaries to meet in triple junctions with interfacial angles approximating 120°. The co-existing ilmenite grains are much smaller and are located interstitially between the larger titaniferous magnetites.

The titaniferous magnetite grains, particularly those in the more highly weathered samples, are characteristically traversed by irregular cracks as illustrated in Plate 13 (A). These fractures do not always coincide with the magnetite cleavage directions and their formation is presumably related to volume changes that occur during oxidation.

10.3.1 The titaniferous magnetite

Titaniferous magnetite represents the dominent opaque phase in these ores and is characterised by the presence of various intergrown Ti-and Al-rich phases as illustrated in Plates 13-15. For descriptive purposes this magnetite can be regarded as the matrix in which the various microintergrowths are located.

The titaniferous magnetites typically exhibit varying degrees of oxidation to martite which proceeds via the formation of intermediate titaniferous maghemite. The oxidation characteristically commences along grain boundaries and moves inwards in an irregular fashion. This two-stage oxidation process preserves the delicate micrometre-sized intergrowths and results in an irregular zonal distribution of martite, titaniferous maghemite and unoxidised magnetite in the grains. The weathered grains commonly consist of an unoxidised core surrounded by an outer zone of

titaniferous maghemite and martite. The unoxidised cores may be absent in the more highly weathered samples and the outermost martitized parts of the grains commonly show hydration to geothite.

In addition to the titaniferous magnetite, the ores are traversed by narrow, sparsely distributed, irregular veinlets of optically homogeneous magnetite as illustrated in plate 13 (B). A well defined boundary is developed between this homogeneous magnetite and the titaniferous magnetite in certain areas as illustrated in Plate 13 (B). The contacts are more diffuse in other areas, particularly near grain boundaries and have the appearance of segregations, rather than veinlets as illustrated in Plates 13 (C-E). This homogeneous magnetite oxidises directly to martite without the formation of intermediate titanomaghemite and the process takes place along its octahedral planes as illustrated in Plates 13 (B-E).

The true magnetite veinlets are generally free from ilmenite and other inclusions, but the segregations commonly contain numbers of small, skeletal and poikilitic ilmenite grains as illustrated in Plates 13 (C-E). There appears to be some crystallographic control of the external morphology of the ilmenite grains in all cases by the octahedral planes of their magnetite hosts. Both types of homogeneous magnetite exhibit a slight brownish-pink colour that might be indicative of the presence of minor TiO_2 remaining in solid solution.

10.3.2 The ilmenite

A wide variety of ilmenite grains are present, both as discrete crystals and as various microintergrowths in titaniferous magnetite. For descriptive purposes seven types of ilmenite are recognised, each type being characterised by differences in grain size and morphology.

10.3.2.1 Coarse granular ilmenite

Large tabular-to irregularly-shaped, elongated ilmenite grains are located interstitially between the large titaniferous magnetite grains as illustrated in Plate 13 (F). The grains range from 0,2 to 1,0mm in length, but are generally less than 0,7mm long. They are commonly present as single crystals, but occasionally may form aggregates of two or more grains. The ilmenites do not exhibit signs of polygonalization where they are in contact either with titaniferous magnetite or other

PLATE 13

KAFFIRSKRAAL TITANIFEROUS IRON ORES

All photomicrographs taken in incident light using oil immersion objectives.

A. The typical appearance of weathered Kaffirskraal titaniferous magnetites showing the presence of numerous irregular fractures (black).

B. A transgressive veinlet of optically homogeneous magnetite showing incipient martitization (white) cutting across titaniferous magnetite.

C. Poikilitic ilmenite grains (dark grey) set in optically homogeneous magnetite (lighter grey) that shows extensive martitization (white).

D. Similar to (C), but with the ilmenite grains (dark grey) showing greater crystallographic control. Note the presence of a typical ulvospinel cloth texture in the titaniferous mangetite on the left hand side of the photomicrograph.

E. Similar to (D), but showing larger, better developed ilmenite grains (dark grey).

F. A cluster of large intergranular ilmenite grains in titaniferous magnetite.

G. Numerous fine magnetite lamellae (white) in ilmenite (dark grey). The white grain is martitized titaniferous magnetite while the white line running diagonally across the ilmenite is a veinlet of martitized late-stage magnetite.

H. A small, irregularly shaped ilmenite grain (dark grey) surrounded by titaniferous magnetite showing the development of very fine ilmenite lamellae and an ulvospinel cloth texture. The lighter areas in the groundmass are due to the presence of titaniferous maghemite.

PLATE 13
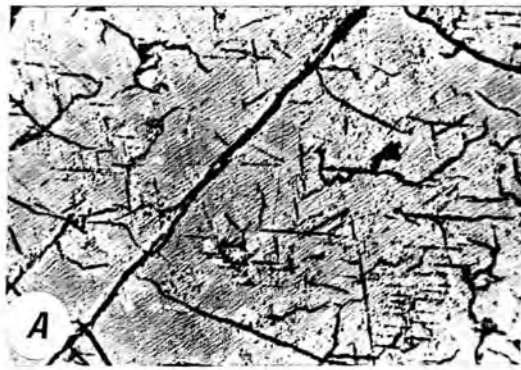
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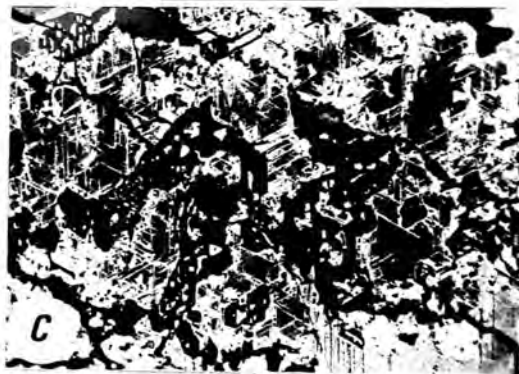
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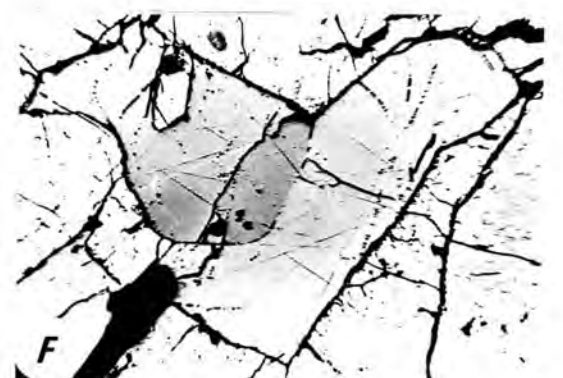
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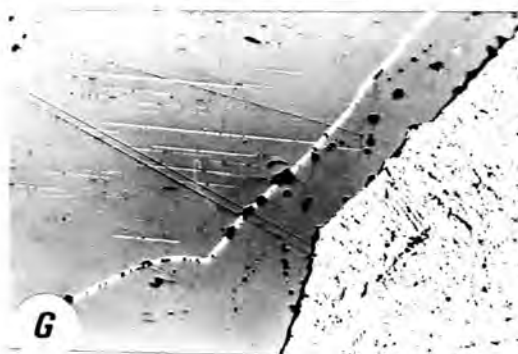
0,1 mm

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ilmenite grains.

The amount of coarse grained ilmenite in the samples is variable and ranges
between approximately 2 and 6 per cent. The ilmenites occasionally contain
large rounded, to subrounded inclusions of titaniferous magnetite that are
compositionally and texturally similar to the surrounding grains. The
larger ilmenite grains occasionally contain very fine, sparsely
distributed magnetite lamellae (Plate 13 (G)). These lamellae are
commonly less than a micrometre wide, but may be up to 40 micrometres
long. They are oriented along the basal planes of their ilmenite hosts
and are generally confined to the central portions of the larger grains,
being absent from regions near grain boundaries. These lamellae have
been oxidised to martite in the majority of samples, but are recognisable
because of the morphological differences between them and hematite
lamellae. _ Magnetite lamellae exhibiting various stages of martitization
are also occasionally present.

10.3.2.2. Fine granular ilmenite

Small, irregularly shaped, and often elongated, ilmenite grains are
present as stringers along the interfaces between co-existing titaniferous
magnetite grains. Similar grains are also irregularly distributed within
the titaniferous magnetites as isolated grains or as stringers that are
often aligned along gently curved paths. Typical examples of these
ilmenite types are illustrated in Plates 13 (H) and 14 (A-B). Their
irregular, elongated forms suggest that they are in many cases composed
of numbers of similarly oriented small grains that have coalesced to form
longer, optically continuous grains.

Numbers of rounded, micrometre-sized spinel grains are typically present
around the peripheries of the smaller ilmenites and are commonly located
within the outer 5 to 10 micrometre wide rims of larger ilmenites.
Somewhat larger spinel grains are sometimes located along the interfaces
between the fine granular ilmenite and the titaniferous magnetite. Both
the internal and external ilmenite grains are often connected to a set of
large sparsely distributed ilmenite lamellae.

10.3.2.3 Large ilmenite lamellae

Numbers of large, sparsely distributed ilmenite lamellae are present
oriented along the octahedral planes of the titaniferous magnetites. They

vary in width from 5 to 10 micrometres and show extreme elongation
with lengths commonly up to 0,2mm and even occasionally as long as 0,4mm.
They are typically spinelliferous and are characterised by the presence
of numerous small, rounded spinel grains that are located along the
ilmenite/titaniferous magnetite interfaces illustrated in Plate 14
(B-D). The sparse distribution of these lamellae and their wide
size variation suggests that more than one size range might be present.

The ilmenite lamellae exhibit gently tapering ends at places where they
intersect or are totally enclosed in titaniferous magnetite as illustrated
in Plate 14 (D). They are occasionally connected to small granular
ilmenite grains with which they may be in optical continuity or else
exhibit different orientations.

The lamellae are very erratically distributed throughout the ores, being
fairly abundant in certain areas, but are virtually absent from others.
On a smaller scale, within a particular polished section, the lamellae
might be quite well developed in a particular titaniferous magnetite,
but are virtually absent from neighbouring grains. The lamellae are
not sufficiently well developed in any of the samples to form a typical
trellis network.

10.3.2.4. Very fine ilmenite lamellae

A second set of very much finer ilmenite lamellae is also present as
illustrated in Plate 14 (E-H). These lamellae are generally less
than 20 micrometres long. They are also sparsely distributed
throughout their titaniferous magnetite hosts and are generally developed
in the immediate vicinity of grain boundaries, cracks and other permeable
features as illustrated in Plate 14 (G and H).

The very fine ilmenite lamellae are also oriented along the octahedral
planes of their titaniferous magnetite hosts, but are only rarely
developed to the extent that well defined trellis networks are formed.
Spinel grains are only rarely associated with these lamellae, but very
small, irregularly shaped, ilmenite grains are sometimes developed at the
ends of these lamellae. The lamellar ilmenite development generally
gives way to a typically coarse-grained ulvospinel-type microstructure
within 20 to 30 micrometres of the fracture or other permeable structure
as illustrated in Plate 14 (H).

PLATE 14

KAFFIRSKRAAL TITANIFEROUS IRON ORES

All photomicrographs taken in incident light using oil immersion objectives.

A. Small, irregularly-shaped ilmenite grains (dark grey) developed
    along the boundary between larger titaniferous magnetite grains.

B. Small, irregularly-shaped ilmenite grains (dark grey) aligned along
    a fracture in titaniferous magnetite containing lamellae ilmenite
    (dark grey). Notice that some of the ilmenite lamellae are connected
    to the ilmenite grains.

C. A large ilmenite lamella (dark grey) with numbers of small spinel
    grains (black) developed along its margins. Abundant
    crystallographically oriented transparent spinel intergrowths (black)
    are also developed in the surrounding titaniferous magnetite.

D. Intersecting large ilmenite lamellae (dark grey) developed in
    titaniferous magnetite.

E. Very fine ilmenite lamellae (dark grey) in titaniferous magnetite.

F. A small, irregular ilmenite grain (dark grey) surrounded by very fine
    ilmenite lamellae.

G. Areas of titaniferous magnetite containing very fine ilmenite lamellae
    and grading into areas in which small patches of ulvospinel cloth
    texture are present. Note the very fine ilmenite grains (dark grey)
    that are located in stringers along the fractures.

H. Typical fine-grained microstructural relationships in the Kaffirskraal
    titaniferous magnetites. Very small ilmenite granules (dark grey)
    are developed along the margins of an arcuate fracture (black).
    Very fine ilmenite lamellae are developed for a short distance on
    either side of the fracture and then grade into a typical ulvospinel
    cloth microtexture.

PLATE 14
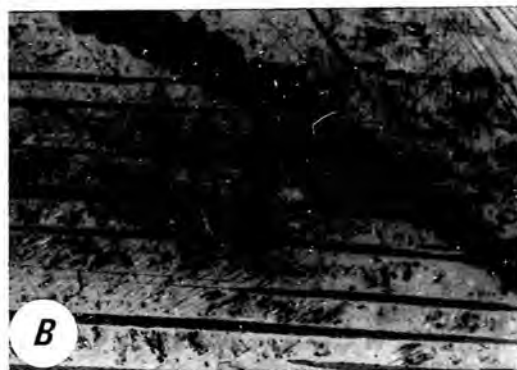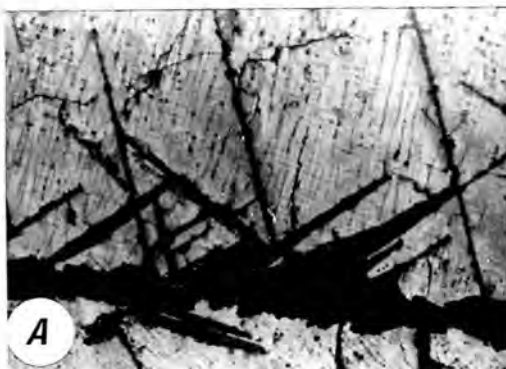
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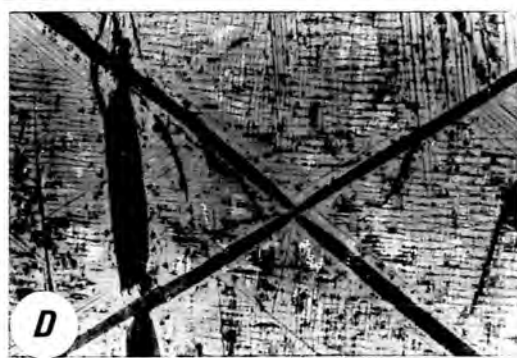
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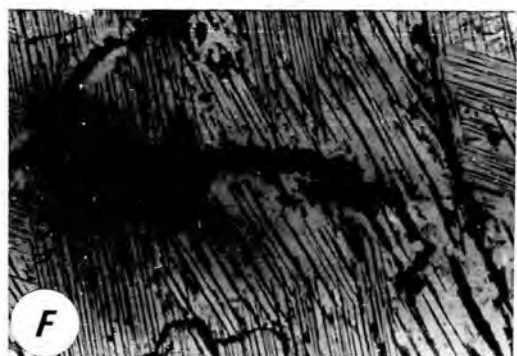
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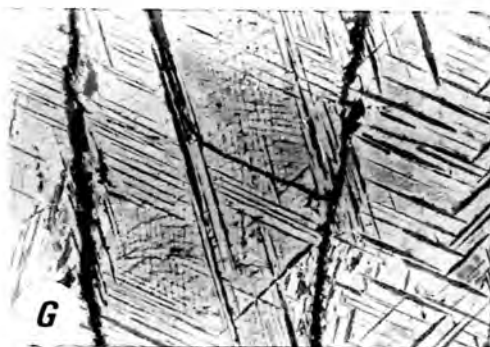
0,015 mm

10.3.2.5. Extremely fine granular ilmenite

A second set of extremely fine-grained, granular ilmenite that is
morphologically similar to the fine granular ilmenite, is also present
in the titaniferous magnetites. These grains are typically less than
3 micrometres across and are generally found as stringers that are aligned
along fractures and other permeable features as illustrated in Plate
14 (G and H). These grains are commonly connected to the ends of the very
fine ilmenite lamellae and are characteristically associated with their
development.

10.3.2.6 Ilmenite derived from ulvospinel

The most abundant and widely developed microstructure in the Kaffirskraal
titaniferous magnetites is the characteristic cloth-like structure formed
by the subsolvus exsolution of ulvospinel. This texture is particularly
coarse and well developed, consisting of a mesh-like network of micrometre
and sub-micrometre sized (originally ulvospinel) lamellae. They are
oriented along the cubic planes of their hosts and break the magnetite
up into a myriad of micrometre-sized cubes as illustrated in Plate 15 (A).
This network is also characteristically developed in the areas between the
larger ilmenite lamellae, but is usually absent from a narrow zone several
micrometres wide immediately adjacent to the lamellae (Plates 14 (B-D), 15
(B-C)).

Exsolved ulvospinel is readily oxidised to ilmenite, but when this occurs
at low temperatures, the orientation of the originally exsolved ulvospinel
is retained by the oxidation product. The weathering of the Kaffirskraal
ores has caused the widespread oxidation of ulvospinel and no unoxidised
ulvospinel was noted, even in the freshest samples. These very fine-
grained microstructures are preserved during oxidation due to the
formation of titaniferous maghemite as an intermediate phase.

The very fine ilmenite lamellae derived from the oxidation of ulvospinel
appears to break down and a coarser, less well-defined texture is
developed in certain areas within the titanomagnetite grains. The
individual lamellae swell and coalsce with neighbouring lamellae to form
larger grains that are in optical continuity as illustrated in Plate 15
(D and E). They form a perforated, sieve-type texture consisting of
abundant rounded inclusions of magnetite and are surrounded by a narrow

PLATE 15

KAFFIRSKRAAL TITANIFEROUS IRON ORES

All photomicrographs taken in incident light using oil immersion objectives.

A. A typical ulvospinel cloth texture developed in titaniferous magnetite. The ulvospinel has been oxidised to ilmenite (dark grey lamellae).

B. Ilmenite lamellae (dark grey) enclosing areas of titaniferous magnetite containing finer ilmenite lamellae and ulvospinel intergrowths.

C. Similar to (B), but showing a well developed ulvospinel cloth texture in the titaniferous magnetite between two large ilmenite lamellae (dark grey).

D. A typical ulvospinel texture showing evidence of coarsening and lamellar breakdown. The ulvospinel has been oxidised to ilmenite (dark grey).

E. Similar to (D), but showing a more advanced degree of modification.

F. Similar to (E), but showing the development of numbers of sieve-like ilmenite grains (dark grey).

G. Transparent spinel lamellae (black) developed parallel to (100) of the titaniferous magnetite host.

H. A partially oxidised titaniferous magnetite grain containing "islands" of unoxidised magnetite (dark grey) surrounded by lighter titaniferous maghemite.

PLATE 15

A

B

0,015mm

C

D

0,015mm

E

F

0,015mm

G

0,015mm

H
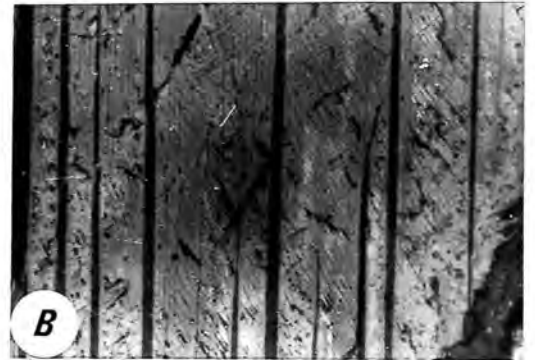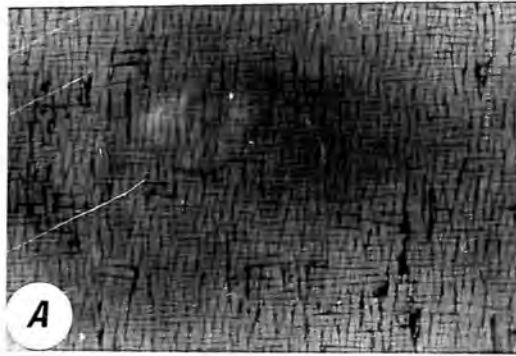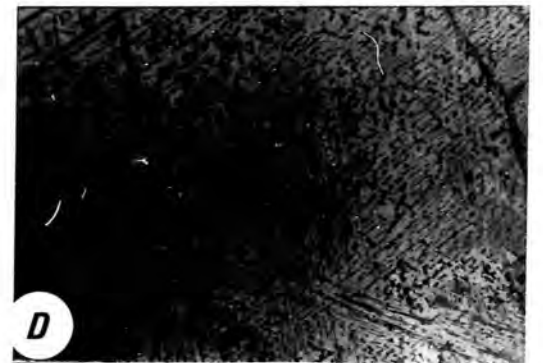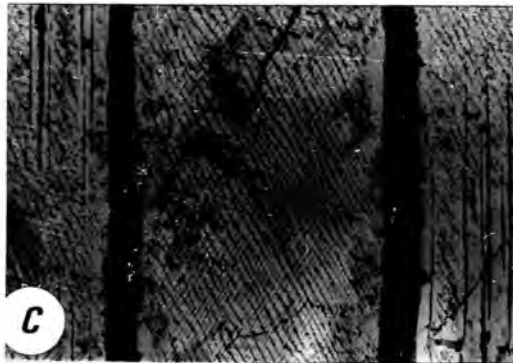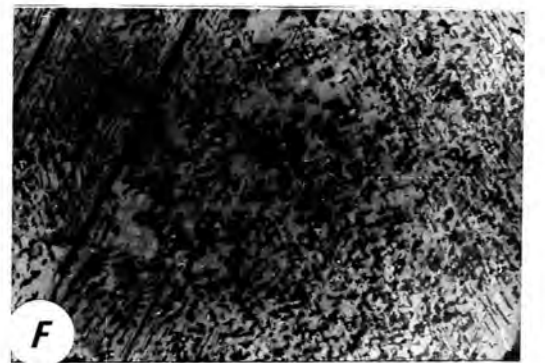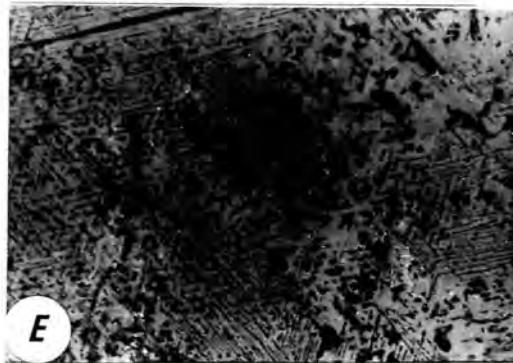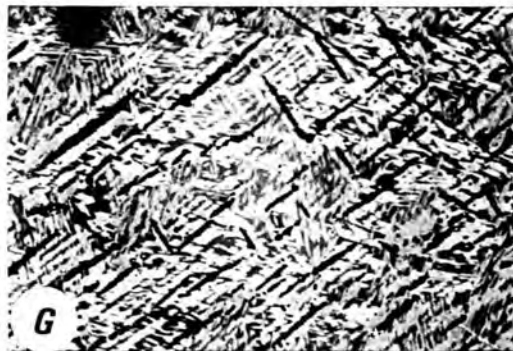
0,1mm

zone of optically homogeneous magnetite in their advanced stage of development as illustrated in Plate 15 (F). These areas merge imperceptibly into areas of normal ulvospinel-type lamellar development, and are commonly developed near grain boundaries.

10.3.2.7 Small skeletal and poikilitic ilmenite grains

This class of ilmenite exhibits a wide range in grain size that varies from less than 10 micrometres up to 0,1mm. The larger grains typically exhibit subhedral outlines and contain abundant poikilitically enclosed grains of rounded, optically homogeneous, magnetite as illustrated in Plate 13 (C). The smaller grains are more skeletal in form and are intergrown with optically homogeneous magnetite as illustrated in Plate 13 (D and E). In part, the morphologies of the smaller grains are crystallographically controlled by the orientation of the octahedral planes of their magnetite hosts.

These types of ilmenite are characteristically located adjacent to, or are enclosed by a zone of optically homogeneous magnetite within a titaniferous magnetite grain, or are present in the narrow transgressive magnetite veinlets. It is conceivable that the small poikilitic ilmenite grains may have developed from the breakdown of very fine ilmenite lamellae described in section 10.3.2.6, but no grains illustrating intermediate stages in this process were noted in the samples examined.

10.3.2.8 Relative proportions of coarse-and fine-grained ilmenite in the Kaffirskraal ores

The relative proportions of coarse-grained granular, fine-grained granular, and lamellar ilmenite present in the Kaffirskraal ores are variable and were determined by point counting. The other fine-grained phases were too small for accurate determination and were included under titaniferous magnetite. The results obtained are presented in Table 13 and illustrate the variations in the relative abundance of these minor phases.

TABLE 13

Relative amounts of ilmenite in the Kaffirskraal ores

Sample No.	HB 6	HB 9	HB 11	HB 12	HB 15
Coarse granular ilmenite	3,2	2,0	4,5	5,5	5,8
Fine granular- and lamellar ilmenite	4,7	4,3	1,0	2,2	2,8
Titaniferous magnetite	92,1	93,7	94,5	92,3	91,4
TOTAL :	100,0	100,0	100,0	100,0	100,0

The coarse granular ilmenite content varies between 2 and 6 per cent while
the amounts of fine granular and lamellar ilmenite are also variable.
The low value (1,0 per cent) reported for HB 11 is due to the virtual
absence of large ilmenite lamellae from this sample.

10.3.3 Transparent spinel

Small amounts of a transparent, aluminium-rich spinel, probably pleonaste,
are present in a number of forms as exsolution bodies in the titaniferous
magnetite. This spinel is a very minor constituent of the ore and shows
a variable distribution, being more abundant in certain samples than in
others.

The pleonaste is commonly present as small rounded, to sub-rounded grains
that vary between 2 and 5 micrometres in diameter. They are localised
along the interfaces between the larger ilmenite lamellae and their
titaniferous magnetite hosts. These grains are occasionally present as
inclusions within the ilmenite lamellae, but are restricted to a relatively
narrow area close to the outer margins of the ilmenite grains.

The bulk of the pleonaste is present as tiny, elongated micrometre-to
sub-micrometre-sized laths that are oriented parallel to the cube faces
of the titaniferous magnetite in a mesh-like array (Plates 14 (C) and 15
(C). Those lamellae are ubiquitously developed and are intermediate in
size between that of the very fine ilmenite lamellae and the ulvospinel
textures. They are more rarely slightly coarser and sometimes have the
appearance of elongated chains of octahedra. These features are

preserved when martitization takes place via the intermediate formation of maghemite.

10.3.4 Weathering of the Kaffirskraal ores

The Kaffirskraal ores are extensively oxidised and hydrated due to surface weathering processes. The ore is fractured and traversed by goethite veinlets that often display delicate botryoidal and concretionary features, while the exposed surfaces have a shiny black coating of goethite. The titaniferous magnetite shows alteration to titaniferous maghemite, martite and ultimately goethite as described in section 10.3.2.1.

The fine-grained ilmenite intergrowths also show evidence of oxidation and decompose to yield poorly-crystalline TiO_2 compounds. The alteration of the ilmenite also commences along grain boundaries and fractures and moves inwards until the grains are completely altered. The spinel and silicates decompose to various clay minerals and are removed during the weathering process.

10.4 Chemical Analyses of the Kaffirskraal Titaniferous Iron Ores

The chemical analyses of five typical Kaffirskraal ores are presented in Table 14 together with analyses from the literature. The low SiO_2 values reported for the samples reflect the small amount of silicate impurities present. The TiO_2 contents are slightly lower than usual for ores of this type, but are nevertheless within the compositional range of titanomagnetites from basic rocks. As indicated in Table 13, only a small portion of this TiO_2 is present as discrete ilmenite grains, the remainder being present as very fine-grained ilmenite intergrowths. The results are not expressed graphically since the exact stratigraphic positions of the analysed samples are not accurately known.

The ores exhibit moderate Al_2O_3 contents of between 1,9 and 3,1 per cent that can be accounted for by the small amounts of exsolved aluminous spinel present in the titaniferous magnetite. The very high Fe_2O_3 values reflect the highly oxidised nature of the ores due to surface weathering processes. Calculations show that there is insufficient FeO to account for all the ilmenite present in the most highly oxidised samples, (HB 9 and HB 11). This indicates that extensive oxidation of Fe^{2+} to Fe^{3+}

TABLE 14

ANALYSES OF KAFFIRSKRAAL TITANIFEROUS IRON ORES

	HB 6	HB 9	HB 11	HB 12	HB 15	J.N.	230	231	M23
SiO_2	2,19	1,04	1,70	1,33	0,65	1,00	N.R	N.R	0,34
TiO_2	12,61	13,28	12,43	13,55	13,04	14,50	12,88	14,76	15,18
Al_2O_3	2,72	1,89	3,14	2,05	2,29	1,33	3,70	3,08	3,55
Cr_2O_3	<0,05	<0,05	<0,05	<0,05	<0,05	–	N.R.	N.R.	0,08
Fe_2O_3	62,61	69,50	70,83	66,53	50,49	67,87	70,12	50,17	39,11
FeO	16,49	10,83	9,28	13,74	29,29	10,06	5,85	26,23	39,15
MnO	0,32	0,21	0,27	0,12	0,36	0,38	0,16	0,64	0,27
MgO	2,88	2,58	2,07	1,42	3,06	2,54	0,82	2,72	1,31
V_2O_5	0,72	0,80	0,90	0,87	0,78	1,48	N.R.	N.R.	0,70
TOTAL :	100,54	100,13	100,62	99,61	99,96	99,16	93,53	97,60	99,69
TOTAL Fe :	56,61	57,03	56,75	57,21	58,08	55,29	53,59	55,48	57,78

J.N. Analysis of Kaffirskraal ore (Nel and Jansen, 1957).

230,231 Analyses of Kaffirskraal ore (Frick, 1975).

M23 Analysis of titaniferous magnetite from seam 11 Bushveld Complex (Molyneux, 1970a, 1972).

N.R. Not reported.

must have occurred in the ilmenites and confirms their altered nature.

The V_2O_5 values range from 0,90 to 0,72 per cent and may reflect a slight decrease in V_2O_5 content upwards in the seam. These values are considerably lower than the 1,48 per cent reported by Nel and Jansen (1957) and Frick (1975) does not report analyses for this element. The reason for this discrepancy is not known, but internal checks carried out during the analyses indicate both an accuracy and a reproducibility of $\pm$ 5 per cent for the given value of V_2O_5.

The MgO values vary between 1,4 and 3,1 per cent and do not appear to be related to the SiO_2 content of the ores. MnO contents are generally low, but also show considerable variation from 0,12 to 0,36 per cent in the new analyses.

10.5 Analyses of Co-existing Ilmenites from the Kaffirskraal Complex

Electron microprobe analyses of co-existing coarse-grained ilmenites from the Kaffirskraal ores are presented in Table 15 together with two analyses of ilmenite from the associated magnetite-clinopyroxenite reported by Frick (1975). Analyses were also made of the fine granular ilmenite and these are presented in Table 16 together with 4 analyses of the smaller poikilitic ilmenite grains.

The ilmenites co-existing with the titaniferous magnetite ores are characterised by high MgO contents that range from 6,2 to 9,3 per cent. These values are among the highest yet recorded for igneous ilmenites from non-kimberlitic sources. The samples were re-analysed together with additional co-existing ilmenites from the ores and consistently high values were obtained. As a further check on the analyses, several previously analysed, low-MgO ilmenites were re-analysed together with a batch of Kaffirskraal ilmenites using various standards and the expected values were obtained, indicating that these high values do not represent an analytical error. Analyses of large ilmenite lamellae in the Kaffirskraal titaniferous magnetites also show characteristically high MgO values.

The analyses of ilmenite from the associated magnetite-clinopyroxenite also show high MgO values (Frick, 1975), but are nevertheless much lower than those reported for the ilmenites from the titaniferous magnetite

TABLE 15

KAFFIRSKRAAL COMPLEX : MICROPROBE ANALYSES OF COARSE GRAINED ILMENITES

Oxide	HB 6	HB 9	HB 11	HB 12	HB 15	HB 5	HB 7	HB 8	HB 13	227	221	K 23
TiO_2	53,13	53,55	54,53	52,29	52,05	53,33	52,23	52,76	52,97	48,19	48,72	52,1
FeO	33,32	33,09	33,27	33,77	34,83	30,64	34,72	34,03	35,13	39,40	42,26	40,1
MgO	7,75	8,12	8,49	7,07	6,22	9,30	6,52	7,13	6,64	1,60	2,47	4,2
MnO	0,62	0,64	0,52	0,59	0,95	0,66	0,65	0,59	0,65	1,09	0,78	N.R.
$*Fe_2O_3$	4,79	5,91	3,67	6,07	6,78	5,91	6,23	5,19	3,99	10,70	6,79	3,5
Al_2O_3	0,12	0,12	0,12	0,13	0,13	0,12	0,12	0,12	0,13	N.R.	N.R.	0,5
Cr_2O_3	0,17	0,17	0,17	0,17	0,17	0,18	0,18	0,23	0,17	N.R.	N.R.	N.R.
TOTAL :	99,90	101,60	100,77	100,09	101,13	100,14	100,65	100,05	99,68	100,98	101,02	100,4

NUMBER OF IONS ON THE BASIS OF 6 OXYGENS

Al^{3+}	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006
Cr^{3+}	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006
Fe^{3+}	0,172	0,208	0,130	0,218	0,242	0,208	0,224	0,190	0,144
Ti^{4+}	1,908	1,890	1,929	1,885	1,873	1,890	1,882	1,899	1,922
Fe^{2+}	1,331	1,298	1,310	1,355	1,393	1,210	1,390	1,364	1,418
Mg	0,551	0,567	0,597	0,504	0,443	0,655	0,466	0,509	0,478
Mn	0,026	0,025	0,022	0,026	0,037	0,025	0,026	0,026	0,026
TOTAL :	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000

NORMATIVE COMPOSITION (MOLE PER CENT)

$FeTiO_3$	66,57	64,88	65,49	67,72	69,64	60,43	69,50	68,20	70,87
$MgTiO_3$	27,55	28,35	29,84	25,22	22,16	32,77	23,31	25,47	23,91
$MnTiO_3$	1,29	1,27	1,13	1,30	1,87	1,28	1,29	1,29	1,30
R_2O_3	4,59	5,50	3,54	5,76	6,33	5,52	5,90	5,04	3,92
TOTAL :	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

* Fe_2O_3 calculated assuming ilmenite stoichiometry.

N.R. not reported.

221 and 227 averages of analyses of two ilmenites from the Kaffirskraal magnetite-clinopyroxenite (Frick, 1975).

K23 analysis of ilmenite from Lease 11, Bushveld Complex (Molyneux, 1970a, 1972).

Note : MgO values have been checked by repeated analyses using a variety of standards.

TABLE 16

KAFFIRSKRAAL COMPLEX : MICROPROBE ANALYSES OF FINE GRANULAR-AND POIKILITIC-ILMENITE GRAINS IN TITANIFEROUS MAGNETITE

Oxide	FINE GRANULAR ILMENITES									SMALL POIKILITIC ILMENITES			
	HB 6	HB 9	HB 11	HB 12	HB 15	HB 5	HB 7	HB 8	HB 13	HB 6	HB 9	HB 13	HB 15
TiO_2	55,23	55,10	54,86	55,29	54,41	54,08	54,55	54,33	51,11	54,97	55,54	54,57	51,32
FeO	33,27	30,81	31,91	34,45	36,80	34,21	34,72	33,62	35,05	32,31	33,99	35,16	36,77
MgO	8,76	10,06	9,49	8,08	6,15	7,70	7,41	8,11	5,55	9,20	8,38	7,35	4,53
MnO	0,80	0,79	0,66	0,90	1,15	0,79	0,89	0,76	1,02	0,70	1,05	0,86	1,28
∗Fe_2O_3	2,31	3,75	2,56	1,36	0,80	3,51	2,71	2,40	6,54	3,27	1,28	0,80	5,51
Al_2O_3	0,11	0,12	0,11	0,12	0,13	0,12	0,12	0,12	0,14	0,12	0,12	0,12	0,13
Cr_2O_3	0,16	0,18	0,17	0,17	0,18	0,19	0,17	0,24	0,18	0,17	0,17	0,16	0,18
TOTAL :	100,64	100,81	99,76	100,37	99,62	100,60	100,57	99,58	99,59	100,74	100,53	99,02	99,72

NUMBER OF IONS ON THE BASIS OF 6 OXYGENS

Al^{3+}	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006
Cr^{3+}	0,006	0,006	0,006	0,006	0,012	0,006	0,006	0,011	0,006	0,006	0,006	0,006	0,006
Fe^{3+}	0,084	0,128	0,090	0,050	0,030	0,124	0,096	0,087	0,240	0,118	0,044	0,028	0,206
Ti^{4+}	1,952	1,930	1,949	1,969	1,976	1,932	1,946	1,948	1,874	1,935	1,972	1,980	1,891
Fe^{2+}	1,308	1,200	1,256	1,363	1,486	1,359	1,383	1,340	1,429	1,266	1,339	1,418	1,508
Mg	0,613	0,700	0,667	0,569	0,444	0,542	0,526	0,576	0,404	0,641	0,590	0,528	0,330
Mn	0,031	0,030	0,026	0,037	0,046	0,031	0,037	0,032	0,041	0,028	0,043	0,034	0,053
TOTAL :	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000

NORMATIVE COMPOSITION (MOLE PER CENT)

$FeTiO_3$	65,40	60,00	62,84	68,14	74,41	67,90	69,14	67,05	71,45	63,29	66,95	70,87	75,41
$MgTiO_3$	30,65	34,97	33,33	28,45	22,24	27,10	26,29	28,80	20,20	32,07	29,50	26,38	16,49
$MnTiO_3$	1,55	1,54	1,28	1,85	2,33	1,57	1,86	1,58	2,05	1,41	2,13	1,74	2,65
Fe_2O_3	3,40	3,49	2,55	1,56	1,02	3,43	2,71	2,57	6,30	3,23	1,42	1,01	5,45
TOTAL :	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

∗ Fe_2O_3 calculated assuming ilmenite stoichiometry.

Note : Mg values have been checked by repeated analyses using a variety of standards.

seam. The MgO values for the ilmenites are higher than those of their
corresponding bulk ore analyses which indicates a preferrential
partitioning of MgO into the rhombohedral phase during crystallisation.

Recalculation of the analyses assuming stoichiometry indicates the
presence of minor amounts of excess FeO that has been recalculated to
Fe_2O_3 and probably represents hematite in solid solution with the ilmenite.

The MnO values display a slight variation, but cluster around a value of
approximately 0,6 per cent in the new analyses. This value is also
higher than that displayed by their corresponding ore analyses and
indicates that the MnO is also preferentially accomodated in the
rhombohedral phase during crystallisation.

The analyses of the coarse grained ilmenite, fine granular ilmenite
and small poikilitic ilmenite grains from the same ore specimens show a
marked, but constant variation in their MnO and MgO contents. The MnO
values increase progressively from the coarse grained ilmenites through
the fine granular types to the small poikilitic grains. This reflects
the progressive incorporation of this oxide into rhombohedral phase with
falling temperature (decreasing grain size of the two intergrown phases).

The MgO values are more variable. The lowest values are generally
present in the coarse grained ilmenites while the highest values are
found in the fine granular ilmenites. One of the MgO values of the
fine poikilitic ilmenite grains are lower than those in their corresponding
coarse grained ilmenites (HB 15) while three are higher (HB 6, 9 and 13).
These features also reflect the partitioning of MgO into the rhombohedral
phases during different stages of crystallisation.

10.6 Beneficiation

The Kaffirskraal ores generally contain only minor silicate impurities and
require no beneficiation in this respect. The TiO_2 contents of the ores
are too low for the production of high-titania products while the new V_2O_5
analyses also indicate that they cannot be regarded as potential vanadium
ores.

The coarse grained ilmenite present in the samples can be concentrated by
crushing to less than 200 mesh followed by electromagnetic separation.

This ilmenite is commonly present in amounts less than 6 per cent and locally in amounts as low as 2 per cent so that this procedure would not be economically feasible. The small amount of beneficiation that would result from the separation of this 2-6 per cent ilmenite would not bring about any marked improvement in the V_2O_5 content of the magnetic fraction.

The remainder of the TiO_2 reflected in the analyses is present as various fine-grained ilmenite microintergrowths that cannot be liberated by mechanical means.

10.7 Discussion

The titaniferous iron ores of the Kaffirskraal Complex can be compared both chemically and texturally with the ores of the Middle Group of seams of the Bushveld Complex, although they contain slightly less TiO_2. They typically show the development of very fine-grained ulvospinel-type microstructures that are indicative of slow subsolvus cooling under conditions of low oxygen fugacity. The ores, although polygonalized, do not show evidence of having been metamorphosed. The sparsely distributed coarse grained ilmenites might represent a co-precipitated phase, but their mineralogical relationships suggest that they might have formed as high-temperature exsolution products. They are generally elongated along the interfaces between the titaniferous magnetite grains and typically exhibit irregular outlines, suggesting an exsolution origin.

The amount of coarse-grained ilmenite does not appear to have any relationship to the overall TiO_2 content of the ore in which it is present. There is approximately one per cent difference between the highest and lowest TiO_2 values reported in this study while the amount of coarse-grained ilmenite varies between approximately 2 and 6 per cent (equivalent to approximately 1-3 per cent TiO_2). In addition, sample HB 9 contains the lowest amount of granular ilmenite, but exhibits one of the highest total TiO_2 contents.

The magnetite lamellae present in these ilmenites are problematical since the experimental evidence discussed in Part 1 indicates that magnetite is only sparingly soluble in ilmenite, even at elevated temperatures. This magnetite could conceivably represent a true exsolution product since it is only present in minor amounts or else

it might represent reduced, previously exsolved hematite. The reduction of hematite to magnetite takes place under higher oxygen fugacities than that required for ulvospinel stability (Buddington and Lindsley, 1964). The presence of abundant exsolved ulvospinel in a sample would therefore imply that the oxygen fugacities during this period of cooling were low enough to cause the reduction of any exsolving hematite.

Experimental studies by Lindsley and Lindh (1974) indicate that unmixing of an ilmenite-hematite solid solution commences at temperatures below 800°C. For samples containing only limited hematite this unmixing would commence at much lower temperatures. Precise data on the magnetite-ulvospinel solvus are not available, but the experimental data of Vincent et al. (1957) indicate that unmixing commences at temperatures below 600°C. The exsolution of hematite from ilmenite could thus conceivably take place contemporaneously with the exsolution of ulvospinel from titaniferous magnetite.

The lower oxygen fugacities implied by the presence of ulvospinel would thus result in the contemporaneous reduction of exsolving hematite which would then form the typical oriented magnetite lamellae. It is also possible that an essentially stable ilmenite-hematite solid solution containing less than 6 per cent Fe_2O_3 could be reduced in the solid state under suitably low oxygen fugacities. This process might also take place at temperatures high enough to allow exsolution of the insoluble magnetite formed in this manner.

The fine granular ilmenites are interpreted as having formed by external granule oxidation/exsolution. These grains are commonly connected to ilmenite lamellae that are related to the same stage of microstructural development. The rows and stringers of ilmenite grains that are present locally along slightly curved paths within the titaniferous magnetites are also normally associated with fine ilmenite lamellae. These stringers may reflect the presence of more permeable zones within the titaniferous magnetite, possibly related to the presence of cooling cracks. Their mode of origin is interpreted as being essentially the same as that of the smaller, externally exsolved grains and they are developed during the same stage in the cooling history.

The development of a well defined, cloth-like texture of very fine Fe-Ti

oxide lamellae oriented along the cube directions of the titaniferous magnetite indicates that extensive ulvospinel exsolution occurred under conditions of low oxygen fugacity during cooling at temperatures below 600°C. This exsolved ulvospinel subsequently underwent relatively low-temperature oxidation to produce ilmenite that has generally preserved the original shape and orientation of the ulvospinel lamellae. This oxidation may have taken place during a late-stage magmatic event (deuteric oxidation) at low temperatures, but it is also likely to have resulted from the widespread oxidation caused by weathering under near-surface conditions.

Oxygen fugacities were not uniformly low throughout the ore during the period of ulvospinel exsolution and small amounts of extremely fine-grained lamellar ilmenite were also produced. This lamellar ilmenite is typically present in a narrow rim, generally less that 20 micrometres wide, that surrounds the titaniferous magnetite grains and is present along either side of minute cracks that traverse the magnetite. This ilmenite is developed on the same scale as the ulvospinel and although it is developed along the (111) planes, it merges with the (100) oriented ulvospinel lamellae a slight distance away from the grain margins or fractures. This suggests that the ilmenite was formed by an oxidation/exsolution mechanism at the same time as the ulvospinel was exsolving and indicates that differences in oxygen fugacities existed over very short distances.

Slightly higher oxygen fugacities apparently existed in the late-stage residual fluids that were present around the magnetite grains during the final stages of cooling and which could also permeate the grains along cooling fractures and cracks. These fluids would cause oxidation of any exsolving ulvospinel in their immediate vicinity resulting in the formation of ilmenite that would exsolve on (111). The degree to which this oxidation would affect the microstructures of the grain concerned would depend on the initial oxygen fugacity of the fluid and the temperature. These factors would in turn control the rate of oxygen diffusion through the crystal and would determine the distance over which oxidation would occur.

The oxidised rims round the Kaffirskraal titaniferous magnetites are relatively narrow and this suggests that the late-stage fluids were only mildly oxidising with respect to ulvospinel. The presence of minute

"externally exsolved" ilmenite granules along these oxidised fractures suggests that the oxidation process took place at temperatures that were high enough, not only to allow for the development of very fine ilmenite trellis lamellae, but also to allow the migration of some of this material into the fractures and grain boundary regions.

A slight coarsening of the ulvospinel lamellae which eventually leads to their breakdown into more sieve-like texture containing abundant tiny rounded inclusions of magnetite is developed locally at places within certain of the titaniferous magnetites. This texture is developed towards grain boundaries and consists of ilmenite. This ilmenite may originally have been ulvospinel and it merges into surrounding areas showing normal ulvospinel textural development.

It is possible that while normal ulvospinel exsolution was taking place, small areas of higher oxygen fugacity resulted in the oxidation of part of this ulvospinel to ilmenite. Provided that temperatures were low enough at this stage, ilmenite lamellae would not develop, but small granules of ilmenite would be formed instead. The oxidised ulvospinel lamellae would provide suitable nucleation and growth sites for this material which would simply add-on causing the change in morphology. The reasons for differences in oxygen fugacity within a single sample are uncertain, but Bowles (1976) reported variable oxygen fugacities over short distances in the Freetown Complex titaniferous magnetites. The location of these textures near grain boundaries might reflect mild late-stage oxidising conditions in the residual fluids at temperatures below that at which the very fine ilmenite lamellae developed. This would account for the relatively narrow distance over which the texture is developed.

The larger poikilitic and skeletal ilmenite grains are problematical. They are characteristically surrounded by areas of optically homogeneous magnetite and at places are present in late-stage transgressive magnetite veinlets. The surrounding optically homogeneous magnetite together with the complicated morphologies of the grains suggest that they have formed by the diffusion of Ti-ions from the surrounding areas, but the conditions under which this could have occurred are uncertain. It would have been expected that the more typical ilmenite lamellae would have been developed had temperatures been high enough to allow for the required degree of

diffusion to take place.

Small amounts of water or other fluid phases might become locally trapped in the late-stage intercumulus liquid in certain areas within the ores. Loss of hydrogen from this entrapped water would increase the oxygen fugacities and cause oxidation in the marginal areas of surrounding titaniferous magnetite grains. The resulting increased oxygen fugacities might have been high enough locally to cause internal granule oxidation/exsolution of ilmenite in these areas. These conditions of higher fluid pressure would exist only locally within the ores and might approximate the hydrothermal conditions underwhich ionic mobilities are increased at lower temperatures. Lindsley (1962) discussed the experimental investigation of the iron-titanium oxides under hydrothermal conditions in order to speed up sluggish reaction rates at low temperatures.

The increased low-temperature ionic diffusion would result in the continued growth, coalescence and partial spheroidization of these internal grains giving rise to the poikilitic ilmenite grains. The breakdown and coarsening of the oxidised ulvospinel networks might also have originated in this manner, but under milder oxidizing conditions, or perhaps under conditions of lower ionic mobility. The homogeneous magnetite associated with these grains commonly shows varying degrees of martitization, even when the enclosing titaniferous magnetite is unoxidised. This martitization might, in part, be due to local oxidation associated with the formation of the poikilitic ilmenite grains. These textures are not commonly encountered in the ores examined during this study which suggests that relatively unusual conditions are necessary for their development.

Late-stage, optically homogeneous, transgressive magnetite veinlets have been noted in all the ores examined and are particularly well developed in certain samples from the Trompsburg Complex (this report). They might represent a lower temperature magnetite that crystallised from residual, iron-rich late stage fluids. Should this be the case, then it is possible that the skeletal- and poikilitic- ilmenite grains in these veinlets may have crystallised together with the magnetite from residual Ti-ions present in the postulated late-stage fluids. This mechanism would account for the morphological differences between these

ilmenites and those produced by oxidation/exsolution, but its feasibility is by no means certain and would require further investigation. This mechanism would not account for these grains developed within the titaniferous magnetites.

Frick (1975) reported that the Kaffirskraal titaniferous magnetites are highly aluminous, but when the range of values obtained during this study (including Frick's analyses) are compared with the values obtained for samples from other basic complexes they can be regarded as being only moderately aluminous. e.g. Kaffirskraal (1,33-3,70 per cent), Bushve 1 (2,15-5,52 per cent) ; Rooiwater (1,23-6,3 per cent); Mambula (5,63-8,39 per cent) ; and Trompsburg (3,41-5,90 per cent). The titaniferous magnetites from the associated magnetite - clinopyroxenite, are however, more aluminous (Frick, 1975).

The high MgO values reported for the co-existing ilmenites are unusual and are amongst the highest yet recorded from non-kimberlite sources. Ilmenites from basaltic igneous rocks generally contain less than 4 per cent MgO (Thompson, 1976), although higher values of up to 10 per cent have been reported in ferrian ilmenites intergrown with titaniferous magnetites in trachybasalts (Anderson, 1968a). Kimberlitic ilmenites are characteristically MgO-rich (up to 19 per cent) (Mitchell, 1973), but it is generally agreed that they have formed at great depths, possibly within the mantle (Thompson, 1976), and are consequently different from those in basaltic intrusions. Limited information is available on the factors controlling Mg-distribution in terrestrial basaltic ilmenites, but studies on lunar and kimberlitic materials may have some bearing on this matter.

A compilation of data from a variety of rock types by Lovering and Widdowson (1968) suggested that the MgO contents of ilmenite are controlled largely by the MgO/FeO ratios of their host rocks and that they are not influenced to any extent by the temperature and pressure conditions. Mitchell (1973) noted a range of 6 to 19 per cent MgO in kimberlite ilmenites and suggested that it resulted from a variation in MgO/FeO ratios in the kimberlitic magma during crystallisation. Studies of lunar ilmenites by Steele (1974) and Nehru et al. (1974) showed a systematic relationship between MgO/FeO ratios in the ilmenites and co-existing minerals as well as their host tocks. In a review of lunar

mineralogy, Smith and Steele (1976) concluded that the Mg/Fe ratios of the ilmenite increase with an increase in the bulk Mg/Fe ratio of the host rock and that Mg is transferred from the co-existing silicates to the ilmenite with increasing temperature.

In contrast to these geochemical controls, Haggerty (1973a) suggested that the high MgO contents of certain lunar ilmenites are due to crystallisation from an ultrabasic liquid under high pressures. Similarly, Haggerty (1975) suggested that the high MgO content of kimberlitic ilmenites is also controlled by pressure, rather than temperature or oxygen fugacity. Mitchell (1977) investigated the geochemistry of kimberlitic ilmenites in more detail and concluded that their Mg/Fe ratios do not reflect large Mg/Fe variations in the magma, but are due to the variation of some parameter such as temperature, oxygen fugacity or silica activity.

Thompson (1976) investigated the chemistry of ilmenites crystallised within the anhydrous melting range of a tholeiitic andesite at pressures between 5 and 26 kb. and noted variations in minor element (Mg,Mn,Al) contents. These experiments showed that the MgO contents of the crystallised ilmenites are not related to either their temperature or pressure of formation. Instead, they appear to be controlled by the Mg/Fe distribution between the solid and liquid phases at various stages of crystallisation.

The geological relationships exhibited by the Kaffirskraal Complex appear to rule out the effects of high pressure crystallisation in controlling the formation of Mg-rich ilmenite. The well defined chill zone and contact aureole of the Complex (Frick, 1975) suggests that it was emplaced into the Ventersdorp lavas in a relatively cool geological environment such as exists at a relatively high level in the crust. Subsequent crystallisation would thus take place under relatively low pressures, possibly similar to those under which various other basic intrusions containing low-MgO ilmenites solidified. Further evidence for the low pressure crystallisation of the Kaffirskraal Complex is afforded by presence in the fine-grained marginal noritic zone of phenocrystic orthopyroxene that shows signs of resorption. Frick (1975) suggested that this mineral may have crystallised at pressures above 5 kb, but on intrusion into areas of lower pressure it would become unstable and would thus have been reabsorbed.

The coarse grained Mg-rich ilmenites in the Kaffirskraal ores are thought to have formed largely by exsolution from an original high-temperature iron-rich spinellid phase so that their compositions must be related to that of the titaniferous magnetite. This is supported by the presence of Mg-rich ilmenites as internal granules within the titaniferous magnetite and which were formed as oxidation/exsolution products. The compositions of these smaller intergrown phases must also reflect aspects of the original compositions of their hosts.

The geochemical and mineralogical environment of the Kaffirskraal titaniferous magnetite is also notably different from that in other layered intrusions. The Kaffirskraal ores are associated essentially with clinopyroxene while the ores from other Comples are interlayered with plagioclase-rich rocks such as gabbro, anorthosite or troctolite e.g. Skaergard (gabbro), Rooiwater (metagabbro), Usushwana (gabbro), Mambula (gabbro), Trompsburg (troctolite) and Bushveld (troctolite, gabbro, anorthosite).

Frick (1975) has suggested that the lack of plagioclase in the magnetite-clinopyroxenite might be due to the effects of high water pressure during crystallisation that would depress the anorthite field in the diopside-anorthite system. These high water pressures would also imply high oxygen fugacities due to loss of hydrogen during crystallisation and would account for the abundant development of titaniferous magnetite. The abundant ulvospinel development and paucity of lamellar ilmenite, however, indicate that the post-crystallisation cooling occurred under conditions of low oxygen fugacity.

Frick (1975) discussed the mafic nature of the Kaffirskraal parental magma and drew attention to certain geochemical and petrological similarities between the Kaffirskraal Complex and zoned ultramafic complexes described by Taylor and Noble (1969) that commonly show the development of magnetite-clinopyroxenite. The analyses of both the marginal norite and associated magnetite-clinopyroxenite rocks of the Kaffirskraal Complex (Frick, 1975) show high MgO/FeO ratios. This suggests that the Mg contents of the titaniferous magnetite would have been controlled by the Mg/Fe^{2+} distribution between the solid and liquid phases during the crystallisation of the Kaffirskraal magma according to the data of Thompson (1976). Other factors such as

oxygen fugacity and silica activity may also have controlled the MgO contents of the opaque oxides.

The precipitation of the copious quantites of titaniferous magnetite necessary to form the 8m thick ore seam must have been preceded by extensive iron-enrichment of the residual magma before crystallisation of the magnetite-clinopyroxenite and other iron-rich differentiates. Precipitation must have been initiated by some oxidation process as discussed in section 3 leading to the formation of a high-temperature, iron-rich spinel containing minor amounts of Mg, Al, V and Mn that were also present in the residual magma. On cooling, the exsolution of ilmenite commenced with the Mg preferentially migrating out of the spinel structure into the rhombohdral phase. Similarly, exsolution of an aluminous spinel containing some Mg (pleonaste) was also initiated and continued down to low temperatures.

Large ilmenite grains in basic igneous rocks characteristically contain more MgO than their co-existing titanigerous magnetites (Vincent and Phillips, 1954,; Bowles, 1977). The co-existing mafic silicates, (olivine and/or either ortho-or clinopyroxene, or both) also contain variable, but generally much larger amounts of MgO. This suggests that the partitioning of MgO between the various co-existing mafic and oxide phases during the crystallisation of the magma is controlled by some factor other than the initial MgO/FeO ratio of the liquid. On the basis of experimental studies in the system $MgO-FeO-Fe_2O_3-SiO_2$ Speidel and Osborn (1967) noted that the composition of olivine, pyroxene and magnesioferrite (spinel) in equilibrium with vapour at sub-solidus temperatures changes as a function of temperature and oxygen fugacity. They concluded that the Mg/Fe ratio in olivine, orthopyroxene and magnetite might be significantly different at lower temperatures than at the time of crystallisation. In particular, they noted that the Mg/Fe ratio would increase in olivine and also increase to a lesser extent in orthopyroxene, but would simultaneously decrease in the magnetite.

Speidel (1970) noted in a further series of experiments including TiO_2 that the MgO content was higher in the spinel phase than in the co-existing rhombohedral one at high temperatures and moderately high oxygen fugacities. This relationship was, however, reversed at lower

oxygen fugacities and corresponds to the situation in naturally occurring minerals. The effects of additional minor phases such as Al, V and Mn might also be important in controlling Mg partitioning between co-existing phases.

The occurrence of Mg-rich ilmenite in the Kaffirskraal ores can be interpreted in terms of the experimental results of Speidel and Osborn (1967) and Speidel (1970). A small amount of Mg would have been incorporated into the spinel phase during crystallisation at elevated temperatures. This amount varied between approximately 1,5 and 3 per cent (expressed as MgO, Table 14) and was probably not only controlled by the MgO/FeO ratio of the magma, but also by the temperature and oxygen fugacity.

The MgO content of the spinel phase would then begin to decrease on slow cooling under suitable oxygen fugacities. The Mg would normally be partitioned into any suitable co-existing femic silicate phase such as olivine or pyroxene. These phases are, however, virtually absent in the ore-rich horizons with the result that the Mg would have to be incorporated into one or other of the oxides present. A portion of the Mg would be incorporated into the pleonaste component of the titaniferous magnetite. The amount of pleonaste formed will in turn be determined largely by the quantity of Al_2O_3 present.

Calculation of the normative amounts of pleonaste, $(Mg, Fe) O.Al_2O_3$, or even spinel $(MgO. Al_2O_3)$, in the Kaffirskraal titaniferous iron ores indicates the presence of at least 0,7 to 1,8 per cent excess MgO. A further portion of this excess MgO might be present in the extremely minor, but variable amounts of associated clinopyroxene. Any remaining excess Mg would have incorporated into the titaniferous magnetite during crystallisation. According to the data of Speidel (1970), this Mg would subsequently become incorporated into the rhombohedral phases produced either by exsolution or contemporaneous oxidation/exsolution.

The high Mg contents of these ilmenites is a result of their occurrence in volumetrically small amounts and reflects the strong partitioning of this element into the rhombohedral phase. The presence of high Mg contents in the various smaller-sized intergrown ilmenites also indicates that this process remained operative over a considerable period during cooling.

Variable MgO values have been obtained for the different ilmenites because they do not all represent exactly the same stage of exsolution or oxidation/exsolution. Differences in size and morphology exist between the analysed grains and indicate that they formed under somewhat different conditions, even though they are classified under the same broad categories. The relative amounts of the different morphological ilmenite types varies from sample to sample as reflected in Table 13 while the amounts of Al_2O_3, transparent spinel development and co-existing clinopyroxene are also variable. These features would all influence the MgO partitioning and the reported variations reflect the complex interplay of these processes.

It is interesting to note that the analyses of co-existing coarse-grained ilmenites from various titaniferous iron ores in the Bushveld Igneous Complex also exhibit rather high MgO values. Molyneux (1970a, 1972) reported MgO values ranging between 3,4 and 5,8 per cent for ilmenites from these ores which are also higher than those for ilmenites from basic igneous rocks. The MgO analyses of ilmenites from the Mambula Complex are also high (1,7-6,6 per cent) while those from the Trompsburg Complex (next section) are even higher (4,9-8,7 per cent). These analyses suggest that the Mg contents of the various exsolution product ilmenites in these ores are strongly dependent on the original MgO content of the titaniferous magnetite. It might be noted in this respect that the ilmenites of the Rooiwater and Usushwana Complexes exhibit more "normal" MgO contents and that the overall MgO values of the corresponding ores are also relatively low. (it is assumed that the bulk of the ilmenite in these ores originated by oxidation/exsolution of an original homogeneous spinel phase).

Very much lower MgO values (1,6 and 2,5 per cent) were reported for the co-existing ilmenites in the magnetite-clinopyroxenite of the Kaffirskraal Complex by Frick (1975). This feature might be due to the preferential incorporation of the Mg expelled from the titaniferous magnetite into the co-existing clinopyroxene on cooling rather than into the rhombohedral phase. This behaviour is also in accord with Speidel's (1970) experimental data.

The MnO reported in the titaniferous magnetite ore analyses is also largely

present in the rhombohedral phases (Vincent and Phillips, 1954) ;
Neumann, 1974). The partitioning of MnO between the co-existing cubic
and rhombohedral phases has been studied in detail and the subject has
been recently reviewed by Neumann (1974). Numerous investigators, in
particular Buddington and Lindsley (1964), Anderson (1968b), Czamanske and
Mihalik (1972), Duchesne (1972) and Elsdon (1972) have reported the
enrichment of MnO in ilmenites relative to their co-existing titaniferous
magnetites. They also noted that the amount of MnO in the ilmenite
increases towards the later stages of crystallisation in various
fractionated rock types.

Buddington and Lindsley (1964), Anderson (1968b) and Duchesne (1972)
reported that the MnO content of the ilmenite increased with decreasing
temperature of crystallisation. Neumann (1974) reported that the MnO
contents of ilmenite exsolution lamellae are generally higher than those
in the co-existing separate grains.

The ilmenite grains in the Kaffirskraal ores exhibit a distinct
enrichment in MnO relative to their corresponding bulk ore analyses.
The MnO contents of the ilmenites also increase with a progressive
decrease in their size and suggests that the increase is related to
decreasing temperatures of formation. These features are in accordance
with the commonly observed behaviour of MnO in these minerals. By
analogy , the behaviour of Mn during crystallisation and subsolidus
cooling might be similar to that of Mg and this aspect requires further
experimental investigation.

A portion of the coarse-grained Kaffirskraal ilmenite might conceivably
have been co-precipitated rather than exsolved, in which case, their
high MgO contents can also be interpreted in the light of Speidel's (1970)
experimental results. Speidel (1970) also noted that the amount of
rhombohedral phase dissolved in the spinel phase decreases with an
increase in MgO content and this might account for the extreme paucity
of broad ilmenite lamellae (possibly true exsolution bodies) in the
Kaffirskraal titaniferous magnetites.

10.8 Genesis of the Kaffirskraal Ores

Frick (1975) envisaged the formation of the ore-rich seam as resulting
from the in situ crystallisation - differentiation of a second phase of

intruded magma that gave rise to the magnetite-clinopyroxenite and ore-rich layer. The chemical and textural relationships together with small-scale igneous layering are interpreted as being due to crystal settling processes. Frick (1975) noted that, although the complex is layered, it has certain affinities with zoned ultramafic complexes.

The mineralogical and textural evidence suggests that the genesis and microstructural evolution of the Kaffirskraal ores can be interpreted as follows:-

1. The 8m thick titaniferous magnetite seam was formed as a cumulate rock by normal fractional crystallisation processes from an iron-enriched residual magma as envisaged by Frick (1975). The titaniferous magnetite-rich layer formed during this process by the accumulation of an initially homogeneous spinellid phase containing Fe, Ti, Al, Mg, V and Mn together with possible minor amounts of co-precipitated ilmenite. Factors such as post-cumulus growth, removal of intergranular fluids by filter-pressing and annealing may also have played an important role in the development of this layer. Minor entrapped silicate liquid crystallised as clinopyroxene.

2. At the commencement of cooling, exsolution of a titanium-rich rhombohedral oxide phase was initiated resulting in the formation of several per cent by mass of intergranular ilmenite and possibly some of the larger ilmenite lamellae. At slightly lower temperatures the finer-grained intergranular ilmenites and sparsely distributed ilmenite lamellae were formed. These phases probably represent true exsolved ilmenite and correspond to the external granule exsolution described by Buddington and Lindsley (1964) and their formation is in agreement with the data of Anderson (1968b). This type of exsolution is thought to cease once temperatures drop below about 750°C while any ilmenite present in amounts greater than about 5 per cent by mass must have been formed by a contemporaneous oxidation (Buddington and Lindsley, 1964; Anderson, 1968b). The nature and location of these lamellae and grains suggest that they nucleated at grain boundary imperfections and that the grains grew externally while the lamellae grew into the titaniferous magnetite. Grain boundary adjustment would also have occurred under the annealing

effects of high temperature leading to the formation of polygonal grains having interfacial angles approximating 120°.

3. Once the temperature had dropped to below approximately 900°C, exsolution of the aluminous spinel would have commenced. At the higher temperatures nucleation would have preferentially occurred at grain boundary imperfections along the magnetite boundaries and along the interfaces between ilmenite lamellae and titaniferous magnetite resulting in the formation of small grains. At lower temperatures, lower ionic mobility would result in an increase in supersaturation away from pre-existing spinel granules resulting in the development of fine pleonaste lamellae along (100) of their hosts. The period of spinel exsolution would thus overlap somewhat with the lower temperature portion of stage 2 and would continue down to the temperatures at which exsolution effectively ceases.

4. The relatively minor development of ilmenite lamellae suggests that cooling through the temperature interval of approximately 750 to 600°C took place under conditions of low oxygen fugacity. These conditions favoured the stability of a homogeneous magnetite-ulvospinel solid solution so that virtually no exsolution of titanium-rich phases took place. It is possible that occasional local fluctuations in oxygen fugacity occurred resulting in slightly more oxidising conditions. Minor amounts of lamellar ilmenite would have been produced parallel to (111) of the titaniferous magnetite hosts during this process.

5. With continued slow cooling the magnetite-ulvospinel solvus is intersected at approximately 600°C (Vincent et al., 1957), and exsolution of ulvospinel along (100) of the host commences under conditions of low oxygen fugacity. These conditions prevailed during cooling down to temperatures of several hundred degrees resulting in the development of a well defined, ulvospinel cloth texture.

During cooling through this temperature range, exsolution of any excess hematite from ilmenite would also occur. The oxygen fugacities required for ulvospinel stability are lower than those

required for the reduction of hematite to magnetite so that
magnetite lamellae would be developed in the coarser-grained
ilmenites by a contemporaneous reduction/exsolution process.

Local fluctuations in oxygen fugacity, possibly related to changes
in the interstitial fluids, occurred during this phase of cooling,
so that mildly oxidising conditions existed around grain boundaries
and along fractures. This resulted in the formation of ilmenite
by a contemporaneous oxidation/exsolution process instead of
ulvospinel, in the areas immediately adjacent to the zones of higher
oxygen fugacity. This ilmenite was then exsolved as very fine
lamellae oriented along (111) and occasionally formed small
"external" granules along the fractures. These textured suggest
that nucleation of this ilmenite commenced at dislocations along
the fractures where oxygen fugacities were highest and then grew
inwards along the octrahedral planes for as far as the prevailing
oxygen fugacities and rates of diffusion would allow.

6. Slight oxidation of the ulvospinel network may have occurred locally
at lower temperatures due to increased oxygen fugacities. This
resulted in the conversion of the pre-existing (100) ulvospinel to
ilmenite which represents a crystallographically unstable orientation.
Temperatures may have still been high enough at this stage for
continued oxidation/exsolution of ilmenite to take place which would
be precipitated around the oxidised ulvospinel lamellae to produce
the coarsening effect that is developed locally. Incipient diffusion
of this converted ilmenite to a more stable crystallographic
arrangement may also have contributed to the development of this
texture. The areas of poikilitic ilmenite may have formed locally
under the highest oxygen fugacity conditions.

7. Transgressive veinlets of optically homogeneous magnetite were formed
by precipitation from late-stage residual fluids during the final
stages of crystallisation. The textural evidence also suggests that
the minor amounts of poikilitic and skeletal ilmenite present in the
veinlets may have been precipitated from the same fluids.

8. Oxidation and hydration of the Kaffirskraal ores in the zone of
surface weathering has resulted in their partial martitization,

maghemitization and the development of abundant secondary goethite and hematite. Large scale oxidation of ulvospinel to ilmenite would have taken place during this stage although the possibility of this oxidation having occurred during stage 7 should not be overlooked.

10.9 Conclusions

1. The vanadium-bearing titaniferous iron ores of the Kaffirskraal Complex can be compared chemically and mineralogically with simiar ores from other Igneous Complexes. There are, however, distinct differences in the geological environment of this deposit which suggest that it originated from a slightly different magma-type than that usually responsible for the formation of stratiform basic intrusions.

2. The presence of the Kaffirskraal titaniferous iron ores in a discrete layer towards the upper part of a mafic intrusion is in accord with their development by normal crystallisation-differentiation processes that are operative in Complexes of this nature.

3. The Kaffirskraal ores are characterised by a well-developed ulvospinel cloth texture in the titaniferous magnetite and by a paucity of lamellar or granular ilmenite.

4. The larger-sized ilmenite grains are characterised by relatively high MgO contents that are amongst the highest yet reported in these minerals from non kimberlitic sources. The high MgO contents reflect the composition of original high temperature spinel phase and demonstrate the preferential partitioning of Mg into the rhombohedral phase during cooling.

5. The ores contain only minor quantities of silicate impurities and as much would require no beneficiation. Separation of the very small percentage of coarser-grained ilmenite would have no marked significance.

6. The ores are characterised by moderately low TiO_2 values and contain only between 2 and 6 per cent coarse-grained ilmenite that is recoverable by standard ore dressing procedures. The remainder of

the TiO_2 is present in a variety of extremely fine-grained microintergrowths that cannot be separated by mechanical means.

7. The V_2O_5 analyses reported for these ores are at variance with the published values and suggest that the vanadium content is too low for their consideration as potential ores.

8. The low TiO_2 and V_2O_5 contents of these ores together with their limited ore reserves suggest that they do not represent suitable raw materials for the production of either high-titania or V_2O_5 products. Their close proximity to the Vereeniging-Vanderbijlpark area may, however, increase their economic potential.

9. The Kaffirskraal Complex should provide a suitable suite of samples that can be used to study the partitioning of Mg and Mn between the co-existing phases, both in the ore-rich layer and underlying silicate-rich rocks. Detailed electron microprobe analyses of the various intergrown Ti-rich phases would also provide information on the partitioning of these elements between cubic and rhombohedral phases with decreasing temperature.

11. THE TITANIFEROUS IRON ORES OF THE TROMPSBURG IGNEOUS COMPLEX

11.1 Introduction

A large positive gravity anomaly was discovered near the Orange Free State town of Trompsburg during 1942 and was subsequently investigated in more detail by geophysical techniques. Seven exploratory boreholes were drilled in the area during the period 1946 to 1948 and these revealed the presence of a basic igneous complex at a depth of approximately 1000m beneath a cover of younger Karoo rocks. A detailed amount of the geophysical exploration programme has been given by Buchmann (1960) while the petrography of the complex has been described by Ortlepp (1955, 1959).

The available data suggest that the complex is roughly circular in plan with a diameter of approximately 48 km. It is between 1800 and 3000m thick and is composed of gabbro with locally developed layers of olivine gabbro and anorthosite. The uppermost zone intersected in the bore holes consists largely of 300m of troctolite in which 19 titaniferous magnetite-rich seams ranging from several centimetres up to 4,5m in thickness are developed. Small, local concentrations of titaniferous iron ore associated with gabbro are also present at greater depths.

The complex is intrusive into marble that is correlated with the Malmani dolomite and is overlain unconformably by a sequence of younger Karoo rocks (Ortlepp 1955, 1959). The complex has been dated at $1372^{\pm} 142$ million years by Davies et al. (1970) and thus represents the "youngest" of the complexes investigated.

11.2 Samples Investigated

Mr. R. Fouche of General Mining kindly gave permission for the original Trompsburg borehole core to be used in this study. Samples, in the form of short lengths of split core, were collected from the upper portion of borehole TG 2. Unfortunately, after nearly 30 years, many of the distinguishing marks on the core trays have become illegible, and although the presence of numerous titaniferous magnetite-rich layers was evident, their exact stratigraphic position could not always be determined.

The relative positions of the samples examined are shown in Table 17. The position of several samples is not certain and they are marked with an asterisk. The numbers of the samples refer to specimens that were chemically analysed, but a large number of other specimens were also

microscopically examined.

TABLE 17

THE DISTRIBUTION AND THICKNESS OF TITANIFEROUS MAGNETITE SEAMS IN BOREHOLE TG 2, TROMPSBURG IGNEOUS COMPLEX.

SEAM NUMBER (ARBITARY)	THICKNESS OF SEAMS (M)	DEPTH OF SEAMS BELOW SURFACE (M)	SAMPLE NUMBERS (this report)
19	2,5	1247,5	8/1 - 8/5
18	4,6	1259,8	8/6-8/16
17	2,4	1265,5	24/2-24/6
*16	0,4	1381,9	17/2-17/5
15	1,8	1388,6	7/1- 7/6
14	2,0	1399,9	7/7- 7/9
13	0,5	1407,5	12/1-12/5
12	0,6	1421,5	4/1- 4/4
11	1,3	1423,7	4/8- 4/10
10	2,7	1434,0	4/13-4/25
9	1,8	1466,6	11/1-11/7
8	1,5	1486,1	10/1-10/8
7	1,4	1499,5	10/10-10/17
6	0,8	1550,1	9/1 - 9/3
5	2,4	1575,1	3/19-3/28
*4	0,7	uncertain	2/16
3	0,1	uncertain	not sampled
2	0,5	1651,9	15/1-15/4
1	0,6	1653,2	15/8-15/11

Data compiled from Buchmann (1960)
* Sample positions uncertain

Ortlepp (1955,1959) also reported the occurence of massive titaniferous magnetite layers in borehole TG 1, and local ore-rich concentrations in borehole TG 4, but these occurrences were not investigated during the present study.

11.3 Description of the Ores
Nineteen titaniferous magnetite-rich seams ranging from 150mm to 4,5m in

thickness were intersected in the upper 300m of borehole TG 2 as
indicated in Table 17. The seams are generally well developed and
are separated by variable thicknesses of troctolite. The troctolite
consists of plagioclase with lesser amounts of olivine, titaniferous
magnetite, ilmenite and, more rarely, augite. The opaque oxide content
of the troctolite is highly variable.

The ores range from essentially pure, silicate-free types to more impure
varieties containing up to 30 per cent silicates. Olivine and augite
are the most common silicates in the ores while plagioclase is only
rarely present. This is in marked contrast to its appearance as a
dominant phase in the associated troctolites. Small, but variable
amounts of apatite are present in some of the silicate-rich ores and
their concentrations may locally reach up to 15 per cent.

According to Ortlepp (1959) the plagioclase is labradorite and its
composition varies between An_{52} and An_{58} in the troctolite and associated
ores. The olivine is unusally magnesium-rich considering its association
with such iron-rich rocks and ranges from Fa_{26} to Fa_{31}. Pyroxenes are
only sparingly present and are usually augitic in composition. These
mineral compositions are apparently typical for the Complex as a whole
and they characteristically display little compositional variation with
stratigraphic height (ortlepp, 1959). Textural relationships suggest
that the olivine and plagioclase crystallised simultaneously to form an
allotriomorphic texture while the opaque oxides crystallised in the
interstices at a later stage (Ortlepp, 1959).

The silicates generally appear fresh and unaltered in the troctolites,
but in contrast, they are typically altered to varying degrees in the
ores.

Olivine is the most abundant silicate in the ores and is present as
rounded to sub-rounded grains that are commonly completely surrounded
by opaque oxides. The olivine sometimes shows the development of a
very narrow outer border of possibly more iron-rich composition where
it is in contact with the opaque oxides. The olivine grains are
commonly extensively serpentinized and are traversed by veinlets of
secondary magnetite. Volume changes associated with the serpentini-
zation process have resulted in the widespread fracturing of surrounding

opaque oxides and other silicates. The fractures in the surrounding
minerals are commonly filled with serpentine and late-stage secondary
magnetite that appears to have migrated from the serpentinized olivine
into the expansion cracks. The serpentine in the veinlets is finely
granular and is composed of innumerable tiny lath-shaped crystals that
have grown transversly across the fractures.

The plagioclase in the ores may be either fresh or partially altered,
but it is occasionally completely replaced by fine-grained, scaly
aggregates of sericite, epidote, calcite and other secondary mineral.
The plagioclase grains are typically separated from neighbouring opaque
oxides by narrow, well defined reaction rims of biotite and/or brown
hornblende. The augite is generally unaltered and does not usually
exhibit a reaction relationship towards the opaque oxides, although
a narrow zone of amphibole may sometimes be present between them.

The Trompsburg ores also exhibit other forms of late-stage alteration
in addition to the serpentinization. Many of the ores are fractured
and are traversed by irregular veinlets, many of which contain late-
stage magnetite. Certain samples show evidence of late-stage
dissolution of titaniferous magnetite from zones parallel to fractures
which has resulted in a porous texture. The exsolved aluminous spinels
in these areas have also been altered to a softer, unidentified phase,
possibly diaspore.

The titaniferous magnetites in the silicate-rich ores occasionally show
incipient peripheral alteration and replacement by fine grained sphene
and chlorite aggregates. This form of alteration has occasionally
progressed further to form sphene and chlorite aggregates that contain
relicts of oriented ilmenite lamellae. These more highly altered
samples are commonly traversed by irregular veinlets of calcite, sericite,
epidote, chlorite and other fine-grained alteration products. These veinlets
commonly exhibit minor compositional zoning parallel to their lengths.
The plagioclase in these samples is generally completely altered to
saussurite while the augite is altered to uralite and chlorite. Minor
amounts of ilvaite are also present in some of the silicate-rich samples.

The Trompsburg ores and the various silicate-rich types commonly contain
small amounts of sulphide that can locally reach as high as 30 per cent

(Ortlepp, 1959). The sulphides are present both as large grains and as smaller irregular veinlets that exhibit various replacement relationships.

The Trompsburg ores are characteristically TiO_2-rich and exhibit a wide range in the ratio of coarse grained ilmenite to titaniferous magnetite. Coarse grained ilmenite is commonly the dominant opaque phase in the associated troColites and some of the silicate-rich ores, but becomes progressively subordinate with respect to titaniferous magnetite as the amounts of silicate impurities decrease. Only minor amounts of coarse granular ilmenite are generally present in the ore-rich specimens. The titaniferous magnetite grains are also commonly very much larger in the ore-rich layers than in layers where the silicates are more abundant.

The opaque oxides occupy the interstices between the silicates in the silicate-rich samples and generally exhibit rounded to smoothly curved grain boundaries. The silicates become separated from each other as the opaque oxide content increases so that they are present as isolated rounded grains that vary from 1 to 5mm in size in the ore-rich samples. The grain boundaries between the titaniferous magnetites and ilmenites are also generally straight to gently curved, but in detail they are highly spinelliferous and irregular.

The silicate-poor samples in contrast, consist essentially of very large titaniferous magnetite grains that are commonly more than 10mm across and exhibit a well defined polygonal relationship towards each other. Coarse ilmenite grains, generally between 2 and 5mm in size are sparingly present in these ores and are located interstitially between the larger titaniferous magnetites. The ilmenite/titaniferous magnetite grain boundaries are generally straight to gently curved on a large scale, but they are highly spinelliferous and irregular on a fine scale.

The titaniferous iron ores of the various seams exhibit remarkably similar microstructures, although there are minor differences that reflect slight fluctuations in conditions during crystallisation. Several zones of apatite-rich magnetite rocks were noted during the study and appear to be restricted to the zones above the uppermost titaniferous magnetite seam (19) and above the 1,8m thick seam at 1389m (seam 15). These rock types

were not specifically searched for during sampling and it is possible
that they might be more extensively developed.

Ortlepp (1955,1959) reported that ingeous layering was not well-developed
in the Trompsburg Complex and stressed that its constituent minerals do
not exhibit any marked compositional trends with increasing stratigraphic
height.   Examination of the Trompsburg cores during the collection of
the titaniferous magnetite samples indicated the presence of a wide
variety of cumulus rock types, particularly in borehole TG 2 which
contained the ore-rich seams.   Investigation of the titaniferous
magnetites revealed the presence of locally abundant sulphide
mineralization and a study of this is currently being undertaken by
Mr. C.T. Logan at NIM.

Logan (personal communication, 1977) has recognised the presence of
numerous macrorhythmic layers within certain sections of the Trompsburg
core.   In particular, he has noted the presence of at least 19 cyclic
units in a single core tray containing approximately 60m of core.   The
units vary in thickness between 1 and 3m and consist typically of a thin
olivine-rich or dunitic layer that grades upwards into a gabbro with a
decrease in olivine content.   Magnetite then appears as a cumulus phase
and may become the dominant phase, in some cases forming a definite
ore-rich seam or layer.   The magnetite content decreases sharply with
increasing height and the rock becomes plagioclase-rich, locally forming
an anorthosite.   The cycle is then repeated.

The thickness of individual layers is highly variable and they are not
always present in each cyclic unit.   These features indicate that the
petrology of the Trompsburg Intrusion is far more complex than suggested
by Ortlepp's reports.   Further petrographic and mineralogical
investigations of this Complex are currently in progress and it is hoped
that they will provide additional data that will help explain the various
features exhibited by these ores.

The Trompsburg ores are characteristically TiO_2, Al_2O_3 and MgO-rich
and their titaniferous magnetite display a wide range of microstructures
that have resulted from the exsolution and oxidation/exsolution of Ti-and
Al-rich phases.   The individual components of the ores are discussed more
fully in the following sections.

11.3.1 <u>Titaniferous magnetite</u>

The Trompsburg titaniferous magnetites are characterised by the presence of numerous, generally very fine-grained, intergrown Ti- and Al-rich phases as illustrated in Plates 16-20. The grain size of the titaniferous magnetite varies between 1 and 2mm in the silicate-rich ores, but appears to increase progressively as the proportion of silicates decreases so that larger grains of more than 10mm in size are present in the purer samples.

The titaniferous magnetite grains tend to exhibit rounded, elongated forms in the silicate-rich samples and appear moulded around the co-existing silicates. They often completely enclose smaller, rounded olivine grains while well-developed, spinelliferous grain boundaries are developed between them and co-existing coarse granular ilmenite. Grain boundaries are more difficult to observe in the ore-rich samples on account of the large size of the titaniferous magnetite crystals, but the enclosed silicates are generally rounded to sub-rounded while the opaque oxides exhibit differing degrees of polygonalization.

The grain boundaries between the titaniferous magnetites and silicates appear as smooth curves under low magnification, but in detail they are commonly serrated and irregular due to numbers of small transparent spinel grains arranged along the grain boundaries. The grain boundaries are similar, irrespective of whether a reaction rim is developed between the silicates and titaniferous magnetites or not. The biotite reaction rims that separate titaniferous magnetite from plagioclase commonly contain abundant, micrometre-sized, rounded magnetite grains.

The Trompsburg titaniferous magnetite is generally fractured due to volume changes associated with the serpentinization of olivine, the degree of fracturing being directly related to the abundance of olivine in a particular sample. The fractures are generally filled with serpentine, and to a lesser extent, by an optically homogeneous magnetite (Plate 16 (A). Other late-stage processes, in addition to the serpentinization effects, have also led to the development of distinctive features in the titaniferous magnetites. The fractures in many of the samples have been filled with graphite while some dissolution of the titaniferous magnetite and its exsolved aluminium-

rich spinels appears to have taken place in adjacent areas. This
dissolution has progressed to such an extent in some samples that the
titaniferous magnetite has a distinctly porous appearance (Plate 16 (B
and C)). Minor amounts of pyrrhotite, and to a much lesser extent,
pentlandite, are commonly present along the fractures together with
graphite (Plate 16 (A)).

Dissolution and replacement of titaniferous magnetite by fine-grained
sphene and chlorite aggregates has occurred in certain samples,
particularly the silicate-rich ores. This form of alteration is
confined largely to exposed surfaces along fractures and grain
boundaries so that the complete replacement of small grains is only
rarely observed. This form of alteration appears to have preferentially
attacked the magnetite and the very fine-grained microintergrowths so
that the larger ilmenite lamellae originally present in the host are
preserved in their crystallographic orientations in the complex sphene/
chlorite aggregates (Plate 16 (C)). The degree of magnetite dissolution
can often be determined by the presence of narrow ilmenite lamellae that
are apparently only slightly affected by this process. After
dissolution of the magnetite from the grain boundary areas, these
lamellae remain projecting into the intergranular area so that their
lengths give an indication of the amount of magnetite that has been
dissolved (Plate 16 (D)).

11.3.2 Homogeneous late-stage magnetite

Narrow, irregular, late-stage veinlets of optically homogeneous magnetite
are commonly present in the Trompsburg ores and exhibit transgressive
relationships towards both opaque oxides and silicates. These veinlets
cut across the various lamellar structures in the titaniferous magnetites
and clearly post-date them. This magnetite is generally somewhat lighter
coloured than the associated titaniferous varieties and is free from fine
grained inclusions.

The bulk of this magnetite appears to have been derived from the
serpentinisation of the olivine and is found both in the altered olivine
and in the serpentine-filled fractures in the associated minerals. In
some cases a veinlet which is developed in an opaque oxide can be followed
into a neighbouring serpentinised olivine where it probably originated.

A small amount of the late-stage magnetite might also have been precipitated from iron-rich fluids formed during the dissolution of titaniferous magnetite and its replacement by sphene.

11.3.3 Ilmenite

Ilmenite is present in the Trompsburg ores in a wide variety of forms that include both discrete grains and numerous complex microintergrowths with titaniferous magnetite. The coarser types of lamellar ilmenite are generally not well developed while trellis-like ilmenite intergrowths are generally rare and are apparently confined to specific seams. The various types of ilmenite can be characterised by differences in grain size and morphology that are described in sections 11.3.3.1 to 11.3.3.8.

11.3.3.1 Coarse granular ilmenite

Coarse grained ilmenite is commonly the dominant opaque phase in the more silicate-rich rocks where it is present as relatively large grains that vary between 1 and 5mm in size. These grains generally exhibit gently curved outlines and appear to be interstitial to the silicates about which they are moulded. The amount of ilmenite decreases with respect to titaniferous magnetite as the proportions of silicates in the samples decreases so that it is commonly only a minor phase in the ore-rich seams. Between 20 and 25 per cent by volume of coarse-grained ilmenite is commonly present in the silicate-rich ores while only between 5 and 10 per cent is developed in the silicate-poor ores. The ilmenite grains in the ore-rich samples exhibit a similar grain size to those in the silicate-rich ores, but are generally slightly elongated or show signs of polygonalization.

The ilmenite/titaniferous magnetite grain boundaries are generally highly spinelliferous and are characterised by the presence of abundant, small rounded spinel grains located along the interfaces. The spinel grains range in size from 1 to 20 micrometres and produce highly irregular, sutured boundaries as illustrated in Plate 16 (E-G). These spinel grains are more rarely present as a string of impurities that are located within the ilmenite parallel to their grain boundaries, but generally within 20 micrometres of it.

These ilmenite grains are also generally highly fractured due to the

PLATE 16

TROMPSBURG TITANIFEROUS IRON ORES

All photomicrographs taken in incident light using oil immersion objectives.

A.   Typical appearance of the Trompsburg ores. The titaniferous magnetite (left hand side of photomicrograph) contains abundant exsolved pleonaste (oriented black rodlets). The ilmenite (right hand side of the photomicrograph) exhibits a spinelleferous rim along its contact with the magnetite. The minerals are traversed by fractures (black) containing coarse pyrrhotite (white).

B.   Alteration of titaniferous magnetite (dark) in areas adjacent to fractures (black).

C.   Late-stage alteration of titaniferous magnetite (dark grey) revealing the ilmenite trellis networks.

D.   Spinelliferous ilmenite lamellae (grey) projecting beyond the margins of their titaniferous magnetite host (white) into the silicate matrix (black).

E.   Sub-parallel fractures (black) traversing both ilmenite (grey) and titaniferous magnetite (light). Note the spinelliferous ilmenite rim developed along the contact between the ilmenite and titaniferous magnetite.

F.   Similar to (E) but taken under higher magnification to show the finer microstructural details of the spinelliferous ilmenite rim.

G.   A row of pleonaste grains (black) located along the interface between ilmenite (dark grey) and multi-phase titaniferous magnetite (lighter).

H.   Ilmenite (grey) tranversed by numerous serpentine-filled fractures (black).

PLATE 16

A

1,0 mm

B

0,015 mm

C

1,0 mm

D

0,015 mm

E

1,0 mm

F

0,025 mm

G

0,015mm

H
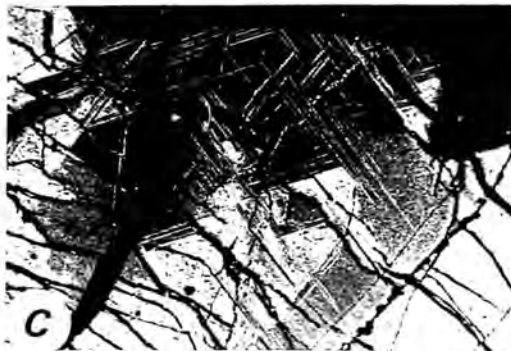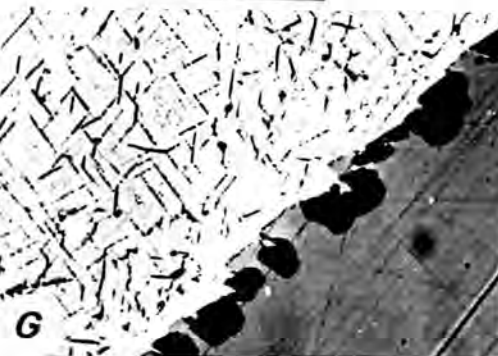
0,15 mm

serpentinization of olivine as illustrated in Plate 16 (E and H). The grains are also traversed by irregular, late-stage veinlets of serpentine, optically homogeneous magnetite, graphite, and more rarely, sulphides (Plate 17 (A and B)). The ilmenites only very rarely show the development of stress-twin lamellae even though they are extremely fractured.

The larger ilmenite grains typically contain small numbers of narrow magnetite lamellae that are oriented parallel to their basal planes. These lamellar or plate-like bodies are generally less than 3 micrometres in width, but show extreme elongation and may be up to 0,06mm in length, although they are commonly shorter. These lamellae generally exhibit sharp terminations and occasionally contain small inclusions of aluminous spinel. The spinel is generally present as small segments of the lamellae and is commonly developed near their ends. Lamellae of pure spinel are also occasionally present in the ilmenite. Small, rounded, micrometre-sized grains of spinel are occasionally present along the interface between the ilmenite and larger magnetite lamellae. Sparsely distributed spinel lamellae of a similar size and orientation are also occasionally present (Plate 17(B)).

A second type of very much coarser lamellar intergrowth of titaniferous magnetite is also present oriented along the basal planes of some of the larger ilmenite grains as illustrated in Plate 17 (C). This intergrown titaniferous magnetite is optically similar to that of the larger co-existing grains. This magnetite is highly aluminous and contains numerous small grains of transparent spinel arranged along the ilmenite/magnetite interfaces while narrow spinel lamellae are occasionally present along the (100) planes of the magnetite. Various extremely fine-grained exsolved Ti-rich phases are also commonly present towards the centres of the wider lamellae.

The titaniferous magnetite lamellae vary in width from 5 to 50 micrometres and may be up to 0,2mm long. They are generally of uniform thickness, but may occasionally pinch and swell along their length. Their terminations are commonly sharp and do not taper gently. Small rounded inclusions of titaniferous magnetite are also occasionally present in the ilmenite.
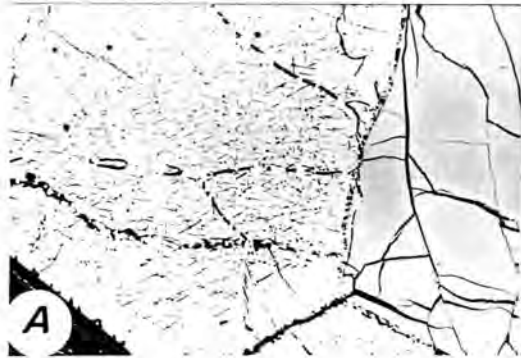
PLATE 17

TROMPSBURG TITANIFEROUS IRON ORES

All photomicrographs taken in incident light using oil immersion objectives.

A. Fractured ilmenite (grey) showing the development of pyrrhotite (light) along some of the fractures. The difference in colour of the pyrrhotite is due to reflection pleochroism.

B. Similar to (A), but small numbers of transparent spinel rodlets (black) are present in the ilmenite.

C. A plate-like inclusion of multi-phase titaniferous magnetite (lighter) in ilmenite (darker) traversed by a serpentine-filled fracture.

D. An aggregate of small irregular ilmenite grains (dark grey) and pleonaste (black) developed along a permeable zone within a titaniferous magnetite grain.

E. Similar to (D), but the ilmenite grains have coalesced to form a veinlet.

F. Broad spinelliferous ilmenite lamellae (grey) extending to the margins of their titaniferous magnetite hosts where they become wider.

G. Ilmenite lamellae (dark grey) containing abundant pleonaste (black).

H. Sparsely distributed fine spinelleferous ilmenite lamellae (dark grey) in titaniferous magnetite (light) containing abundant exsolved pleonaste (black).

PLATE 17
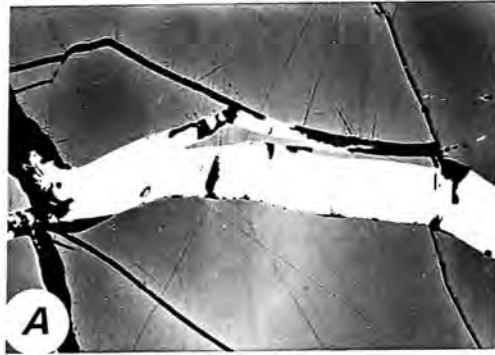
0,015 mm

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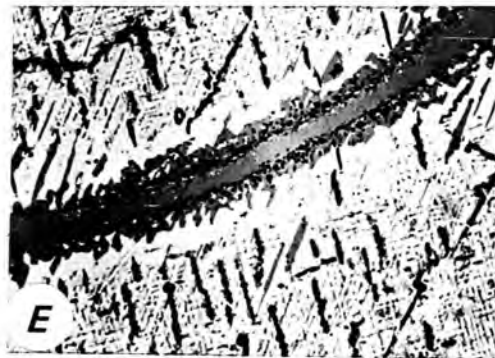
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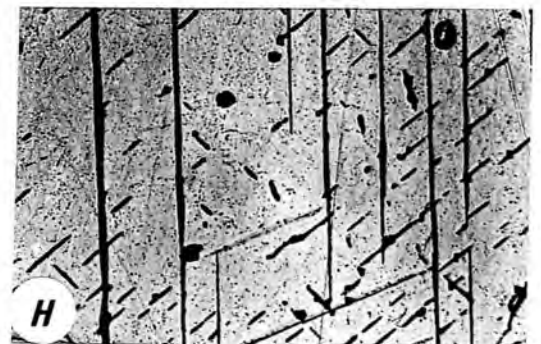
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11.3.3.2 Fine granular ilmenite

Small elongated, or irregularly shaped ilmenite grains are occasionally present within the titaniferous magnetite grains or are located along the interfaces between neighbouring magnetite grains. These grains range from 0,02 to 0,1mm in size and are typically spinelliferous, having numbers of very much smaller, transparent spinel grains arranged around their margins where they are in contact with titaniferous magnetites. These fine granular ilmenites are also sometimes connected to the broad ilmenite lamellae that occasionally cut across the titaniferous magnetites.

The amount and size of the spinel grains associated with the ilmenite appears to be controlled largely by their size. The spinel is generally abundant around the larger grains, but is less well-developed around the smaller grains and may even be absent from the smallest ones.

Many of the smaller ilmenite grains exhibit highly irregular outlines and are sometimes arranged in stringers along curved fractures or permeable zones within the titaniferous magnetites (Plate 17 (D and E)). These ilmenite grains are commonly connected to a set of finer ilmenite lamellae that are developed along either side of the permeable zone. These lamellae and small ilmenite grains are also generally in optical continuity.

11.3.3.3 Broad ilmenite lamellae

Broad ilmenite lamellae, usually between 7 and 20 micrometres wide, but occasionally wider, and up to 0,4mm long are sparingly present along the oactahedral planes of the titaniferous magnetites as illustrated in Plate 17 (F). These lamellae are generally very rare and are only very occasionally developed to the extent where they form a distinct trellis network.

These lamellae are highly spinelliferous and are characterised by the presence of large numbers of very small, transparent spinel grains. The spinels are not only located along the ilmenite/titaniferous magnetite interfaces, but are present within the ilmenite and are commonly aligned in rows parallel to the lamellar boundaries (Plate 17 (G)). The titaniferous magnetite in the immediate vicinity of these ilmenite lamellae is generally devoid of the finer grained ilmenite microintergrowths for a distance of up to 0,02mm from the lamellae (Plate 17 (G)).

The lamellae that are completely enclosed within the titaniferous
magnetite generally exhibit a well defined, narrow, lensoid shape
with gently tapering ends.   In contrast, the lamellae that extend
to the grain boundaries commonly exhibit a slight degree of thickening
towards the grain boundary, reaching their broadest development at the
grain boundary itself.   These lamellae also occasionally protrude a
slight distance from their host titaniferous magnetite and may be joined
to small ilmenite grains.

Fracturing and displacement of the host titaniferous magnetites during
serpentinization of the associated olivine is commonly controlled by
the lamellae.   They provide planes of weakness along which separation
can preferentially occur.

11.3.3.4 Fine ilmenite lamellae

A second series of finer ilmenite lamellae are sporadically developed
along the octahedral planes of the titaniferous magnetites, but are
rarely abundant enough to form a well defined trellis network.   They
range from 1 to 5 micrometres in width and are generally extremely
elongated, locally attaining lengths of 0,25mm.   They are generally in
the form of flattened lenses with gently tapering ends, although more
complex morphologies are sometimes developed (Plates 17 (G) and 18 (A-B)).

These lamellae are generally spinelliferous, but not to the same extent
as the broad lamellae.   Rows of small, rounded, transparent spinel grains
are generally arranged along the ilmenite/titaniferous magnetite interfaces
in the usual manner.   The smaller ilmenite lamellae are generally less
spinelliferous than the larger ones in this class and in some cases the
smaller bodies are completely free of marginal spinel.   A narrow zone
of inclusion-free, optically homogeneous, titaniferous magnetite
approximately 10 micrometres wide is generally present around these
lamellae.   The titaniferous magnetite present between these lamellae at
a greater distance typically contains an abundance of other finer
intergrown phases.

These lamellae are generally not well developed in the Trompsburg
titaniferous magnetites and with the exception of samples 17/2 and 24/5
they are virtually absent from these ores.   Where present, they are
more commonly located near grain boundaries and along early-formed

fractures. They are also occasionally connected to small irregular
ilmenite grains that are developed along fractures or other permeable
zones within their hosts.

11.3.3.5 Very fine spinelliferous ilmenite lamellae

This type of intergrowth represents the common groundmass texture in
the titaniferous magnetites in samples 4/4-15 and 12/4-5 and is
characteristic of ore-rich samples from this level in the Complex.
These textures are very distinctive and are not developed to any extent
in titaniferous magnetites from other levels in the Complex. They do
not represent a variant of the fine-grained ilmenite lamellae described
above since the titaniferous magnetite between these lamellae appears
optically homogeneous and free from other inclusions even under the
highest magnification (2000X, oil immersion). These lamellae are
approximately a micrometre wide and vary between 10 and 20 micrometres
in length. They generally form a well developed trellis network and
are oriented along the octahedral planes of their host grains (Plate
18 (C)). They commonly exhibit a wide range in grain size over a
small distance within the same grain and merge into areas consisting
of extremely fine-grained, rounded inclusions of spinel and ilmenite
that are at the limit of optical resolution ("salt and pepper texture").

The ilmenite lamellae are distinctly lens-shaped and have gently tapering
ends, especially where they intersect each other. Myriads of micrometre-
sized rounded spinel grains are typically located along the ilmenite/
titaniferous magnetite interfaces and occasionally form part of the lamellae.
Other coarser forms of spinel are typically absent from grains showing this
type of microstructural development.

11.3.3.6 Extremely fine ilmenite lamellae

A set of extremely fine grained ilmenite lamellae approximately 1
micrometre thick and up to 10 micrometres in length are occasionally
developed in the Trompsburg titaniferous magnetites. They are also
developed along the octahedral planes of their hosts, but are typically
free of fine-grained spinel intergrowths (Plate 18 (D)).

The lamellae are generally best developed along a narrow zone bordering
grain boundaries and along fractures, but may also be present further into
the titaniferous magnetites where they are most commonly developed in areas

PLATE 18

TROMPSBURG TITANIFEROUS IRON ORES

All photomicrographs taken in incident light using oil immersion objectives.

A. Fine intersecting ilmenite lamellae (grey) parallel to (111) in titaniferous magnetite containing abundant exsolved pleonaste (black) parallel to (100).

B. Fine ilmenite lamellae (grey) developed parallel to (111) of titaniferous magnetite cut by pleonaste lamellae that have exsolved parallel to (100). Note that the pleonaste lamellae appear to consist of rows of octahedra.

C. Very fine spinelliferous ilmenite lamellae (dark grey) in titaniferous magnetite. Tiny pleonaste grains are black.

D. Extremely fine ilmenite lamellae (grey) developed along (111) of the Ti-magnetite cut by pleonaste lamellae (black) developed along (100).

E. Typical ulvospinel cloth texture viewed along (100). Extremely fine pleonaste grains are black.

F. Same as (E), but viewed along (111) showing the 3-fold symmetry.

G. Similar to (E), but showing the development of several larger ulvospinel "boxes".

H. Similar to (G), but showing a much more pronounced development of this ulvospinel texture.

PLATE 18
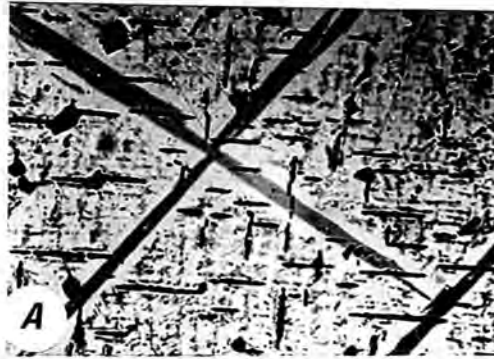
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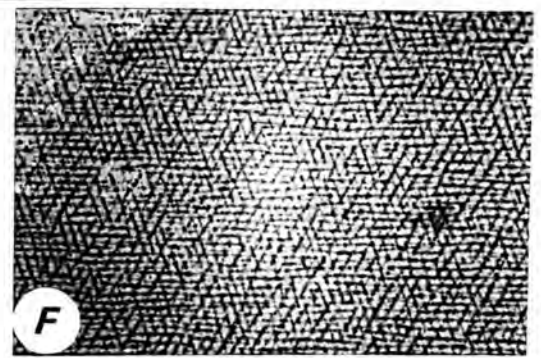
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between the fine ilmenite lamellae. These lamellae generally merge imperceptibly into ulvospinel-type textures and are more common in the silicate-rich ores, being virtually absent from some of the pure types. Very small, micrometre sized ilmenite granules are occasionally developed at the ends of these lamellae where they protrude into fractures.

11.3.3.7 Extremely fine granular ilmenite

Very small, micrometre sized ilmenite granules are rare in the Trompsburg titaniferous magnetites and are occasionally present in narrow stringers that are aligned along minor fractures or other permeable features. These grains are generally irregular in shape and are commonly connected to the extremely fine ilmenite lamellae described above.

Similar sized, irregular to rounded ilmenite grains are present in the areas between well-developed ilmenite trellis networks. These textures are rare and have only been noted in samples 17/2 and 24/5 that are characterised by an abundance of very fine lamellae.

Aggregates of very small, rounded ilmenite grains are occasionally developed around the periphery of the larger and more sparsely distributed spinel lamellae. These aggregates are commonly arranged in a rectangular pattern around each spinel lamella at a distance of several micrometres and produce the effect of a "frame" surrounding the spinel. These structures might, in part, represent oxidised ulvospinel.

11.3.3.8 Ulvospinel and its oxidation products

The characteristic cloth-like structure formed by the sub-solidus exsolution of ulvospinel is the most abundant and widely developed microstructure in the Trompsburg ores. This microstructure is particularly coarse and well developed in the samples and consists of a mesh-like network of micrometre and sub-micrometre sized ulvospinel lamellae. These lamellae are orientated along the cubic planes of their hosts and divide the magnetite groundmass into a myriad of micrometre-sized cubes (Plate 18 (E and F)). Certain ulvospinel lamellae are occasionally better developed and textures similar to those in Plate 18 (G and H) are formed. Frameworks of coarser ulvospinel are also developed around the larger spinel lamellae (Plate 19 (A and B)).

Exsolved ulvospinel is readily oxidised to ilmenite, but when this occurs at low temperatures, the orientation of the originally exsolved ulvospinel is retained by the oxidation product. Ortlepp (1959)noted the presence of unaltered ulvospinel in these ores, but the present microscopic investigation shows that much of the ulvospinel has been oxidised to ilmenite. X-ray powder diffraction traces reveal broad, irregular magnetite peaks which partly reflect the very fine-grained size of the individual magnetite fragments, the present of the aluminous spinel, optically homogeneous magnetite and possibly some unoxidised ulvospinel that all have similar d-spacings. It is possible that the partial oxidation of this ulvospinel may have occurred during 30 years of storage under atmospheric conditions. It is also possible that oxidation of ulvospinel at the surface of the polished sections may have occurred during their preparation.

The normally very fine-grained ulvospinel lamellae are oxidised to ilmenite at places within the titaniferous magnetites and the texture breaks down to yield a less-well defined microstructure. The individual lamellae swell and coalesce with neighbouring lamellae to form larger grainsthat are in optical continuity. They form a perforated sieve type texture containing abundant rounded magnetite inclusions in their more advanced stage of development and are surrounded by a narrow zone of optically homogeneous magnetite (Plate 19 (C and D)). This advanced stage is rarely reached, however, and these forms of microstructural modification merge imperceptibly into the areas of normal ulvospinel-type textural development.

11.3.4 Spinel and other aluminous phases

The aluminous nature of the Trompsburg titaniferous magnetite is reflected in the abundant development of transparent, aluminium-rich spinels probably close to pleonaste in composition. They are present in a wide variety of forms and, also exhibit a considerable range in grain size. These intergrowths are extremely well developed in the titaniferous magnetite from both the silicate-rich and silicate-poor ores, but are virtually absent from those in the apatite-rich rocks.

The spinel is commonly present in various types of spinelliferous ilmenite rims as small, rounded grains that range from 20 down to less than 1 micrometre in size as decribed in the preceeding sections. Numbers of small spinel grains, generally between 10 and 15 micrometres in size are

# PLATE 19

TROMPSBURG TITANIFEROUS IRON ORES

All photomicrographs taken in incident light using oil immersion objectives.

A.   Exsolved pleonaste (black) present as lamellae and rows of small
     grains in titaniferous magnetite showing an ulvospinel cloth texture.

B.   Pleonaste lamellae (black) surrounded by boxworks of ulvospinel
     (dark grey) and surrounded by titaniferous magnetite containing
     small grains of ilmenite (or ulvospinel) and pleonaste ("salt and
     pepper" texture).

C.   Coarsening of ulvospinel lamellae (dark grey), now oxidised to
     ilmenite developed in titaniferous magnetite.

D.   Similar to (C), but showing replacement of part of the Ti-rich phase
     by a dark unidentified phase (possibly pleonaste or diaspore).

E.   A large pleonaste grain(black) with skeletal outer margins in
     titaniferous magnetite.

F.   A large, more rounded pleonaste grain (black), containing a blade
     of pyrrhotite (white) enclosed by titaniferous magnetite.

G.   Pleonaste lamellae (black) exsolved parallel to (100) of
     titaniferous magnetite.

H.   Similar to (G), but viewed along (111) showing the 3-fold symmetry
     in this orientation.

PLATE 19
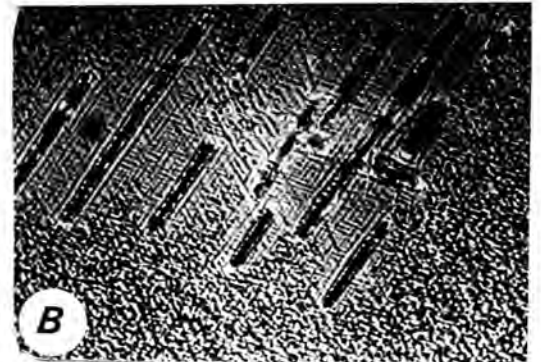
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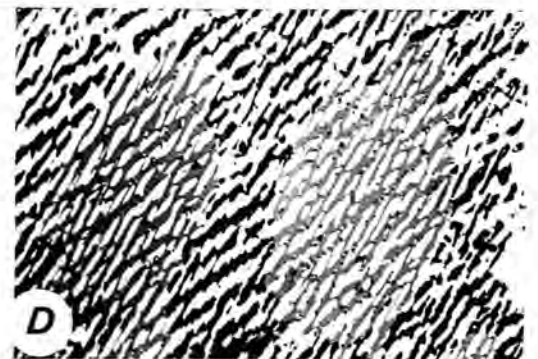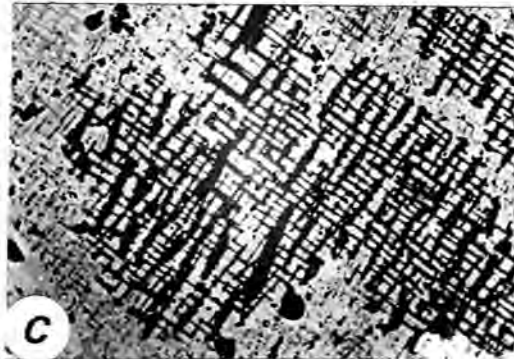
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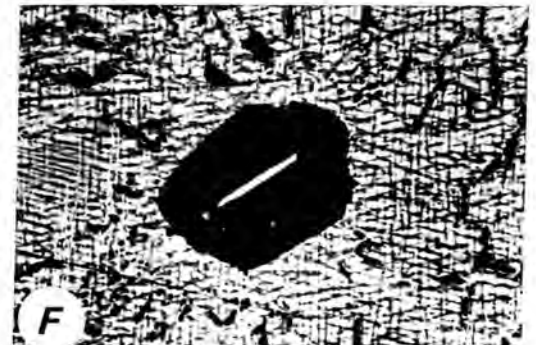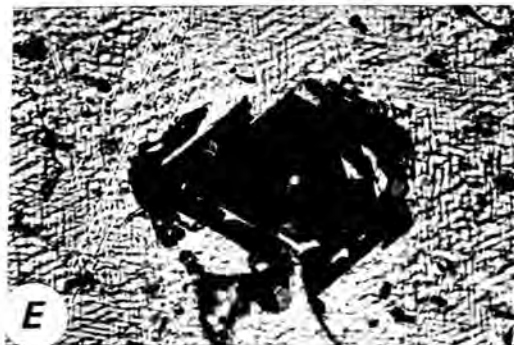
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also commonly present around the peripheries of the titaniferous
magnetite grains.

Isolated, generally rounded, spinel grains between 10 and 30 micrometres
in size are often irregularly distributed throughout the titaniferous
magnetite in areas devoid of lamellar spinel. These grains are typically
surrounded by a zone up to 20 micrometres wide that is devoid of other
fine-grained spinel intergrowths (Plate 19 (G and H)). A small proportion
of these larger grains are slightly greyer in colour than the usual
exsolved transparent spinels and they commonly contain a small, lath like
inclusion of sulphide, generally pyrrhotite, at their centre (Plate 19(F)).
Molyneux (1970a,1972) reported the presence of similar grains in the
Bushveld titaniferous magnetites and has identified them as diaspore.
These grains were not identified positively in the Trompsburg ores, but
they might well be diaspore rather than spinel.

The transparent spinel is also present as well-defined lamellae that are
oriented along the cube planes of their hosts to form a grid-like pattern
(Plate 19(G and H,A)). These lamellae vary in length from 5 to 40
micrometres, but are generally only 1 to 3 micrometres in width. They
are generally less than 20 micrometres long and it is only rarely that
the longer types are developed.

Small, octahedral spinel grains are sometimes developed at the intersection
of two sets of the larger lamellae. The spacing of the lamellae is also
dependent on size and the larger lamellae are generally spaced further apart.
The spinel lamellae cut across all types of lamellar ilmenite except for
the very finest microintergrowths (plate 20 (B and C)). The larger lamellae
occasionally appear to consist of chains of octahedra that are joined end
to end (Plate 18 (B)).

The spinel lamellae and larger grains are absent from some of the
titaniferous magnetites and their place is taken by a myriad of tiny,
sub-micrometre-sized spinel grains. These grains are at the limits of
optical resolution and are intergrown with an extremely fine-grained
Ti-rich phase that cannot be properly resolved. These areas of magnetite
have an overall highly speckled appearance under high magnification that
is perhaps best described by the term "salt and pepper" texture. These
areas tend to merge into areas showing the development of the more normal

types of spinel exsolution bodies within the same grain. This type of microstructure is commonly developed in titaniferous magnetites that contain very fine, spinelliferous ilmenite lamellae.

The spinel appears to have been altered to a very much softer phase in areas showing signs of magnetite dissolution. This phase is extremely fine grained and was not identified, but might possibly be diaspore, gibbsite, chlorite or some other secondary Al-rich mineral.

11.3.5 Graphite

Graphite is ubiquitously present in the more titaniferous magnetite-rich Trompsburg ores and is generally developed as veinlets along many of the numerous late-stage fractures that traverse the samples (Plate 20 (C and D)). These veinlets range from 0,1mm down to several micrometres in width and commonly contain small, but variable amounts of magnetite, serpentine and several types of sulphide. The graphite is present as soft flaky crystals that exhibit extreme pleochroism and are occasionally bent. The crystals are generally oriented with their prominent cleavage perpendicular to the sides of the fractures, but they are also found oriented along the length of the fractures.

Transgressive graphite veinlets are present in both the ilmenite and titaniferous magnetite and graphite commonly appears to replace the spinel that was originally present in intergrowths in both these minerals (Plate 20 (D and E). This replacement takes place in the neighbourhood of the veinlets and the graphite also locally replaces the magnetite lamellae in ilmenite where they are cut by graphite veinlets. Scaly graphite aggregates are also commonly developed around many of the sulphide grains.

The transgressive nature of the graphite veinlets indicates that they are late-stage phenomena while they also cut across the various fine ilmenite lamellae which can often be matched up across the veinlets. The extremely fine grained ilmenite lamellae are unfortunately too short so that it is not clear whether or not they are cut and displaced by the graphite.

Polishing of the graphite is very difficult in view of its very soft nature in comparison with the very much harder opaque oxides. Reasonable results were obtained in many cases, as illustrated in the photomicrographs.

## PLATE 20

TROMPSBURG TITANIFEROUS IRON ORES

All photomicrographs taken in incident light using oil immersion objectives.

A.   Pleonaste lamellae (black) showing a wide range in size in
titaniferous magnetite.   Note the abundance of lamellae along
certain zones.

B.   Typical pleonaste lamellae (black) in titaniferous magnetite.
Note the presence of several larger, euhedral pleonaste grains
(black).

C.   Typical titaniferous magnetite showing a broad ilmenite lamella
(dark grey) and exsolved pleonaste (black).   An irregular graphite-
filled veinlet is present roughly parallel to the ilmenite.   Note
the presence of pleonaste lamellae within the ilmenite.   The small,
lighter coloured and irregular grains to the left of the veinlet at
the top of the photomicrograph consist of graphite.

D.   A transgressive graphite-filled veinlet.   The graphite has grown
transversely across the fracture and its banded appearance is due to
the extreme reflection pleonchroism of this mineral.

E.   Graphite (light) replacing a pleonaste lamella (centre of
photomicrograph).   The other darker coloured bodies contain graphite
and another unidentified phase, possibly diaspore.

F.   A pyrrhotite grain (white) showing partial oxidation to magnetite
(grey).   The sulphide is located between ilmenite (slightly darker
grey) and titaniferous magnetite (full of inclusions).   The
transgressive veinlet (black) contains minor pyrrhotite (white)
and some magnetite (grey).

G.   Similar to Plate 19 (C), but with portion of the original ulvospinel
or ilmenite being replaced by pyrrhotite (white).

H.   A basal section of an apatite crystal (black) set in ulvospinel cloth-
textured titaniferous magnetite containing spinelliferous ilmenite
lamellae (dark grey).

PLATE 20

A

0,2 mm

B

0, 015 mm

C

D

0, 015 mm

E

0,015 mm

F

0,5 mm

G

H
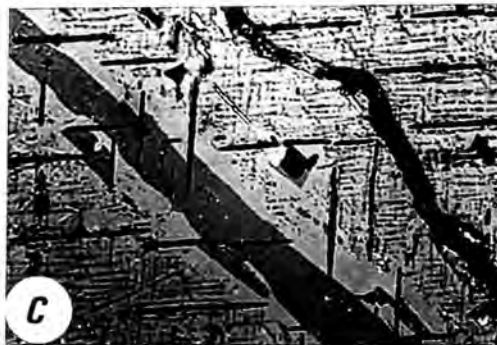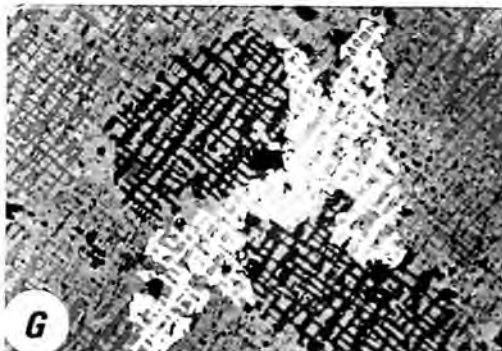
0,015 mm

11.3.6 Sulphides

The Trompsburg ores generally contain small, but variable amounts of sulphide mineralization. Ortlepp (1959) noted that the sulphide concentrations locally reached as high as 30 per cent, but these samples were no longer available for investigation.

The sulphides are generally present as discrete grains in the intergranular areas between oxides or as transgressive veinlets. Replacement of very fine grained spinel intergrowths by sulphides has also been noted in some of the altered titaniferous magnetites.

Pyrrhotite is the most common sulphide and it is present both as discrete rounded grains up to 3mm across and as narrow irregular, transgressive veinlets (Plate (F)). The pyrrhotite is nickel-rich and commonly shows the development of pentlandite exsolution flames. It also shows alteration to magnetite. This process commences along grain boundaries and fractures and moves inwards into the grain in an irregular fashion. The pyrrhotite veinlets also commonly show evidence of alteration to magnetite, but it is difficult to distinguish this magnetite from that produced during serpentinization unless some unoxidised pyrrhotite is present. These veinlets also commonly contain serpentine, late stage magnetite, graphite and other secondary minerals as illustrated in Plate 16 (A). It also occasionally replaces the fine-grained magnetite in the titaniferous magnetite grains (Plate 20 (G)).

Pentlandite is probably the next most common sulphide and it is present both as discrete grains and as exsolution bodies in pyrrhotite. The pentlandite grains are generally associated with pyrrhotite grains, but they generally are much smaller and distinctly rounded. They are commonly surrounded by graphite aggregates and are sometimes fractured and veined by graphite and late-stage magnetite.

Chalcopyrite is also present in small amounts as discrete grains and is generally associated with the complex pyrrhotite - pentlandite grains, although it has been noted on its own. The sulphides were not studied in detail, but it is probable that a wide range of Ni-Fe-Co and Cu-Fe sulphides might be found if specifically searched for.

11.3.7 Apatite

Several zones of fine-to medium-grained apatite-bearing ore-rich rocks were encountered during the course of this study as indicated in Table 21. The ratio of silicates to opaque oxides in these samples is approximately equal while the apatite is present in amounts ranging from 5 to 15 per cent by volume. This type of material was not specifically sampled so that ores containing higher concentrations of apatite might be present.

The apatite exhibits a highly variable grain size that ranges from several micrometres up to approximately 0,3mm. It is present as prismatic hexagonal crystals that are generally sub-rounded to rounded in outline, although euhedral grains are occasionally present, particularly in the fine-size ranges (Plate 20 (H)).

The apatite was not investigated in detail, but it is most probably the normal fluorapatite found in basic rocks (Brown and Peckett, 1977). It appears to be preferentially enclosed in, or located adjacent to both the ilmenite and titaniferous magnetite grains and is locally abundant enough to produce a well-defined poikilitic texture. In contrast to its association with the opaque oxides, it is only present in minor amounts as inclusions within the associated silicates. Olivine and augite are commonly present in these rocks types while plagioclase is a rare constituent. Apatite is generally not present in more than trace quantities in the majority of ores examined.

The titaniferous magnetite associated with the apatite characteristically displays a coarse, well-defined, ulvospinel-type microstructure and is virtually devoid of fine grained, transparent spinel intergrowths. Other types of lamellar ilmenite intergrowths are also rarely developed, and where present, are only slightly spinelliferous. This is in marked contrast to the normal silicate-rich ores that usually exhibit a greater proportion of lamellar intergrowths.

11.4 Chemical Analyses of the Trompsburg Titaniferous Iron Ores

The chemical analysis of 18 typical Trompsburg ores are presented in Table 18 together with two analyses from the literature.

The small, but variable amounts of SiO_2 reflect the minor amounts of silicate

TABLE 18

ANALYSES OF TROMPSBURG TITANIFEROUS IRON ORES

Seam	1	2	4	5	6	7		8		9	13	14	16	17	18		19		a 5	a 10
Oxide	15/11	15/1	2/16	3/19	9/1	10/17	10/14	10/8	10/1	11/1	12/2	7/8	17/2	24/5	8/16	8/8	8/4	8/1	21-718	21-117
SiO_2	3,88	2,26	2,91	3,12	1,15	0,94	1,39	0,64	1,97	2,75	3,13	6,04	0,62	3,24	1,98	3,28	2,12	3,78	4,00	0,33
TiO_2	15,23	15,61	15,49	16,33	17,44	16,63	17,40	15,14	19,99	16,27	14,71	13,57	17,09	14,85	15,43	15,26	20,14	17,96	14,40	15,32
Al_2O_3	3,86	4,60	4,39	4,93	4,65	5,08	4,82	4,68	4,24	5,49	4,56	3,41	4,84	5,90	4,24	4,68	4,23	4,24	5,15	5,31
Cr_2O_3	0,16	0,22	0,40	0,18	0,28	0,19	0,27	0,20	0,10	0,12	0,41	0,48	0,61	0,14	0,50	0,46	0,22	0,41	N.R.	N.R.
Fe_2O_3	36,56	39,71	35,86	35,40	35,83	33,57	37,41	36,31	32,61	34,17	35,50	33,63	37,76	33,89	35,56	33,96	30,84	33,38	35,04	36,16
FeO	33,87	32,75	34,54	35,19	34,24	37,10	34,08	36,04	35,61	36,55	35,28	34,88	33,33	37,24	34,09	35,44	36,23	35,56	29,99	32,87
MgO	4,13	3,98	4,13	3,97	4,54	4,54	4,27	4,42	4,46	3,82	6,03	4,67	3,66	4,07	5,04	5,12	4,19	4,96	5,96	4,54
MnO	0,36	0,33	0,36	0,51	0,41	0,37	0,38	0,35	0,51	0,34	0,34	0,69	0,36	0,45	0,36	0,36	0,33	0,32	0,41	0,31
V_2O_5	0,80	0,76	0,80	0,78	0,76	0,77	0,70	0,72	0,63	0,87	0,65	0,63	0,77	0,77	0,78	0,71	0,70	0,65	1,10	1,82
TOTAL :	98,85	100,22	98,88	100,41	99,30	99,19	100,72	98,50	100,12	100,38	100,61	97,80	99,04	100,55	97,98	99,27	99,00	101,26	96,05	96,66
TOTAL Fe :	51,80	53,23	51,93	52,11	51,67	52,32	52,65	53,41	50,49	52,31	52,25	50,63	52,32	52,65	51,37	51,30	49,73	50,99	47,82	50,84

a Analyses of Trompsburg titaniferous iron ore (Ortlepp, 1955, 1959).

N.R. not reported.

impurities, usually serpentinized olivine, in the ores. The TiO_2
contents vary between 13,6 and 20 per cent, but are generally above
15 per cent and are in the typical range expected for ores of this
nature.

The Al_2O_3 contents vary between 3,4 and 5,9 per cent and, since the ores
contain only minor plagioclase, the bulk of this is present in the
various exsolved spinel phases in the titaniferous magnetite. Cr_2O_3
values are consistently low, but in some samples values of between 1,5
and 0,6 per cent are reported. No chromite or chrome-spinel was
identified in the ores and this oxide is most probably held in solid
solution in the magnetite.

The Fe_2O_3 contents of these ores are low when compared to similar ores
from surface exposures and reflect their unweathered nature. The FeO
values are correspondingly high and when the analysis are recalculated
in terms of ilmenite, a small amount of excess FeO remains in certain
samples indicating the presence of some unoxidised ulvospinel.

The V_2O_5 values range between 0,63 and 0,83 per cent and are very much
lower than the values reported by Ortlepp (1955,1959). The reason for
this discrepancy is not known, but acceptable values were obtained during
duplicate analyses which indicate a reproducability of at least $\pm$ 0,05
per cent of the reported value. The V_2O_5 values do not show a continual
decrease upwards in the sequence, but instead appear to indicate the
presence of 3 broad cycles, each of which is characterised by decreasing
V_2O_5 contents upwards.

The MgO values vary between 3,7 and 6,0 per cent and can be accounted
for by the presence of serpentinized Mg-rich olivine. The values do
not vary systematically with SiO_2 content, however, which indicates that
some of the MgO must be present in one or other of the opaque phases or
their exsolution products. The MnO values vary between 0,3 and 0,7 per
cent, but do not show any marked variation with position in the sequence.

11.5 Analyses of Coarse-Grained Ilmenites from the Trompsburg Complex
Electron microprobe analyses of the co-existing coarse-grained ilmenite
from the chemically analysed Trompsburg ores are presented in Table 19.

TABLE 19

MICROPROBE ANALYSES OF COARSE GRAINED ILMENITES.

	1	2	4	5	6	7	7	8	8	9	13	14	16	17	18	18	19	19
	15/11	15/1	7/16	3/19	9/1	10/17	10/14	10/8	10/1	11/1	12/2	7/8	17/2	24/5	8/16	8/8	5/4	5/1
TiO_2	53,43	53,05	51,22	53,50	53,35	53,15	54,81	53,09	53,55	53,72	53,67	52,18	51,96	51,77	54,44	54,33	53,31	53,91
FeO	35,74	33,99	34,59	35,74	32,37	33,85	33,24	31,94	33,36	34,29	32,35	37,42	33,82	33,34	32,89	32,69	34,19	32,52
MgO	6,97	7,37	6,09	6,54	8,41	7,48	8,68	8,50	7,99	7,53	8,63	4,90	6,90	7,04	8,67	8,73	7,36	8,67
MnO	0,59	0,55	0,65	0,79	0,57	0,57	0,58	0,56	0,57	0,60	0,56	0,69	0,59	0,58	0,57	0,56	0,57	0,53
$*Fe_2O_3$	4,71	4,07	6,63	4,55	5,03	3,51	3,83	5,10	4,63	4,79	4,47	5,83	6,71	8,87	3,43	3,75	4,15	3,99
Al_2O_3	0,12	0,12	0,11	0,12	0,12	0,12	0,11	0,13	0,13	0,12	0,12	0,16	0,14	0,12	0,12	0,12	0,14	0,12
Cr_2O_3	0,13	0,17	0,19	0,17	0,17	0,17	0,17	0,16	0,17	0,17	0,19	0,22	0,23	0,18	0,17	0,18	0,17	0,13
TOTAL :	100,99	99,32	99,48	101,41	100,02	98,85	101,42	99,48	100,40	101,22	99,99	101,40	100,35	101,90	100,29	100,36	99,89	99,87

NUMBER OF IONS ON THE BASIS OF 6 OXYGENS

	1	2	4	5	6	7	7	8	8	9	13	14	16	17	18	18	19	19
Al^{3+}	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006
Cr^{3+}	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,006	0,012	0,006	0,006	0,006	0,006	0,006
Fe^{3+}	0,170	0,144	0,244	0,160	0,176	0,128	0,134	0,182	0,164	0,170	0,158	0,214	0,242	0,312	0,118	0,130	0,150	0,142
Ti^{4+}	1,909	1,922	1,872	1,914	1,906	1,930	1,927	1,903	1,912	1,909	1,915	1,887	1,870	1,838	1,935	1,929	1,919	1,923
Fe^{2+}	1,392	1,369	1,405	1,420	1,287	1,367	1,301	1,275	1,324	1,355	1,282	1,505	1,355	1,318	1,301	1,290	1,369	1,290
Mg	0,494	0,530	0,441	0,463	0,596	0,540	0,604	0,605	0,565	0,531	0,610	0,353	0,492	0,497	0,611	0,616	0,527	0,613
Mn	0,023	0,023	0,026	0,031	0,023	0,023	0,022	0,023	0,023	0,023	0,023	0,029	0,023	0,023	0,023	0,023	0,023	0,020
TOTAL :	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000	4,000

NORMATIVE COMPOSITION (MOLE PER CENT)

	1	2	4	5	6	7	7	8	8	9	13	14	16	17	18	18	19	19
$FeTiO_3$	69,61	68,45	70,22	71,00	64,34	68,36	65,03	63,75	66,19	67,76	64,11	75,29	67,77	65,91	65,06	64,65	68,49	64,53
$MgTiO_3$	24,68	26,48	22,04	23,14	29,81	27,00	30,20	30,23	28,25	26,56	30,48	17,63	24,60	24,86	30,54	30,78	26,33	30,63
$MnTiO_3$	1,14	1,16	1,31	1,57	1,14	1,16	1,12	1,15	1,14	1,14	1,14	1,45	1,15	1,14	1,14	1,13	1,15	1,00
R_2O_3	4,57	3,91	6,43	4,29	4,71	3,48	3,65	4,87	4,42	4,54	4,27	5,63	6,48	8,09	3,26	3,55	4,03	3,84
TOTAL :	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

* Fe_2O_3 calculated assuming ilmenite stoichiometry

Note : MgO values have been checked by repeated analyses using a variety of standards.

The Trompsburg ilmenites are characterised by high MgO contents that range from 4,9 to 8,7 per cent and are similar to those present in the Kaffirskraal Complex (this report). These values are among the highest yet recorded for igneous ilmenites from non-kimberlitic sources. The samples were re-analysed in a batch together with several previously analysed low-MgO ilmenites using various standards and the expected values were obtained which suggests that these results do not reflect a systematic analytical error. The MgO values are also higher than that shown by the bulk ore analyses which indicates that the MgO is preferentially incorporated in the rhombohedral phase.

The MnO values are fairly constant in the vicinity of 0,6 per cent, rarely reaching as high as 0,8 per cent.

Recalculation of the microprobe analyses assuming stoichiometry indicates the presence of minor amounts of excess FeO that is recalculated as Fe_2O_3 and is regarded as hematite in solid solution in the ilmenite. The iron-rich nature of these larger ilmenites is also reflected by the presence of the crystallographically oriented magnetite lamellae.

11.6 Beneficiation

The Trompsburg Igneous Complex is covered unconformably by approximately 1000m of younger sediments so that the utilization of its ores appears remote. The new V_2O_5 analyses presented in this report also indicate that they are too low grade to warrant exploitation. In view of this, no beneficiation tests were carried out.

11.7 The Sequence of Ores in the Trompsburg Complex

One of the problems facing the interpretation of the mineralogical results is the positioning of the ore samples in their correct stratigraphic sequence in the borehole core. The exact position of certain samples is not known (as mentioned in section 11.2), but it was hoped that this study might yield information regarding their correct sequence. It was hoped that the V_2O_5 content of the titaniferous magnetites would be found to decrease systematically upwards in the sequence as illustrated by the Skaergaard, Bushveld, Rooiwater and Mambula Complexes. No similar overall trend was however apparent from the analyses and Ortlepp (1955,1959) reported a value of 1,80 per cent V_2O_5 in ores approximately halfway up the sequence while an ore from 180m lower down in the sequence

has a value of only 1,10 per cent V_2O_5.

Ortlepp (1955,1959) has commented on the lack of compositional variation in the Trompsburg minerals with stratigraphic height and this feature is also displayed to a certain extent by the titaniferous iron ores. A tabulation of the samples with respect to their known or estimated heights in the borehole is given in Tables 17 and 21. This reconstruction appears to indicate the presence of three zones, or cycles, in which the V_2O_5 contents of the lowest ore-rich seams are approximately 0,8 per cent and decrease systematically upwards to values of approximately 0,65 per cent, whereupon the sequence is repeated.

The apatite-rich zones appear to be located towards the top of the second (above seam 15) and third (above seam 19) cycles. No apatite-rich samples were found towards the top of the first cycle, but this might be due to imperfect sampling.

It is also possible to group the ores into six basic types based on the nature of the titaniferous magnetite intergrowths. The variations in the microstructural development reflect differences in oxygen fugacity during cooling and certain textural types appear restricted to definite stratigraphic levels. The essential features of the textural types are given in Table 20 while their distribution is indicated in Table 21.

TABLE 20

TEXTURAL CLASSIFICATION OF THE TROMPSBURG TITANIFEROUS MAGNETITES

TYPE	RELATIVE fO_2 DURING COOLING	DISTINGUISHING FEATURES	NOTES
1	Very low	Abundant ulvospinel, ilmenite trellis lamellae virtually absent. Abundant fine-grained spinel lamellae.	The most common microstructure. Extensively developed in cycle 1 and part of cycle 3.
2	Low	Extensive coarse-grained ulvospinel. Apatite crystals of various sizes. Virtually no aluminous spinel.	Characteristic texture in the apatite-rich ores which are restricted to the upper portions of cycles 2 and 3.
3	Low	Moderate amounts of ulvospinel with a minor development of fine ilmenite trellis lamellae interspersed with ulvospinel. Fine grained aluminous spinel lamellae.	Relatively rare. Type 1 grades into this type which is commonly developed as a local variant.
4	Moderate	Virtually no ulvospinel, minor broad ilmenite lamellae, abundant fine ilmenite lamellae of various types. Fine-grained aluminous spinel lamellae.	A very rare texture. Restricted to samples near to 17/2.

TABLE 20 (cont.)

TYPE	RELATIVE fO$_2$ DURING COOLING	DISTINGUISHING FEATURES	NOTES
5	High	No ulvospinel, minor broad ilmenite lamellae. Abundant fine spinelliferous ilmenite lamellae set in an optically homogeneous titaniferous magnetite groundmass. No lamellar aluminous spinel.	A characteristic texture developed in the ores of cycle 2. Not developed elsewhere.
6	Highest reached	No ulvospinel, minor broad ilmenite lamellae. Abundant medium-sized ilmenite trellis lamellae. No very fine-grained groundmass textures. Granules of fine-grained ilmenite developed between ilmenite lamellae. Abundant fine-grained lamellae.	A very rare texture. Restricted to sample 24/5.

The textures containing abundant ulvospinel indicate that the sub-solidus cooling took place under relatively low oxygen fugacities at almost all levels in the Complex. Certain textural types are however restricted to specific zones as illustrated by type 5 that is typical of cycle 2 and type 2 which is found in the apatite-rich areas. Samples 17/2 and 24/5 appear to have cooled under conditions of relatively high oxygen fugacity that are not characteristic of the Complex as a whole. Their position at the bottom of cycle 3 that otherwise exhibits type 1 textures might indicate that they are incorrectly positioned.

TABLE 21

VARIATION IN V_2O_5 CONTENT AND MICROSTRUCTURAL DEVELOPMENT OF THE

TROMPSBURG TITANIFEROUS MAGNETITES WITH INCREASING HEIGHT

SEAM NUMBER	V_2O_5 CONTENT (%)	DOMINANT MICROSTRUCTURAL TYPE	CYCLE
Apatite-rich Zone		2	
19	0,65	1	
	0,70	1	
18	0,71	1	3
	0,78	1 - 2	
17	0,77	6	
16	0,77	4	
Apatite-rich Zone		2	
15	–	?	
14	0,63	2	
13	0,65	3 - 5	2
12	–	5	
11	–	5	
10	–	5	
9	0,87	1	
8	0,63	1 - 2	
	0,72	1 - 2	
7	0,70	1	
	0,77	1	
6	0,76	1 - 2	1
5	0,78	1	
4	0,80	1	
3	–	?	
2	0,76	?	
1	0,80	1	

The other minor elements do not appear to exhibit any systematic
variation between the ores from different levels and cannot be used
to refine the sample distribution to any marked extent.   Ortlepp (1959)
concluded that the Complex is a composite body on the basis of a lack of
compositional variation in the Trompsburg minerals and proposed that its
peculiar iron-enriched nature was due to its derivation from the fractional
crystallisation of magma at depth.   His data do not indicate the presence
of relatively small scale cyclic features in the Complex, but this might
be due to his sampling at rather widely spaced intervals.

The analytical data obtained have not been particularly helpful in
elucidating the correct sequence in the Trompsburg ores and the lack of
marked mineralogical variations in the titaniferous magnetites over a
vertical distance of approximately 300m is problematical.   The
replenishment of the iron-enriched magma by successive heaves of
fractionated magma might account for the observed reversals in V_2O_5
content in the three broad cycles and other compositional variations in
the ore.   The distribution of samples as indicated in Table 21 must be
regarded with caution and it is hoped that a future drilling programme
may establish the correct sequence.   The recognition of an extremely
well developed cyclic repitition of units (Logan, personal communication)
indicates that the relationships during crystallisation were probably
far more complex.

11.8 Discussion

The Trompsburg ores can be distinguished both chemically and texturally
from those of the other Complexes studied and they also differ in that
the serpentinized olivine is the dominant silicate impurity.   Certain
of the apatite-bearing silicate-rich ores closely approach the
composition of the olivine-apatite-magnetitites of the Villa Nora area
of the Bushveld Complex (Grobler and Whitfield, 1970) . None of the
samples examined contains more than 15 per cent apatite, but it is possible
that ores containing greater amounts might be present.

The large ilmenite grains appear to have been co-precipitated together
with the titaniferous magnetite while their relatively large size also
suggests a similar mode of occurence in the silicate-poor ores.   The
relative abundance of coarse-grained ilmenite in the silicate-rich ores

and its contrasting paucity in the silicate-poor ores has also been noted
in other basic intrusions. Vincent and Phillips (1954) reported a
similar relationship in the Skaergaard intrusion and suggested that
sufficient oxygen was available during the precipitation of the silicate-
rich ore to allow for the high-temperature crystallisation of ilmenite.
During the crystallisation of the ore-rich bands, however, they suggested
that insufficient oxygen was available and this resulted in the formation
of ulvospinel which remained in solution in the titaniferous magnetite.
Molyneux (1970a) reported a similar relationship in the Bushveld ores.

The formation of magnetite requires the oxidation of some Fe^{2+} to Fe^{3+}
which implies that the formation of a titaniferous magnetite seam requires
a large-side oxidative effect as discussed in section 3. An ulvospinel-
magnetite solid solution is generally co-precipitated together with an
ilmenite-hematite solid solution during the normal crystallisation of
basic rocks and their compositions are controlled largely by temperature
and oxygen fugacity (Buddington and Lindsley, 1964).

The factors controlling the relative amounts of cubic and rhombohedral
phases that would be precipitated at any particular stage and the
fractionation of Ti between them have, however, not been investigated.

An extensive literature survey has shown that titaniferous magnetite
ores and titaniferous magnetites from basic rocks (in particular,
homogeneous single-phase titanomagnetites from chilled basalts) invariably
contain less that 25 per cent TiO_2 (approximately equal to 70 per cent
ulvospinel). Annersten et al. (1973) studied magnetite-ulvospinel solid
solutions using x-ray diffraction and Mössbauer spectroscopy techniques
and concluded that the Ti was incorporated in both the tetrahedral and
octrahedral sites in the range 20 to 70 mole per cent ulvospinel. At
higher concentrations, the substitution takes place mainly in the
octahedral sites or the smaller ions may possibly substitute in the
tetrahedral sites. This relationship suggests that the incorporation
of Ti into the magnetite lattice might take place relatively easily up
to 70 mole per cent ulvospinel, but would take place with greater difficulty
at higher Ti concentrations. This might account for the apparently
limiting TiO_2 content of 25 per cent in titaniferous magnetite.

Ilmenite is formed from Fe^{2+} and Ti^{4+} and can be precipitated once magma

of the appropriate composition enters the ilmenite stability field
on cooling. The precipitation of magnetite requires that some
oxidation of Fe^{2+} to Fe^{3+} occurs and it is possible that some of the
available Ti might be preferentially incorporated into the crystallising
cubic phase rather than into ilmenite. During normal crystallisation
(of basic igneous rocks) the oxygen fugacities are such that, although
some magnetite is formed that can accomodate up to 25 per cent TiO_2,
sufficient Ti remains in the magma to allow for the co-precipitation
of ilmenite. During large-scale oxidation and the formation of abundant
magnetite, much of the TiO_2 might become incorporated into a magnetite-
ulvospinel solid solution and insufficient remain available for the
co-precipitation of ilmenite. Re-equilibration of TiO_2 between the
co-existing rhombohedral and cubic phases will subsequently continue to
take place during slow cooling as discussed by Buddington and Lindsley
(1964).

The high-temperature crystallising spinel might conceivably act as a
TiO_2 scavenger and preferentially take up the available titanium in the
form of a magnetite-ulvospinel solid solution to a limiting value of
approximately 25 per cent TiO_2. The rate of this magnetite precipitation
from the iron-enriched residual liquid is controlled by the prevailing
oxygen fugacity which will concequently also control the rate of TiO_2
removal from the magma. The greater the amount of magnetite that is
precipitated at any particular time, the larger will be the amount of
TiO_2 removed from the magma resulting in a decrease in the rate of
ilmenite precipitation. The possible reasons for the large-scale changes
in oxygen fugacity in the cooling magma have been discussed in section 3.

At times when copious quantities of magnetite are formed, such as during
the precipitation of a titaniferous magnetite cumulate layer, it is
conceivable that the bulk of the available TiO_2 will be incorporated into
the spinel phase with the result that little or no discrete ilmenite will
be co-precipitated. In cases of more extreme oxidation, the amount of
magnetite precipitation might become so great that the overall TiO_2 content of
the magnetite drops below 25 per cent due to its depletion in the magma
and there is no co-precipitation of ilmenite.

Conditions in the magma would return to normal after a widespread magnetite
precipitation event and the TiO_2 content of the residual liquid would again

increase. Lower oxygen fugacities would allow for the precipitation of only relatively minor titaniferous magnetite and ilmenite crystallization would again be initiated. Coarse-grained ilmenite and titaniferous magnetite are commonly developed in rocks only a short distance above the titaniferous magnetite cumulate layers which suggests that there is either a rapid return to normal conditions or else other factors might also have been involved in the formation of these layers. It is possible that the rate of magnetite precipitation increased so dramatically as a result of sudden oxidation that it completely overwhelmed the ilmenite which continued to precipitate at the normal rate. The ilmenite would then have accumulated as a minor phase in the resulting spinel-rich cumulate layer and the amount of co-precipitated ilmenite present would reflect the rate of magnetite crystallisation. The common occurrence of increasing amounts of granular ilmenite with a progressive increase in silicate content in the Trompsburg rocks also suggests that this is in part due to the relative decrease in the amount of magnetite precipitating at any stage, allowing for the accumulation of other phases. This proposed mechanism can account for the apparently antipathetic relationship between coarse-grained co-existing ilmenite and titaniferous magnetite in basic rocks. Alternatively, the oxidation event responsible for the extensive titaniferous magnetite crystallisation might also change the physcio-chemical conditions of the melt so that it is no longer in the ilmenite stability field.

Ortlepp (1955,1959) favoured the view that the Trompsburg magma was volatile-rich which led to the formation of abundant Fe^{3+}. The resultant large amount of oxygen caused the crystallisation of abundant magnetite rather than a ferrous silicate (fayalite) so that a foresteritic olivine was formed in an iron-rich environment. The experimental data of Speidel and Osborn (1967) indicate that a Mg-rich olivine co-exists with an Fe-rich spinel phase and liquid at temperatures above 1300°C and moderately high oxygen fugacities. The relationships in the $MgO-FeO-Fe_2O_3-SiO_2$ system are complex and are dependent on both temperature and oxygen fugacity (Speidel and Osborn, 1967). The presence of additional elements such as Al and Ti as well as volatiles would alter the phase relationships and might depress the temperatures to levels more acceptable in a crystallising basic magma.

Speidel and Osborn (1967) also noted that the Mg distribution between the

various co-existing phases in equilibrium with vapour at sub-solidus
temperatures also changes as a function of temperature and oxygen
fugacity.   In particular, the Mg content of the olivine will be higher
than that in the co-existing pyroxene and spinel phases if the oxygen
fugacity is held constant during equilibrium cooling or decreases at
a moderate rate.   The olivine will thus exhibit an increased MgO
content on cooling while that of the co-existing spinel will decrease.

The silica deficient nature of the Trompsburg magma during the
crystallisation of the ores is reflected in the abundance of
co-precipitated olivine instead of other ferromagnesian silicates.   The
Mg-rich nature of the olivine is largely a result of the partitioning
of this element into the silicate rather than oxide phases and is not
anomalous in view of the experimental data of Speidel and Osborn (1967).
The chemical composition of the Trompsburg magma must, however, have been
rather different to that of the other basic complexes investigated and
would probably fall into the category of a basic magma of low silica
activity according to the data of Carmichael et al. (1974).

The co-existing coarse-grained ilmenites are also Mg-rich (4,8-8,7 per
cent) and the discussion of similar ilmenites from the Kaffirskraal
Complex in section 10.7 is equally applicable here.   The MgO-rich nature
of these ilmenites indicates its preferential partitioning into the
rhombohedral rather than cubic phases in accordance with the experimental
data of Thompson (1976) and Speidel (1970).

The extensive fracturing of the opaque oxides during volume changes
associated with the serpentinisation of olivine has increased the
permeability of the Trompsburg ores and increased the surface areas along
which reactions can occur.   The variety of late-stage products
indicate that a complex series of interactions were involved which
included late-stage magmatic fluids and were controlled by the fugacities
of oxygen and carbon dioxide.   The various alteration and secondary
mineralization processes must also have been operative concurrently or
been related in time   because of the intimate association of many of
their products.

The extensive olivine serpentinization occurred at a late stage after
the crystallisation of the ores was largely complete as the related
fractures transgress all the larger scale microstructures such as

ilmenite lamellae. Serpentinized olivine is present in ores recovered
from a depth of more than 300m below the pre-Karoo surface so that
the serpentinization is unlikely to be the result of near-surface
weathering processes. The presence of sulphides, graphite and sphene
along with serpentine and magnetite in the filled fractures indicates
that the alteration might have occured at slightly elevated temperatures,
possibly during the later stages of cooling after the majority of
microstructures had developed in the ores. The serpentinization of
olivine, particularly the magnesian varieties, takes place readily in
the presence of water at temperatures below 400°C (Deer et al., 19 a).

The alteration of titaniferous magnetite to sphene during late-stage
magmatic processes has been discussed with reference to the Usushwana
Complex in section 8.8 and is equally applicable here. The formation
of sphene and associated alteration products is less pronounced than
in the Usushwana Complex and is restricted to certain portions of some
of the ore- and silicate-rich layers. This is in contrast to the other
types of late-stage phenomena that are very much more widely distributed.
This local sphene development and the lack of evidence suggesting that
the Complex has been metamorphosed implies that the alteration is related
to late magmatic processes similar to those reported for the Bushveld
Complex by Willemse (1969) and Molyneux (1970a).

The greatest amount of sphene development is associated with the presence
of secondary veinlets containing sericite, epidote and calcite. The
plagioclase in these samples is generally extremely saussuritized while
the pyroxene is uralitized and the serpentinized olivine replaced by
calcite. These factors suggest the presence, at least locally, of a
carbonate-rich fluid phase during this period of cooling.

The alteration and sphene development appears to have taken place at
somewhat higher temperatures as suggested by Desborough (1963) and
Davidson and Wyllie (1968). Portion of the late-stage magnetite might
have been precipitated as a direct result of this process. The Ti
required for sphene formation can be supplied from the ulvospinel in the
magnetite while the Ca and Si are available either in the associated
plagioclase or late-stage fluids.

The alteration of the transparent exsolved spinel generally takes place

in the areas adjacent to the sites of sphene development which suggests
a relationship between them. The exact nature of the alteration product
is not known, but it might be a chlorite, diaspore or high-alumina clay
such as gibbsite.

The sulphide mineralization appears to encompass both primary and
secondary types. The larger primary grains of nickeliferous
pyrrhotite and pentlandite are locally abundant and resemble the opaque
oxides in form, being moulded around the earlier-formed silicates.
These sulphides are commonly surrounded by, and are sometimes veinel by
graphite. Small amounts of pyrrhotite, and less commonly pyrite, are
present in the narrow transgressive veinlets where they are associated
with other late-stage phases. The pyrrhotite more rarely shows minor
replacement of the titaniferous magnetite. These sulphides are
secondary in nature and their presence indicates that sulphur fugacities
were also locally important during the late-stage processes.

Sulphides of the pyrrhotite-pentlandite-chalcopyrite groups are commonly
found in basic intrusions. Liebenberg (1970) described their local
concentration as intercumulus phases in anorthosites immediately below
the Main and Upper magnetite seams of the Bushveld Complex. He also
reported the presence of small amounts of sulphide in the other rock
types including the titaniferous iron ores and concluded that they
crystallised from the intercumulus liquid. Von Grunewaldt (1976)
described the association of sulphides and titaniferous magnetite in
the Upper Zone of the eastern Bushveld Complex. Many features shown
by these sulphides are also exhibited by the Trompsburg ores and, in
particular, secondary sulphides, usually pyrrhotite, are associated with
secondary magnetite, serpentine and ilvaite while primary intercumulus
sulphides of the pyrrhotite-chalcopyrite-pentlandite-cubanite association
are also present. The secondary pyrrhotite occasionally replaces
titaniferous magnetite.

The occurrence of sulphides in basic rocks has been reviewed by Maclean
(1969) and Haughton et al. (1974), who showed that silicate melts with
high FeO contents are capable of dissolving increased amounts of sulphur
since it forms bonds with the Fe^{2+} in the melt. The sulphur solubility
is also dependent on oxygen fugacity since as it increases, more
oxidation of Fe^{2+} to Fe^{3+} will occur, resulting in the formation of
magnetite. The crystallisation of magnetite in turn lowers the FeO

content of the magma which consequently reduces the sulphur solubility causing the precipitation of sulphide.

The occurrence of sulphide associated with spinel-rich layers in basic intrusions has been reviewed by Irvine (1975b) who suggested that the addition of silica to a mafic melt might cause the precipitation of a sulphide-rich liquid. The mechanism is based partly on the relative differences in the crystal field stabilization energies of Fe^{2+} in o..ide, silicate and sulphide structures. The introduction of excess silica into a cooling basic silicate melt just saturated with olivine or pyroxene and sulphide liquid would reduce the number of octahedral sites in the silicate liquid. The Fe^{2+}, Ni^{2+} and Cu^{2+} that normally occupy these sites would thus be preferentially expelled. The dissolved sulphur in the melt is, however, bonded largely to those ions so that it will also be expelled resulting in the separation of a sulphide liquid.

Buchanan (1976) reported that sulphide concentrations are commonly associated with magnetite in Bushveld rocks from the Bethel area. He also concluded that the sulphur solubility in iron-rich magmas is dependent on FeO activity and the oxidising influence of increasing oxygen fugacity. Buchanan (1976) also noted that the sulphide-rich concentrations are associated with the marker horizon in the Bethel area and attributes their formation to an increase in oxygen fugacity caused by an influx of fresh magma at this level. Von Grunewaldt (1976) concluded that the abundance of sulphide in the Bushveld Upper Zone is a result of crystallisation conditions that led to an increase in sulphur in the residual melt while fractional crystallisation raised the FeO content and so increased sulphur solubility. The influx of a large amount of fresh, undifferented magma then added more sulphur to the melt which became further saturated as crystallisation proceeded until conditions were reached that were favourable for the separation of a sulphide liquid.

The presence of large sulphide grains in the Trompsburg igneous rocks and their association with titaniferous magnetites is comparable with similar occurrences in other complexes and can be explained in an analogous manner. The late-stage sulphide veinlets are, however, more problematical and their presence suggests the presence of sulphur,

possibly in the form of SO_2, as a component of the late magmatic fluids.
SO_2 is a common constituent of magmatic gases (Gerlach and Nordlie, 1975b)
so that sulphur would presumably also be a component of late-stage
magmatic fluids. The iron necessary for the formation of pyrrhotite or
pyrite would also be available from the serpentinization of olivine and,
to a lesser extent, from the dissolution of magnetite. Crystallisation
of late-stage sulphide would thus take place locally along the fractures
where the correct physico-chemical conditions were attained.

Late-stage oxidation of both granular- and vein-type pyrrhotite to form
magnetite is a common feature in these ores and appears to post-date all
other features. This oxidation has destroyed portion of the original
secondary pyrrhotite and it is not possible to distinguish it under the
microscope from the magnetite produced by serpentinization.

This type of pyrrhotite may consequently have originally been more widely
distributed. The common association of this pyrrhotite with secondary
magnetite and graphite in the veinlets indicates the operation of complex
crystallisation processes during the later stages of volatile activity.

The presence of abundant graphite along many of the fractures and its
replacement of spinel exsolution bodies also indicate that it is a
late-stage crystallization product. The origin of this graphite and
its common association with titaniferous magnetite and sulphides is
also problematical, but suggests a complex interplay of late-stage fluid
processes involving changes in oxygen, carbon-dioxide and sulphur
fugacities, as well as composition and temperature.

The author has not been able to locate any literature dealing specifically
with the occurrence of graphite and titaniferous magnetite although
Ramdohr (1969) reported that the association is commonly developed in
titaniferous iron-ores and that the graphite is "orthomagmatic". It
was not noted in the ores from the other deposits examined while
Molyneux (1970a,b) does not report its presence in the Bushveld ores
either. Leibenberg (1970) reported the common association of graphite
with sulphides in the Vlakfontein nickel deposit in the Bushveld Complex.
Vermaak (1976) suggested that the graphite in the Vlakfontein ores formed
by the reduction of CO_2 in a reducing environment within the vincinity
of the sulphides.

The probable source of the carbon in the graphite of the Tromsburg ores was in either CO or CO_2 that was present in the late-stage fluid or gaseous phases. Two possible sources of CO or CO_2 exist ; (i) large quantities would have been produced by decarbonation reactions associated with the thermal metamorphism of the dolomitic country rocks, and (ii) they are common components of volcanic gases and are present in small amounts in the magma (Gerlach and Nordlie, 1975a, b). The large amount of graphite in these ores and its apparent absence from other similar ores suggests that in this case the carbon was introduced during metamorphism of the country rocks.

The deposition of late-stage graphite in the Trompsburg ores might be anologous to the precipitation of carbon in the cooler, upper parts of a blast furnace. This is a common phenomenon and involves relatively low temperature (400-500°C) reactions involving the reduction of iron oxides and the formation of C and CO_2 (Newton, 1959). The large amount of titaniferous magnetite would tend to buffer the oxygen and carbon dioxide fugacities during cooling while the abundance of exsolved ulvospinel indicates relatively reducing conditions during sub-solidus cooling. Carbon monoxide decomposes at temperatures between 400 and 500°C to yield carbon and CO_2 (Habashi, 1969) so that a reaction of this type might also be involved in the graphite precipitation.

The extensive serpentinization of the olivine suggests the presence of water-rich fluids at some stage during the late-stage cooling history and this would have also affected the graphite stability relationships. Carbon is metastable in the presence of hot water vapour and decomposes to yield CO and H_2O (Newton, 1959 ; Habashi, 1969). The association of graphite with sulphides and magnetite in the late-stage veinlets thus poses numerous problems and highlights the complex interplay of reactions that took place during the later stages of the cooling of this Complex.

The presence of apatite in the Trompsburg ores is not unusual since it is commonly present in the late-stage fractionation products of large basic intrusions such as the Skaergaard and Bushveld Complexes (Wager and Brown, 1968). Willemse (1969a) reported the appearance of apatite approximately 900m above the main magnetite seam in the Bushveld Complex. It continues to be present at higher levels and is locally an important constituent of the rocks. Apatite-rich zones are also

present in the Rooiwater Complex (van Eeden et al.,1939) while rocks resembling the Trompsburg apatite-rich ores have been described from the Villa Nora area of the Bushveld Complex (Grobler and Whitfield,1970).

The occurence of iron-titanium oxide-apatite ores has been reviewed by Philpotts (1967) who noted that many of these ores have a ratio of two parts opaque oxide to one part apatite. Experimental data indicate the existence of a eutectic between the oxide and apatite phases at this composition and that this eutectic mixture forms an immiscible liciu with a silicate melt of dioritic composition. Grobler and Whitfield (1970) reported the presence of small globular chlorite inclusions in the Villa Nora apatites and speculated that they might indicate liquid immiscibility between the apatite-magnetite and silicate melt.

The Trompsburg apatite is present in variable amounts, but the ratio of opaque oxides to apatite is invariably much greater that 2 to 1. The preferential association of the apatite with the opaque phases, either as inclusions or as discrete grains arranged along their grain boundaries is in sharp contrast to its virtual absence from the associated silicates. This feature is noteworthy and suggests a relationship between the opaque oxides and apatite. The apatites contain abundant fluid inclusions and small, rounded opaque intergrowths together with other pale-coloured, unidentified phases, some of which might be chlorite. The apatite-rich zones appear to be located towards the top of cycles 2 and 3 which suggests that they crystallised from the phosphorous-rich residual liquids of these two postulated magma influxes.

The highly aluminous nature of the Trompsburg ores is reflected in the abundance of a wide variety of exsolved, transparent aluminous spinel phases. They resemble the ores of the Mambula Complex in this respect and the discussion in section 9.7 is equally applicable here. The Trompsburg ores are located in a relatively Al-rich troctolitic environment that is developed both above and below the seams. These rocks also exhibit relatively low SiO_2 contents (Ortlepp, 1959). A mechanism of the type suggested by Carmichael et al. (1974) in which the titaniferous magnetites of magmas of low silica activity become relatively enriched in Al_2O_3 presents a possible explanation of this phenomenon.

11.9 <u>Genesis of the Trompsburg Ores</u>

Ortlepp (1955,1959) considered that the Trompsburg Complex was emplaced
as a composite sheet-like body and that the titaniferous magnetite ores
form distinct layers. He concluded that the differentiation was
controlled largely by clinopyroxene fractionation while the high Fe_2O_3
content of the gabbros and abnormal association of massive iron-ore with
troctolite are due to high oxygen fugacities during cooling.

The mineralogical and textural evidence present here suggest that the
genesis and microstructural evolution of the Tromsburg ores was as follows:-

1. The various ore-rich layers formed as cumulate rocks during fractional
   crystallisation of an iron-enriched mafic magma as discussed in section
   3. A fresh influx of fractionated iron and sulphur-rich magma occurred
   after the crystallisation of the cycle 1 seams. Continued crystallisa-
   tion resulted in the formation of the cycle 2 seams and their associated
   sulphide mineralisation. Phosphorous became concentrated in the
   residual liquid towards the end of this cycle resulting in the
   appearance of locally abundant apatite. A further influx of iron-
   rich magma gave rise to the cycle 3 seams which also show late stage
   apatite crystallisation. The V_2O_5 content of the magnetite decreases
   from approximately 0,8 per cent at the base of each cycle to 0,6 per
   cent at the top.

2. The titaniferous magnetite-rich layers formed by the accumulation of an
   initially homogeneous high-temperature spinellid phase containing Fe, Ti,
   Al, Mg, V and Mn together with small, but variable, amounts of olivine,
   ilmenite, augite and plagioclase. The opaque oxides are generally
   cumulus minerals, but they might represent inter-cumulus phases in the
   more silicate-rich samples. The association of sulphides with the ores
   at certain levels might be due to the separation of an immiscible
   sulphide liquid.

3. Post-cumulus growth processes, the removal of intergranular fluids by
   filter-pressing and annealing may also have played an important role
   in the development of ore-rich horizons. Minor entrapped silicate
   liquid would have crystallised as various silicate phases or might have
   contributed to the development of late-stage reaction rims between early-
   formed oxides and silicates.

4. At the commencement of cooling, exsolution of a titanium-rich, rhombohedral oxide phase was initiated in the spinel resulting in the formation of several per cent by mass of intergranular ilmenite and possibly some of the larger ilmenite lamellae. This is probably true exsolved ilmenite and corresponds to the "external granule" exsolution described by Buddington and Lindsley (1964) and is in agreement with the data of Anderson (1968b). This type of exsolution is thought to cease once temperatures drop below about 750°C and any ilmenite present in amounts greater than 5 per cent would have formed by a complex oxidation/exsolution process. The nature and location of these lamellae and grains suggest that they nucleated at grain boundary imperfections with the grains growing externally while the lamellae grew into the titaniferous magnetites. Grain boundary adjustment would also have occurred due to adcumulus growth and annealing at these temperatures leading to the formation of polygonal grains having interfacial angles approximating 120°.

5. Once temperatures had fallen to below approximately 900°C, exsolution of the aluminous spinel would have commenced. Nucleation would have preferentially occurred at grain boundary imperfections at the higher temperatures resulting in the growth of small grains along the titaniferous magnetite grain boundaries and along ilmenite lamellae. Lower ionic mobility with decreasing temperature results in an increasing supersaturation away from the pre-existing spinel granules and leads to the development of fine spinel lamellae along (100) of the titaniferous magnetite. The period of spinel exsolution overlapped with the lower-temperature portion of stage 4 and continued down to the temperatures at which exsolution effectively ceases. The spinelliferous ilmenite rims would have developed during grain-boundary adjustment during this period.

6. The microstructural development in the temperature range between approximately 750 and 600°C is dependent largely on oxygen fugacity and a variety of textural types developed, as shown in Table 20. The oxygen fugacities were sufficiently low for the bulk of the ores during this stage of cooling and favoured the stability of an homogeneous magnetite-ulvospinel solid solution and only minor exsolution of Ti-rich phases occurred (types 1 and 2). Increases in oxygen fugacity occurred locally during this stage leading to the

oxidation/exsolution of fine ilmenite trellis lamellae along (111) of
the magnetite (types 4,5 and 6).

7. The magnetite-ulvospinel solvus is intersected at approximately 600°C
and exsolution of ulvospinel along (100) of the magnetite commences
under conditions of low oxygen fugacity (Vincent et al.,1957). The
bulk of the Trompsburg microstructures developed under these
conditions, but oxygen fugacities were higher locally resulting in the
oxidation/exsolution of various-sized, very fine-grained ilmenite
lamellae. The ratio of ilmenite to ulvospinel is dependent on oxygen
fugacity and ilmenite is formed at the expense of ulvospinel. The
range of textural types from 3 to 6 reflect progressively increasing
oxygen fugacities and a consequent decrease in ulvospinel content.

Cooling through this temperature range would also result in the
continued exsolution of aluminous spinel and the numerous dislocations
along ilmenite lamellar grain boundaries would have provided
nucleation sites resulting in spinelliferous rims round the smaller
lamellae as well. Hematite exsolution from ilmenite would also occur,
but in the bulk of the ores the oxygen fugacities were lower than those
required for the reduction of hematite to magnetite. This resulted in
the formation of magnetite lamellae in the coarser-grained ilmenites
by a contemporaneous reduction/exsolution process.

Local fluctuations in oxygen fugacity also occurred at this time,
presumably related to the movement of interstitial fluids so that minor
lamellar ilmenite was developed around grain boundaries and along
fractures, even in some of the ulvospinel-rich ores.

8. Cooling to lower temperatures would result in a continuous
re-equilibration process between co-existing oxides and silicates while
exsolution or oxidation/exsolution would continue until diffusion
rates became too slow and effectively ceased. The microstructural
development would be essentially complete at this stage which would
have been at temperatures of "several hundred degrees" (Buddington and
Lindsley, 1964).

9. Late-stage volatile activity became important towards the close of

stage 8 and the local dissolution of magnetite occurred resulting in
sphene and chlorite precipitation. Widespread serpentinization of
olivine resulted in the extensive fracturing of the ores and produced
larger surface areas for reaction. A complex influence of late-stage
fluids resulted in the alteration of transparent spinel and the
deposition of late-stage graphite and sulphide along the fractures
together with serpentine and secondary magnetite. Oxidation of part
of the pyrrhotite to magnetite occurred and it is possible that local
oxidation of exsolved ulvospinel lamellae to ilmenite also occurred.
Temperatures were too low, however, to allow for any microstructural
modification of the intergrown phases to occur.

11.10 Conclusions

1. The Trompsburg vanadium-bearing titaniferous iron ores can be compared
   chemically and mineralogically with similar ores from other basic
   complexes. These ores are Al- and Mg-rich in contrast to the usual
   types and are associated with an environment rich in magnesian olivine.

2. The development of the Trompsburg titaniferous iron ores in discrete
   layers towards the upper parts of a large gabbroic intrusion is in
   accord with their having developed by the normal crystallisation -
   differentiation processes that are operative within intrusions of
   this type.

3. The minor element contents of the titaniferous magnetites do not exhibit
   a progrssive variation with increasing height in the Complex. The
   V_2O_5 variation suggests the presence of at least 3 cyles of
   crystallisation that might reflect the influx of fresh magma into the
   intrusion.

4. Considerable amounts of apatite are developed towards the top of cycles
   2 and 3. Apatite precipitation is a characteristic feature of late-stage
   magmatic crystallisation and its development at these levels also
   supports crystallisation from separate influxes of magma.

5. The Trompsburg ores vary between essentially pure titaniferous
   magnetite-rich layers through to various silicate-rich types containing
   up to 40 per cent olivine, augite and plagioclase. The silicate-rich
   ores are characterised by an abundance of large, coarse-grained

ilmenites, but their relative abundance decreases with respect to titaniferous magnetites as the silicate content decreases. The silicate-poor ores contain only minor granular ilmenite.

6. The grain size of the titaniferous magnetites in the silicate-poor ores is very much larger than the silicate-rich types. This coarsening in grain-size might reflect the operation of sintering processes in the spinel-rich layers during the earlier stages of cooling.

7. The Trompsburg titaniferous magnetites are characterised by the widespread development of ulvospinel that is indicative of subsolidus cooling under conditions of low oxygen fugacity. The local development of lamellar ilmenite indicates the presence of higher oxygen fugacities in certain areas.

8. The aluminous nature of the Trompsburg titaniferous magnetites is reflected in the widespread development of transparent spinel microintergrowths. These are developed in a wide variety of morphologies that are indicative of precipitation at various stages during the cooling process.

9. The co-existing coarse-grained ilmenites are particularly Mg-rich and exhibit MgO contents that are amongst the highest yet reported from non-kimberlite sources. Their high MgO contents reflect the preferential incorporation of this element into the rhombohedral phase during cooling.

10. The olivines in the Trompsburg ores have been extensively serpentinised and the resulting volume changes have resulted in widespread fracturing of the associated opaque oxides and silicate phases. The fractured minerals are extensively veined by serpentine and homogeneous magnetite derived from the altered olivine.

11. The Trompsburg ores have undergone extensive late-stage alteration resulting in the precipitation of variable amounts of late-stage graphite and sulphides along the numerous fractures. Minor dissolution of titaniferous magnetite has also occurred and has been locally replaced by sphene and chlorite aggregates.

12. The Trompsburg opaque oxides exhibit a wide range of complex relationships, both between themselves and their co-existing silicates. These relationships require further study and, in particular, the factors governing crystallisation in this Complex require detailed investigation.

13. The recognition of numerous thin cyclic units in the Trompsburg Complex associated with the titaniferous magnetite precipitation indicates that the crystallisation processes are far more complex than is suggested by earlier reports. A more detailed study of the mineralogical relationships over a realtively small vertical distance in the Complex should provide information that might account for the overall lack of well-defined minor element fractionation trends in the Trompsburg titaniferous magnetites.

14. The opaque oxides from a number of rock types ranging in composition from virtually oxide-free types to pure ores should be examined in order to determine the differences that exist between these phases when present in different concentrations. This would also provide information on the relationships between co-existing coarse-grained ilmenite and titaniferous magnetite.

15. The reported V_2O_5 analyses are at variance with the previously published values and indicate that it is present in insufficient quantity to warrant recovery. The contents range between approximately 0,6 and 0,8 per cent V_2O_5 and vary from seam to seam.

16. The complex is covered by approximately 1000m of younger sedimentry rocks and its ores cannot be considered as possible raw materials for V_2O_5 or high-titania slag production in view of the availability of suitable material from other more readily assessible sources.

12. CONCLUDING NOTE

This investigation has revealed the existence of chemical, mineralogical and microstructural differences between the various investigated South African titaniferous iron ores. The microstructural differences are largely a result of variations in sub-solidus cooling conditions, and are in some cases due to metamorphism.

The chemical differences are a result of slight variations in the compositions of the magmas from which the ores crystallised as well as variations in the crystallisation conditions.

The differences in bulk chemistry between the ores from the five Complexes are summarised in figure 5. The ores from each Complex plot in a specific field and there is only a small degree of overlap between several of the Mambula and Trompsburg analyses.
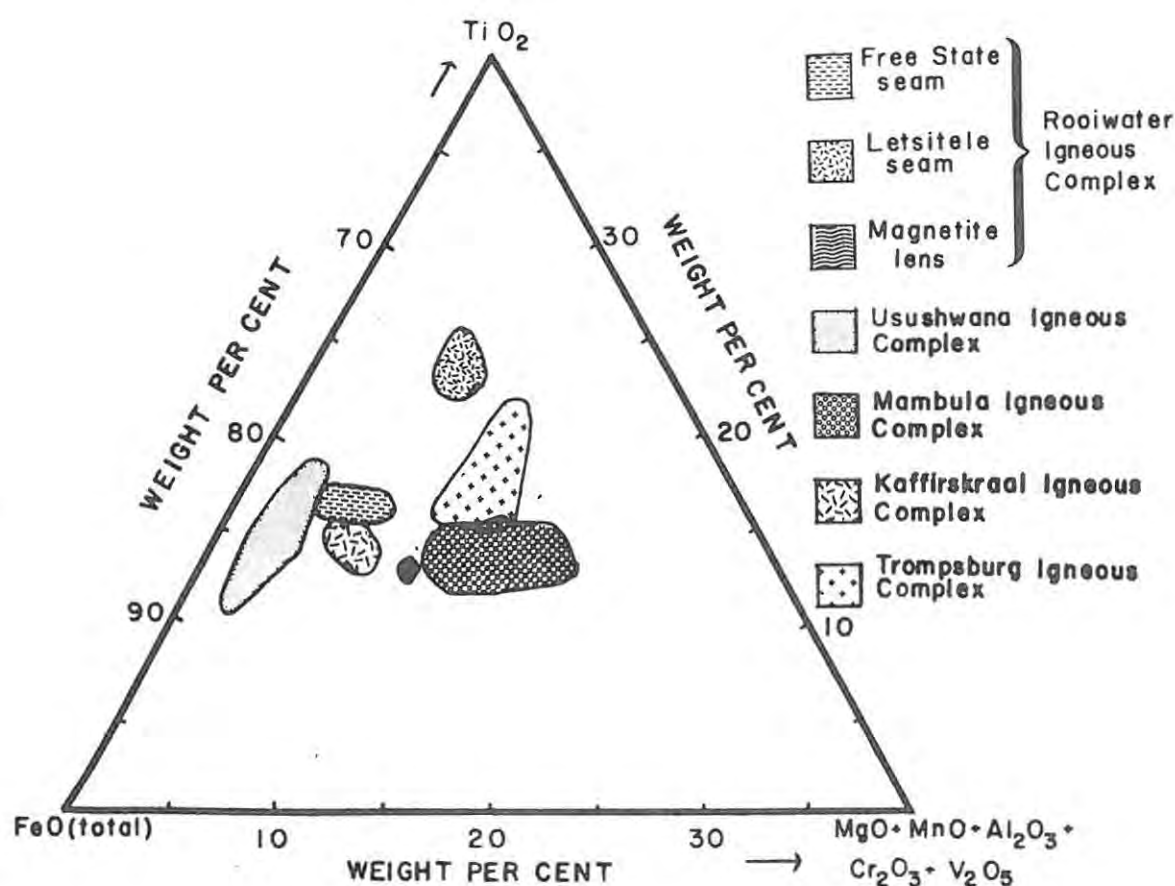
FIGURE 5: The range in chemical composition of the titaniferous iron ores of the Rooiwater, Usushwana, Mambula, Kaffirskraal and Trompsburg Complexes.

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APPENDIX 1.

MINERAL SEPARATION PROCEDURES.

A). At Rhodes University.

1). Half- to two-kilogram samples of rock were sawn into thin slabs on a diamond saw and were then broken into small pieces using a jaw-crusher. These fragments were then crushed by passing them through a roller-crusher with hardened steel rollers. Several passes were made through the crushers with the sample being sieved between each crushing and the less than 85 mesh fraction removed. The process was continued until all the material had been reduced to less than 85 mesh.

2). The rock powders were then mechanically sieved into the following 3 size fractions to facilitate mineral separation: (i) 85-120 mesh, (ii) 120-200 mesh, (iii) less than 200 mesh.

3). Each size fraction was deslimed by washing in water and a primary heavy mineral concentrate was prepared using a Haultain Superpanner.

4). The primary heavy mineral concentrates were then oven dried at $80^{o}C$.

5). The magnetic fraction was separated from each concentrate under acetone using a powerful permanent magnet. The samples were then again oven dried at $80^{o}C$.

6). The ilmenite was recovered from the remaining heavy mineral concentrate by means of repeated electromagnetic separations. The electromagnetic separator was set with both forwards and sideways tilts of 25° and was run at a current strength of approximately 0,2 amp.

B). At the National Institute for Metallurgy.

The method adopted was essentially the same, except the crushing was carried out in a "Siebtechniek" swing mill and the primary heavy mineral concentrate was prepared by means of heavy liquid separations using bromoform with a specific gravity of 2,89. This concentrate was subjected to a further separation using methylene iodide with a specific gravity of 3,2. The samples were washed with acetone and allowed to dry under infra-red lamps.

STANDARDS USED DURING WET CHEMICAL ANALYSES AND THE AVERAGE OF DUPLICATE

ANALYSES MADE ON THEM

	+ K1	K1	+ K7	K7	+ K8	K8	+ K12	K12	+ BS4	BS4	+ STD1	STD1	+ STD2	STD2	+ STD3	STD3	+ STD4	STD4
SiO_2	–	–	< 0,05	–	< 0,05	–	–	–	0,11	–	–	–		–		–	–	–
Al_2O_3	–	–	0,67	–	0,20	–	–	–	0,08	–	–	–		–		–	2,82	–
Fe_2O_3	7,61	7,82	10,33	9,68	13,50	13,65	10,57	10,91	8,36	9,79		1,62		24,51		22,91	–	28,87
FeO	21,30	21,00	24,44	25,03	24,72	24,10	22,97	22,17	40,36	38,50		0,72		14,61		21,11	54,37	27,98
MgO	14,24	14,38	11,49	11,56	10,44	10,81	12,02	11,99	0,57	0,64		0,02		0,43		0,03	3,03	3,00
CaO	0,11	0,10	0,38	0,32	0,02	0,03	0,32	0,31	0,10	0,09		0,02		0,09		0,09	0,20	0,15
TiO_2	52,87	52,84	51,85	51,83	50,10	50,56	51,96	51,73	49,54	49,99	96,20	96,42	58,8	58,72	54,2	54,20	36,61	36,47
Cr_2O_3	3,14	3,21	0,20	0,33	0,54	0,59	1,64	1,80	0,04	0,03	0,37	0,34		0,29		0,01	0,16	0,19
MnO	0,26	0,18	0,15	0,14	0,18	0,15	0,23	0,19	0,48	0,46	–	0,06		0,19		1,51	–	0,07
V_2O_5	–	–	0,26	–	0,20	–	–	–	0,20	–	–	–		–		–	0,46	–
TOTAL:	99,53	99,53	99,77	98,89	99,90	99,89	99,71	99,10	99,84	99,50	96,57	99,16		98,84		99,86	97,65	96,73

Sources of standards used : + indicates the standard, the unmarked analyses represent the average of duplicate determinations.

K1,K7, K8 : portions of large discrete kimberlite ilmenite nodules

K12 : kimberlite ilmenite concentrate from the Wesselton Mine

BS4 : ilmenite concentrate from the beach sand east of the Fish River (near the Old Woman's River mouth).

These five samples were analysed by the General Superintendence Co. S.A. (Pty) Ltd., Johannesburg as project 90173 and dated 26th March, 1973.

The methods used were : SiO_2 - gravimetric ; Al_2O_3, MgO, CaO, Cr_2O_3, V_2O_5 - atomic absorbtion spectroscopy ; TiO_2, MnO - spectrophotometric, FeO, Fe_2O_3 - volumetric.

Std 1 : Rutile concentrate - purchased from the Bureau of Analysed Samples, Middlesborough, England.

Std 2 and 3 : Ilmenite concentrate - purchased from the Bureau of Analysed Samples, Middlesborough, England.

Std 4 : A hemo-ilmenite concentrate supplied by Dr.Z.Katzendorfer, Quebec Bureau of Natural Resources, Canada.

APPENDIX 3

STANDARDS USED IN ELECTRON MICROPROBE ANALYSES

	1	2	3	4
SiO_2	0,49	0,43	–	0,11
TiO_2	1,51	51,88	54,01	50,16
FeO	23,57	40,87	23,23	33,40+
MgO	8,16	–	11,45	10,68
MnO	0,19	1,07	0,18	0,43
CaO	–	–	0,17	–
NiO	0,23	–	0,17	–
ZnO	0,11	–	–	–
CoO	0,10	–	–	–
Fe_2O_3	10,14	5,56	8,78	–
Al_2O_3	14,99	0,04		0,13
Cr_2O_3	39,71	–	1,52	3,46
V_2O_5	0,46	–	–	–
Na_2O	–	0,08	–	–
TOTAL :	99,66	99,93	99,51	98,37

Nature and Source of Standard :

1) Chromite from the Merensky Reef ex Dr.S.A. de Waal, NIM, Randburg.

2) Ilmenite ex Dr.K.Snetsinger, NASA, Moffet Field, California.

3) Kimberlite ilmenite ex Dr.C.Frick, S.A. Geol. Surv.

4) Kimberlite ilmenite ex Anglo American Research Laboratories, Crown Mines, Johannesburg.

+ Total Fe as FeO

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