Controls on the Distribution of Manganese in Banded Iron-Formations (BIF) of the Palaeoproterozoic Transvaal Supergroup, South Africa

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ABSTRACT

The 2.65 to 2.05 Ga Transvaal Supergroup comprises one of the best-preserved and largely continuous successions in the world of Banded Iron-Formation (BIF), a chemical sedimentary rock composed of fine (mm to cm scale) interbanded iron-rich and iron-poor bands, developed atop the Archaean Kaapvaal Craton of southern Africa. The Transvaal BIF sequence contains at its upper stratigraphic part, an intriguing interlayered BIF-Mn association, namely the Hotazel Formation in the Kalahari Manganese Field, which constitutes the largest land-based manganese deposit on record. The genesis of the Hotazel deposits, and their exact significance in terms of atmosphere-hydrosphere-biosphere evolution, remain as elusive as they are challenging. In this thesis, an attempt is made to illuminate the origin and diagenesis of the Hotazel Formation and its post-depositional hydrothermal modification, through a highresolution geochemical study of the narrowest of the three BIF-Mn sedimentary cycles present in the Hotazel stratigraphy. This approach is coupled with a preliminary geochemical study of the distribution of Mn in older BIF of the Transvaal Supergroup as well (Kuruman and Griguatown Formations), so as to test recent models that causally link all BIFs in the Transvaal Supergroup under a common and evolving palaeo-environment of deposition. The results indicate that the cyclic deposition of the Hotazel BIF and enveloped Mn-rich sediments would have taken place in a stratified basin with a well-developed chemocline in terms of the vertical distributions of Mn and Fe, much like recent anoxic stratified basins such as the Orca Basin in the Gulf of Mexico. The increased Mn abundances as Mn-bearing ferrous carbonates in the upper part of the Griguatown BIF predating the Hotazel strata, also seems to lend support to the notion that the two BIFs are temporally interlinked as part of a broader sedimentary continuum. Finally, the largely conservative behaviour of Mn and associated elements during hydrothermal alteration of the Hotazel rocks is re-assessed, and renewed emphasis is placed on the possibility that brine metasomatism may have been a key factor in Mn redistribution and residual enrichment.

DECLARATION

I declare that the thesis entitled: "Controls on the distribution of manganese in banded iron-formation (BIF) of the Palaeoproterozoic Transvaal Supergroup, South Africa" is my own work, that it has not been submitted for any degree or examination in any other university, and that all sources used or quoted have been indicated and acknowledged by complete references.

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1. INTRODUCTION, BACKGROUND AND SCOPE

1.1. TERMS AND DEFINITIONS

The term "Banded Iron Formation (abbr. BIF)" is conventionally used in the literature to describe a chemical sedimentary rock with a characteristically layered/banded texture, whereby bands of fine-grained iron-rich material are interlayered with bands dominated by microcrystalline quartz (chert). The scale of banding is known to range from sub-mm- to dm-thick, whereas individual bands can extend laterally over 100's of km (Gross, 1983). A variety of Fe-minerals can be seen in BIF, ranging from magnetite forming essentially mono-minerallic laminae, to chert bands rich in one or more Fe-rich carbonate or silicate mineral species such as siderite, minnesotaite, greenalite and stilpnomelane, among others.

Various classification schemes have been proposed in the past for the subdivision of BIF deposits on the basis of mineralogy, geochemistry, age, tectonic and palaeo-environmental setting. The classification of Gross (1983) into three key types utilising a combination of the above parameters (Figure 1.1), stands to date as the most widely used of these schemes.

Superior-type Iron Formation

BIF deposits belonging to the *Superior-type* are those deposited on stable, near-shore continental platform settings. They are characterized by a general lack of deformation, extensive lateral continuity, and association with lithologies such as platform carbonates, carbonaceous shales and quartz-arenites (Beukes and Gutzmer, 2008). Although the age range of the Superior-type BIFs extends from 3.5 to 1.8 Ga, a clear peak in their volume deposited was reached at *ca*. 2.5 Ga. It was during the latter time when two of the key BIF-hosting sequences of the world were formed, namely those of the Hamersley Group in Australia, and of the Transvaal Supergroup in South Africa (Klein, 2005).

Algoma-type Iron Formation

The mostly Archaean-age (3.5 to 2.7 Ga) *Algoma-type* constitutes the second class of BIF as defined by Gross (1983). Algoma-type BIFs are thought to have been deposited at or close to volcanically-active submarine environments, hence their common litho-stratigraphic association with volcanic rocks and siliciclastic sediments (Beukes and Gutzmer, 2008). Algoma-

type BIFs are commonly a key component of Archaean greenstone belts, and for that reason they are usually highly deformed and metamorphosed at mid- to high grades of regional metamorphism. This makes the reconstruction of their original depositional basins and estimations of volumes of sediment deposited very difficult to interpret (Klein, 2005).



Figure 1.1: Distribution of BIF across time, with relative depositional volumes also illustrated. The Transvaal Supergroup near the peak of BIF abundance is selected (Klein, 2005).

Rapitan-type Iron Formation

The *Rapitan-type* BIF shows an intimate stratigraphic association with thick sequences of glaciogenic deposits of Neoproterozoic age, interpreted to reflect global-scale glacial events. One of the additional key characteristic of these otherwise volumetrically small BIF occurrences is their temporal association with manganese-rich sediments. A good example of such a BIF-Mn association is reported by Klein and Ladeira (2004) from the Urucum deposits of Brazil. The renewed global-scale deposition of BIF during the Neoproterozoic combined with low latitude palaeo-magnetic data available for several of the deposits, have lent key support for the so-called *Neoproterozoic Snowball Earth* event, itself interpreted to be the main cause of temporary marine anoxia at that time which subsequently led to the deposition of Fe- and Mn-rich chemical sediments (Kirschvink, 1992; Klein and Beukes, 1993; Young, 2002; Klein and Ladeira, 2004; Klein, 2005).

1.2. PALAEO-ENVIRONMENTAL SIGNIFICANCE OF BIF

Compared to both the Algoma- and Rapitan-type BIF, the number of worldwide occurrences and geographic distribution of Superior-type BIF are relatively few and limited. However, this does not overshadow their importance in terms of the biological, chemical and climatic evolution of the atmosphere and oceans in the early Earth. The dominance of Superior-type BIFs specifically over the time interval 2.6 to 2.2 Ga, has rendered them prime targets for research into early Earth environments and processes across a period of major global change. It is widely accepted that at about 2.3 Ga ago, the redox state of the atmosphere shifted from anoxic to oxic (Bekker *et al.*, 2004); and this event has been termed the Great Oxidation Event (abbr. GOE) by Holland (2005), even though some authors argue that several events of shortlived oxygenation ("whiffs" of oxygen) may well have preceded the GOE (Anbar *et al.*, 2009). Proposed biological changes across the GOE include a possible shift from anaerobic photoferrotrophy to oxygenic photosynthesis, whereas a number of authors also argue for a causal connection between the GOE and one of the earliest events of global-scale glaciation (Snowball Earth) as encapsulated by the Huronian deposits of Canada (Kirschvink *et al.*, 2004; Kopp *et al.*, 2008).

In the above context, the Transvaal Supergroup of South Africa has its rightful place as one of the most complete archives of BIF-deposition during the critical interval between 2.6 to 2.2Ga. The following sections provide background information on the Transvaal Supergroup and its BIF component, and culminate in the presentation of the aims and objectives of the present thesis.

1.3 THE TRANSVAAL SUPERGROUP

The 2.65 to 2.05 Ga Transvaal Supergroup is a platformal succession consisting of chemical sedimentary rocks that developed over large parts of the Kaapvaal Craton of southern Africa (Figure 1.2). It is developed in two spatially separated basins, the *Transvaal Basin* in the central part of the Kaapvaal Craton and the *Griqualand West Basin* along the western edge of the craton, the latter extending beneath younger Kalahari deposits into southern Botswana (Beukes and Gutzmer, 2008). The Griqualand West Basin is composed predominantly of chemical sedimentary deposits of carbonates and banded iron formation (BIF) interbedded with minor glacial and volcanic units, and will constitute the focus of this thesis. Preserved outcrops of the Transvaal Supergroup cover an area of *ca.* 190,000 km² and is believed to have originally

covered the entire Kaapvaal Craton >600,000 km², attaining a total stratigraphic thickness of up to 11 km (Knoll and Beukes, 2009).



Figure 1.2: Locations of the sub-basins that make up the Transvaal Supergroup of southern Africa (after Moore *et al.,* 2001).

The stratigraphy of the Transvaal Supergroup is composed of a large variety of lithologies that display complex lateral and vertical facies variations across the basin. An analysis of these facies changes show that the individual Formations of the Transvaal Supergroup were deposited in environments that ranged from deep-water basinal settings right through into very shallow-platform settings above normal wave base (Klein and Beukes, 1989; Beukes and Klein, 1990; Klein, 2005; Beukes and Gutzmer, 2008).

1.4. THE GRIQUALAND WEST BASIN

The Griqualand West Basin of the Transvaal Supergroup overlies the western to south-western rim of the Archaean Kaapvaal Craton, and contains one of the stratigraphically best developed, continuous and laterally extensive Superior-type BIF preserved in the geological record. The basin consists of a conformable succession of carbonates, siliciclastics, BIF, and minor volcanics, as shown in a relatively simplified form on Table 1.1 (based on information from Horstmann and Hälbich, 1995; Polteau *et al.*, 2006; Beukes and Gutzmer, 2008; Knoll and Beukes, 2009).

Table 1.1: Stratigraphic subdivisions of the major formation of the Griqualand West Basin (after Polteau *et al.,* 2006).

Supergroup	Group	Subgroup	Formation	Lithology	Approx.thickness (m)		
		Voëlwater	Mooidraai (2.394 Ga)	Carbonate, chert	300		
	Postmashurg	VOElWater	Hotazel BIFs, Mn		250		
	1 0001110000118		Ongeluk	Andesitic lava	900		
			Makganyene	Diamictite	50-150		
			Rooinekke	BIF, dolomite	100		
			Naragas	Shale, siltstone			
Transvaal		Koegas	Kwakwas	Riebeckitic slate	240-600		
		(2.415 Ga)	Doradale	BIF			
	Ghaap		Pannetjie	Quartz wacke, shale			
			Griquatown (2.432 Ga)	Clastic-textured BIFs	200-300		
		Asbestos Hills	Kuruman (2.465 Ga)	Microbanded BIFs	150-750		
		Campbellrand	(2.557 Ga)	Carbonate, shale, chert	1500-1700		
		Schmidtsdrif	(2.642 Ga)	Shale, quartzite, lava, carbonate	10-250		

Due to its position on the structurally stable Kaapvaal Craton, the Griqualand West Basin and the Transvaal Supergroup as a whole are exceptionally well preserved, have experienced very little deformation, and were only subjected to burial temperatures in the range of 120 to 210°C at pressures of less than 2 kb (Miyano and Beukes, 1987; Cornell *et al.*, 1996; Johnson *et al*, 2003; Klein, 2005; Knoll and Beukes, 2009). It is only along the south-western corner of the Griqualand West Basin where the Kaapvaal Craton is jutted against the adjacent Namaqualand metamorphic belt, that the Transvaal rocks have experienced intense deformation (Altermann and Hälbich, 1991).

1.4.1 The Ghaap Group

Beukes (1983, 1984, 1987), Klein and Beukes (1989), and Beukes and Klein (1990) have produced a considerable body of research work with primary emphasis on the stratigraphy, sedimentology, geochemistry and depositional palaeo-environment of the *Ghaap Group*, the

stratigraphically lower part of the Transvaal Supergroup in the Griqualand West Basin. Particular emphasis in the above studies was placed on elucidating key stratigraphic transitions between the Campbellrand Subgroup and overlying Kuruman and Griquatown BIF Formations, as well as between the latter two BIF Formations.

The lower, *Campbellrand Subgroup* represents an up to 1,7 km-thick platformal carbonate succession, which ranges from stromatolitic, shallow-shelf deposits that thin out along the SW margin of the Kaapvaal Craton into a carbonate succession of finely laminated non-stromatolitic deposits. The carbonate deposits are composed mostly of dolomite and lesser limestone, with reworked micritic and biogenic material and unusually pyrite-rich carbonaceous shales, especially at their topmost part (Beukes, 1983, 1984, 1987; Klein and Beukes, 1989; Horstman and Hälbich, 1995; Beukes and Gutzmer, 2009).

The Campbellrand Subgroup is conformably overlain by a maximum of 1000 m thick BIF of the *Asbesheuwels Subgroup*; the latter is described in more detail in Chapter 3, hence only a brief reference is made here. Beukes (1983, 1984) and Beukes and Klein (1990) describe the lower member of the Asbesheuwels Subgroup, the *Kuruman Formation*, as a typically microbanded BIF with very fine mm-scale rhythmic banding that grades upward the stratigraphy from meso-and microbanded chert-magnetite-siderite BIF into more granular chert-carbonate-magnetite BIF. The finely laminated (microbanded) Kuruman BIF thus grades upwards into the mesobanded and more granular-textured BIF of the *Griquatown Formation*. Such facies transitions are very uncommon in the geological record and have essentially only been described from the Transvaal Supergroup (Beukes, 1980, 1983, 1984; Klein and Beukes, 1990; Beukes and Klein, 1990). However, in spite of the obvious textural differences between the Kuruman and Griquatown BIFs both are hard to distinguish geochemically and are therefore thought to have been deposited under broadly similar palaeo-environmental conditions (Beukes and Klein, 1990).

Beukes and Klein (1989) and Klein and Beukes (1990) describe the development of the Ghaap Group as an evolving depositional system, whereby the Campbellrand carbonates developed in a shallow-water regressive-stage of the depositional basin that experienced high organic carbon productivity and carbonate precipitation. Subsequent drowning of the basin by deep waters depleted in organic carbon and enriched in Fe, led to the deposition of the conformably overlying Kuruman Formation, which is composed of finely-laminated BIF rich in magnetite and Fe-silicate minerals. The progressively shallowing basin eventually recorded a transition from the deposition of the microbanded BIF facies of the Kuruman Formation into the mesobanded to granular and more carbonate-enriched BIF of the Griquatown Formation, the latter representing in-situ reworked material above wave-base (Beukes and Klein (1990).



Figure 1.3: (a) Simplified geological map of the Griqualand West Basin of the Transvaal Supergroup in the Northern Cape Province; (b) regional, NNE to SSW cross-section showing reconstructed lateral facies variations across the primary basin (from Beukes and Klein, 1990).

1.4.2 The Postmasburg Group

The Postmasburg Group forms the stratigraphically uppermost part of the Transvaal Supergroup in the Griqualand West Basin and attains a total thickness of up to 1.5 km. The 50 - 150 m-thick glaciogenic *Makganyene Formation* at the base of the Postmasburg Group, is composed of coarsely bedded and massive diamictites with clasts ranging in shape from angular to sub-rounded, and in size from 0.5 - 30 cm, as well as lesser BIF, sandstone and shale. These glacial sediments are conformable with the overlying *Ongeluk Formation* volcanics as

they interlayer finely, whilst small volcanic fragments are observed in the upper diamictite layers (Visser, 1971; Kirschvink *et al.*, 2000; Polteau *et al.*, 2006).

The Ongeluk Formation attains an average thickness of ~600 m, and is a continental-type basaltic andesite that consists of a series of sub-aqueous extrusions preserved as pillow lavas, massive lava flows and hyaloclastites. The transition of the Ongeluk Formation with the overlying *Hotazel Formation* is marked by an increase in hayloclastite with intercalated jasper and chert at the contact with the Hotazel sediments (Kirschvink *et al.*, 2000; Polteau *et al.*, 2006; Schneiderhan *et al.*, 2006). Kirschvink *et al.*, (2000) observe that at the transition between the Ongeluk and Hotazel Formations, a 0.5 - 1m thick unit of jaspilitic sediment containing small drop stones and sandy horizons is present, which texturally resembles the siliciclastic facies seen in the Makganyene Formation at the base of the Postmasburg Group.

The uppermost part of the Postmasburg Group is represented by the Hotazel and Mooidraai Formations which are best preserved in the northern corner of the Griqualand West basin and specifically in the area known as the Kalahari Manganese Field (abbr. KMF) (Tsikos and Moore, 1997; Tsikos *et al.*, 2001, 2003; Polteau *et al.*, 2006). The Hotazel Formation overlies conformably the Ongeluk volcanic rocks and is characterized by a cyclic succession of microbanded, rhythmitic BIF interlayered with well-laminated Mn-rich layers. The transitional intervals between BIF and Mn take the form of laminated lutites characterised by a strong red colouration due to the abundance of very fine-grained hematite. The three sedimentary cycles of BIF \leftrightarrow hematite lutite \leftrightarrow Mn-rich sediment that develop in the Hotazel Formation exhibit remarkable lateral constancy over an area of *ca*. 400 km², making the KMF one of the largest land-based resources of manganese metal globally (Laznicka, 1992; Astrup and Tsikos, 1998). A more detailed reference to the stratigraphy of the Hotazel Formation will be made in Chapter 2.

The *Mooidraai Formation* is a carbonate unit that develops conformably at the stratigraphic top of the Postmasburg Group, in the form of micro-laminated to massive Fe-bearing limestone and occasionally dolomite (Tsikos *et al.*, 2001). The contact between the Mooidraai and Hotazel Formations is marked by intraclastic carbonate material that appears to record synsedimentary slumping, and is occasionally interbedded with sideritic chert (Beukes, 1986; Tsikos *et al.*, 2001; Polteau *et al.*, 2006; Schneiderhan *et al.*, 2006).

1.4.3. Age Controversies in the Griqualand West Basin

A summary of published absolute ages for rocks of the Transvaal Supergroup in the Griqualand West Basin, has been compiled and shown on Table 1.2. With regard to the sedimentary units of the sequence, the basal Archaean Schmidtsdrif Formation of the Ghaap Group records an age of 2.56 Ga; the Gamohaan Formation of the Campbellrand Subgroup approximately 2.52 Ga; the Kuruman Formation around 2.47 Ga; and finally, the Mooidraai Formation at the top of the Transvaal stratigraphy has yielded a diagenetic age of 2.39 Ga. An obvious discrepancy ensues, however, when the published whole-rock age of the Ongeluk Formation is considered (Table 1.2; Cornell *et al.*, 1996).

Table 1.2: Published ages for various stratigraphic units of the Transvaal Supergroup in the Griqualand West Basin (Armstrong *et al.*, 1991; Barton *et al.*, 1994; Horstmann and Hälbich, 1995; Cornell *et al.*, 1996; Sumner and Bowring, 1996; Altermann and Nelson, 1998; Bau *et al.*, 1999; Johnson *et al.*, 2003; Pickard, 2003; Sumner and Beukes, 2006), Fairey *et al.*, (2013).

Geological Unit	Age (Ma)	Literature Source	Methodology		
Mooidraai dolomite	2394 ± 26 Ma	Bau et al., (1999) and Corfu et al., (2009)	Pb/Pb whole rock		
			U-Pb discordia intercept		
Mooidraai dolomite	2392 ± 23 Ma	Fairey <i>et al.,</i> (2013)	U-Pb discordia intercept		
Ongeluk Lava	2034 ± 139	Armstrong, 1987 in Horstmann and Hälbich (1995)	Rb/Sr whole rock		
Ongeluk Lava	2238 ± 87/92	Armstrong, 1987 in Horstmann and Hälbich (1995)	Pb/Pb whole rock		
Ongeluk Lava	2222 ± 13 Ma	Cornell <i>et al.</i> , (1996)	Pb/Pb whole rock		
Makganyene Fm	2436 ± 7 Ma	Moore <i>et al.</i> , (2013)	U-Pb Zircon age		
Koegas Subgroup	2415 ± 6	Kirschvink et al., (2000)	Pb/Pb whole rock		
Griquatown Fm.	2432 ± 31	Trendall et al., 1990, In Johnson et al., 2003	U-Pb Zircon age		
Kuruman IF (Upper)	2465 ± 5	Pickard (2003)	U-Pb Zircon age		
Kuruman IF (Lower)	2478±6	Pickard (2003)	U-Pb Zircon age		
Gamohaan Fm. (Upper)	2516 ± 4	Altermann and Nelson (1998)	U-Pb Zircon age		
Gamohaan Fm (Lower)	2521 ± 3	Sumner and Bowring (1996)	U-Pb Zircon age		
Nauga Fm: 480m above base	2549 ± 7	Altermann and Nelson (1998)	U-Pb Zircon age		
Nauga Fm: 450m above base	2552 ± 11	Barton et al., (1994) and Altermann and Nelson (1998)	U-Pb Zircon age		
Schmidtsdrif Fm (Campb. Fm.)	2557 ± 49	Jahn et al. (1990) in Horstmann and Hälbich (1995)	Pb/Pb whole rock		
Ventersdorp Supergroup	~ 2.2 Ga	Armstrong et al., 1986 in Sumner and Bowring (1996)	Rb-Sr and Pb-Pb whole rock		
Ventersdorp Supergroup	2643 ± 80 Ma	Van Niekerk and Burger, (1978) in Sumner and Bowring (1996)	U-Pb zircon		
Ventersdorp Supergroup	2714 ± 8	Armstrong et al., (1991)	U-Pb Zircon age		

At 2.22 Ga, the age of the Ongeluk volcanics would invalidate that of the Mooidraai Formation, and requires that a ~200 Ma hiatus exists between the Ghaap and Postmasburg Groups. Many authors (e.g. Evans *et al.*, 1997; Mapeo *et al.*, 2006), assume this to be the case, although the

existence of an erosional unconformity has been challenged by Visser (1971), Moore *et al.*, (2001, 2011), Polteau (2004) and Polteau *et al.*, (2006), based on field evidence. Furthermore, Sumner and Bowring (1996) suggest that because a variety of Pb-Pb and Rb-Sr whole-rock isotopic data from various lithologies of the Transvaal Supergroup indicate ages of ~2.2 Ga (including the underlying 2.6 to 2.7 Ga Ventersdorp Supergroup; see Table 1.2), the latter might well reflect an overprinting episode of regional metamorphism.

The lack of resolution in the age of particularly the Postmasburg Group bears major implications in terms of palaeo-environmental reconstructions. In the simplest of terms, the genesis of Hotazel Formation and its contained manganese deposits are inconclusively dated in the context of the GOE, i.e. the Hotazel either predates or post-dates the latter. This age-related issue will be briefly revisited in Chapter 3 of this thesis.





1.5. MANGANESE IN THE GRIQUALAND WEST BASIN: AIMS AND OBJECTIVES

As mentioned earlier in this chapter, major manganese deposits of economic significance and associated with BIF, occur twice in the geological record (Figure 1.4): the Neoproterozoic Rapitan association exhibits a causal connection with global-scale glaciation, whereas the Kalahari deposit in the Palaeoproterozoic Hotazel Formation is arguably the largest and oldest BIF-hosted deposit on record, and it is unique with respect to its age, size, and clear syngenetic character to the enclosing Hotazel Formation BIF.

The mineralogy and geochemistry of the Hotazel Formation and the processes that have led to its primary deposition and subsequent local upgrading to high grade Mn-ore, are topics that have been dealt with in a large number of publications (Boardman, 1964; De Villiers, 1960, 1970, 1983; Beukes, 1983; Kleyenstüber, 1984, 1985; Nel *et al.*, 1986; Miyano and Beukes, 1987; Kleyenstüber, 1993; Gutzmer, 1983; Cornell and Schütte, 1995; Grobbelaar *et al.*, 1995; Beukes *et al.*, 1995; Gutzmer and Beukes, 1995, 1996; Tsikos and Moore, 1997, 2005; Tsikos *et al.*, 2001, 2003, 2010). Proposed models for the deposits of the KMF have covered a diverse variety of genetic processes, ranging from large-scale epigenetic replacement mechanisms, to submarine volcanogenic-exhalative activity, to chemical sedimentation in a pre- or post-GOE anoxic to mildly oxic ocean-atmosphere system. Some authors also implicate a direct genetic connection between the deposition of the Hotazel BIF-Mn Formation and a Palaeoproterozoic Snowball Earth event as manifested, in part, by the Huronian-age diamictite of the Makganyene Formation (Tsikos and Moore, 1998; Kirschvink *et al.*, 2000).

Arguably one of the most intriguing questions around the manganese deposits of the Transvaal Supergroup, concerns the staggering volume of manganese hosted within the Hotazel BIF, by comparison with the essentially Mn-barren BIF sequence of the Ghaap Group (Kuruman and Griquatown Formations). To this end, the recent work of Tsikos *et al.*, (2010) provides a new look into the deposition of the Hotazel Formation as part and parcel of a chemically (and possibly biologically) evolving palaeo-depositional environment leading up to the GOE: the Hotazel BIF and its Mn enrichment are therefore tentatively linked with the older BIFs of the Ghaap Group, as products of chemical deposition in a terminal depositional setting preceded by large-scale deposition of Mn-poor BIF.

In light of all the above, the main objective of this thesis is to illuminate the various controls of the association between manganese and BIF in the Transvaal Supergroup. This is approached in three discrete and at the same time complementary ways:

- The first Chapter (2) following the Introduction (1), represents a rigorous, high-resolution mineralogical and geochemical study of a complete BIF-Mn cycle in the Hotazel Formation. This is a first study of its kind pertaining to the Hotazel succession, and was undertaken with a view to help decipher as much as possible the primary and diagenetic environment of deposition of the Hotazel sediments and especially the processes that led to the cyclic development of BIF and Mn-rich sediment in the Hotazel succession. This is achieved by focusing on the middle and stratigraphically narrowest BIF-Mn cycle of the Hotazel Formation as an analogue for the entire sequence.
- The second Chapter (3), presents a low-resolution bulk-rock petrographic and geochemical study across the Kuruman and Griquatown Formations, with emphasis on the distribution of manganese across the examined BIF stratigraphy. The focus here is to identify any systematic behaviour of manganese up-section; provide some plausible explanations regarding the controls for such distribution; and evaluate these in the context of the entire Transvaal Supergroup and particularly the stratigraphically younger, Mn-enriched Hotazel Formation.
- The final Chapter (4), represents a brief look into secondary alteration and metal enrichment processes in the Hotazel Formation, with emphasis on the relative geochemical behaviour of manganese along with selected other major, minor and trace components during post-depositional fluid-rock interaction, and on any new evidence for the geochemical nature of the latter.

The thesis concludes with a brief Chapter (5) which provides a synopsis of the findings and arguments presented in the preceding chapters and includes some suggestions for future research.

2: HIGH-RESOLUTION STUDY OF A SINGLE Mn-Fe CYCLE OF THE HOTAZEL FORMATION: INSIGHTS INTO PRIMARY DEPOSITION AND DIAGENESIS

2.1. INTRODUCTION

The mineralogy, geochemistry, and origin of the Mn-bearing horizons within the Hotazel Formation and the processes that have led to their primary deposition and subsequent upgrading to high grade Mn-ore, have been described and discussed in a large number of publications by Boardman (1964); De Villiers (1960), (1970), (1983); Beukes (1983); Kleyenstüber (1984, 1985); Nel et al., (1986); Miyano and Beukes (1987); Kleyenstüber (1993); Gutzmer (1983); Cornell and Schütte (1995); Grobbelaar et al., (1995); Beukes et al., (1995); Gutzmer and Beukes (1995); Gutzmer and Beukes (1996); Tsikos and Moore (1997); and Tsikos et al., (2001, 2003, 2010). In earlier years, most authors linked the genesis of the Hotazel succession to the underlying Ongeluk volcanic sequence, owing to their obvious stratigraphic association observed in the field. Hence, the formation of the Fe-Mn cyclicity in the Hotazel Formation was interpreted as a result of sedimentary processes intermittently charged with volcanically-sourced exhalations, thus assigning the genesis of the entire sequence largely to volcanogenic models (e.g. Kleyenstüber, 1984; Cornell et al., 1995). In recent years however, emphasis has been placed primarily on the cyclic nature of the deposits and the importance of primary sedimentary processes in the context of an evolving atmosphere-ocean system (e.g. Tsikos et al., 2010). This has effectively relegated the role of volcanism as merely a possible source for the metals in the Hotazel package of sediments. Even though the origin of the Hotazel Formation remains to date a key topic of research and debate, the research approach applied in this chapter has been influenced to a great degree by the most recent ideas and arguments.

2.2. AIMS AND OBJECTIVES

This chapter presents a high-resolution mineralogical and geochemical study across a single, complete Fe-Mn cycle out of the three contained in the Hotazel Formation, and specifically the middle Mn-layer, or "manganese marker" as informally referred to by mining geologists

in the field (Figure 2.2). This middle Mn layer records the thinnest of the three such cycles in the Hotazel strata (*ca*. 10 m stratigraphic thickness in the drillcore section studied here) and therefore can be regarded as a condensed analogue of the entire sequence, making it ideal for the detailed analysis of the mineralogical and geochemical changes that occur as the lithologies grade, from the host BIF to the Mn-rich layer itself, via hematite-rich transitional lithologies referred to as hematite lutites (see Chapter 1 for more details).

Examination of such variations was accomplished through the application of a wide variety of analytical techniques on samples collected every 20 - 25 cm on average. These included standard mineralogical analyses via XRD on bulk powders; bulk analyses of major element oxides and trace elements by X-ray Fluorescence (XRF); carbon isotope analyses of the bulk carbonate and organic carbon fractions of the samples; and finally Fe and Mn speciation analyses (Poulton and Canfield, 2005), which essentially determine the abundance and distribution of Fe and Mn contained in different mineral fractions within an individual sample. The latter technique has not been applied to samples from the Hotazel Formation, and in combination with the other data, provide important new insights into the deposition and diagenesis of the Hotazel deposits in the context of Fe and Mn cycling. The results and arguments presented in this chapter further illuminate the primary and early burial environments of these unique deposits, and especially the possible controls for the conspicuous Fe-Mn cyclicity, with the aid of additional literature information from suitable modern environmental analogues.

2.3. STRATIGRAPHY OF THE HOTAZEL FORMATION

The Hotazel Formation is developed in the KMF (Figure 2.1) in the northern part of the Griqualand West basin. It is composed of three Mn-rich sedimentary horizons interbedded with BIF, as illustrated in the simplified stratigraphic column of Figure 2.2. The stratigraphic base of the Hotazel Formation comprises volcaniclastic ("hyaloclastic") deposits at the interface with underlying massive volcanic rocks of the Ongeluk Formation. Pillow structures variously observed in the latter, along with the obvious sedimentary character of the overlying volcaniclastic deposits themselves, suggest a sub-aqueous environment of volcanic extrusion (Tsikos and Moore, 1997). The Hotazel and Ongeluk Formations, along with the

Mooidraai Formation at the very top of the sequence, stratigraphically constitute the Voëlwater Subgroup (Beukes, 1983).



Figure 2.1: (a) Geological map of the Griqualand West basin of the Transvaal Supergroup in the Northern Cape of South Africa, highlighting the Kalahari Manganese Field (KMF) hosting the Hotazel Formation. (b) Simplified map of the KMF showing localities of some presently active mines (from Cabral *et al.*, 2011).

The intimate stratigraphic association between BIF and Mn is the most characteristic and arguably intriguing feature of the Hotazel Formation (Tsikos *et al.*, 2003). It is developed as three cyclical lithological units that display subtle and very gradual mineralogical changes stratigraphically upwards from:

- Chert-magnetite (+Fe-carbonate, +Fe-silicate) microbanded BIF; grading into:
- Hematite- and Mn carbonate-rich lutite; which, in turn, grades into:
- Braunite-kutnahorite Mn-rich horizons,

and back again to BIF *via* a hematite lutite transition. The upper and lower Mn-units in the Hotazel Formation attain maximum thicknesses up to 25 m and 45 m respectively, whilst the

middle Mn-unit is a relatively thinner horizon of an average of ~3 m in thickness. As indicated earlier, the latter is the specific focus of this chapter. Due to the very gradual stratigraphic transitions from the Fe-rich to the Mn-rich layers of the Hotazel Formation, the thickness of the middle Mn marker is conventionally bracketed by absolute Mn contents and Mn/Fe ratios of minimum commercial viability. Currently, mainly the lowermost Mn-unit is mined, either as primary carbonate-rich Mn-ore containing marginally economic grades of 38 to 40 wt. % Mn, or as high-grade hydrothermally altered Mn-ore (not exceeding 5 m in stratigraphic thickness in most cases) in the northern KMF, at grades generally >44 wt. % Mn (Nel *et al.*, 1986; Gutzmer and Beukes, 1995). Much of the previous work on the Hotazel Mn ore horizons have understandably placed emphasis on the processes that led to the secondary metal upgrading of the ores in the northern part of the KMF.



Figure 2.2: Stratigraphic subdivision of the Transvaal Supergroup, with the position of the Hotazel Formation highlighted and illustrated in log form. Modified after Tsikos *et al.*, (2001, 2010).

2.4. SAMPLE SELECTION AND METHODOLOGY

2.4.1 Drillcore Location

Farm Gloria is situated in the north-eastern part of the KMF, and geographically borders the area dominated by hydrothermally altered, carbonate-lean, high-grade Mn ore (N'Chwaning and Wessels Farms). The Gloria Mine itself, however (Figure 2.1b), operated by ASSMANG Ltd who kindly sponsored this research, is an underground mining operation exploiting relatively low-grade, braunite/kutnahorite-rich Mn ore from the lowermost Mn layer. The latter is akin in terms of mineralogy and geochemistry to the Mamatwan-type low-grade ore that dominates the remainder of the KMF to the south (Kleyenstüber, 1984; Tsikos and Moore, 2003), but is stratigraphically much thinner (generally <10 m) by comparison.

The intersection targeted for this study is captured in drillcore GL 81 in the Gloria area, which was obtained as part of an ongoing drilling program by ASSMANG aimed at delineating extensions and grade variations, of the Mn ore-body currently targeted at Gloria Mine. The Hotazel Formation stratigraphy in this area of the KMF is very well preserved, albeit relatively thinner overall than in the southernmost parts of the KMF (see Tsikos *et al.*, 2003 for more details), and usually the drillcore material obtains records of 100% core recovery. Drillcore GL 81 constitutes no exception in the latter respect.

2.4.2 Logging, Sample Selection and Processing

A complete cycle from the relatively thin middle Mn-unit was logged (Figure 2.3) and sampled in relatively high resolution, with samples extending well into the under- and overlying BIF enveloping the Mn-layer. The complete section of core logged extends from 349.77 to 360.20 meters below surface, with the total 10.43 m of core section captured initially through 35 individual samples. Sample collection was guided by careful description of the lithology and at least subtle macroscopic variation in mineralogy and/or textures, bearing in mind at the same time the need to capture the individual sub-units logged with sufficient statistical resolution where possible. Some of the samples collected were later sub-sampled, and resulted in a complete set of 40 half-core samples. Sample depths and accompanying descriptive information are summarised and are available in Appendix I.

For further processing, each half-core sample was carefully divided into two quarter sections with a core cutter. One quarter was used to produce a polished thin section, whilst the other half was crushed to a fine powder for bulk analyses. This permits the direct correlation between the petrographic features observed for each sample in thin section, and the bulk mineralogical and geochemical results.



Figure 2.3: Lithological log and sample positions across the BIF-MnF-BIF cycle of the middle manganese layer from drillcore GL 81 near Gloria Mine in the KMF.

2.4.3 Analytical Techniques

In conjunction with basic petrography, a wide range of analytical techniques were applied to all samples for the purposes of this study (more detailed technical descriptions are provided in Appendix II). Specifically, all 40 samples were analysed for:

- Major elements oxides (by X-Ray Fluorescence on fusion discs);
- Trace elements (by X-Ray Fluorescence on pressed powder pellets);
- Bulk mineral identification (by X-Ray Diffraction on powdered samples);
- Iron and manganese speciation (through sequential extraction of different mineral fractions, and analysis of each for Fe and Mn by Atomic Absorption Spectrometry);
- Bulk Fe²⁺/Fe_{Total} determinations (by iron titration);
- Total carbon and total organic carbon content (by conventional bulk C analyses);
- Carbon isotope ratios on bulk carbonate and organic fractions (by gas-source mass spectrometry).

2.5. MINERALOGY

2.5.1. Macroscopic Descriptions

Identification of minerals based on macroscopic observations alone is an ominous task in rocks such as those examined here, due to their extremely fine-grained nature. General observations can still be made in some instances, such as the presence of hematite which is easily identifiable over large parts of the studied section by its intense red colouration; or of magnetite, which develops usually in discrete and highly magnetic mm-scale laminae within the BIF. The presence of carbonates is also relatively easily verifiable in the Mn-rich parts of the stratigraphy on the basis of previously published textural descriptions (Kleyenstüber, 1984). Outside these phases, however, confident determination of mineralogy can only be performed in the laboratory.

As seen in Figure 2.4, mineralogical and textural changes are very subtle and gradual across the studied section, making the task of defining end-member lithotypes difficult. However, the broad delineation of the expected three main lithologic types comprising the Fe-Mn cyclical unit is readily possible (Figure 2.5): this includes BIF at the base of the cycle, increasing gradually in modal hematite content up-section into hematite lutite proper, and gradually into a dark Mn-rich horizon, with the same layering repeating up-section in reverse.



Figure 2.4: Core sections displaying the very gradual textural and colour changes observed across the stratigraphy of the middle Mn marker. Note the consistently very fine grained habit and mm-scale rhythmic alternation of light and dark bands. The arrows on the core point downward the stratigraphy with the base (sample labelled G 32) composed of dark-coloured lutite at the contact with BIF (not shown). Progressive reddening marks an increase in hematite content up-section. The central unit (marked by sample G 24) represents the more Mn-rich interval, which grades upwards into a hematite-rich lutite and back into BIF.



Figure 2.5: Hand specimens of the three main lithotypes of the Hotazel Formation. (A) Finely laminated, alternating layers of dark magnetite and light coloured chert and carbonate minerals. (B) Dark red hematite lutite intercalated with abundant large white carbonate ovoids and laminae, which are also present in the Mnhorizon shown in (C), but with much more abundant and smaller ovoids than in the hematite lutite. The scale of hand specimens are shown against a mm-scaled ruler.

The BIF specimen displayed in Figure 2.5A exhibits the characteristic micro-banded nature of the Hotazel BIF at the flanks of the middle Mn layer, with mm-scale, light-coloured chertrich bands containing subordinate carbonates and Fe-silicates, interlayered with dark, magnetite-rich bands. Banding becomes less developed albeit still distinct in the very finegrained hematite lutite and Mn-rich lutite specimens of Figure 2.5B and 2.5C respectively, both of which contain characteristic light-coloured (ranging from whitish to pinkish grey in hand-specimen) laminae rich in carbonate minerals. The broad lithologic subdivision encapsulated in the cores displayed in Figure 2.5, namely BIF; carbonate/hematite-rich unit; and main Mn-rich unit, will be variously used in the sections that follow, with reference to the bulk mineralogical and geochemical results obtained from the same materials, and the discussion and arguments that will be based on those results.

2.5.2. X-ray Diffraction

Results from the XRD analyses of all samples collected from section GL 81 is summarised in Table 2.1, and illustrated in Figure 2.6, which is detailed further with mineralogical identifications based on the petrography section that follows. In general, the majority of minerals determined here are characteristic of diagenetic to a very low-grade metamorphic environments not exceeding 210 °C in burial temperatures (Miyano and Beukes, 1987; Klein, 2005). However, it is important to point out the presence of microcrystalline calcic garnet (andradite) in selected samples from the lower half of the examined section. Subsequent to the collection of samples for this specific part of the study, the author was informed by the company that the drillcore GL8 1 was drilled in proximity to a dolerite dyke (which is of unidentified origin). It is therefore possible that the otherwise unusual occurrence of andradite in this section, owes its origin to a potentially minor and largely isochemical thermal effect on the Hotazel BIF samples, whereby andradite may form as a result of a decarbonation reaction between ankerite, magnetite and quartz. Consequently, samples with andradite may have suffered partial carbonate loss, which is cautiously assumed for the purposes of this study that it did not have any significant fractionation effect on the bulk carbonate carbon isotope composition obtained from the same samples.

The mineralogical results shown in Figure 2.10 correspond broadly to the three main lithologic groups defined in earlier sections, namely the BIF, Mn-rich layer and carbonate/hematite layer, and forms the benchmark for subsequent data presentation and discussion. In particular, the absence of XRD-detectable quartz is a mineralogically defining feature of both the hematite/carbonate-rich layer (G 16.b to G 3), as well as the Mn-rich layer (G 21 – G 30) (see also in this respect: Miyano and Beukes, 1987). The tabulated

mineralogy is depicted in comparison to the major element oxide compositions in Figure 2.10.

Table 2.1: Mineralogy of the middle Mn cycle in drillcore GL 81. Minerals identified by XRD are shown with dots (•) (dark grey: major; light grey: minor); those by petrography are shown with 'X' (green: major; white: minor).

		OXID	ES		CARB	ONATE	S	SILICATES			OTHER				
Sample	Qtz.	Mag.	Hem.	Ank.	Calc.	Kutn.	Rhod.	Brau.	Min.	Frie.	Gre.	Stilp.	And.	Pyr.	Bar.
G 1	•	•			Х				Х			Х			
G 2.a	•	•			Х				Х			Х			
G 2.b	•	•													
G 3	Х	•	Х		•	•									
G 4	Х	•	Х		•	•			•						
G 5	Х	•	Х		•	•					•				
G 6		•	Х		•	•			Х	•					
G 7		•	•			•			Х						
G 8			•			•				•					
G 9			•			•					•				
G 10.a			•		•	•			Х		•				
G 10.b			•		•	•	•				•				
G 11		•	•		•					•					
G 12		•	•		•	•				•					
G 13		•			•	•			•		Х	Х			
G 14	Х	•	Х		•	•							•		
G 15.a	•	•			•	•				•			Х		
G 15.b	•	•			•					•					
G 16.a	Х	•	Х		•	•					•		•		
G 16.b	Х	•			•	•			Х			Х	Х		
G 17	•	•		•									•		
G 18	•	•	Х	•		•						Х	•		
G 19	•	•		•								Х			
G 20	•	•	•		•						•		•	Х	
G 21	Х	•	•	•		•				•					
G 22	Х		•			•				•	•	Х			
G 23	Х		•			•	•	•		•	•				
G 24			•			•	•	•		•					
G 25			•			•	•	•		•					
G 26			•			•	•	•		•					Х
G 27.a			•	•		•	•	•	•						
G 27.b			•	•			•	•							
G 28			•	•			•	•							
G 29			•												
G 30	Х	Х	•							•					
G 31	•	•	•									Х			
G 32	•	•	•									Х			
G 33	•	•	•						Х				Х		
G 34	•	•	•						Х				•	Х	
G 35	Х	•	•			•			•				•		

	Identification through:					
Mineral abundance	XRD	Petrography				
Major	•	Х				
Minor	•	Х				





Figure 2.6: X-ray Diffraction profiles of samples across the stratigraphy with the peaks of main mineral components highlighted. These results displaying mineralogical changes are used in the lithological subdivision of the Hotazel BIF-Mn-rich formation-BIF cycle.

2.5.3. Petrography

Basal Banded Iron Formation unit (G 35 – G 33)

Microbanded BIF at the stratigraphic base of the examined section is texturally characterized by fine-grained, mm- to cm-scale thick bands (up to 2 cm thickness in some instances), with band alternation following the predictable pattern between iron-oxide-rich

layers and Fe-poor, microcrystalline chert-rich bands containing carbonate and silicate minerals (Figure 2.7A).

The dark Fe-rich bands are composed of opaque oxide grains of predominantly magnetite at the base (sample G 35), giving way to magnetite-hematite intercalations stratigraphically higher up (sample G 33). In general, magnetite is present as well-formed euhedral crystals that range in size from 10 μ m to larger \geq 0.5 mm diameter crystals, whereas hematite is present as extremely fine grains (<10 μ m), either in discrete laminae or as occasionally disseminated grains between larger magnetite micro-crystals in magnetite-dominated bands (Figure 2.7D). The oxides occur in a matrix of quartz with lesser Fe-rich silicates and carbonate minerals. Interstitial quartz and carbonate grains are commonly in the form of minute anhedral and subhedral crystals respectively, up to 0.4 mm in diameter; while quartz, in particular, exhibits irregular sutured edges. Other silicate minerals occur as needles and sprays of minnesotaite and fibrous stilpnomelane within the quartz-carbonate matrix. Modal abundances of magnetite *versus* silicate and carbonate phases vary from sample to sample, with the lowermost sample containing relatively fewer magnetite microbands. Moving up stratigraphy, alternations of "dusty" hematite with magnetite bands is clearly displayed under reflected light as shown in Figure 2.7C.

Light-coloured, Fe-poor bands are composed mainly of quartz and carbonate minerals, and host abundant sprays and needles of minnesotaite and/or very fine-grained flaky greenalite. Bands composed mainly of stilpnomelane are easily identified by their pervasive brown colour and fibrous habit (Figure 2.7A), often containing interspersed ankerite rhombohedra and clusters of microcrystalline quartz (Figure 2.7B). Disseminated magnetite and hematite grains are commonly dispersed throughout all chert-rich bands, regardless of the exact paragenesis in each instance.

As indicated earlier, andradite is present in the basal BIF as a later replacement mineral at the boundaries of oxide and quartz-carbonate bands, and displays a characteristic poikilitic texture, forming euhedral hexagonal crystals up to 0.5 mm in diameter. The stratigraphically lowest sample (G 35) displays the highest modal abundance of andradite, in the form of light-coloured bands that have been almost completely replaced by grains of andradite in a matrix of (lesser) quartz and carbonate.



Figure 2.7: Photomicrographs of microlaminated BIF. A: transmitted light image of alternating light and dark banding. Opaque bands consist of magnetite with interstitial, very fine grained hematite. Banding is produced by varying mineralogical composition: the light band is stilpnomelane-dominated. B: Very fine grained stilpnomelane, containing dispersed ankerite rhombohedra, clusters of microcrystalline quartz and fine disseminated hematite. C: Reflected light photomicrograph of interlayered hematite and magnetite. D: Transmitted light photomicrograph of a magnetite band, with a small anhedral grain of hematite in between.

Upper Banded Iron Formation units (G 20 – G 17, G 2.b – G 1)

The BIF in these intervals is very finely-laminated (microbanded) and characterised by the classic rhythmic alternations between Fe-poor and Fe-rich layers. Abundant magnetite, quartz and lesser Fe-silicates and carbonates are the key species here. Magnetite comprises the bulk of the oxide bands with small ($\leq 1 \mu$ m), finely dispersed grains of hematite present as well-developed subhedral to euhedral micro-crystals, ranging from $<10 \mu$ m to $>100 \mu$ m in diameter. Magnetite crystals are commonly also disseminated throughout the interlayered quartz-carbonate bands which range in thickness from 50 µm up to 1.5 cm (Figure 2.8), and

contain abundant very fine-grained silicates, mostly minnesotaite, greenalite and friedelite (the positive identification of the latter was determined by XRD).

An interesting textural feature in the upper BIF samples is mm- to cm-thick bands composed entirely of calcite with a very distinctive texture referred to by Sumner and Grotzinger (1996) as herringbone calcite. This texture is specifically manifested by large elongated individual grains of calcite (Figure 2.8C and D), that develop perpendicular to banding and containing inclusions of fine-grained oxides and silicates that preferentially concentrate along individual grain margins. The herringbone calcite bands are capped at their upper boundary by up to 0.5 mm-thick bands of euhedral magnetite, enveloped in a chert greenalite-rich matrix (Figure 2.8D).

Finally, andradite crystals (Figure 2.8E and F) are also occasionally observed at the boundaries between bands of magnetite and those of microcrystalline quartz, again forming large (>1 mm diameter) poikilitic sub- to euhedral crystals with a well developed zonal pattern from rim to core as illustrated in Figure 2.8F.

Middle, Mn-rich carbonate lutite (G 32 – G 21)

The Mn-rich layer is composed of Mn-silicates, Mn-carbonates and minute hematite grains. Texturally, this unit also exhibits distinct banding: Mn-rich bands are composed of finegrained braunite and friedelite, along with abundant, complexly zoned ovoids of carbonate (Figure 2.9E) which may reach up to 2 cm in diameter. The Mn-rich bands are intercalated with bands of kutnahorite that display compositional zoning (Figure 2.9B). The zoned ovoids contain cores of fibrous friedelite (Figure 2.9C and D) surrounded by Mn carbonates (kutnahorite and possibly minor rhodochrosite). The transition from the basal BIF to the Mnrich unit is highly gradational, and is marked by a striking modal decrease in magnetite bands and corresponding increase in very fine-grained hematite ones. Here, carbonate mineralogy and textures are comparable to those seen in the Mn-rich interval. The banding of hematite and magnetite is most visible in hand specimens as alternating red (hematite) and black (magnetite) bands, and is further confirmed microscopically as seen earlier in the petrography section. Magnetite is distinctly absent from the Mn-rich unit.



Figure 2.8: Mineralogy and textural features of Unit 4 the upper BIF. A: Coarsely banded BIF of the stratigraphically lowermost samples of Unit 4. B: Microlaminated bands of the uppermost BIF samples. C: Bands of herringbone calcite capped by large 0.4 mm euhedral magnetite crystals, the rims which are displayed in D, as rims of greenalite at the base and top of bands of magnetite. Euhedral andradite crystals are displayed in E at the boundary between magnetite and quartz carbonate bands. The zoned texture of andradite grains are displayed in F.


Figure 2.9: Mineralogy and textures of the manganese rich layer. All photomicrographs taken under transmitted light. A, B and E show the abundance of ovoids and lamellae that range in size from 5 mm to 100 μ m. Both the ovoids and lamellae are often mineralogically zoned from rim to core. The rims are composed of thin 20 μ m diameter bands of microcrystalline quartz and or friedelite which grade into bands of kutnahorite and rhodocrosite. The ovoid core is composed of fibrous aggregations of friedelite displayed by C and D, which are magnifications of the cores of the lamellae of B, and ovoid core of 2.9E. Fibrous aggregations of friedelite forms light coloured haloes around entire ovoids, the rim of the halo around the ovoid (2.9E) is magnified in Figure 2.9F.

Hematite/carbonate-rich iron formation (G 16.b – G 3)

The carbonate/hematite-rich horizon within the upper stratigraphic portion of the studied section is enveloped by BIF. It is also texturally similar to the typical microlaminated BIF by its characteristic cm-scale alternating bands dominated by magnetite, hematite and Mn carbonate (mainly kutnahorite). Quartz contents are very low or absent from this unit, and are thus essentially undetectable by XRD.

Magnetite- and hematite-rich bands here range in thickness from 0.4 mm to >2 cm, while kutnahorite bands are comparatively thinner at <0.2 mm. As with the Mn-rich layer, abundant ovoids and mm-thick laminae of carbonate are commonly present. Hematite dominates samples from this unit to such a degree that samples G 9 to G 10.b are composed almost entirely of hematite with lesser kutnahorite ovoids/laminations, and little to no magnetite.

2.6. GEOCHEMISTRY OF THE Fe-Mn CYCLIC UNIT

2.6.1. Major Element Oxides

Tabulated major element oxide compositions of all samples analysed from the middle Mn unit of drillcore GL 81, are available in Appendix III. Stratigraphic profiles for selected major element oxides are displayed in Figure 2.10. The composition of all samples is dominated by SiO₂, FeO, MnO, MgO and CaO, whereas the minor element oxides TiO₂, Al₂O₃, K₂O, and P₂O₅ are present in very low and largely invariant concentrations, and are therefore not considered any further here.

As expected, BIF samples (G 35 - G 33, G 20 - G 17, G 2.b - G 1) are characterised by compositions dominated strongly by FeO and SiO₂, which together make up more than 75 % of the total sample mass on average for each sample. Indeed, the highest SiO₂ and total Fe oxide concentrations across the entire stratigraphic section are observed in BIF samples (Figure 2.10). In terms of the remaining major element oxides, the carbonate-associated oxides MgO and CaO record average wt. % values of 4.1 and 5.91 respectively, with the

basal BIF samples generally being more Ca-enriched. Bulk MnO does not exceed the value of 3 wt. %.

Highest MnO contents are observed in the Mn-rich horizon (G 32 - G 21), with an average value at 18 wt. % and a maximum at 33.6 wt. %. Here, CaO contents are also comparatively high, between 10.2 to 23.2 wt. %, confirming the substantially carbonate-rich nature of this unit. FeO and SiO₂ respectively make up 31.1 and 17.8 wt. % on average. MgO at a mean value of ~5 wt. % essentially makes up the remaining composition of samples.

The most abundant component in the hematite- and carbonate-rich unit (G 16.b – G 3) is total Fe as FeO, which comprises up to 47 wt. % of each sample by mass, at an average of 28.46 wt. %. In order of decreasing abundance the following major element oxides are present in wt. % averages of: CaO (15.9), SiO₂ (15) MnO (11.8) and MgO (5.9).



Figure 2.10: Major element oxide compositional profiles and main mineralogy of samples across the banded iron formation-manganese rich layer cycle section.

In terms of stratigraphic behaviour, the profiles for the major oxides of Si and Fe exhibit an apparent sympathetic relationship, whilst also anticorrelating strongly with the bulk CaO and MnO profiles (Figure 2.10). MgO shows no systematic behaviour, as it is known to be accommodated both in carbonate and in silicate minerals (Klein, 2005). The relationship between Fe+Si against Ca+Mn, essentially reflects the simple albeit important broad distinction between the two key end-member rock types in the Hotazel sequence, namely Mn-impoverished, Fe/Si-rich BIF and carbonate/Mn-rich rock.

2.6.2. Trace Elements

Samples of BIF are well documented for containing very low concentrations in the majority of trace elements (e.g. Klein, 2005). Similarly, trace element analyses for the samples from drillcore GL 81 display very low values across all lithological sub-units, as defined and examined here. The elements: Mo, Nb, U, Rb, Th Pb, Ni, Sc, and LREE (Ce, Nd, La) are all either at or below the detection limit in the greater majority of samples, while by contrast, the trace elements with concentrations consistently above the detection limit are Zr, Y, Sr, Co, Cr, V, Zn, Cu, and Ba (illustrated as profiles in Figure 2.11).

With respect to BIF samples (G 35 - G 33, G 20 - G 17, G 2.b - G 1), none of the trace elements illustrated in Figure 2.11 aside from Cr and occasionally Zn, have values that exceed 50 ppm. Similarly, the Mn-rich unit (G 32 - G 21) has very low abundances in all trace elements except for Ba. With regard to the hematite/carbonate-rich interval (G 16.b - G 3), the highest trace element values are observed for Sr and Ba. These two elements have a well-constrained mineralogical association in BIF, with the former being hosted almost exclusively in the carbonate fraction whereas the latter represents minute abundances of barite.

The profiles of Figure 2.11 provide little meaningful stratigraphic information for the behaviour of most trace elements analysed for. Probably the most notable relationship is that between Ba and Sr, which appear to be most strongly enriched in the carbonate/hematite-rich unit. As the latter also happens to be relatively enriched in MnO by comparison to adjacent BIF (Figure 2.10), it may be tentatively regarded as a second Mn sub-cycle in the studied sequence.

CHAPTER 2: HIGH RESOLUTION STUDY OF THE CYCLIC FE-MN OF THE HOTAZEL FORMATION



Figure 2.11: Trace element compositional profiles of the BIF-MnF cycle. Values are displayed in parts per million (ppm).

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2.6.3. Fe and Mn Speciation and Ratio Relationships

Iron and manganese speciation techniques that involve the sequential dissolution, extraction and analysis of various mineral fractions from sediments and rocks, have not been applied widely (if at all) in the geochemical research of BIF. This is surprising when one considers that BIFs are both very fine-grained and poly-minerallic rocks, and thus do not lend themselves for various types of mineral-specific geochemical work, unless chemical (pre-) treatment of the rocks is implemented. In this study (and this also applies to a similar application in Chapter 3 of this thesis), the Fe-speciation technique as developed by Poulton and Canfield (2005) was used, with a view to providing a better insight into the speciation of Fe and Mn in the examined sequence. From that point of view, this specific study represents probably the first attempt to read in more detail the mineral-specific stratigraphic signals of Fe and Mn in (a portion of) the Hotazel sequence, and elucidate the possible primary and/or diagenetic factors that controlled variations in their distribution.

Before the speciation data for this study are presented and discussed, it is important to note that refinement and adaptation of the speciation technique of Poulton and Canfield (2005) for the rocks analysed here, was not employed for the purposes of this study. The author understands that the "blind" application of the said technique is likely to yield spurious results for at least some of the rock samples examined here (and those in Chapter 3 later), in the absence of prior experimental laboratory tests. Consequently, the speciation results of this work do not prove in their own right that each of the mineral group-fractions that were chemically treated in the laboratory (i.e. carbonate, oxide, silicate) reacted optimally to the added reagents, i.e. >99 % of their abundance by mass was brought into solution. Therefore, the possibility of incomplete (partial) dissolution effects and cross-contamination across the different fractions, at least with respect to Fe and Mn, remains open.

It is important to also define upfront the mineral groups that were targeted through the chosen dissolution technique: based on the stepwise dissolution protocol used (Poulton and Canfield, 2005) and the mineralogy of the rocks under investigation, the carbonate fraction represents mixtures of calcite, ankerite and/or kutnahorite; ferric oxides include essentially

only hematite; ferrous oxides are only magnetite; whilst the remaining minerals are all lumped in the silicate fraction. For the purposes of simplicity and convenience in the way of data presentation and discussion, the relative percentages of the different fractions in each sample resulting from the speciation analyses (i.e. carbonate, hematite, magnetite and silicate) were re-calculated from the raw speciation data to the total Fe and Mn abundances for each sample as determined via XRF. Finally, whereas four Fe speciation fractions have been determined, the Mn speciation is reported in three, with the two oxide fractions grouped together for simplicity.

Bearing in mind all the above, the speciation data are illustrated as stratigraphic area plots in Figure 2.12, which adjacently include profiles for bulk Fe # (i.e. ratio of ferrous to total Fe) and bulk carbonate carbon determinations. There are some key signals and relationships across stratigraphy that are worth noting for the subsequent discussion and modelling:

- Despite the generally high abundance of carbonate carbon in the rocks, Fe bound in the carbonate fraction is from very low to virtually absent across the entire section, thus suggesting very little Fe-carbonate. By contrast, the bulk of Mn contained in the examined sequence is hosted in the carbonate fraction, with two clear peaks at the Mn-rich unit and the hematite/carbonate unit;
- Hematite-bound Fe shows a relatively invariant behaviour across stratigraphy, except for a peak at the transition between the basal BIF and overlying Mn-rich unit;
- Peaks in magnetite Fe as determined by speciation analyses is seen in the BIF intervals, as expected, and correspond directly to Mn minima, suggesting a clear antithetic relationship between magnetite and Mn enrichment;
- Substantial silicate-bound Fe is detected mainly in BIF samples from the lower and middle parts of the examined section, whereas small abundances of silicate-bound Mn characterises both intervals of high Mn, presumably due to the presence of braunite and friedelite.
- There is a striking antithetic relationship between total Mn and Fe number, which implies a close sympathetic correlation between high Mn content and correspondingly high ferric - relative to ferrous - Fe abundance. This is in conjunction with similar mineralogical evidence from previous studies on the Hotazel Formation and associated Mn-rich units (e.g. Tsikos *et al.*, 2003, 2010).



Figure 2.12: Fe and Mn speciation data, plotted as area profiles, as well as Fe # (Fe 2+/ (Fe 2+) + (Fe 3+)), $\delta^{13}C_{Total}$ and the total carbon in wt. % of samples from the cyclical unit. On the speciation area plots the carbonate fraction of Fe and Mn is displayed in blue and purple respectively. On the Fe area plot hematite and magnetite values are displayed separately.

The above points are further reinforced by the ratio profiles displayed in Figure 2.13, which utilise elemental oxides with speciation data ratios. Notable here is the good sympathetic relationship between the selected speciation ratio data with the bulk-rock MnO/CaO ratio, particularly with regard to the two high-Mn intervals in the stratigraphy. This implies that the selected speciation data faithfully reflect the ones from bulk geochemistry.



Figure 2.13: The Fe# of the Mn-Fe cycle plotted against the ratio of major element oxides CaO/MgO and MnO/CaO, and the speciation ratios Mn_{Carbonate}/Fe_{Carbonate}, Mn_{Carbonate}/Fe_{Hematite}, and Fe_{Hematite}/Fe_{Magnetite}.

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2.6.4. Bulk Carbon Isotopes

Analyses for total carbonate carbon, total organic carbon (TOC), and respective stable isotope values are illustrated in the stratigraphic profiles in Figure 2.14. It must be noted upfront that the carbonate mineralogy of the Hotazel rocks is known to be complex both from this study and previous ones (Tsikos et al., 2003), with ankerite and calcite dominating the BIF units whilst kutnahorite and Mn-bearing calcite (plus minor rhodocrosite in a few instances) characterise the manganese-rich horizons. For the purposes of this study, no mineral-specific sequential extraction of carbonate-carbon (as CO_2) fractions was attempted, firstly because BIF carbonates show systematic isotopic variation which has previously been interpreted to record a similar origin; and secondly because sequential extraction techniques specifically for Mn carbonates through reaction with phosphoric acid at different temperatures, has proven to be relatively ineffective (Tsikos, 1999). For the same reason, oxygen isotope data for the carbonates become meaningless and thus are neither included in the Appendix nor presented here. Instead, emphasis is placed on the bulk carbonate-carbon isotope record, on the assumption that it records common and comparable processes of carbon isotope fractionation across all different lithologic units in the examined section, irrespective of exact carbonate mineralogy in each instance.

The isotopic profiles of Figure 2.14 exhibit a *ca*. 7 ‰ range in variation between bulk $\delta^{13}C_{carb}$ values, from as high as -3.9 ‰ to as low as -11.2 ‰, respectively recorded in samples from BIF and the main Mn-rich unit. Despite this relatively large range, the stratigraphic profile displays a relatively smooth progression from high to lowest \square values at the basal BIF-Mn transition of the examined section and into the main Mn-rich interval, followed by a gradual increase stratigraphically higher. This contrasts with the relatively more erratic variation in bulk carbonate carbon abundance across the stratigraphy, which fluctuates from as low as sub -0.1 wt. % to as high as 8 wt. %. By contrast, bulk $\delta^{13}C_{TOC}$ values of the very low contents of TOC (less than 0.2 wt. % in all instances) show a much narrower range of values of ~2 ‰ (between -29 ‰ and -27 ‰), but a much "noisier" stratigraphic profile than that for bulk carbonate, with frequent and sharp peaks and troughs. There appears to be no clear lithologic control in the variation of the organic isotope data, although it could be argued

that the main Mn-rich horizon appears to record the lowest I values. Finally, the broadly antithetic relationship between the Fe # stratigraphic profile and that for bulk carbonate carbon contents, suggests a broadly positive relationship and thus likely cogenetic behaviour between modal hematite and carbonate material.



Figure 2.14: Profiles across the middle BIF-Mn cycle, drillcore GL 81, of: Fe # (Fe²⁺/ Fe²⁺+Fe³⁺), bulk $\delta^{13}C_{carb}$, bulk carbonate carbon, Total Organic Carbon, and $\delta^{13}C_{TOC}$.

2.7. DISCUSSION

2.7.1. The Hotazel Formation in the Context of Early Earth Evolution.

Before attempting to model the primary depositional environment of the Hotazel Formation and elucidate the causes behind the conspicuous cyclicity of Fe- and Mn-rich sediment that makes up the entire sedimentary succession, it is important to highlight two key points of contention that, directly or indirectly, surround the genesis of these enigmatic deposits. These points need to be taken into account during attempted reconstruction of the depositional palaeo-environment of deposition of the Hotazel strata, and can be summarised as follows:

Timing and Relationship to the GOE

As indicated in the introductory chapter of this thesis, the absolute depositional age of the Hotazel Formation remains elusive. Authors are divided into those who advocate a <2.2 Ga age on the basis of the underlying Ongeluk volcanics (e.g. Kirschvink *et al.*, 2004), against those who support a >2.4 Ga age based on the age of the overlaying Mooidraai carbonates (Fairey *et al.*, 2013). This controversy has an obvious and significant bearing with respect to the GOE, which on the basis of a combination of several lines of evidence is placed at approximately 2.3 Ga (Figure 2.15). These lines of evidence include amongst others the disappearance of mass independent fractionation (MIF) of S isotopes between 2.45 and 2.32 Ga (e.g. Farquhar *et al.*, 2000, 2011; Bekker *et al.*, 2004;, Guo *et al.*, 2009); a post -2.48 Ga significant increase in Cr abundances in BIF (Konhauser *et al.*, 2011); and increasingly abundant oxidized Fe(III) in palaeosols between 2.5 and 2.0 Ga (e.g. Rye and Holland, 1998; Holland, 2006; Murakami *et al.*, 2011). Simply speaking, on current geochemical, geological and geochronological evidence, it remains unresolved whether the Hotazel Formation post-dates the GOE, or pre-dates it.



Figure 2.15: Cumulative history of O_2 released through geological time (Kump, 2008; Schlesinger and Bernhardt, 2013).

Primary Fe/Mn Oxidative Mechanism/s.

It is a fact that abiotic and/or biological mechanisms of primary Mn precipitation are hardly considered in published models that attempt to reconstruct the deposition of BIF, for the simple and obvious reason that the abundance of Mn in BIF is demonstrably very low. This in itself, understandably hampers efforts to model the deposition of the Hotazel Formation. By contrast, with regard to Fe, both Fe-photosynthesizers and cyanobacteria have variously been suggested to have contributed to the deposition of BIF in general. Since earlier years, abiotic or microbially-catalysed reaction of Fe(II) with dissolved O₂ released during cyanobacterial oxygenic photosynthesis, has been thought to have been a key mechanism for primary precipitation, (e.g. Cloud, 1973); there is mounting evidence in recent years,

however, that direct microbial oxidation of Fe(II) during anoxygenic photosynthesis (e.g. photoferrotrophy) may instead have been the prevailing primary precipitation mechanism of Fe in the ferric form (e.g. Konhauser *et al.*, 2002; Kappler *et al.*, 2005; Crowe *et al.*, 2008). To complicate matters further, Trouwborst *et al.* (2007) note that these two metabolic pathways (i.e. oxygenic photosynthesis *versus* photoferrotrophy) are not mutually exclusive, as both mechanisms are known to precipitate Fe (hydr-)oxides in marine environments today. Moreover, although organic geochemical evidence for the existence of cyanobacteria prior to the GOE has been variously presented from biomarker studies of ~2.7 Ga black shales in Australia and South Africa (e.g. Summons *et al.*, 1999; Brocks *et al.*, 1999, 2003; Eigenbrode *et al.*, 2008). Waldbauer *et al.*, 2009), recent studies that refute such evidence cast doubt on the robustness of biomarker records for the onset of oxygenic photosynthesis (Rasmussen *et al.*, 2008). The above, in combination with the contentious age of the Hotazel Formation, places the matter of primary Fe and Mn oxidation for the Hotazel sediments into the realm of speculation.

2.7.2. Diagenesis in the Hotazel Formation

There is a considerable volume of literature on BIF, most of it published in the past 10 years or so, which is dedicated to petrographic and geochemical evidence in support of diagenetic models being responsible for much of the mineralogical and isotopic characteristics of BIF as observed today. The combination of petrographic textures, carbon and Fe isotope ratios as well as laboratory-based experiments (e.g. Johnson *et al.*, 2008; Heimann *et al.*, 2010; Posth *et al.*, 2013), are used to suggest that at least the carbonate component in BIF (mainly siderite and ankerite) as well as magnetite and selected silicate mineral species (e.g. minnesotaite), owe their origin to early diagenetic redox processes involving ferric oxyhydroxides and co-precipitated organic matter. The specific mechanism postulated for such diagenetic transformations is Dissimilatory Iron Reduction (abbr. DIR) by heterotrophic Fereducing bacteria, which utilise the coupled oxidation of organic carbon through ferric Fe reduction as their energy source (Johnson *et al.*, 2008, 2013). Apart from the predominantly ferrous mineralogy of BIF, the chief geochemical parameters used in the widespread support of DIR as the key overprinting diagenetic mechanism are the low \mathbb{P}^{13} C values of BIF

carbonates in conjunction with highly variable but generally low bulk ⁵⁷Fe values. The former, in particular, are interpreted to signify that the carbon in BIF carbonates is partly of marine inorganic origin and partly from organic matter remineralisation during diagenesis. This results in intermediate carbon isotope values recorded in siderite and ankerite that lie between the typical end-member values for aqueous marine bicarbonate (~0 ‰) and marine organic matter (~-28 ‰) (Tsikos *et al.*, 2003).

The carbon isotope data presented in earlier sections of this Chapter fit directly into the diagenetic mode of origin as described in the foregoing. Crucially, the same process seems to also apply in the case of the manganese-rich horizon in the examined intersection of drillcore GL 81; in fact, the generally lower values in manganese carbonate suggests a potentially even more "organic" source for the carbon in the latter. There is, however, a curious feature in the data from across the entire sequence, namely that variation in the ¹³C values appears relatively small by comparison to the fluctuations in the relative abundance of carbonate-carbon in individual samples. That is to say, there is a relative constancy in the isotope data across the entire length of the studied section, particularly within individual lithologic units, irrespective of the modal abundance of carbonate in the samples. This suggests a curious relative invariance in the contributions of organic versus inorganic carbon to the carbonate fraction of the rocks, which is arguably difficult to reconcile through processes occurring within the sediment pile alone. Therefore, one could argue that precipitation of at least a portion of the carbonate contained in the Hotazel strata may have been derived through direct precipitation from a seawater column where organic carbon cycling may have operated, in order to account for the isotopically depleted isotope signatures. As will be seen in the next paragraph, such a process is indeed observed in extant anoxic basins that could be used as analogues for the palaeo-environment of the Hotazel succession, and perhaps it ought to be considered more seriously in future studies on the origin of carbonates in BIF and associated Mn-rich sediments where applicable.

2.7.3. Possible Modern Environmental Analogues

The most likely modern analogues for the primary precipitation of ferruginous and possible manganiferous sediments akin to the Hotazel Formation, are summarized in Table 2.2.

The best documented of the three environments is the *Black Sea*, with bottom waters enriched in both Fe and Mn, but with a water column that is methane-saturated and euxinic, i.e. sulphidic (Yigiterhan *et al.*, 2011). The Hotazel stratigraphy is however extremely sulphide-poor with no supported documentation of isotopic evidence for the primary existence of methane in the system (as displayed by strongly depleted carbon isotope values).

Table 2.2: Comparing the Archaean Ocean with its modern analogues (adapted from Crowe *et al.*, 2008), including data from Trefry *et al.*, (1984), Trouwborst *et al.*, (2006) Crowe *et al.*, (2008), Dellwig *et al.*, (2012), Schnetger and Dellwig, (2012).

	Archaean	Lake Matano		Orca Basin	Black Sea
Components	Ocean	Mixed Layer	Anoxic Layer	Anoxic brine	Anoxic Layer
Fe (II)	40-120 μmol.liter ⁻¹	0	140 µmol.liter ⁻¹	0.028 µmol /liter	0.000092 μmol
					/liter
Mn (II)		0	9.5 µmol.liter⁻¹	22,000 μg/liter	5 μmol.liter
O ₂	<0.08% PAL *	Saturated	<1 µmol.liter ⁻¹	0 μmol.liter	0 μmol.liter
SO ²⁻ 4	<200 µmol.liter ⁻¹	<20 µmol.liter ⁻¹	<0.1 µmol.liter ⁻¹	<1 µmol.liter	400 μmol.liter
PO ³⁻ 4	0.03-0.29µmol.liter ⁻	<0.025 µmol.liter ⁻¹	9 µmol.liter⁻¹		7 μmol.liter
SiO _{2(aq)}	670-220 μmol.liter ⁻¹	300 µmol.liter⁻¹	420 μmol.liter ⁻¹		
рН	>6.5	8.6	7.0	6.5	
Euphotic zone	<150 m	<130			
Stratification		~100 pycnocline		~2240m	75-125 m
				Halocline/pycnocline	redoxcline

*PAL, Present atmospheric levels

With high ferrous Fe and low sulphate concentrations in its deep anoxic bottom waters, *Lake Matano* in Indonesia is described by Jones *et al.*, (2011) as a prime modern analogue for the chemistry and biology of Archaean and early Proterozoic oceans. The low sulphate concentrations of the Lake are below that of the Archaean ocean leading to the complete removal of sulphate within the upper chemocline, allowing the accumulation of high Fe solute concentrations to depth. Jones *et al.*, (2011) also documented that sulphide concentrations are below what is required to support sulphide-driven anoxygenic

phototrophy, concluding that the bacterial population in Lake Matano is largely sustained by photoferrotrophy supporting the hypothesis that the oxidation of Fe drives the metabolism of a prominent bacterial population.

The *Orca Basin* is however arguably the best analogue for modelling considerations in this chapter. It is a permanently stratified submarine depression situated in the Gulf of Mexico, with anoxic bottom water conditions formed by a strong pycnocline induced by dense brines. The rich brines are formed by the leaching of salt diapirs cropping out of the surrounding sea floor (Tribovillard *et al.*, 2009); governing the density of the anoxic hypersaline bottom layers and leading to its hydrodynamic stability (Schijf, 2007). The significant increase of the salinity of the anoxic bottom waters coincides with the redox transition horizon of the basin. Van Cappellen *et al.* (1998) focused on the distribution of dissolved and particulate Fe and Mn in the stratified water column, and observed that the high dissolved Mn(II) levels (>400 μ M) at a salinity of 60 – 180 ‰ NaCl equivalent, results from dissimilatory (microbial) reduction of Mn oxides and coupled organic matter oxidation, while the precipitation of Mn carbonate in the high-salinity zone (>180 ‰) is the main removal mechanism of Mn to the sediments (Van Cappellen *et al.*, 1998). Significantly, Van Cappellen *et al.*, (1998), performed chemical extractions on sediments from the Orca Basin which suggests that Mn is indeed largely associated with the carbonate mineral fraction.

2.7.4. Depositional Modelling

Arguably the most striking feature that needs to be accounted for in any proposed depositional model for the Hotazel Formation, is the cyclic deposition of Fe- and Mn-rich sediment across the original proto-basin. That cyclicity has been discussed to some degree previously (e.g. Beukes 1983; Tsikos and Moore, 1997) though probably not exhaustively. The current study has moved that discussion one step further, by focusing on the same style of cyclicity yet on a scale where subtle changes from one facies to the next can be effectively tracked through a high-resolution analytical approach. What has become readily apparent from the preceding sections and all relevant data presented, is that the examined 10m-thick BIF-Mn-BIF cycle of drillcore intersection GL 81, is in fact a much more intricate succession of Fe and Mn sedimentary rock, characterised by at least 5 different lithologic intervals (two of which are Mn-enriched), almost unperceptively grading into one another.

This pattern suggests an environment and style of deposition which were fluctuating appreciably over relatively short time scales, and probably in response to a variety of potential driving factors, be it tectonic, climatic, biological, or any combination thereof.

It is envisaged that the fluctuations between Fe and Mn deposition in the examined section and across the overall Hotazel Formation by extension, must have taken place in an environment with well-established stratification with respect to both Fe and Mn. Such stratification is thought to have mimicked the one in the Orca Basin of Mexico, as illustrated in Figure 2.16B, which is a more generalised depiction of the depth profiles at Orca Basin observed by Van Cappellen *et al.* (1998) and shown in Figure 2.16A. The diagram essentially shows a two-pronged depth profile in distributions of Fe and Mn, with an upper Mn/Fe_(aq) maximum, and a lower Fe/Mn_(aq) maximum. The high Mn spike would owe its origin due to processes of redox cycling within the water column in the presence of organic matter, much like with biologically-mediated diagenetic processes of Fe (and/or Mn) cycling within the upper pile of anoxic marine sediments.

Alternate cycles of Fe- and Mn-dominated deposition could conceivably form as a result of superimposed changes in sea-level against the redoxcline of Figure 2.17: for example, according to the transgression-regression model of Beukes (1983) and Tsikos and Moore (1997), seawater regressions and resultant shallowing could cause Mn-dominated precipitation along with Fe-oxide (hematite), whereas during a transgressive cycle, Fe-rich deposition would be favoured. Variations of such a model can then be refined depending on the exact mechanism of Fe precipitation: if, for example, both Fe and Mn were forming as primary oxy-hydroxides, then subtle redox changes associated with the transgressive-regressive cycles can adequately explain the cyclic pattern of sedimentation observed. In this instance though, the present assemblages would require an added reductive "blanket-like" overprint during diagenesis, via biological Fe and Mn reduction respectively, in order to account for the partly reduced mineralogical character of the rocks with respect to both Fe and Mn mineral species across the examined succession.



Figure 2.16: (A) Dissolved Mn (II) and Fe (II) vertical distributions across the stratified water column of the Orca Basin, Gulf of Mexico. (B) Similar concentration gradients as of (A), but of aqueous Fe and Mn as Mn/Fe and Fe/Mn ratios across the chemocline. Modified after Van Cappellen *et al.*, (1998) and Tribovillard *et al.*, (2009).

The alternative scenario to the above would be if manganiferous carbonate deposition may have taken place, at least in part, as a primary mechanism within the water column, as recorded in the Orca Basin and also implied earlier in this chapter for the Hotazel succession. In such a case, deposition of hematite along with primary Mn carbonate and perhaps Mn (oxy-)hydroxide as well, may have been transiently possible during the more oxic (regressive) phase of the system. Fe-dominated precipitation would have taken place during a transgressive, relatively more reduced phase of precipitation, whereby the rate of reductive Mn cycling in the water column would have outpaced that of its oxidation and/or carbonate formation. Transitional stages of deposition to the foregoing two extremes may have resulted in the deposition of transient, Mn-bearing and especially carbonate-rich sediment, as recorded in the hematite/Mn-bearing carbonate sub-cycle in the upper part of the studied section.



Figure 2.17: A conceptual depositional model for the Hotazel sediments in a well-stratified anoxic water column of the Palaeoproterozoic ocean.

2.8 SUMMARY AND IMPLICATIONS

The conspicuously threefold chemical cyclicity observed in the Hotazel Formation with respect to Fe and Mn, was examined mineralogically and geochemically across a single such cycle with a view to providing a plausible depositional/diagenetic model that can account for its development.

Irrespective of whether or not the Hotazel sediments were deposited by biological or abiotic oxidation processes, it is concluded that the Hotazel Fe-Mn succession must have formed in a well-stratified depositional environment not only in terms of the redoxcline but especially with respect to a well-defined gradient in the relative abundance of Fe versus Mn in

solution. The exact nature of the primary precipitates remains unresolved, as it is deemed possible that both high valence species (i.e. oxyhydroxides of Fe and Mn) and reduced phases (e.g. Mn carbonates) may have formed out of the water column. This suggests further study into the primary depositional mechanisms of Fe in BIF in general and Fe plus Mn in the succession in particular, with special emphasis on the possibility of primary reduced Mn and Fe precipitation (e.g. as carbonate) during BIF formation.

However, the model proposed here provides new constraints concerning the bigger picture of the atmosphere-biosphere-ocean system in the early Palaeoproterozoic. Mineralogical stratification as observed in the cyclicity of Mn and Fe is only observed from the Palaeoproterozoic Hotazel strata and is not mirrored in formations from any modern depositional environment. This suggests that it is not only possible, but very likely that sediments of the Hotazel Formation experienced deposition under an anoxic environment, and is therefore a pre-GOE occurrence.

3. CONTROLS AND IMPLICATIONS OF THE DISTRIBUTION OF MANGANESE ACROSS BIF OF THE LOWER TRANSVAAL SUPERGROUP

3.1 INTRODUCTION AND AIMS

Although worldwide BIF occurrences are known to constitute ideal protoliths for high-grade massive hematite Fe-ores (e.g. Dalstra and Guedes, 2004), commercial Mn deposits in direct association with BIF are very rare (Laznicka, 1992). In the few cases where exploitable Mn mineralisation is directly associated with BIF, the deposits are generally small and of marginal economic importance (e.g. Woodi-Woodi, Australia: Blake *et al.*, 2011) and their genesis is commonly attributed to supergene or multi-stage hydrothermal enrichment processes at the expense of carbonate-rich BIF. Truly syngenetic Mn deposits in BIF are, by contrast, extremely rare; as a matter of fact, the only deposit on record where a clear syngenetic litho-stratigraphic association between BIF and Mn-rich sedimentary rock occurs, is the manganiferous Hotazel Formation dealt with in Chapter 2 of this thesis and revisited in Chapter 4. Furthermore, even bulk Mn contents in world-class BIF of the Neoarchaean and Palaeoproterozoic (such as those of the Hamersley Province of Australia) very seldom exceed the value of 0.5 wt. % (Klein, 2005), which in view of the high concentrations of Fe in the same rocks suggests that BIF is, in fact, a rock with Fe/Mn ratio substantially higher than that of average mafic crust (Qin and Humayun, 2008).

Recently, Tsikos *et al.*, (2010) introduced a conceptual model that may account for the origin of the extraordinarily large deposits of Mn in the Hotazel BIF as develop in the KMF. The model implicates directly, - and essentially for the first time - the entire BIF succession of the Transvaal Supergroup, and specifically the thick Kuruman and Griquatown BIFs of the Asbesheuwels Subgroup that stratigraphically underlie the Hotazel Formation. The model of Tsikos *et al.*, (2010) essentially proposes that the Hotazel strata may have formed in a terminal, chemically evolved depositional palaeo-environment, at least with regard to its Mn enrichment in solution and the highly depleted isotope signature of the coexisting aqueous Fe reservoir. Such a notion further requires that the entire succession of BIF succession across the Transvaal Supergroup – namely the Kuruman, Griquatown and Hotazel BIFs – essentially track a continuous process of chemical sedimentation, during

which Mn enrichment ensued as a result of Rayleigh distillation processes in a common depositional palaeo-environment through time.

Should the model of Tsikos *et al.*, (2010); a hypothesis that will be addressed in this Chapter; hold true, then there may well be geochemical signals recorded in the Kuruman/Griquatown BIF succession that can be thought to herald the highly-enriched in Mn, terminally resulting in the deposition of the Hotazel Formation. The most obvious of such signals would conceivably be in the form of a progressive enrichment in Mn relative to Fe in the upper parts of the Griquatown BIF. However, to date there has been no published information whatsoever on the chemical stratigraphy of the entire Kuruman and Griquatown BIF succession, particularly with respect to Mn. This Chapter constitutes the first attempt to fill this void in the literature, in the form of a low-resolution study of the bulk and speciation geochemistry of the Kuruman and Griquatown BIF. This is done through the use of two highly suitable drillcore intersections that collectively capture the respective stratigraphic interval, drilled in the early-to-mid 1990's. Drilling was carried out by the mining company SAMANCOR that exploited Mn ore in the KMF prior to BHP-BILLITON-HMM; the latter company inherited and kindly provided access of the said cores to the author and her supervisors, for the purpose of the present study and beyond.

3.2 REGIONAL GEOLOGY OF THE ASBESHEUWELS SUBGROUP

The geological setting and the mineralogical and chemical compositions of the Kuruman and Griquatown BIFs of the Asbesheuwels Subgroup have been comprehensively described by Beukes (1978, 1980a, 1980b, 1983, 1984) and thereafter revisited by Miyano and Beukes (1984); Miyano *et al.*, (1987), Van Wyk (1987), Klein and Beukes (1989), Beukes and Klein (1990), Beukes *et al.*, (1990), Hälbich *et al.*, (1993), and Horstmann and Hälbich (1995).

The Asbesheuwels Subgroup as part of the lower Ghaap Group, is developed in the Griqualand West Basin of the Transvaal Supergroup, covering the western rim of the Archaean Kaapvaal Craton (Figure 3.1). The Kuruman and Griquatown Iron Formations (IF) are composed almost entirely of BIF, and together constitute the Asbesheuwels Subgroup, conformably overlying the mostly dolomitic Campbellrand Subgroup. The Ghaap Group is

terminated upwards by the siliclastic Koegas Subgroup which overlies the Asbesheuwels Subgroup BIF in the southern part of the Griqualand West Basin, but is apparently not developed north of the Griquatown (growth) fault.



Figure 3.1: Simplified geological map highlighting the distribution of outcropping Kuruman, and overlying Griquatown Formations across the Griqualand West basin.

Overlying the Ghaap Group is the Postmasburg Group which comprises (from base to top) the Makganyene diamictite, Ongeluk volcanic, Hotazel BIF-Mn and Mooidraai carbonate Formations. The contact relationship between the Ghaap and Postmasburg Groups remains contentious, with some authors interpreting it as a ~200 Ma unconformity (e.g. Kirshvink *et al.*, 2004) whilst others interpret it as conformable (Moore *et al.*, 2003, 2011).

The Kuruman Formation consists essentially of autochthonous BIF comprising alternating microbanded and mesobanded siderite-chert-magnetite macrocycles. In the south (Prieska-Koegas area) the Kuruman BIF is separated from the Campbellrand Subgroup by several tens of meters of the Naute Black Shale, consisting mainly of pelitic rocks and some intercalated cherts (Horstmann and Hälbich, 1995). **The Griquatown Formation** conformably overlies the Kuruman BIF, consisting of predominantly clastic-textured, granular BIF, with interbedded microbanded facies, massive ferruginous carbonate/Fe silicate cherts and Fe lutites. The geochemical and mineralogical similarities of the Griquatown and Kuruman BIFs with other Proterozoic and Archaean counterparts elsewhere in the world, suggests that they are typical archives of large-scale BIF deposition at the Archaean-Proterozoic boundary.

3.3 DEPOSITIONAL ENVIRONMENT OF THE KURUMAN AND GRIQUATOWN BIFS

As displayed in Figure 3.2 and described by Beukes (1984), the Kuruman and Griquatown BIFs are interpreted to have been deposited in a wide variety of sedimentary environments, ranging from basinal to shallow epeiric sea, supratidal flat and possibly fresh-water lake.

The microbanded Kuruman BIF was deposited in an open shelf environment along the western margin of the Kaapvaal craton. As suggested by Beukes (1984) photosynthesizing organisms would have flourished in the basin promoting the precipitation of Fe carbonate and Fe-oxide in discrete microbands, in an environment where silica would have largely been deposited during periods of volcanic quiescence. The upper part of the Kuruman BIF consists of siderite-Fe silicate rhythmites deposited in a toe-of-slope environment and rhythmites with grainflow bands deposited along a platform slope. The top of the Kuruman BIF consists of orthochemical as well as allochemical, clastic-textured facies BIF which would have been deposited along a platform edge. During episodes of explosive volcanic activity,

bands of volcanic ash preserved in the present sedimentary record as stilpnomelane lutites were deposited, leading to a sequence of stacked stilpnomelane lutite-ferhythmite macrocycles on the open shelf.



Figure 3.2: Stratigraphic subdivisions and lithologic units of the Griqualand West Supergroup (Beukes, 1984).

Granular-facies BIF of the Griquatown Formation was deposited in a relatively shallowwater, storm-dominated epeiric sea by comparison to the palaeo-environment where microbanded facies Kuruman BIF would have typically precipitated. Siderite and hematite lutite were deposited in the low-energy subtidal zone of the epeiric sea below normal wave base, whereas granular BIF would have formed in high-energy shoals, and banded Fe silicate lutite in platform interior, lagoonal environments (Beukes, 1984). The epeiric sea deposits are overlain by conglomerates which are referred to by Beukes (1984) as *disclutites*; these would represent storm-dominated supratidal flat deposits. Basin fill culminated in the deposition of lacustrine greenalite bandlutite and deltaic siliciclastics at the top of the BIF sequence (Beukes, 1984).

3.4 SAMPLE SELECTION AND METHODOLOGY

The locations of drillcores Hex 5 and Gas 1 is displayed in Figure 3.3. Both intersections capture a continuous section of the stratigraphy from the northern part of the Transvaal basin, where the Koegas Subgroup is not developed. Drillcore Hex 5 captures the lower part of the Ongeluk Formation, the entire Makganyene Formation and approximately the upper half of the Asbesheuwels Subgroup. Drillcore Gas 1 was drilled down to the uppermost part of the Asbesheuwels Subgroup (Griquatown BIF) and continued right through the entire BIF stratigraphy, i.e. through the remainder of the Griquatown and entire Kuruman BIF, and into the underlying Campbellrand dolomites (Figure 3.2).



Figure 3.3: Locality of the KMF within the Griqualand West Basin (left), and localities of the drillcores Hex 5 and Gas 1 (right).

A total of 28 samples were collected from drillcore Hex 5, which straddles the entire Griquatown BIF, the upper part of the Kuruman BIF, and extending at its top into the lowermost part of the Makganyene Formation, displayed in Figure 3.5.



Figure 3.4: Stratigraphy of the Transvaal Supergroup as captured in drillcore intersections Hex 5 and Gas 1, with corresponding sample positions. The microbanded Kuruman BIF is shown in dark grey and the upper, predominantly granular mesobanded Griquatown BIF in light grey.

The sampled interval extends from 647.71 to 935.25 m below surface, and covers 286.54 m of BIF stratigraphy at a resolution of approximately one sample every 10 m of stratigraphic section. A total of 27 samples were collected from drillcore Gas 1. With approximately half of the lower section complimenting that of Hex 5, as it intersects the entire Kuruman BIF, whereas the upper half correlates directly with the Griquatown BIF intersection of drillcore Hex 1 (Figure 3.4). The entire sampled interval of drillcore Gas 1 straddles 451.44 m of the BIF stratigraphy of the Transvaal Supergroup in the area, at a sampling resolution of one sample every 15 to 20 m on average. Macroscopic descriptions and sample depths of all samples are provided in Appendix I.



Figure 3.5: Lithological log of the gradational transition from BIF of the Griquatown Formation into the overlying Makganyene diamictite, from drillcore Hex 5.

All samples collected represent halved sections of core of lengths generally ranging from 10 to 15 cm. Sub-sections of no more than 5 cm length were then further quartered, with the one quarter used for the production of a thin section whereas the other quarter was to be crushed into sample powder. The sample powders were processed in the laboratory for the subsequent analyses of the samples via XRD (bulk mineralogy), XRF (major and trace element geochemistry) and Fe/Mn speciation analyses. Detailed descriptions of the analytical techniques and methodology are provided in Appendix II.

3.5 MINERALOGY

3.5.1 Macroscopic Descriptions

As typically the case with BIFs in general, the very fine-grained nature of the rocks in both the Kuruman and Griquatown BIFs, hinders identification of most minerals with the naked eye. BIF of the Kuruman Formation is easily identifiable in the field by its striking and welldefined mm- to cm-scale, laminated to microbanded texture of rhythmically alternating Ferich and Fe-poor bands. In hand specimen, identification of riebeckite is comfortably made through its characteristic blue colour, whereas the tentative identification of the Fe silicates greenalite and stilpnomelane can be made on the basis of the green and brown colouration of chert bands respectively containing each mineral. Otherwise, the only other relatively confident mineral identification is with respect to the abundant and essentially monominerallic magnetite laminae. Figure 3.6 displays characteristic images of Kuruman BIF.

The Griquatown BIF is contained almost in its entirety in both drillcores sampled, and the respective intersections correlate well laterally on a variety of scales. Careful logging in conjunction with published descriptions of the Kuruman and Griquatown BIFs by Beukes and Klein (1990), reveals that the lowermost part of drillcore Hex 5 captures the uppermost part of the microbanded, riebeckite-rich BIF from the Groenwater Member of the Kuruman Formation, represented by the lowermost sample Hex 24. The overlying Riries Member is developed, but rather obscured by the occurrence of a dolerite sill ~10 m thick (also seen in drillcore Gas 1). This zone contains the first sedimentological evidence in its upper part, of granular BIF textures in the form of thick cm-scale bands of granular chert with irregular

contact relationships and draped by thin laminae of magnetite (Figure 3.7). These textures herald the transition into the predominantly granular-textured Griquatown BIF sequence that follows stratigraphically higher for the remaining part of the examined drillcore intersection. That transition is marked by the Ouplaas Member, a ca. 2.5 m thick unit characterised by a basal conglomeratic bed (Figure 3.8A), and containing 10 to 30 cm thick bands of greenalite lutite with wavy and lenticular bedding ("podding"), intercalated with fine-grained bands of magnetite and chert (Figure 3.8C). The same stratigraphy is largely replicated with minor variation in drillcore Gas 2 as well, making lateral correlation between the two sets of drillcores feasible on sedimentological grounds alone.



Figure 3.6: High resolution photograph of very finely-banded rhythmitic BIF from the Kuruman Formation. Red arrows indicate mm-scale laminations composed predominantly of magnetite. Blue bands in core section (A) are composed of riebeckite, while the greenish colour of (B) is indicative of abundant greenalite. Section (C) with its brownish green appearance contains abundant Fe-silicates (stilpnomelane and greenalite). Scale is in mm; abbreviations are: Qtz-Quartz, Mag-Magnetite, Rieb-Riebeckite, Green-Greenalite, Stilp-Stilpnomelane.



Figure 3.7: Photograph of the Kuruman-Griquatown transitional zone displaying dm-thick, coarse granular chert bands interlayered with finely laminated magnetite and chert (±carbonate) layers. As indicated by the arrows on the photograph, both lithologies are draped by fine-grained magnetite bands which is indicative of this transition zone. Core section (A) displays thick, granular chert bands (whitish-grey) overlain by thick bands of magnetite, whilst core sections (B) and (C) shows bands of chert overlain by thin laminae draped with magnetite.



Figure 3.8: Photograph of lithological units across the Ouplaas Member at the base of the Griquatown BIF. The disrupted banding of section (A) terminated in the basal core band of conglomeratic chert in (B), which is overlain by fine-grained greenalite lutite seen in (C), but becomes largely absent in the core section of (D).

The Griquatown BIF overlying the Kuruman BIF, is bound at its base by a conglomeratic horizon referred to as the Danielskuil "Marker" displayed in Figure 3.9A, a unit indicative of

the First Upper Crocidolite Zone of the Danielskuil Member (Beukes and Klein, 1990). As highlighted in Figure 3.9E, the marker horizon consists of flattened, 0.5 to 1.5 cm peloidal chert pods alternating with fine (1 mm) wavy magnetite laminae. The conglomeratic marker fines upwards through a transitional zone (Figure 3.9B and C) into mesobanded BIF containing alternating decimetre-thick chert/carbonate/magnetite bands (Figure 3.9D).



Figure 3.9: Lithologic features of the First Riebeckite Zone of the Griquatown Formation. The conglomeratic Danielskuil Marker (A) is shown in detail in (E) The marker conglomerate fines upwards in the transitional horizons of (B) and (C) into overlying mesobanded Griquatown BIF observed in (D).

The Danielskuil Member consists of an upper and lower riebeckite-rich zone separated by a riebeckite-poor chert-rich zone which in turn is bound by dm-thick, dark stilpnomelane felutite beds. The remainder of the upper sequence comprises largely mesobanded facies BIF with abundant granular textures, whereby riebeckite-rich chert bands are intercalated with thick, mesobanded to micro-banded chert-siderite Fe-lutite and granular Fe-lutite mesobands. Chert mesobands are either finely laminated, granular, or massive (Figure 3.10D and C), whereas Fe-lutite mesobands are more commonly finely banded (Figure 3.10B to E). The abundance of riebeckite generally wanes stratigraphically upwards.



Figure 3.10: Photograph displaying the typical meso- to macrobanded texture and riebeckite-rich nature observed throughout most of the stratigraphic expanse of the Griquatown BIF. The lower portion of (A) displays the disrupted texture of reworked material, while a large riebeckite/chert macroband, and riebeckite rich pods are shown in (C) and (D) respectively. The large riebeckite band of (C) is itself internally banded. Section (B) displays the dm-scale thickness of bands.


Figure 3.11: High magnification photographs of sections of Griquatown BIF. (A) chert mesobands, containing variable modal riebeckite and interbedded with magnetite; (B) a large granular stilpnomelane-ankerite-rich band overlain by a riebeckite-rich one hosting large carbonate (ankerite) rhombohedra. Scale is in mm; abbreviations are: Qtz-Quartz, Magn-Magnetite, Rieb-Riebeckite, Stilp-Stilpnomelane, Ank-Ankerite.

3.5.2 X-ray Diffraction

The bulk mineralogy of the 55 samples collectively obtained from the Kuruman and Griquatown BIFs for the purposes of this study was determined by XRD (Figure 3.12), and the results comprehensively summarised in Figure 3.13. Essentially all samples are found to contain quartz, magnetite, and a variety of carbonate and Fe-silicate minerals. Hematite was undetectable via XRD in any of the samples analysed. Quartz is detected in every sample and is often the most abundant mineral present, whereas the spectral responses for magnetite and carbonate minerals vary depending on modal abundance from sample to sample. Silicate minerals, most commonly minnesotaite but also stilpnomelane, riebeckite and greenalite, are generally barely detectable to undetectable via XRD and are only picked up in a few particularly Fe silicate-rich samples. Of the carbonate minerals, both ankerite and siderite are detected, with the former being most abundant. Calcite is rare. Overall, the XRD analyses of the powered samples did not reveal any significant variation between the bulk mineralogical compositions of the Kuruman and Griquatown BIFs.





Figure 3.12: X-ray Diffraction profiles for samples collected across the Kuruman and Griquatown BIFs. Samples from drillcore Hex 5 section are shown on the left-hand column, whereas those from drillcore Gas 1 are shown on the right.



Figure 3.13: Bulk mineralogical composition of all samples across the Asbesheuwels Subgroup, as identified by XRD. Samples from the Hex 5 core section are indicted in black, while Gas 1 core section samples are displayed in brown.

3.5.3 Petrography

Microbanded Kuruman BIF

Under the petrographic microscope, the Kuruman BIF is typified by its microbanded texture whereby layering is defined by rhythmically alternating Fe-rich and Fe-poor assemblages, on scales ranging from µm- to cm-thick. Kuruman BIF samples predominantly are made up of microcrystalline quartz (chert) bands containing variable abundances of carbonate (ankerite, siderite) and/or Fe-silicate minerals (greenalite, stilpnomelane, riebeckite and/or minnesotaite), often with some disseminated magnetite as well; which alternate with essentially mono-minerallic magnetite bands. Riebeckite, in particular, is a common mineral constituent in the Kuruman BIF, where it forms mono-minerallic, wavy and often contorted bands of thicknesses up to several cm in some instances, as well as in the form of needle-like fine disseminations and sprays in a matrix of microcrystalline chert (±carbonate).



Figure 3.14: Photomicrographs of the mineralogy and microtextural features of the Kuruman BIF. (A) Interlayered, mm-scale carbonate- and greenalite-rich bands, shown in more detail in (B). (C) Abundant magnetite disseminations adjacent to a thin magnetite band, interlayered with greenalite-, stilpnomelane- and quartz/ carbonate-rich bands. (D) Magnetite band enveloped by blue riebeckite rims and very fine-grained quartz.

Granular Griquatown BIF: Fe lutites to granular facies

The presence of cm to dm-scale mesobands characterize the largest part of the Griquatown BIF, in marked contrast to the microbanded texture that typifies the Kuruman BIF. Although the lower and upper portions of the Griquatown BIF share similar textural characteristics, the stratigraphically lower section appears to be volumetrically more dominated by finegrained Fe-lutite assemblages (Figure 3.15) whereas the latter records increasing abundances of granular facies assemblages (Figure 3.16). Silicate- and carbonate-rich banded Fe-lutites that dominate the lower Griquatown (as also described by Beukes and Klein, 1990), are typically composed of interlayered stilpnomelane and riebeckite-rich bands that contain abundant Fe-carbonate grains in a matrix of microcrystalline quartz. Magnetite is a relatively lesser constituent in this specific facies, but it is present either as fine disseminations or less commonly as thin mono-minerallic microbands. Stilpnomelane-rich bands are very fine-grained, commonly hosting ankerite rhombohedra that exhibit clear zonation from rim to core, while riebeckite-rich bands are usually composed of masses of fine riebeckite fibers in a matrix of microcrystalline quartz and carbonate. In quartz-rich meso-bands, riebeckite fibres show unhindered growth patterns (Figure 3.15F) while in carbonate-rich bands, riebeckite fibres may grow around, and are concentrated along, the edges of carbonate crystals (Figure 3.15C and E)

Granular facies increasingly dominate the upper stratigraphic portion of the Griquatown BIF and are composed predominantly of granular-textured chert and Fe carbonate. These bands of apparently in situ reworked material, consist of rounded 200 µm diameter particles of carbonate and quartz, which form discrete layers up to 10 cm thick. The granular bands are interbedded with Fe-silicate (mainly stilpnomelane) lutites containing magnetite laminae as more commonly observed in the stratigraphically lower Griquatown BIF (Figure 3.16A). Towards the stratigraphic top, granular Griquatown mesobands become volumetrically more dominant whilst interbedded Fe-lutites are generally thinner and more infrequent. Granular facies BIF shows a narrow range in clast size and shape: whereas most bands are well-sorted with fragments of similar sizes and shapes, in some instances (Figure 3.16D) elongated granules up to 100 µm wide and 300 µm long, which appear to be aligned with their long axis sub-parallel to bedding orientation. These seemingly imbricated clasts are enveloped by thin rims of carbonate grains. The rounded clasts are more often hosted in microcrystalline quartz, though greenalite and carbonate-hosted clasts are also observed.



Figure 3.15: Transmitted light photomicrographs of representative mineralogical and textural features of the mesobanded Griquatown Formation. (A) Banding defined by the layering of coarse grained carbonate in chert adjacent to magnetite and stilpnomelane-rich bands; (B) layering of fine-grained, stilpnomelane-rich and stilpnomelane-poor, carbonate-bearing chert with abundant disseminated magnetite grains. (C) Riebeckite-rich chert band containing abundant large, euhedral, zoned ankerite crystals, with at least three identifiable zones. (D) Crudely banded masses of fibrous riebeckite concentrated around microcrystalline carbonate aggregates (E) riebeckite-rich chert on a sharp contact with a carbonate-rich band. (F) Fine riebeckite sprays in a matrix of microcrystalline quartz band.



Figure 3.16: Transmitted light photomicrographs of representative mineralogical and textural features of granular facies Griquatown BIF. (A) Granular beds form thick 0.5 to 1 cm thick layers of rounded peloidal grains that overly finer grained bands. (B) Two granular bands interbedded with a thin <1 mm band of siderite Fe lutite. (C to E) Higher magnification images of granular beds which display in more detail varying textures observed. (C) Rounded and elongated pelloidal granules composed of chert and carbonate, hosted in a matrix of microcrystalline quartz and euhedral carbonate crystals ranging in size from 10 to 100 μ m. (D) Bands that contain predominantly elongated chert granules rimmed with fine-grained carbonates and set in a matrix of microcrystalline quartz here, may display apparent imbrication patterns. (E) Similar elongated granules as in (D) this time set in a greenalite-rich matrix.

3.6 GEOCHEMISTRY OF THE KURUMAN AND GRIQUATOWN BIFs

3.6.1 Major Element Oxides

Selected major element oxide compositions for drillcores Gas 1 and Hex 5 are displayed as stratigraphic profiles in Figure 3.17. The remaining element oxides (TiO₂, Al₂O3, K₂O, Na₂O and P₂O₅) are present in generally very low abundances which are either largely invariant or very erratic across the stratigraphy, and thus contain little meaningful information. Most of these elements are attributed to the fluctuating relative detrital fraction in the rocks, whereas Na₂O is an exception in this regard, as it is associated with samples that contain significant riebeckite which is widely thought to be of late diagenetic/metamorphic origin. However, the origin of riebeckite in these rocks and in BIF, in general, is beyond the scope of this study, and for that reason, the original samples were collected with care in order to avoid as much as possible visually thick riebeckite laminae.

The first point to stress here is that all samples analysed from Hex 5 and Gas 1 drillcores, are invariably dominated by SiO₂ and FeO, which together make up on average, a third to a fourth of the total rock mass (in wt. %) in each instance. With regard to total Fe (as FeO) alone, a general distinction can be drawn between the Kuruman and Griquatown BIFs, with the former being enriched in FeO by a few percentage values on average (39 *versus* 32 wt. %). Concerning the remaining elements, i.e. MgO, CaO and MnO, CaO shows a measurable increase up the stratigraphy which is particularly evident in the upper 50 m or so of the Hex 5 intersection. In absolute terms, this increase is from 2 to 5 wt. % in the Kuruman BIF samples to a maximum of 11 wt. % in the Griquatown BIF. This increase is broadly mimicked also by the MgO stratigraphic profile, although not as strikingly, due to the non-specific partitioning of Mg in carbonates as well as Fe silicate minerals. The underlying mineralogical reason for these signals is simple: the Griquatown BIF, and much more impoverished in magnetite. As a result, the carbonate-associated element oxides of CaO and MgO show a clear increase up section whereas total FeO shows broadly the opposite.

With regard to MnO, it is present across the stratigraphy from consistently very low values in the Kuruman BIF, to occasionally percentage-level MnO contents in the Griquatown BIF. With respect to average MnO values, there is an increase from approximately 0.3 wt. % in the Kuruman Formation to 1.2 wt. % in the Griquatown Formation. The latter, however, has a significant standard deviation, as MnO maxima of up to 4.4 wt. % in the Griquatown BIF are observed, in the form of at least two distinct spikes. The corresponding increase mentioned above in carbonate-associated components over the same portion of the stratigraphy, hints towards a possible association of the Mn with the bulk carbonate fraction of the rocks. The signals are therefore interrogated further in the speciation section that follows.



Figure 3.17: Graph displaying profiles of major element oxide values.

3.6.2 Trace Elements

As expected, trace element abundances in the Kuruman and Griquatown BIFs are observed to be as low as they typically are reported in BIFs of South Africa and coeval BIF worldwide (Klein 2005, and references therein). Selected stratigraphic profiles for most elements where statistically relevant data were available are displayed in Figure 3.18. All other elements analysed for, via the XRF technique, are either too close to the respective lower limits of detection, or below them, so are not considered further.

All elements shown in Figure 3.18 display no systematic stratigraphic variations, except for a subtle and very general increase up-section in selected elements, such as Rb and Sr, which are respectively due to the ever so slight increase in detrital component in the Griquatown BIF relative to the Kuruman BIF, and the substantial increase in modal carbonate in the former. Occasional spikes are also seen in the abundances of elements of possible detrital origin, such as Zr, Cr, V and Sc, especially in the uppermost portion of drillcore Hex 5 near the contact with the overlying Makganyene Diamictite. This is a feature that should be kept in mind with regard to future isotopic research targeting some of these elements (e.g. Cr) in these or similar rocks elsewhere: isotopic analyses of elements at low abundances combined with an apparent detrital origin, are probably unlikely to provide reliable proxies for water-column processes in the original depositional environments of BIF.



Figure 3.18: Stratigraphic profiles for selected trace element concentrations in parts per million (ppm) across the Kuruman and Griquatown BIFs as captured in drillcores Hex 5 and Gas 1.

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3.6.3 Fe and Mn Speciation

Application of speciation analyses in the Kuruman and Griquatown BIFs was done in a similar way with the approach used in Chapter 2 of this thesis, with respect to the Hotazel Formation. The reader is therefore referred to the relevant section of Chapter 2 for more details. The main difference here as compared to the Hotazel Formation, is that the rocks are geochemically and mineralogically much simpler. Crucially, there are no discrete Mn-rich layers anywhere in the BIF sequence, and hematite is also practically absent from all samples collected. As a result, the speciation analyses were carried out in the laboratory and reported here in essentially three steps, representing the total carbonate, total oxide (effectively only magnetite) and total silicate fraction of the samples. All results are included in Appendix III and are graphically shown in the profiles of Figure 3.19.

The first point to mention here which also contrasts significantly with what is seen in the Hotazel strata, is that there is a significant portion of the total Fe hosted in the carbonate fraction of the rock. This is clearly a function of the relatively high abundance of modal ankerite and siderite in the rocks as discussed earlier, mainly in the Griquatown BIF but also occasionally in the Kuruman BIF as well. With respect to the total oxide-hosted Fe fraction, this is prominently higher in most samples from the Kuruman BIF but is also seen in the Griquatown BIF as well. An apparent antithetic relationship seems to be recorded in the oxide-hosted *versus* carbonate-hosted Fe speciation profiles, i.e. high carbonate Fe seems to correspond to low magnetite Fe in a given sample, although the statistical significance of that relationship is questionable considering that the opposite occurs in some samples as well. Finally, the silicate-hosted Fe profile exhibits no apparent systematic distribution across stratigraphy, but it is worth noting that the Fe in the silicate fraction is significant in absolute terms, as it makes up to a third of the total Fe in the rocks and is occasionally even higher.



Figure 3.19: Area plots of Fe and Mn speciation data from all samples across the Kuruman and Griquatown BIFs in drillcores Gas 1 and Hex 5. Juxtaposition of the stratigraphic logs and corresponding speciation profiles is based on descriptive lithological information alone.

The Mn speciation profiles are arguably the most insightful in the context of this chapter. It is conspicuously evident from the profiles of Figure 3.19, that all but a small fraction (less than 10 % by mass) of Mn in the examined rocks is hosted in the carbonate fraction, whether the samples represent the Kuruman or the Griquatown BIF. The significance of this feature is investigated further in the selected bulk-rock and speciation ratio profiles of Figure 3.20.

The combined stratigraphic profile of CaO/FeO in the examined sections reinforces in a slightly different way the earlier conclusion about the upper portion of the Griquatown stratigraphy, where modal carbonate dominates over modal oxide (essentially magnetite). It is over the same section, in which the carbonate-hosted Fe fraction also dominates over the Fe oxide fraction with two distinct peaks of anomalously high carbonate abundance relative to oxide. These spikes correspond directly to the high bulk MnO spikes seen in Figure 3.17 and in the speciation profiles of Figure 3.19.

However, this only reinforces the earlier point that Mn is largely hosted solely in the carbonate mineral fraction, and that high modal carbonate will reflect on high bulk MnO in the rocks as well. What is not known though, especially in the absence of mineral chemical data, is whether the carbonate fraction in itself becomes more manganiferous with stratigraphic height. This can be resolved further in the profile that utilises the ratio of carbonate-hosted Mn speciation data over corresponding samples for carbonate. It becomes much more evident here that the carbonate fraction of the upper Griquatown samples indeed becomes substantially more manganiferous with stratigraphic height, as the said carbonate-specific Mn/Fe ratio increases from as low as 0.01 in the Kuruman BIF to as high as 0.1 to 0.15 in the upper approximately 50 m of the Griquatown BIF.



Figure 3.20: Profiles of major element oxide ratios CaO/FeO and FeO/SiO₂, as well as Fe-Mn speciation ratios $Fe_{Carbonate}/Fe_{Oxide}$ and $Mn_{Carbonate}/Fe_{Carbonate}$

3.7 DISCUSSION AND CONCLUSIONS

The key conclusion emerging from the present Chapter is that the Kuruman/Griquatown BIF succession that stratigraphically pre-dates the Hotazel Formation, indeed becomes more manganiferous with stratigraphic height. This point in itself could be tentatively used in support of these rocks containing a "precursor signal" of increasing Mn content with time, which ultimately led to the anomalous event of high Mn deposition in the Hotazel Formation stratigraphically higher. However, it is also important to emphasize here that Mn is entirely hosted in the carbonate fraction of the rocks (as with much of the Mn in the Hotazel strata), therefore it has a strict mineralogical affiliation and is present almost entirely in a divalent (i.e. reduced) form. Understanding the possible processes that have controlled its mineralogical and stratigraphic distribution thus becomes quite challenging as that distribution has to be linked directly to the origin of Fe carbonates in the Kuruman and Griquatown succession. Specifically, the questions raised can be grouped according to the two possible modes of origin of the carbonates:

Diagenesis. Is the Fe carbonate fraction in the Kuruman and Griquatown Iron formation entirely diagenetic in origin? If so, was the Fe and Mn contained in these rocks initially in a high valence state in the sediment (e.g. as oxyhydroxides), and were they both subsequently reduced in the presence of organic carbon as the main electron donor? Moreover, was Mn reduction by carbon quantitative relative to Fe within the sediment (as thermodynamically expected), i.e. no diffusive loss occurred out of the sediment into the overlying water column? And if Mn was quantitatively reduced, what primary processes controlled the fluctuations in primary Mn supply to the sediment in the first place, as evidenced by the relevant data profiles shown in this section?

Primary precipitation. Is the Fe carbonate of primary origin, at least in part? That is, is there a possibility that the carbonate fraction of the sediments potentially carries with it a signal of increasing Mn (relative to Fe) abundance in solution in the overlying water column with time? If so, what were the exact mechanisms of primary carbonate sequestration and why/how did they change with time, so as to produce more manganiferous carbonate in progressively younger precipitates? And how possible is it that such a signal was faithfully preserved during diagenesis and burial, as it is clear that the carbonates in BIF are at least

texturally modified? Is this Mn signal recorded similarly in coexisting carbonates such as siderite and ankerite, for example?

The above list of questions is not exhaustive and will keep growing unless a much more rigorous examination of the carbonate petrography and geochemistry of the Kuruman and particularly Griquatown BIF is conducted. This investigation have to use detailed petrography on a variety of scales, combined with a variety of micro-analytical and bulk-rock geochemical techniques, as well as stable isotope applications for at least C (carbonate and organic where possible) as well as Fe. Such research was beyond the scope of this thesis but is currently being carried out by other postgraduate researchers.

4. SECONDARY CONTROLS OF MANGANESE RE-DISTRIBUTION AND ENRICHMENT IN THE HOTAZEL FORMATION: THE ROLE OF FLUIDS

4.1 BACKGROUND

The Hotazel Formation of the Palaeoproterozoic (2.65 to 2.05 Ga) Transvaal Supergroup hosts a world class resource of Mn comprising >10 billion tons of ore, ranging in grade from 20 to 48 wt. % Mn metal (Tsikos and Moore, 2005). This resource, known as the KMF (the geographical area in which the Hotazel Formation is preserved) is estimated to account for approximately 50 % of the world's known land-based reserve of Mn ore (Laznicka, 1992; Klemm, 2000; Tsikos *et al.*, 2003). The KMF comprises five structurally preserved erosional relics of the Hotazel Formation, the locations of which are displayed in Figure 4.1a (Gutzmer and Beukes, 1995; Astrup and Tsikos, 1998). The small Hotazel and Langdon Annex deposits to the east of the main KMF are down-faulted blocks of the Hotazel package that have formed graben structures and experienced subsequent hydrothermal and supergene enrichment producing Hotazel "supergrade" ore with >60 wt. % Mn, which have essentially been mined out. The Avontuur and Leinster deposits to the north are thought to be of subeconomic grade, although they have not been exhaustively explored to date (Astrup and Tsikos, 1998).

The main deposit in the KMF is the largest of the five indicate above, extending over an area of approximately 400 km². Here, the bulk of all reported ore reserves and economic production is from the stratigraphically lowermost of the three Mn-beds observed in the Hotazel Formation (see also Chapter 1 of this thesis for more details). It has a maximum thickness of 45 m at the Mamatwan mine, which decreases to between 4 to 8 m towards the northern KMF at the Gloria, Wessels and N'Chwaning areas (Gutzmer and Beukes, 1995; Astrup and Tsikos, 1998). The middle Mn-horizon, referred to as the "middle marker" is the thinnest of the three Mn units (on average between 1 to 3 m stratigraphic thickness) and is of no economic significance. The upper Mn-horizon can reach a thickness of up to 12 m in certain areas of the KMF, has been mined locally, and constitutes a potentially important future resource in the NW area of the KMF where hydrothermal alteration and metal upgrading have occurred (Gutzmer and Beukes, 1995; Tsikos *et al.*, 2003).



Figure 4.1: Location of the KMF in South Africa, displaying the five preserved erosional relicts of the Hotazel Formation (top); and a detailed view (bottom) of the main basin in the KMF, including the conceptual boundary separating areas with the two main ore types found. Adapted from Chetty and Gutzmer (2011).

Two main ore types are encountered in the KMF:

- Primary to early diagenetic, low-grade sedimentary ore composed of 20 to 38 wt. % Mn, referred to as <u>Mamatwan-type</u>, after the homonymous locality in the southernmost KMF where open-cast mining of such ore has been ongoing for the past few decades. Mamatwan-type ore is composed of a lutitic assemblage of braunite and lesser hematite, containing abundant ovoids and laminae of Mn carbonates, mainly kutnahorite but also Mn-rich calcite (see Kleyenstüber, 1984; and Tsikos *et al.*, 2003, amongst others).
- Enriched, high-grade, <u>Wessels-type</u> Mn ore, containing >44 wt. % Mn, which spatially makes up only about 5 % or so of the entire area of the KMF, occurs at its north-western margin where intense block-faulting and thrusting are prominent structural features. In apparent association with the latter structure is recorded a complex hydrothermal alteration event, which has evidently caused the removal of mainly carbonate material from a Mamatwan-type "protore", leading to upgrading of the deposit to a coarse-grained calcic braunite-hausmannite-bixbyite assemblage (Gutzmer and Beukes, 1995; 1996). The possible complexity of that hydrothermal process was more recently revisited by Tsikos and Moore (2005), who invoke at least two discrete hydrothermal events, namely a supergene alteration process followed by circulation of fluids of high salinity. The relative role of these two events in terms of metal upgrading, however, remains to be resolved.

4.2 SECONDARY ENRICHMENT MODELS

The processes of secondary metal enrichment from low-grade Mamatwan-type to highgrade Wessels-type Mn ore have been described, investigated and discussed by numerous authors, namely Boardman (1964), De Villiers (1960, 1970, 1983), Beukes (1983), Miyano and Beukes (1987), Kleyenstüber (1993), Gutzmer (1993), Beukes *et al.*, (1995), Cornell and Schütte (1995), Grobbelaar *et al.*, (1995) Gutzmer and Beukes (1995), Gutzmer and Beukes (1997), Astrup and Tsikos (1998), Moore *et al.*, (2001) Tsikos *et al.*, (2003), and Tsikos and Moore (2005). Prevailing models for the genesis of carbonate-free, Mn-enriched ore envision a single major event of fault-controlled hydrothermal fluid flow, accompanied by metasomatic alteration due to lateral infiltration of hydrothermal fluids away from the faults and into the surrounding Hotazel Formation (Beukes *et al.*, 1995; Gutzmer and Beukes, 1995). This process is demonstrated to have been accompanied by significant mass loss, compaction and resultant residual Mn enrichment (Gutzmer and Beukes, 1997).

Alternative ideas for processes of metal upgrading in the northernmost KMF were first put forward by Tsikos et al., (2003). On the basis of secondary alteration patterns recorded in the host Hotazel BIF, rather than the contained Mn ores themselves, they suggested that alteration and enrichment may have been controlled by an overlying erosional unconformity between the Hotazel and the younger silisiclastic succession of the Mapedi Formation at the base of the Olifantshoek Supergroup. This unconformity is specifically best developed at the northern and western part of the KMF. Tsikos et al., (2003) specifically observed that the upper part of the Hotazel BIF immediately below said unconformable contact has experienced pervasive oxidation and leaching of carbonate resulting in the residual enrichment in Fe. By contrast, lower down in the stratigraphy the hosting BIF ranges from incipient altered and dolomitised, to essentially unaltered even deeper. This pattern of alteration is interpreted due to a largely "top-down" fluid circulation and resultant alteration and enrichment process. It is interesting to note here that, recently, Gutzmer et al., (2012), stress that the mineralogical and geochemical effects of supergene alteration along the Hotazel-Olifantshoek unconformity and the timing of its development, are both aspects that are very poorly documented and constrained and thus require further study.

Irrespective of the competing models mentioned in the foregoing, there is general consensus in the literature that the Hotazel strata in the northernmost KMF have experienced a multistage fluid-rock interaction history. This is supported not only by the range and variation of alteration characteristics in the ores and host-rocks across all three dimensions, but also by the vast and diverse range of common to exceptionally rare secondary mineral species present in vugs and veins and along fault zones in the area. This has contributed to a general lack of agreement about the nature of the hydrothermal fluids implicated and to the relatively wide range of temperatures (from <200° to >400° C) reported for them (Dixon, 1985; Miyano and Beukes, 1987; Gutzmer and Beukes, 1996; Lüders *et al.*, 1999; Cairncross *et al.*, 2000; Tsikos *et al.*, 2003; Tsikos and Moore, 2005). The scope for further research on these aspects therefore remains wide open.

4.3 TIMING OF HYDROTHERMAL METAL ENRICHMENT

Efforts to date the hydrothermal alteration event/s that led to the enrichment of the Hotazel Mn ores in the northernmost KMF, have been hampered by the same reasons that also render the hydrothermal enrichment process in the same area inadequately constrained: this is the complete lack of outcrop of the Hotazel Formation, which means that all modelling attempts have to be based on drillcore material and underground exposures. Notwithstanding the latter, some authors have attempted to date the hydrothermal upgrading event by focusing on mineral species that: (1) are thought to record such events on the basis of field evidence; and (2) lend themselves for the application of radiometric dating. For example, Gnos et al., (2003) dated the potassic mineral sugilite which occasionally occurs in metasomatic zones and vugs in direct association with highgrade Mn ore, via ⁴⁰Ar-³⁹Ar dating. The age yielded by the sugilite dating is 1048.1 ± 5.9 Ma, and has been attributed to a hydrothermal event linked to the Neoproterozoic Namaqua-Natal Orogeny. The basis for that interpretation is strengthened by U-Pb and Rb-Sr ages of 1020 to 1085 Ma of magmatic emplacement in the Namaqua area (Barton, 1983a, 1983b), as well as a 1060 to 1030 Ma SHRIMP U-Pb zircon age which records the orogenic episode, crustal thickening and magmatism (Robb et al., 1998). It is concluded by Gnos et al., (2003) that hydrothermal activity causing the enrichment in Mn in the northernmost KMF can be tenuously linked to collisional tectonics and probably occurred during the peak of metamorphism along the edge of the Kalahari craton.

4.4 AIMS AND OBJECTIVES

The final aim of this thesis and specific goal of this Chapter, is to shed further light into secondary metal upgrading processes in the northernmost part of the KMF, by focusing on a narrow part of the Hotazel succession that contains a complete Fe-Mn cycle. For that reason, the high-resolution geochemical record of the middle Mn-horizon as approached in Chapter 2 of this thesis, is coupled here with a similar high-resolution approach of the corresponding stratigraphic interval from the N'Chwaning area in the northern KMF where hydrothermally-altered, high-grade Mn ore occurs. The key objective is to compare and contrast the bulk geochemical and mineralogical records from the two intersections, analyse

the behaviour of Mn, Fe and other associated elements across stratigraphy, and provide new constraints where possible as to the nature of fluid processes that appear to have affected the BIF and Mn-ore alike.

4.5 SAMPLE SELECTION AND METHODOLOGY

The middle Mn unit of drillcore GL 81 from the Gloria Farm locality as dealt with in Chapter 2, and specifically the bulk geochemical and mineralogical data as presented and discussed in the same chapter, is considered here as the Hotazel Formation protolith.



Mine	Name	Status	Mine	Name	Status
1	Black Rock	UG closed	9	Perth	OC closed
2	Wessels	UG operating	10	Smartt	OC closed
3	N'Chwaning	UG operating	11	Mamatwan	OC operating
4	Gloria	UG operating	12	Adams	OC closed
5	Hotazel	OC closed	13	Middleplaats	OC closed
6	Langdon-Annex	OC closed	14	Telele/Kongoni	Prospect
7	Devon	OC closed	15	Mukulu	Prospect
8	York	OC operating			

Figure 4.2: Map of the KMF displaying farm boundaries. Note the distribution of the high-grade Wessels-type ore, and low-grade Mamatwan-type ore displayed in pink and grey respectively. Adapted from Astrup and Tsikos (1998).

Against that dataset the middle Mn unit of drillcore Nch 91 F is examined, which provides the enriched end-member section of high-grade Wessels-type Mn ore from the northwestern N'Chwaning area. Localities of both borehole intersections are illustrated in Figure 4.2 and their logs shown in Figure 4.3 on the same vertical scale.

The enriched, middle Mn-unit of Nch 91 F was logged and sampled in detail, with the sampling extending into the under- and overlying BIF. The complete Fe-Mn cycle is captured over a total of 5.90 m of core thickness, extending from 591.50 to 597.40 m below surface. 17 individual samples were taken from across the section, based on macroscopic textural and mineralogical variations, and bearing in mind the need for a relatively high-resolution approach to ensure good statistical reproducibility. From the initial 17 samples, 3 were subsequently sub-sampled in the laboratory, resulting in a total set of 20 samples. More detailed descriptions and sample depths are summarised and provided in Appendix I.

Samples were obtained as quartered-core sections from the original drillcore intersection. Each sample was carefully further split in the laboratory with a core cutter, allowing one half to be used towards the production of a polished thinsection, whilst the other half was crushed to fine powder for bulk mineralogical analysis by XRD as well as bulk geochemical analyses via XRF. Comprehensive descriptions of the analytical techniques and methodology used are provided in Appendix II.



Figure 4.3: Lithological log and sample positions across the metasomatically upgraded BIF-MnF-BIF transition of the middle manganese unit from Nch 91 F from the Black Rock Mine.

4.6 MINERALOGICAL EXAMINATION

4.6.1 Macroscopic Observations

Due to the fine-grained nature of the rocks under investigation, macroscopic mineralogical identification during sampling of drillcore Nch 91 F was virtually impossible for all phases except hematite and quartz. The former occurs in its characteristic brick-red "dusty" appearance across large part of the examined section of drillcore Nch 91 F. The latter dominates in light-coloured (microcrystalline quartz), but the potential presence of other light-coloured minerals such as carbonate in such bands is impossible to determine with the naked eye.

Texturally, the hand specimens collected from drillcore Nch 91 F display semi-massive to characteristically banded textures on a variety of scales across the section, occasional dissolution cavities (vugs), and very subtle changes in mineralogy as reflected by corresponding changes in colour and to a lesser extent grain size. The hand specimens of BIF displayed in Figure 4.4 and those of Mn-rich counterparts as shown in Figure 4.5, encapsulate the main textural attributes of the samples collected.



Figure 4.4: BIF core specimens from different stratigraphic horizons that display varying textures and mineralogy. (A) illustrates fine-grained alternating bands rich in magnetite and hematite-rich chert; (B) displays common vuggy textures in chert bands; whereas (C) shows a cherty end-member BIF.



Figure 4.5: Hand specimens from the middle Mn interval. Note the massive textural character displayed in (A), and the appearance of fine-grained bands of hematite at the transition (base) into the Mn-rich horizon (B).

4.6.2 Bulk Mineralogy via XRD

The bulk mineralogy of samples from drillcore Nch 91 F is comprehensively presented in Table 4.1, based on the diffractograms of Figure 4.6 and enriched with petrographic observations. It should be noted that, contrary to drillcore GL 81, the evidently more condensed, subtler in terms of textural variation and oxidised intersection in drillcore Nch 91 F, permits a somewhat more crude subdivision of only three lithotypes for presentation purposes, namely Mn-rich unit and the two enveloping Fe-rich units. Samples from drillcore Nch 91 F are mineralogically simpler than those from core section GL 81. BIF at its base (Nch 14 to 17) and top (Nch 1 to 6) is composed almost entirely of quartz, magnetite and hematite, whilst the Mn-rich unit is dominated by braunite. The Mn-silicate mineral, friedelite, was detected only from two samples via XRD in the uppermost BIF, whereas aegirine is detected in samples flanking the Mn-rich horizon.

Table 4.1: Bulk mineralogy of the Fe-Mn of the middle Mn horizon. Minerals identified by XRD are indicated with (•) (dark grey: major; light grey: minor), and those from microscopy by (X) (green: major; white: minor).

	OXIDES		CARBONATE	SILICATES			SULP		
Sample	Quartz	Magnetite	Hematite	Hausm	Kutnahorite	Friedelite	Braunite	Aegirine	Pyrite
Nch 1	٠	•	•						Х
Nch 2.a			•			•			
Nch 2.b			•			•			
Nch 3	٠	•	•			Х			
Nch 4	•	•	•						
Nch 5	٠	•	•						
Nch 6	•		•					•	
Nch 7		Х	Х			Х	Х	Х	
Nch 8			•	Х			•		
Nch 9		Х	•		Х		•		
Nch 10.a		Х	•		•		•		
Nch 10.b			•		•		•		
Nch 11	Х		•	Х		•	•		
Nch 12.a		•	•			•	•		
Nch 12.b	Х	Х	•			•	•		
Nch 13		Х	•						
Nch 14		•	•					•	
Nch 15		•	•			Х		Х	
Nch 16		•	•						
Nch 17	1	•	•						1

	Identification through:			
Mineral abundance	XRD	Petrography		
Major	•	Х		
Minor	•	Х		





Figure 4.6: (A) X-ray Diffraction profiles of the BIF samples from the N'Chwaning section, with main peaks of the key mineral components highlighted. The main minerals detected are quartz, hematite and magnetite and the silicates aegirine and friedelite. (B) X-ray Diffraction profiles of samples across the middle Mn horizon, with the main peaks of key mineral components highlighted. The main minerals detected here are hematite, the Mn-silicates braunite and friedelite, and kutnahorite.

4.6.3 Petrography and Mineralogy

Banded Iron Formation (samples Nch 1 to 6, and Nch 14 to 17)

As indicated in the XRD results, the mineralogy of BIF samples is simple, and composed predominantly of magnetite, hematite, microcrystalline quartz (chert) and negligible carbonate material. Magnetite is present commonly in microcrystalline subhedral form, whereas hematite develops as both fine grained interstitial particles in discrete bands, as well as in relatively larger well-formed subhedral plates, where it is likely forming at the expense of pre-existing magnetite through pseudomorphic oxidation (martitisation). The finely Fe-rich and Fe-poor interlayered texture characteristic of the primary lithology is still well preserved, but the scale of banding is relatively reduced compared to that seen in BIF from drillcore GL 81, with bands exceeding 1 cm in thickness being very occasional and occurring mainly in chert-rich portions of BIF.

Direct evidence of dissolution and mass-loss is recorded through the common occurrence of stylolites, which are observed in BIF samples from above and below the Mn horizons (Figure 4.7C and D). A key mineralogical association particularly with samples flanking the Mn-rich interval is that of aegirine, which appears to texturally overprint pre-existing chert-Fe oxide assemblages. Aegirine is an end-member Na-pyroxene and is present in its highest abundance in the samples enveloping the Mn-rich horizon. The occurrence of aegirine has been discussed before in this thesis and elsewhere (Tsikos and Moore, 2006), and is potentially significant as its chemical composition would signify a metasomatic overprint on the Hotazel rocks, by comparison to their essentially Na-free composition in areas where no alteration occurs (e.g. see drillcore GL 81, Chapter 2 of this thesis).

Manganese-rich horizon (samples Nch 8 to 13)

Similarly with the Fe-rich samples, primary layering is still observed in the Mn unit, though the banding is often contorted. The mineralogy is dominated by fine-grained braunite, along with variable hematite, occasional minute grains of hausmannite interstitial to braunite, and traces of magnetite. Minor microcrystalline quartz and lesser euhedral secondary carbonates are also variously observed, especially as secondary vug-fills.



Figure 4.7: Transmitted and reflected light photomicrographs of mineralogical and textural features from samples across the BIF. (A) Displays microcrystalline quartz hosting hematite and magnetite, while (B) displays a reflected light image of a similar section to (A) where the nature of very fine-grained particles of hematite versus large euhedral crystals of magnetite is highlighted. (C) and (D) show stylolites associated with a banded aggregate of magnetite crystals (black) and brown aegirine, which in image (C) defines a boundary between a band dominated by carbonate from the overlying microcrystalline quartz-rich band. (E) Overgrowths of brown euhedral aegirine on quartz. (F) Interbedded magnetite and microcrystalline quartz. Abbreviations used: Mag. –magnetite, Hem. –hematite, Qtz. –quartz, Carb. - carbonate, and Aeg. –Aegirine.



Figure 4.8: Photomicrographs of selected mineralogical and textural features observed in the Mn-rich horizon. Reflected-light photomicrograph of the fine-grained texture of contorted braunite-rich laminae in image (A) and (B). Note the difference in crystallinity between individual laminae in (A), which likely reflect primary variations in the replaced mineralogy. (C) Reflected light image of anhedral hausmannite particles surrounding larger braunite grains. (D) Transmitted light photomicrograph of vugs filled with recrystallized quartz. Abbreviations used: Mag. –magnetite, Hau. –hausmannite, Qtz. –quartz.

4.7 COMPARATIVE CHEMICAL STRATIGRAPHY

The key objective of this Chapter is to attempt a chemo-stratigraphic comparison between the middle Mn unit and adjacent BIF from the Nch 91 F intersection to the corresponding GL 81 one, with a view to understanding further mechanisms of bulk geochemical change during processes of fluid alteration and metal upgrading. For that reason, relevant data from the drillcore section GL 81 are drawn directly from Chapter 2 of this thesis, where the primary and diagenetic environment of the Hotazel Formation was discussed. The section of drillcore GL 81 is considered as a suitable unaltered protolith to the one of drillcore Nch 91 F examined in this Chapter. This otherwise reasonable assumption encloses some obvious potential pitfalls that relate to any primary lateral variations in thickness, mineralogy and/or geochemistry that may have existed between the intersection GL 81 and the true precursor lithology of intersection Nch 91 F. This must always be kept in mind in all ensuing interpretations.

As the GL 81 intersection was subdivided into 5 distinct lithologic units whereas section Nch 91 F was only subdivided into three, the comparative exercise employed in the forthcoming sections required some further adaptation to account for that and thus facilitate data presentation and interpretation. This was done in the following sections on the basis of the stratigraphic distribution of the key major element oxides across the examined GL 81 stratigraphy, namely FeO and MnO, as the most likely constituents to have behaved conservatively during hydrothermal alteration. Specifically, the Fe-rich portion of section Nch 91 F overlying the Mn-rich horizon was further subdivided into three sub-sections, on the basis of a Mn peak observed within the said intersection. As will be also seen in subsequent sections, the Mn "sub-cycle" recognised in the GL 81 section appears to be replicated in section Nch 91 F, albeit in a stratigraphically much more condensed form as recorded in essentially only two samples only (Nch 2.a and b; see also Appendix III). This Mn-rich "subcycle" in drillcore Nch 91 F (and any considerations arising from it), is therefore confined within the narrow interval that is defined by the midpoint between samples Nch 2.a and Nch 1 above, and the corresponding mid-point between samples Nch 2.b and Nch 3 below.

4.7.1 Mass Balance Considerations

The first step in the comparative exercise as introduced in the foregoing paragraphs, is to construct an equivalent "enriched" intersection of the middle Fe-Mn cycle of drillcore GL 81, on the basis of the mineralogical and geochemical information presented in this chapter for corresponding intersection Nch 91 F, and in light of available literature information (Gutzmer and Beukes, 1997). Simply speaking, the exercise involves first an artificial "decarbonation process", whereby all bulk geochemical data of intersection GL 81 are recalculated to the original analytical totals for all samples on a CaCO₃- and MgCO₃-free basis,

i.e. by subtracting the bulk CaO, MgO and CO_2 contents of the samples. The percentage of mass-loss that corresponds to this numerical re-calculation is then removed as corresponding reductions in the stratigraphic thickness of each of the five sub-units examined, on the added – and arguably over-simplistic – assumption that no density changes accompanied the alteration process. Therefore, the calculated mass loss is conveniently also translated directly into volume loss and resultant stratigraphic compaction, in the absence of any density data which were beyond the scope of this study.

The result of the above process is the production of a conceptually "altered" (i.e. carbonatefree and stratigraphically condensed) section GL 81, as graphically shown in Figure 4.9. Corresponding numerical results are also included in Table 4.2.

Unit	Gl 81	Gl original	A: Volume	B: Vol.	Reduced	Nch	Nch 91 F
	Samples	Thickness	lost (wt. %)	remaining	thickness	Thickness	Samples
		(m)		(wt. %)	(m)	(m)	
5	G1-G2.b	0.43	8.4	91.6	0.39	0.48	Nch 1-Nch2.a
4	G3-G16.b	3.68	45.2	54.8	2.02	0.67	Nch2a-b
3	G17-G20	1.07	15.1	84.9	0.91	1.06	Nch 3-Nch 6
2	G21-G32	4.34	27.5	72.5	3.15	3.09	Nch 8-Nch 14
1	G33-G35	0.78	20.5	79.2	0.62	0.60	Nch 15-Nch17
		10.30 m			7.08 m	5.90 m	
		Total			Total	Total	

Table 4.2: The volume lost (in %) of samples from the Gloria core, is compared with observed thickness from the correlative N'Chwaning Units.

A: Vol. lost (wt. %) = MgO+CaO+CO₂ B: Volume remaining (wt. %) = Total Vol. – $(MgO+CaO+CO_2)$

There are a few key points that emerge at this stage of the exercise, before further geochemical data analysis across stratigraphy is presented : firstly, considering all underlying assumptions mentioned earlier, the estimated "altered" thickness of intersection GL 81 (~7 m) compares reasonably well to the stratigraphic thickness of intersection Nch 91 F (~6 m). This agrees with the widely-held view that secondary metal enrichment in the northernmost KMF has resulted primarily due to decarbonation of the original protolith (Gutzmer and
Beukes, 1997; Tsikos *et al.*, 2003). Moreover, the biggest disparity between the calculated GL 81 thicknesses and those of section Nch 91 F for the five defined sub-units, lies with the stratigraphically upper Mn sub-cycle. The latter is also the most carbonate-rich and second-thickest sub-member of the entire section, and therefore is most prone to error in the calculation process involved. It is also possible that it corresponds to a part of the original stratigraphy that was characterised by relatively larger lateral thickness variation in the original environment of deposition, over short geographical distances; in other words, it is so thin in section Nch 91 F because it may already have been substantially thinner prior to the alteration process, than what is seen in drillcore GL 81.



Figure 4.9: Simplified logs illustrating the thicknesses of the 5 sub-units comprising the middle BIF-MnF-BIF cycle. The left hand log displays the observed unit thicknesses measured from the pristine Gloria core log (GL 81), while the middle log section displays the thicknesses of the recalculated Gloria units that has undergone decarbonation (the removal of CaCO₃, (as CO₂+CaO) and MgO). The log on the left of Figure 4.9 displays the observed unit thicknesses measured N'Chwaning core, Nch 91 F.

4.7.2 Geochemical Considerations across Stratigraphy

Selected re-calculated compositions of section GL 81 on a carbonate-free basis have been plotted along with the true analyses of section Nch 91 F against their respective reducedand true-thickness stratigraphic profiles (Figure 4.10). All element oxides included are those analysed for via XRF but for CaO and MgO for obvious reasons, whereas the trace elements will not be discussed in this context but in more general terms at the end of this section.

Major Element Profiles

With respect to the overall stratigraphic patterns observed (Figure 4.10), there is good correspondence between the two sections in the plotted data for SiO₂, total Fe (as FeO) as well as MnO, whereas the remaining elemental oxides (i.e. Na₂O, TiO₂, Al₂O₃, K₂O and P₂O₅) display a comparatively more variable and thus erratic distribution across stratigraphy. This may also be due to the generally very low abundances for all these components (except for Na₂O, which will be discussed separately below) which could entail a strong element of analytical artefacts in the reported data (e.g. inconsistent levels of precision and accuracy in the instrumental measurements).

When respective absolute abundances for each section are considered, the following points become apparent:

- Bulk SiO₂ does not seem to behave in an entirely conservative fashion during the alteration process: whereas in the Fe-rich and Mn-lean parts of the stratigraphy the absolute data profiles show a reasonably good match (particularly in the portion of the studied sections between the two Mn maxima), within the Mn-enriched units themselves, a relative loss of Si of several wt. % units can be postulated.
- With respect to total Fe (as FeO), things are somewhat more complex: Fe appears to behave conservatively in the middle part of the examined section between the two Mn maxima, but behaves dissimilarly in the two portions where highest Mn is recorded. Specifically, in the main Mn unit, the calculated abundances of total Fe significantly exceed those read in the samples from Nch 91 F, yet the opposite appears to be the case in the high Mn "sub-cycle" higher in the stratigraphy. Therefore, just like Si, Fe cannot be regarded as behaving entirely conservatively

during alteration and upgrading, unless much of the disparity in the two profiles is attributed to primary, (i.e. pre-alteration) lateral variations in geochemical composition.

- Bulk MnO profiles are those that appear to display the most conservative behaviour in the Fe-rich portions of the examined sections, but not in the Mn-rich units themselves. Importantly, the relative enrichment that seems to be recorded in the main Mn unit is well over and above that expected via simple decarbonation of a GL 81-like protolith. This can conceivably be accounted for by the relative reductions in the abundances of Fe and Si in the same sections as discussed earlier. By stark contrast, the stratigraphically higher Mn sub-cycle related to the hematite/carbonate unit, appears more enriched in Mn in the artificially decarbonated GL 81 section than in Nch 91 F. If this effect is not due to primary lateral variations as discussed previously, a possible cause may be sought in the mineralogical differences between the two Mn-enriched intervals: Mn in the upper hematite-carbonate unit is almost entirely carbonate-hosted (unlike the main Mn unit where much of it is hosted in braunite) and much of it may have been remobilised via later fluid alteration.
- The situation regarding the profiles for Na₂O is somewhat intriguing: whereas the abundance of bulk-rock Na in the GL 81 section is negligible across the entire profile, the intersection from drillcore Nch 91 F displays two characteristic spikes of high Na (a percentage level increase in one instance), naturally coinciding with the samples that contain appreciable abundances of aegirine. This feature is not encountered for the first time, but in fact adds to the knowledge of high-Na zones on the flanks of all three manganese cycles of the Hotazel Formation as described and discussed before (Tsikos and Moore, 2005). It therefore becomes apparent that the section under examination has suffered a clear metasomatic overprint, which has involved the introduction of substantial Na from hydrothermal fluids into the rocks. Concerning the reason for the curious distribution of high Na in those two discrete spikes, they may owe their origin to the dissimilar behaviour of Na upon reaction of Na-rich fluids with rocks of the Hotazel Formation: as proposed by Tsikos and Moore (2005), precipitation of a Mn-free sodic/ferric silicate like aegirine may have been favoured by reactions between a highly saline fluid and rocks containing large abundances of

hematite and free quartz, like those that characterise particularly the hematitelutite transitions between the Mn-rich units and adjacent BIF.



Figure 4.10: Profiles of major element oxide compositions of samples across the middle BIF-Mn-rich layer cycle section. The major oxide components: SiO_2 , FeO, MnO and Na_2O that are observed to show significantly large changes are displayed in the top part of the Figure, while the behaviour of components that are present in very low concentrations (TiO₂, Al₂O₃, K₂O, P₂O₅) are displayed at the bottom part.

Trace Elements

With respect to the trace elements analysed, the very low (often very near or below the instrumental limit of detection) abundances for most of them, render considerations involving trace elements in the present context to be difficult and potentially spurious. On the basis of a few trace elements whose abundances are consistently above detection limit, namely Cr, V, Cu, Pb, Ni, and Ba, it is evident that they are substantially enriched relative to their likely precursor protolith. A mere comparison between average Cr abundances in the Fe-rich/Mn-lean portions of core GL 81 versus those of core Nch 91 F, suggests a near 9-fold enrichment from 33 ppm to 305 ppm. Similarly, V, Pb, and Ni display increases in average concentration respectively from 10 ppm to 50 ppm; undetected to 58 ppm; and undetected to 16 ppm. In the Mn-rich unit, increases in the concentration of Cr, V, Cu, Pb, Ni and Ba are also observed, particularly with respect to Cu, Pb, Ni and Ba: Cu increases more than 3-fold from 25 to 86 ppm; Pb increases from undetectable to 83 ppm; Ni from 8 to 26 ppm; and Ba from 29 to 264 ppm. These apparent enrichments appear unlikely to have been produced via conservative processes of decarbonation of a suitable precursor, and probably require net introduction via fluid metasomatic processes or significant geochemical re-constitution of the rocks during the alteration event/s, similarly to the earlier contention about the introduction of Na into the system.

4.8 SUMMARY AND IMPLICATIONS

From the simple yet quite novel geochemical exercise presented in the foregoing sections, it becomes apparent that the alteration and metal upgrading that has been experienced by the Hotazel rocks in the northernmost KMF is geochemically complex, and can hardly be accounted for by mechanisms of fluid-induced dissolution, mass-loss and relative residual enrichment alone. Moreover, the relative behaviour of individual major constituents – like Mn, Fe and Si – is variable across mineralogically and chemically dissimilar lithologic sub-units that comprise the Hotazel strata. Fe-rich portions of the Hotazel have apparently responded differently to circulating fluids than Mn-rich portions did to the same fluids, and the same can be said between carbonate-rich and carbonate-lean stratigraphic intervals. Crucially, the geochemical case-study presented here has also reinforced previously

documented processes and models which involve a significant metasomatic overprint in the Hotazel rocks. Whether or not this metasomatic event was the sole or even main mechanism responsible for alteration and metal enrichment in the Hotazel succession, remains to be verified. It most certainly though, appears to be related to the circulation of highly saline, sodic fluids, at some point in the geological history of these rocks, which appear to have introduced enrichments in at least a certain suite of elements, which besides Na also include Ba, Pb, Cu, V and Zn.

From a geochemical point of view, the suite of elements associated with the enrichment event, fits the description of alkali-rich, low-temperature brines of connate origin, which are variously implicated in processes of base metal ore-formation, such as of Pb-Zn deposits of the MVT type like those seen in association with dolomitic rocks of the basal Transvaal Supergroup (i.e. the Pering area; Gutzmer, 2005). A causal metallogenic link therefore remains between various styles of mineralisation seen on a regional scale in diverse rocks of the Transvaal Supergroup, and calls for further and more intensive research into its causes, fluid sources, timing and controls.

5. SYNOPSIS – SUGGESTIONS FOR FUTURE WORK

The key findings that emerged out of the present study are summarised below in three points corresponding directly to the three main parts of this research:

Chapter 2: Reconstruction of the primary depositional environment of the Hotazel BIF-Mn Formation in the upper part of the Neoarchaean-Palaeoproterozic Transvaal Supergroup, was approached through the detailed petrographic and geochemical examination of a complete, relatively narrow (~10 m-thick), BIF-Mn-BIF cycle of the three present in the Hotazel succession. The results indicate that the palaeo-environment of deposition of the latter must have corresponded to a chemically stratified marine basin, with strong and wellestablished water-column gradients in dissolved Mn and Fe. First-order stratigraphic variations in the style of deposition from Fe-rich to Mn-rich and back must have occurred in response to sea-level changes and attendant redox fluctuations against such water-column stratification. No new constraints, could be provided on the relative role of primary manganese and iron precipitation versus subsequent diagenetic modification in producing the assemblages observed today, but the possibility of at least primary precipitation of Mn carbonate having being transiently operative, was highlighted. However, the model proposed here does provide new constraints concerning the bigger picture of the atmosphere-biosphere-ocean system in the early Palaeoproterozoic. Mineralogical stratification as observed in the cyclicity of Mn and Fe is only observed from the Palaeoproterozoic Hotazel strata and is not mirrored in formations from any modern depositional environment. This suggests that it is not only possible, but very likely that sediments of the Hotazel Formation experienced deposition under an anoxic environment, and is therefore a pre-GOE occurrence.

Chapter 3: The Kuruman and Griquatown BIF sequence that predates the Hotazel Formation, was examined petrographically and geochemically on low resolution, with a view to reading and elucidating any recorded stratigraphic signal in the distribution of Mn. The existence of Mn enrichment in the studied drillcore sections Hex 5 and Gas 1 is specifically recorded in the upper part of the Griquatown BIF, with Mn hosted exclusively in the carbonate fraction. Crucially, the latter itself appears to become progressively more

manganiferous up-section. This result lends broad support to the suggestion that the Kuruman, Griquatown and Hotazel BIFs are likely to be genetically linked through a common and chemically evolving palaeo-environment of deposition, at least with respect to Mn. However, the exact causes, controls and implications of the behaviour of Mn across the entire BIF stratigraphy of the Transvaal Supergroup remain very fertile topics for future research.

Chapter 4: Is essentially the final Chapter of this thesis, the topic of post-depositional, fluiddriven alteration and metal upgrading of the Hotazel Fe-Mn Formation was revisited. This was done through a high-resolution petrographic and bulk geochemical examination of its middle BIF-Mn-BIF cycle, in an area where such effects are recorded and against the corresponding unaltered stratigraphic interval as comprehensively examined in Chapter 2 earlier. The results show that neither Mn nor other major components of the examined section behave entirely conservatively during fluid alteration; that the relative mobility behaviour of each element may vary depending on the exact nature of the protolith in each instance; and that a clear metasomatic introduction of certain chemical constituents (Na, associated alkalis and selected base metals) has taken place. The possibility that a highly saline (Na-rich) brine may have been the main fluid agent causing metasomatic alteration and metal upgrading in the Hotazel rocks, is therefore further reinforced.

It is the hope of the author that the present thesis and the results, arguments and ideas contained within it, will at least provide a springboard for further research on these spectacular rocks. The primary origin of the Hotazel succession and its post-depositional modifications certainly seem to remain very fertile subjects for future research. Similarly, a more detailed look into the Griquatown and Kuruman BIFs – with respect not only of the stratigraphic distribution and mineralogical association of Mn but of other redox-sensitive elements as well – will be absolutely essential in illuminating further the history of the Earth's early oceans and atmosphere, during one of the most important intervals in its geochemical and biological evolution. It is hoped that this thesis has at least succeeded in stimulating more such research towards those directions.

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APPENDICES

APPENDIX I: Sample Localities and Sample Data

A total of 122 samples were collected for this study, providing insights into the geochemical evolution across the stratigraphy of the lower and upper part of the BIF stratigraphy of the Transvaal Supergroup. Individual sample lists from each drillcore are provided in this section. Samples from the BIFs of the Asbesheuwels Subgroup were obtained from two drillcore sections Hex 5 and Gas 1, both of which are from the area to the east off the Kalahari Manganese Field, as shown in Figure A1. These core sections were sampled at Hotazel, courtesy of BHP - Billiton - Hotazel Manganese Mines. A total of 55 samples were taken from the Asbesheuwels BIFs, 28 samples from the Core of Hex 5 and 27 from Gas 1. The Hotazel Formation was sampled from two drillcores from the Black Rock mine, one from the Gloria area and one from N'Chwaning, courtesy of ASSMANG. The unaltered middle Mnrich horizon was sampled at high resolution from core GL 81, which yielded 40 samples. The stratigraphically equivalent altered (metal upgraded) Mn-horizon and adjacent BIF was sampled from drillcore Nch 91 F, from which 20 samples in total were collected.



Figure A1: Geological position of the Kalahari Manganese Field within the Griqualand West Basin and localities of the drillcores used in this thesis.

Table I.1: Individual sample depths and macroscale descriptions of samples from both the Hex 5 and Gas 1drillholes that span across the entire stratigraphy of the Asbesheuwels Subgroup.

No	Sample	m.b.s.	Lithology
1	Nel 1	647.71	Chert-magnetite banded iron formation (plus diamictite clasts)
2	Nel 2	651.48	Chert-magnetite banded iron formation
3	Nel 3	653.19	Chert-magnetite banded iron formation
4	Nel 4	656.13	Riebeckite poor, cherty granular banded iron formation
5	Hex 1.a	660.90	Riebeckite-rich granular textured banded iron formation
6	Hex 1.b	663.00	Riebeckite-rich granular textured banded iron formation
7	Hex 2	672.40	Riebeckite-rich granular textured banded iron formation
8	Hex 3	685.40	Riebeckite-rich granular textured banded iron formation
9	Hex 4	693.80	Riebeckite-rich granular textured banded iron formation
10	Hex 5	705.80	Riebeckite-rich granular textured banded iron formation
11	Hex 6	722.40	Riebeckite poor, cherty granular banded iron formation
12	Hex 7	733.40	Riebeckite poor, cherty granular banded iron formation
13	Hex 8	744.20	Riebeckite-rich granular textured banded iron formation
14	Hex 9	752.80	Riebeckite-rich granular textured banded iron formation
15	Hex 10	766.90	Riebeckite-rich granular textured banded iron formation
16	Hex 11	780.10	Riebeckite-rich granular textured banded iron formation
17	Hex 12	792.00	Riebeckite-rich granular textured banded iron formation
18	Hex 13	802.40	Riebeckite-rich granular textured banded iron formation
19	Hex 14	814.20	Riebeckite-rich granular textured banded iron formation
20	Hex 15	827.40	Riebeckite-rich granular textured banded iron formation
21	Hex 16	835.60	Riebeckite-rich granular textured banded iron formation
22	Hex 17	848.90	Riebeckite-rich granular textured banded iron formation
23	Hex 18	863.90	Finely laminated rhythmitic iron formation
24	Hex 19	871.50	Finely laminated rhythmitic iron formation
25	Hex 20	886.50	Finely laminated rhythmitic iron formation
26	Hex 21	898.70	Finely laminated rhythmitic iron formation
27	Hex 23	919.75	Finely laminated rhythmitic iron formation
28	Hex 24	934.25	Finely laminated rhythmitic iron formation
29	Gas 1	149.50	Riebeckite-rich granular textured banded iron formation
30	Gas 2	173.50	Riebeckite-rich granular textured banded iron formation
31	Gas 3	191.50	Riebeckite-rich granular textured banded iron formation
32	Gas 4	200.60	Riebeckite-rich granular textured banded iron formation
33	Gas 5	212.00	Riebeckite-rich granular textured banded iron formation
34	Gas 6	228.50	Riebeckite-rich granular textured banded iron formation
35	Gas 7	244.00	Riebeckite-rich granular textured banded iron formation
36	Gas 8.a	259.00	Riebeckite-rich granular textured banded iron formation
37	Gas 8.b	270.50	Riebeckite-rich granular textured banded iron formation
38	Gas 9	271.00	Riebeckite-rich granular textured banded iron formation
39	Gas 10	282.50	Riebeckite-rich granular textured banded iron formation
40	Gas 11	296.20	Finely laminated rhythmitic iron formation
41	Gas 12	336.40	Finely laminated rhythmitic iron formation
42	Gas 13	354.40	Finely laminated rhythmitic iron formation

		-	
43	Gas 14	366.50	Finely laminated rhythmitic iron formation
44	Gas 15	371.00	Finely laminated rhythmitic iron formation
45	Gas 16	389.50	Finely laminated rhythmitic iron formation
46	Gas 17	403.60	Finely laminated rhythmitic iron formation
47	Gas 18	419.50	Finely laminated rhythmitic iron formation
48	Gas 19	434.20	Finely laminated rhythmitic iron formation
49	Gas 20	441.00	Finely laminated rhythmitic iron formation
50	Gas 21	446.50	Finely laminated rhythmitic iron formation
51	Gas 22	460.50	Finely laminated rhythmitic iron formation
52	Gas 23	473.60	Finely laminated rhythmitic iron formation
53	Gas 24	488.40	Finely laminated rhythmitic iron formation
54	Gas 25	504.80	Finely laminated rhythmitic iron formation
55	Gas 26	512.90	Finely laminated rhythmitic iron formation

Table I.2: GL 81 individual sample depths and macroscale descriptions

No	Sample	Depth	Lithology
1	G 1	349.80 - 349.93	Banded iron formation (BIF)
2	G 2.a	350.035 - 350.065	BIF
3	G 2.b	350.13 - 350.21	BIF (increase in chert bands)
4	G 3	350.38 - 350.455	BIF (increasing carbonate lamellae and Mn bands)
5	G 4	350.53 - 350.565	BIF (increasing carbonate lamellae, Mn bands, and a band of hematite)
6	G 5	350.74 - 350.80	BIF (abundant Mn rich bands)
7	G 6	350.93 - 350.99	BIF (abundant Mn rich bands)
8	G 7	351.07 - 351.22	BIF (abundant Mn rich bands, appearance of hematite)
9	G 8	351.46 - 351.66	BIF/Hematite Lutite
10	G 9	352.05 - 352.165	Hematite lutite
11	G 10.a	352.245 - 352.37	Hematite lutite (minor Mn-rich zone)
12	G 10.b	352.44 - 352.51	Hematite lutite (increased Mn-rich zones)
13	G 11	352.61 - 352.65	Hematite lutite
14	G 12	352.67 - 352.76	Hematite lutite
15	G 13	352.87 - 352.99	BIF
16	G 14	353.105 - 353.18	BIF (bands of hematite)
17	G 15.a	353.24 - 353.34	BIF (bands of hematite)
18	G 15.b	353.39 - 353.46	BIF (increase in carbonate bands, no hematite)
19	G 16.a	353.60 - 353.66	BIF (predominantly oxide bands)
20	G 16.b	353.72 - 353.78	BIF (increase in carbonate bands)
21	G 17	354.06 - 354.27	BIF (bands of hematite, appearance of green bands (low T garnet?))
22	G 18	354.345 - 354.47	BIF (bands of hematite)
23	G 19	354.57 - 354.76	BIF (bands of hematite)
24	G 20	354.86 - 354.99	BIF (green bands (low T garnet?))
25	G 21	355.135 - 355.25	BIF/Hematite lutite
26	G 22	355. 35 – 355.52	Banded manganese with carbonate lamellae
27	G 23	355.68 - 355.77	Banded manganese with carbonate lamellae and ovoids
28	G 24	356.16 - 356.315	Banded manganese with carbonate and ovoids
29	G 25	356.54 – 356.71	Banded manganese with carbonate lamellae

30	G 26	356.94 - 357.165	Banded manganese with carbonate lamellae (rimmed with hematite)
31	G 27.a	356.73 – 356.79	Hematite lutite
32	G 27.b	356.97 – 357.03	Hematite lutite/BIF
33	G 28	358.18 - 358.30	Hematite lutite
34	G 29	358.455 - 358.53	Hematite lutite
35	G 30	358.76 - 358.94	Hematite lutite
36	G 31	359. 095 – 359.195	Hematite lutite
37	G 32	359.32 - 359.41	BIF/Hematite lutite
38	G 33	359.47 – 359.55	BIF
39	G 34	359.74 - 359.94	BIF
40	G 35	360.10 - 360.215	BIF (bands of green (low T garnet))

Table I.3: Nch 91 F individual sample depths and macroscale descriptions

No	Sample	Depth	Lithology
1	Nch 1	591.50 - 591.645	Banded iron formation (BIF). Finely laminated and magnetite-rich
2	Nch 2.a	591.87 – 592.0	BIF (large voids within carbonate bands)
3	Nch 2.b	592.0 - 592.40	BIF (large voids within carbonate bands)
4	Nch 3	592.57 – 592.84	BIF (increase in banding size, hematite-magnetite-carbonate)
5	Nch 4	592.95 - 593.07	BIF (laminated magnetite and hematite, voids present)
6	Nch 5	593.18 - 593.54	BIF (magnetite and carbonate-rich, no voids present)
7	Nch 6	593.66 - 593.73	BIF (finely laminated rhythmitic, magnetite-hematite-carbonate)
8	Nch 7	593.93 - 594.05	BIF (brecciated with cm-scale carbonate Mn-silicate band)
9	Nch 8	594.06 - 594.31	Hematite lutite (finely laminated hematite and magnetite)
10	Nch 9	594.31 - 594.60	Banded manganese formation
11	Nch 10.a	594.60 - 594.80	Banded manganese formation
12	Nch 10.b	594.80 - 595.04	Banded manganese formation
13	Nch 11	595.04 - 595.42	Banded manganese formation
14	Nch 12.a	595.42 - 595.70	Banded manganese formation
15	Nch 12.b	595.70 – 595.96	Finely interbanded manganese minerals and hematite
16	Nch 13	595.96 - 596.07	Hematite lutite (finely laminated hematite and magnetite)
17	Nch 14	596.07 – 596.50	Massive textured hematite-rich unit
18	Nch 15	596.62 - 596.80	BIF (magnetite and carbonate bands)
19	Nch 16	596.98 – 597.26	BIF (increase in size of carbonate bands)
20	Nch 17	592.40 - 597.52	BIF (increase in size of carbonate bands)

Appendix II: Analytical Techniques and Methodology

a. Sample Preparation

Sample processing was performed at the Geology Department of Rhodes University. Core section samples were halved using a rock saw, and corresponding halves used for the production of a thin section and powered sample material.

Sample sections were carefully inspected for alteration veins and weathered surfaces which were avoided during sampling or cut out with a rock cutter. Rock chips are then cleaned to remove any contaminating dirt and markings related to the labelling process with distilled water and dried with a compressed air stream, which were then crushed in a swing mill with a steel base and rings for 3 minutes into fine face powder textured material. The steel base and rings were cleaned by crushing quartzite fragments and thoroughly washed with distilled water between each sample. The powder from each sample is stored in clean, carefully labelled glass vials till further use.

b. X-ray Diffraction

Powdered material from all samples used in this study were analysed by the standard x-ray diffraction techniques applied in the Department of Chemistry, Rhodes University. A few grams of powdered sample material was loosely placed on clean glass slides and placed in side-loaded sample holders, and analysed by a Phillips water-cooled diffractometer, using CuKa₁ radiation generated at 40 kv and 20-30 mA. XRD patterns are then detected between 5-60 ° Θ on a scan speed of 30 sec/1° at 0.05° step width. XRD profiles of main mineral phases are identified using CrystalSleuth, internet software designed by Laetsch and Down (2006) using powder diffraction data from the RRUFF mineral database.

CrystalSleuth reference: Laetsch, T., and Downs, R., (2006) Software for Identification and Refinement Form Powder Diffraction Data of Minerals Using the RRUFF Project and American Mineralogist Crystal Structure Databases. Abstracts from the 19th General Meeting of the International Mineralogical Association, Kobe, Japan.

c. H_2O and Loss On Ignition (LOI)

Sample H_2O^- and LOI values were determined at the Geology Department of Rhodes University.

To measure the value of water adsorbed to sample material, referred to as H_2O^{-} , approximately 2 g of sample powder is weighed into cleaned and dried silica crucibles, whose combined weighed is recorded to the forth decimal place. The crucible and sample powder is heated to 110 °C for at least 6 hours, allowed to cool in a covered desiccator and then reweighed to four decimal places. The difference in weight between the initial and heated sample material is the measure of H_2O^{-} .

The crucible and sample material is then transferred back to a preheated furnace and heated at 1000 °C for a further 8 hours. The samples are cooled in a covered desiccator and reweighed to four decimal places, and the weight difference observed during the last heating process corresponds to weight lost from the sample material as structurally bound volatiles, commonly H_2O and CO_2 . However, in samples rich in Fe²⁺ and Mn²⁺ bearing minerals, the LOI value is altered and in some cases masked by weight gain due to the oxidation of Fe⁺² and Mn⁺².

d. X-ray Fluorescence

Major oxides and trace elements are analysed by XRF on a Philips PW 1410 spectrometer in the Department of Geology at Rhodes University, against international and in-house rock standards.

• Major element oxides

Major oxide compositions are determined using the XRF analytical procedure developed by Norrish and Hutton (1969). Following the LOI value determination as described above, the ashed sample powder is immediately mixed in careful proportions with dried sodium nitrate and lithium tetraborate flux, and fused into a glass disk. The disks are analysed by XRF for each major element.

As the samples were known to contain high values of Mn and Fe, standards containing various proportions of Mn to SiO, and Fe to SiO were made against which the value of sample majors are determined.

• Trace elements

The 20 trace elements Mo, Nb, Zr, Y, Sr U Rb, Th, Pb, Co, Cr, V, Ce, Nd, La, Zn, Cu, Ni, Ba, Sc, were determined by XRF on pressed powder pellets.

e. <u>Total Carbon</u>

A combustion method is used to determine total carbon at Mintek, in Johannesburg. A portion of sample is weighed into a ceramic crucible along with an accelerator, and then placed in a furnace where it is heated by induction. Upon heating the carbon in the sample is released and is carried into a stream of high-purity oxygen where it is converted to CO₂. The gas stream is transported into an infrared detector which measures CO₂ quantitatively. Prior to sample analysis, the instrument is calibrated with a certified reference material containing a similar C concentration to that of the samples analysed.

f. <u>Fe²⁺ Content</u>

 Fe^{2+} is determined at Mintek in Johannesburg via titration. A portion of sample is weighed into a platinum dish and a mixture of H_2SO_4 and HCl added. The dish is then covered and the sample boiled on a hot plate, a portion of HF is then added and the mixture boiled again. After removal from the hot plate, the dish is immersed in a boric acid solution, which washes the sample material into solution. An aliquot of phosphoric acid is then added, along with a few drops of sodium diphenylamine sulphonate indicator solution, and the Fe^{2+} is then titrated with a standardized potassium dichromate solution, to a purple end-point.

g. <u>Total Iron</u>

Total Fe was determined at Mintek, also via titration. A weighed portion of sample is fused with sodium peroxide and leached with de-ionised water. The iron is then precipitated with ammonia and filtered, and the precipitate then dissolved in an HCl solution. Stannous chloride is added to reduce the iron, which is then titrated with potassium dichromate using a few drops of sodium diphenylamine sulphonate indicator solution to indicate the end-point.

h. Iron and Manganese Speciation
The sequential extraction procedure developed by Poulton and Canfield (2005), was applied at Newcastle University, United Kingdom, to determine the Fe and Mn content of each of the four main mineral phases that compose the samples concerned in this study.

A small amount of powdered sampled material is sequentially mixed with 4 different compounds to dissolve the entire sample in stages. Between each dissolution step the solution and residual solid are separated by placing the sample mixture in a centrifuge, the solution removed for analysis, and the remaining sample material mixed with the next reactive solution. The four solutions used in the sequential process and the mineral group that it dissolves are:

- Sodium acetate dissolves carbonate phases
- Sodium dithionite dissolves reducible oxides, specifically hematite
- Ammonium oxalate dissolves magnetite
- And hydrofluoric acid dissolves the remaining silicate minerals

The solution from each of the four extraction steps is then analysed for Fe and Mn by atomic absorption.

i. Bulk Organic Carbon isotope analyses (University of Durham)

Powdered sample material was analysed at the University of Durham using the methodology described in Gröcke et al. (1999). Carbon-Isotope values are reported as the Standard Delta (δ) notation relative to Vienna Pee Dee Belemnite (VPDB).

j. Bulk Carbonate Carbon isotope analyses (VU Amsterdam)

Bulk carbonate Carbon Isotope analyses were conducted at the stable isotope lab of the faculty of Earth and Life Sciences at the Vrije Universiteit Amsterdam, with a MAT252 with a Kiel II device, and a Delta+ with GASBENCH for carbonate oxygen and carbon isotope analysis.

Appendix III: Whole Rock Geochemical Data

Bulk rock geochemical data consisting of major element oxides and trace elements determined by X-ray Fluorescence is reported in this Appendix. Major element oxide data are reported in weight percent (wt. %) and their analytical totals are calculated therefrom. Trace element concentrations are reported in parts per million (ppm).

The data is organised into 2 main groups according to their stratigraphic position within the Transvaal Supergroup, with the lower section (Kuruman and Griquatown BIF) comprising samples from drillcore intersections Hex 5 and Gas 1 reported first, followed by the upper section (Hotazel Formation) comprising all samples from drillcore intersections, GL 81 and Nch 91 F. Total Fe-oxide and Mn-oxide concentrations are reported as FeO and MnO correspondingly.

Abbreviations listed are:

LOI: Loss on ignition

BD: below detection

Sample	SiO ₂	TiO₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na₂O	K₂O	P₂O₅	LOI	H₂O⁻	Total
wt. %													
Gas 1	36.23	0.07	0.93	38.42	0.51	3.42	2.39	bd	0.14	0.07	15.89	0.68	98.73
Gas 2	30.76	0.07	0.80	41.28	0.83	4.31	0.32	0.01	1.09	0.04	17.96	0.71	98.19
Gas 3	31.20	0.04	0.51	40.82	0.73	3.53	4.11	0.06	0.60	0.02	16.66	0.46	98.74
Gas 4	78.81	0.02	0.06	10.36	0.16	1.59	2.66	1.08	0.08	0.01	5.50	0.40	100.72
Gas 5	40.80	0.05	0.61	34.94	0.40	3.65	1.25	0.08	1.56	0.01	14.84	0.56	98.75
Gas 6	60.81	0.01	0.08	26.06	0.21	1.25	3.68	0.24	0.09	0.09	7.57	0.27	100.36
Gas 7	49.13	0.02	0.16	36.67	0.25	2.09	0.82	0.81	0.32	0.03	8.03	0.39	98.72
Gas 8.a	21.60	0.02	0.55	38.05	0.50	2.58	0.13	0.02	1.13	0.02	11.67	22.25	98.51
Gas 8.b	51.14	0.01	0.29	25.21	0.89	2.98	2.39	0.01	0.23	0.02	16.70	0.34	99.94
Gas 9	27.80	0.01	bd	45.08	0.66	2.32	7.39	0.30	0.01	0.04	14.88	0.36	98.85
Gas 10	38.19	0.01	bd	43.47	0.16	4.00	0.32	bd	0.04	0.12	11.55	0.66	98.49
Gas 11	31.52	0.01	0.14	37.60	0.63	4.06	3.91	0.01	0.09	0.01	20.59	0.53	99.09
Gas 12	62.93	0.01	bd	27.05	0.21	1.59	1.95	0.67	0.02	0.01	5.05	0.34	99.83
Gas 13	66.80	0.01	0.17	18.85	0.18	2.03	2.54	0.02	0.04	0.02	8.89	0.63	100.17
Gas 14	29.33	0.02	bd	56.04	0.81	3.74	0.78	0.04	0.15	0.19	6.24	0.37	97.62
Gas 15	37.28	0.01	bd	35.33	0.75	2.67	4.17	1.10	0.10	0.16	16.28	0.37	98.21
Gas 16	32.51	0.01	bd	38.03	0.61	3.17	3.30	bd	0.04	0.25	20.15	0.44	98.49

Gas 17	45.43	bd	0.43	43.39	0.10	1.81	1.24	bd	0.17	0.04	6.20	0.32	99.14
Gas 18	37.40	0.01	bd	38.04	0.60	2.84	4.07	0.02	0.03	0.21	15.40	0.27	98.88
Gas 19	44.14	0.01	bd	40.67	0.08	2.00	1.14	bd	0.02	0.03	10.37	0.26	98.71
Gas 20	51.12	bd	bd	39.06	0.10	2.70	0.77	0.11	0.01	0.07	4.88	0.14	98.97
Gas 21	49.45	0.01	bd	42.04	0.07	1.94	0.45	bd	0.04	0.08	4.68	0.11	99.00
Gas 22	46.54	bd	bd	43.02	0.08	1.37	1.33	0.26	0.01	0.08	5.59	0.08	98.35
Gas 23	43.53	0.03	0.17	42.27	0.71	4.65	2.76	0.02	0.19	0.20	4.71	0.28	99.52
Gas 24	37.82	0.01	bd	51.61	0.08	2.10	0.82	0.16	0.02	0.05	5.75	0.12	98.70
Gas 25	38.32	0.04	bd	50.28	0.08	1.63	1.07	0.03	0.02	0.08	6.14	0.26	97.94
Gas 26	43.74	0.03	bd	35.91	0.11	1.80	2.97	bd	0.04	0.04	14.00	0.22	98.87
Sample	sio	TiO		500	Mag	Mao	6-0		ĸo				TOTAL
wt. %	5102	1102	Al ₂ O ₃	reu	WINO	IVIgO	CaO	Na ₂ O	K ₂ U	P ₂ O ₅	LOI	п20-	TOTAL
Nel 1	58.039	0.011	bd	28.537	0.871	1.419	7.399	0.002	0.070	0.050	3.177	0.160	99.855
Nel 2	34.213	0.063	0.292	37.412	0.782	2.693	1.911	bd	0.031	0.073	20.842	0.265	98.577
Nel 3	19.538	0.144	1.552	38.828	0.988	4.256	4.632	0.110	0.517	0.070	27.546	0.623	98.805
Nel 4	33.567	0.062	0.602	26.053	3.331	3.805	6.336	0.046	0.296	0.058	24.717	0.809	99.682
Hex 1.a	21.899	0.060	0.470	27.572	3.980	4.468	10.93 9	0.017	0.190	0.059	28.846	0.699	99.199
Hex 1.b	49.120	0.055	0.275	32.228	0.467	2.131	4.707	0.024	0.166	0.048	9.714	0.474	99.407
Hoy 2													

Hex 3	48.808	0.203	2.829	28.118	0.842	4.968	0.672	0.291	1.091	0.048	8.933	1.849	98.653
Hex 4	28.602	0.027	0.048	36.264	0.874	5.071	9.570	bd	0.152	0.038	18.221	0.444	99.309
Hex 5	58.879	0.034	0.098	18.001	0.938	2.026	4.338	0.012	0.088	0.036	15.244	0.440	100.132
Hex 6	21.968	0.096	0.488	32.490	4.442	4.229	4.845	0.047	0.309	0.085	29.011	0.759	98.740
Hex 7	36.563	0.064	0.557	36.168	0.468	3.947	0.980	0.035	0.999	0.045	18.803	0.559	99.188
Hex 8	41.216	0.056	0.633	29.032	0.787	3.438	2.892	0.331	0.429	0.049	20.198	0.515	99.575
Hex 9	41.944	0.048	0.188	33.640	0.534	3.677	1.400	0.008	0.665	0.019	15.480	0.659	98.261
Hex 10	38.165	0.055	0.416	29.607	3.261	3.815	3.696	0.007	0.875	0.031	19.120	0.339	99.387
Hex 11	36.035	0.060	0.451	36.640	0.582	3.048	5.431	0.072	0.573	0.013	14.962	0.470	98.338
Hex 12	42.485	0.046	0.167	32.871	0.563	3.064	2.824	0.046	0.359	0.009	16.552	0.450	99.436
Hex 13	33.147	0.053	0.369	48.641	0.738	1.915	0.947	0.309	0.443	0.070	11.162	0.495	98.289
Hex 14	64.710	0.044	0.155	24.818	0.086	2.159	0.067	2.865	0.266	0.019	3.010	0.755	98.954
Hex 15	51.226	0.050	0.274	32.752	0.254	2.675	1.655	0.209	0.865	0.015	8.530	0.510	99.015
Hex 16	37.697	0.057	0.345	39.241	0.252	4.685	0.283	0.057	1.044	0.079	14.073	0.675	98.488
Hex 17	32.731	0.044	bd	46.634	0.612	3.424	0.156	0.005	0.921	0.047	12.887	0.643	98.105
Hex 18	41.325	0.032	bd	40.816	0.088	3.002	1.471	0.112	0.137	0.080	11.545	0.405	99.013
Hex 19	48.979	0.035	bd	33.760	0.111	3.312	0.238	bd	0.097	0.028	12.129	0.375	99.064
Hex 20	44.447	0.030	bd	35.938	0.460	2.856	3.174	0.482	0.081	0.007	11.437	0.445	99.358
Hex 21	48.308	0.032	bd	36.529	0.115	2.974	2.120	0.010	0.108	0.067	8.230	0.340	98.832

Hex 23	51.340	0.033	0.078	27.126	0.424	3.779	2.754	0.010	0.112	0.025	13.578	0.410	99.668
Hex 24	54.790	0.037	0.135	28.875	0.282	2.515	3.148	0.175	0.136	0.018	8.891	0.540	99.542
Sample wt. %	SiO ₂	TiO₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K₂O	P ₂ O ₅	LOI	H₂O-	TOTAL
G 1	46.42	0.05	0.83	44.00	0.64	1.48	1.57	0.06	0.10	0.17	4.58	0.426	99.89
G 2.a	44.96	0.05	0.28	39.73	0.86	0.85	5.25	0.02	0.09	0.12	7.30	0.462	99.49
G 2.b	31.12	0.04	0.09	51.14	0.78	0.83	4.93	0.01	0.09	0.17	7.97	0.428	97.16
G 3	10.21	0.05	0.20	38.46	5.20	2.61	19.39	bd	0.19	0.10	21.54	0.536	97.95
G 4	15.12	0.04	0.17	28.32	9.35	6.88	18.01	bd	0.16	0.09	21.35	0.529	99.51
G 5	15.24	0.04	0.13	22.47	11.49	6.78	19.55	bd	0.16	0.09	23.12	0.440	99.07
G 6	15.57	0.05	0.31	21.67	11.30	6.89	19.92	bd	0.17	0.09	23.60	0.524	99.56
G 7	10.11	0.05	0.17	14.32	8.82	5.29	29.24	bd	0.22	0.10	29.78	0.525	98.09
G 8	10.36	0.05	0.19	12.43	14.98	3.39	28.00	bd	0.20	0.09	28.50	0.423	98.19
G 9	13.22	0.04	0.14	16.38	13.39	4.41	24.97	bd	0.18	0.09	26.83	0.750	99.64
G 10.a	12.81	0.05	0.13	18.30	12.82	4.11	24.46	bd	0.19	0.09	26.31	0.725	99.27
G 10.b	14.37	0.05	0.13	22.53	11.46	5.01	21.46	bd	0.17	0.09	23.62	0.714	98.88
G 11	12.67	0.05	0.19	22.10	10.91	4.38	23.50	bd	0.18	0.10	25.26	0.809	99.33
G 12	14.26	0.05	0.20	29.13	6.92	5.49	19.84	bd	0.15	0.10	22.45	0.705	98.59

G 13	14.92	0.05	0.15	28.94	4.49	6.12	21.60	bd	0.16	0.10	22.29	0.460	98.81
G 14	21.12	0.05	0.24	47.10	2.02	8.35	7.38	bd	0.09	0.10	11.68	0.535	98.12
G 15.a	16.82	0.06	0.19	31.02	7.54	3.74	19.45	bd	0.15	0.10	20.15	0.689	99.21
G 15.b	22.33	0.06	0.18	27.27	10.46	3.87	17.02	bd	0.13	0.09	18.33	0.404	99.73
G 16.a	18.70	0.06	0.14	40.74	5.45	5.33	12.44	bd	0.12	0.09	15.11	0.307	98.19
G 16.b	16.41	0.05	0.09	40.98	5.59	4.13	14.34	bd	0.11	0.11	16.30	0.429	98.13
G 17	32.63	0.06	0.04	46.68	3.36	2.75	5.27	0.03	0.10	0.08	7.17	0.176	98.15
G 18	33.77	0.04	0.34	48.86	2.55	5.12	2.10	0.01	0.05	0.07	5.90	0.224	98.81
G 19	36.05	0.04	0.21	33.21	6.06	11.57	4.11	bd	0.07	0.13	8.17	0.655	99.64
G 20	37.98	0.03	0.11	26.68	10.24	8.42	6.30	0.01	0.09	0.14	9.62	0.448	99.60
G 21	7.41	0.04	0.20	33.13	18.93	1.32	15.08	bd	0.12	0.11	21.42	0.149	97.76
G 22	10.43	0.03	0.16	12.19	25.04	1.81	23.15	bd	0.16	0.09	26.60	0.230	99.67
G 23	13.03	0.04	0.13	13.77	33.62	2.46	14.01	bd	0.10	0.08	23.49	0.354	100.73
G 24	16.08	0.03	0.14	12.20	31.57	2.55	16.02	bd	0.12	0.08	22.21	0.195	101.00
G 25	17.46	0.03	0.09	20.86	30.38	2.96	10.23	bd	0.09	0.08	18.58	0.219	100.76
G 26	17.24	0.03	0.14	18.49	23.29	6.61	8.26	bd	0.07	0.07	21.71	0.174	96.19
G 27.a	15.01	0.03	0.05	25.48	22.31	8.05	7.62	bd	0.07	0.08	21.55	0.235	100.24
G 27.b	15.66	0.02	0.03	32.70	17.20	8.23	5.80	bd	0.06	0.07	18.74	0.239	98.51
G 28	14.81	0.03	0.03	42.82	11.38	7.73	5.24	bd	0.05	0.07	16.39	0.284	98.55

G 29	17.28	0.03	0.05	41.09	10.00	8.71	5.13	bd	0.06	0.07	15.54	0.230	97.97
G 30	21.29	0.03	0.01	49.38	5.89	8.65	2.54	bd	0.03	0.09	10.28	0.150	98.19
G 31	29.70	0.04	0.02	51.57	3.57	4.75	0.33	0.01	0.01	0.09	7.59	0.155	97.68
G 32	36.23	0.03	0.08	50.89	0.87	0.84	1.70	0.01	0.02	0.13	7.25	0.099	98.05
G 33	24.27	0.03	0.05	59.25	1.41	1.43	2.17	bd	0.03	0.10	8.72	0.150	97.45
G 34	30.55	0.03	0.14	36.63	2.01	1.74	14.34	bd	0.11	0.12	13.27	0.185	98.95
G 35	38.95	0.04	0.10	26.93	1.94	6.86	13.03	bd	0.11	0.12	12.25	0.145	100.55
Sample	siO.	TiO.	AL.O.	FeO	MnO	MøO	CaO	Na.O	к.О	P.O.	101	н.о.	τοται
wt. %	5102	1102	A1203	100		ingo	cuo	11020	120	1 205	201	1120	TOTAL
Nch 1	36.26	0.02	bd	53.26	1.36	0.08	0.32	0.03	0.02	0.12	5.93	0.28	97.65
Nch 2.a	12.48	0.03	0.25	56.73	12.89	2.37	2.63	0.01	0.03	0.10	8.47	0.282	96.27
Nch 2.b	10.42	0.04	0.11	57.34	13.10	1.72	3.38	bd	0.03	0.03	9.80	0.234	96.21
Nch 3	39.02	0.02	bd	49.90	1.12	0.69	0.25	0.07	0.06	0.07	5.56	0.28	97.04
Nch 4	38.45	0.01	bd	51.64	1.35	0.37	0.23	0.11	0.01	0.05	5.75	0.28	98.26
Nch 5	44.33	0.01	bd	46.51	1.74	0.48	0.42	0.28	0.02	0.06	5.18	0.28	99.31
Nch 6	38.83	0.02	bd	45.14	2.72	1.13	1.82	2.21	0.05	0.06	5.03	0.28	97.29
Nch 8	9.25	0.05	bd	7.81	79.24	0.14	2.27	0.01	0.03	0.11	0.87	0.28	100.05
Nch 9	9.75	0.06	0.04	9.91	75.34	0.09	3.50	0.02	0.06	0.10	1.10	0.28	100.23
Nch 10.a	6.83	0.06	bd	8.46	80.91	0.07	2.63	0.02	0.03	0.11	0.94	0.28	100.32

Nch 10.b	12.65	0.04	0.11	15.02	61.74	0.11	7.17	0.01	0.08	0.11	1.67	0.28	98.99
Nch 11	10.24	0.04	0.01	15.17	68.99	0.25	1.58	0.01	0.04	0.04	1.69	0.28	98.33
Nch 12.a	10.15	0.04	0.09	32.06	47.20	0.26	3.75	0.01	0.04	0.06	3.57	0.28	97.50
Nch 12.b	8.45	0.04	0.21	46.28	31.41	0.45	1.27	bd	0.01	0.11	7.20	0.258	95.68
Nch 13	3.35	0.04	bd	61.53	19.62	0.14	0.64	bd	0.03	0.09	6.85	0.281	92.56
Nch 14	20.29	0.03	0.25	50.84	4.17	0.16	16.49	bd	0.12	0.04	6.66	0.074	99.11
Nch 15	45.41	0.02	0.04	45.31	1.40	0.32	0.68	0.47	0.03	0.13	5.04	0.28	99.12
Nch 16	48.31	0.01	bd	43.22	0.77	0.16	0.56	0.54	0.02	0.04	4.81	0.28	98.42
Nch 17	49.59	0.01	0.08	42.53	0.61	0.89	0.21	bd	0.04	0.04	4.74	0.28	99.01

Sample																				
ppm	Мо	Nb	Zr	Y	Sr	U	Rb	Th	Pb	Со	Cr	v	Ce	Nd	La	Zn	Cu	Ni	Ва	Sc
Gas 1	2	2	11	4	20	1	19	bd	1	10	42	29	10	4	4	21	18	11	9	4
Gas 2	2	2	13	2	9	bd	97	bd	bd	10	47	27	9	1	4	14	24	8	22	3
Gas 3	bd	2	8	2	146	1	97	bd	bd	9	41	15	11	4	1	11	22	6	23	3
Gas 4	3	bd	2	2	44	bd	10	bd	2	bd	34	13	2	1	bd	5	12	6	4	1
Gas 5	bd	2	10	2	21	1	314	bd	3	8	40	13	5	4	3	12	19	11		
Gas 6	2	1	3	2	60	bd	14	bd	bd	bd	35	13	1	1	bd	5	18	6	10	2
Gas 7	2	1	7	bd	13	bd	61	bd	2	5	34	18	bd	2	bd	11	21	6	8	1

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Gas 8.a	bd	2	17	bd	6	bd	264	4	bd	10	21	11	13	6	6	19	22	4	11	1
Gas 8.b	2	bd	bd	2	31	bd	30	1	1	bd	20	6	1	2	bd	11	14	bd	5	bd
Gas 9	3	1	2	4	96	bd	bd	bd	bd	7	35	13	11	6	bd	21	23	5	24	2
Gas 10	bd	2	5	16	6	1	4	3	2	12	19	11	10	4	3	11	21	bd	9	1
Gas 11	bd	bd	2	4	46	bd	10	bd	bd	7	23	11	10	3	bd	13	21	2	15	1
Gas 12	4	2	3	2	16	bd	bd	bd	bd	bd	53	17	1	bd	bd	6	21	4	bd	bd
Gas 14	bd	1	3	15	14	1	21	bd	bd	13	26	12	12	7	5	15	21	bd	10	bd
Gas 15	bd	bd	2	9	79	bd	11	1	3	7	14	7	6	6	2	11	17	1	17	1
Gas 16	bd	bd	2	8	46	1	4	bd	6	6	14	7	7	4	2	15	19	bd	13	1
Gas 17	2	1	bd	4	23	2	23	bd	bd	9	21	9				14	19	bd	11	1
Gas 18	2	1	2	7	49	bd	5	bd	bd	6	29	11				13	22	1	28	2
Gas 19	2	1	4	3	17	bd	bd	1	3	7	35	11				11	24	1	5	1
Gas 20	2	1	bd	4	8	bd	bd	2	1	9	30	10				11	23	bd	4	1
Gas 21	3	1	bd	4	8	bd	bd	bd	bd	13	37	13				8	23	3	4	bd
Gas 22	3	1	bd	3	19	bd	bd	2	bd	12	43	13				9	26	1	5	1
Gas 23	2	1	8	12	13	bd	bd	1	bd	10	21	18	11	8	4	15	17	2	3	2
Gas 24	bd	bd	bd	6	10	bd	bd	bd	1	15	39	14	3	4	bd	18	35	bd	8	1
Gas 25	2	1	bd	7	12	1	bd	bd	bd	12	44	14	6	4	bd	7	25	bd	8	1
Gas 26	3	2	bd	4	9	bd	bd	bd	2	9	35	12	9	1	1	7	19	3	3	1

Sample ppm	Мо	Nb	Zr	Ŷ	Sr	U	Rb	Th	Pb	Со	Cr	v	Ce	Nd	La	Zn	Cu	Ni	Ва	Sc
Nel 1	3	1	2	4	29	bd	2	bd	4	5	24	10	11	6	1	7	18	9	bd	2
Nel 2	2	1	11	12	5	bd	2	1	2	8	31	25	11	8	2	14	19	9	2	3
Nel 3	2	3	34	19	12	1	37	bd	bd	14	57	66	17	6	7	44	31	25	10	6
Nel 4	2	1	5	4	14	bd	16	1	1	bd	20	12	7	3	1	7	13	1	1	2
Hex 1.a	1	1	5	7	24	2	9	2	1	bd	17	12	13	9	3	12	21	7	bd	bd
Hex 1.b	2	1	4	4	14	1	8	1	bd	7	40	16	12	3	2	8	25	7	bd	2
Hex 2	2	1	3	2	17	bd	4	bd	3	6	24	11	3	5	1	8	20	6	bd	2
Hex 3	bd	3	34	6	17	bd	73	2	1	9	64	49	14	5	7	23	17	22	57	6
Hex 4	bd	bd	bd	9	33	bd	2	bd	bd	3	12	6	9	8	bd	12	15	bd	bd	1
Hex 5	bd	1	3	7	44	bd	3	bd	1	bd	26	11	4	4	1	8	14	3	bd	1
Hex 6	bd	1	5	10	84	1	17	bd	2	bd	23	14	12	7	3	11	20	4	17	2
Hex 7	bd	1	9	3	18	bd	96	bd	bd	7	30	15	8	4	bd	11	18	5	14	2
Hex 8	bd	2	8	4	177	bd	30	1	4	4	26	15	7	4	1	11	15	4	20	2
Hex 9	bd	1	5	3	33	bd	66	bd	bd	8	28	13	bd	bd	bd	7	18	2	10	2
Hex 10	bd	1	6	2	49	1	80	bd	2	4	23	9	5	2	1	bd	bd	bd	12	2
Hex 11	bd	bd	6	3	95	bd	69	bd	bd	6	39	15	7	3	bd	bd	6	6	20	3
Hex 12	2	2	5	bd	45	bd	45	bd	1	7	37	11	2	2	1	bd	bd	6.4	16	2

Hex 13	2	1	7	3	22	1	49	1	1	10	59	20	2	3	bd	bd	bd	bd	28	2
Hex 14	2	1	3	bd	3	bd	30	1	4	bd	32	16	2	1	bd	6.1	bd	5.4	11	bd
Hex 15	2	1	4	bd	28	1	115	bd	bd	7	32	13	1	3	1	4.7	bd	bd	7	2
Hex 16	bd	1	7	6	10	bd	203	bd	2	7	27	11	8	3	1	11	22	7	21	2
Hex 17	bd	1	3	3	5	1	167	bd	bd	13	25	10	2	bd	bd	9	21	1	12	bd
Hex 18	2	1	3	9	15	bd	13	bd	bd	8	21	9	4	5	bd	7	18	2	12	1
Hex 19	bd	1	4	9	5	2	9	bd	1	bd	17	8	4	bd	2	5	17	5	9	1
Hex 20	2	1	2	4	42	bd	4	3	2	6	27	10	6	4	bd	7	19	1	10	2
Hex 21	bd	bd	2	8	37	bd	4	3	3	bd	16	8	7	5	2	6	18	bd	1	1
Hex 23	bd	1	3	3	19	bd	4	bd	bd	bd	18	10	7	4	bd	10	15	bd	3	2
Hex 24	3	1	4	3	31	1	5	bd	1	4	38	15	2	2	1	10	20	3	2	2
								Up	per Tran	svaal Sup	ergroup									
Sample ppm	Мо	Nb	Zr	Y	Sr	U	Rb	Th	Pb	Со	Cr	v	Ce	Nd	La	Zn	Cu	Ni	Ва	Sc
G 1	3	bd	8	10	21	bd	4	bd	bd	10	31	22	bd	bd	4	15	25	bd	37	3
G 2.a	2	2	6	19	27	bd	bd	bd	bd	10	36	20	bd	4	bd	13	33	bd	14	3
G 2.b	3	bd	3	11	28	bd	bd	bd	bd	13	35	19	bd	bd	3	15	82	bd	13	3
G 3	bd	bd	5	16	277	bd	bd	bd	bd	26	10	21	bd	8	bd	26	23	bd	97	bd
G 4	bd	bd	4	10	512	bd	bd	bd	bd	41	6	10	bd	4	bd	39	19	bd	95	bd

G 5	bd	bd	4	10	532	bd	bd	bd	bd	39	4	7	9	5	bd	40	18	bd	94	bd
G 6	bd	bd	4	8	577	bd	bd	bd	bd	42	5	6	8	5	bd	41	16	bd	102	bd
G 7	bd	bd	4	9	594	bd	bd	bd	bd	33	4	5	11	9	bd	23	15	4	72	bd
G 8	bd	bd	3	8	546	bd	bd	bd	bd	18	2	6	7	6	bd	21	18	8	80	bd
G 9	bd	bd	4	8	440	bd	bd	bd	bd	20	2	6	bd	7	bd	22	14	bd	32	bd
G 10.a	bd	bd	4	10	417	bd	bd	bd	bd	20	4	6	bd	5	bd	23	18	bd	41	bd
G 10.b	bd	bd	3	8	376	bd	bd	bd	bd	26	5	8	7	4	bd	31	17	bd	44	bd
G 11	bd	bd	5	11	179	bd	bd	bd	bd	27	5	9	bd	4	bd	28	17	bd	38	bd
G 12	bd	bd	5	12	141	bd	bd	bd	bd	30	8	8	8	7	4	36	16	bd	11	bd
G 13	bd	bd	4	10	212	bd	bd	bd	bd	30	7	8	bd	6	bd	49	19	bd	6	bd
G 14	bd	bd	8	12	136	bd	bd	bd	bd	54	18	16	11	7	14	63	19	bd	30	3
G 15.a	bd	bd	4	11	462	bd	bd	bd	bd	11	9	9	bd	8		33	19	bd	40	bd
G 15.b	2	bd	3	12	280	bd	bd	bd	bd	6	6	8	bd	bd	bd	33	17	bd	12	bd
G 16.a	bd	bd	6	12	302	bd	bd	bd	bd	11	10	12	bd	bd	6	49	21	bd	21	1
G 16.b	bd	bd	6	11	352	bd	bd	bd	bd	8	12	11	13	5	12	37	23	bd	17	bd
G 17	bd	bd	4	9	45	bd	bd	bd	bd	14	16	12	bd	bd	bd	37	23	bd	19	2
G 18	bd	bd	5	6	15	bd	bd	bd	bd	13	18	13	bd	bd	bd	37	25	bd	20	2
G 19	bd	bd	4	12	33	bd	bd	bd	bd	bd	7	11	bd	bd	bd	70	16	bd	20	3
G 20	bd	bd	5	15	44	bd	bd	bd	bd	bd	8	12	bd	bd	bd	49	16	5	5	3

G 21	bd	bd	4	12	126	bd	bd	bd	bd	bd	6	13	7	bd	4	19	23	bd	30	bd
G 22	bd	bd	4	6	186	bd	bd	bd	bd	4	2	7	6	4	bd	13	18	8	17	bd
G 23	bd	bd	6	7	133	bd	bd	bd	bd	8	3	6	bd	bd	bd	19	21	8	14	bd
G 24	bd	bd	4	8	123	bd	bd	bd	bd	15	bd	6	bd	bd	bd	19	19	10	6	bd
G 25	bd	bd	5	9	107	bd	bd	bd	bd	11	3	7	bd	bd	bd	22	22	8	14	1
G 26	bd	bd	4	5	96	bd	bd	bd	bd	17	2	6	bd	bd	bd	25	18	8	16	1
G 27.a	bd	bd	4	9	63	bd	bd	bd	bd	26	3	8	bd	bd	bd	30	17	bd	47	2
G 27.b	bd	bd	4	9	45	bd	bd	bd	bd	33	5	11	bd	bd	3	33	21	bd	68	2
G 28	bd	bd	5	10	37	bd	bd	bd	bd	39	8	12	bd	bd	4	31	21	bd	56	2
G 29	bd	bd	7	10	40	bd	bd	bd	bd	52	8	11	bd	bd	bd	36	17	bd	44	2
G 30	bd	bd	6	9	29	bd	bd	bd	bd	21	10	14	bd	bd	4	43	22	bd	46	2
G 31	bd	bd	7	11	130	bd	bd	bd	bd	15	13	8	bd	bd	bd	27	37	bd	4206	1
G 32	bd	bd	8	12	15	bd	bd	bd	bd	7	36	17	bd	bd	bd	11	34	bd	30	2
G 33	bd	bd	7	13	16	bd	bd	bd	bd	13	32	17	bd	bd	bd	13	64	bd	25	2
G 34	bd	bd	6	11	60	bd	bd	bd	bd	bd	19	11	9	7	5	15	22	bd	7	bd
G 35	bd	bd	5	11	56	bd	bd	bd	bd	bd	9	9	bd	bd	bd	37	16	bd	bd	bd
Sample	Мо	Nb	Zr	Y	Sr	U	Rb	Th	Pb	Co	Cr	v	Ce	Nd	La	Zn	Cu	Ni	Ва	Sc
Nch 1	3	bd	7	13	8	bd	bd	bd	12	33	305	50	16	7	14	bd	24	12	15	2
Nch 2.a	3	bd	12	23	21	bd	bd	bd	44	51	60	33	bd	bd	16	17	31	18	47	2

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Nch 2.b	3	bd	11	43	40	bd	bd	bd	72	32	65	36	11	7	18	23	31	15	110	4
Nch 3	4	2	8	8	10	bd	bd	bd	30	32	91	31	BD	8	10	24	27	12		
Nch 4	3	bd	7	7	14	bd	bd	bd	29	15	122	31	bd	bd	6	bd	33	9	194	2
Nch 5	4	bd	7	10	16	bd	bd	bd	27	15	88	27	bd	bd	5	6	24	12	38	1
Nch 6	3	2	7	8	29	bd	bd	bd	26	20	81	65	bd	bd	8	36	21	8	578	2
Nch 8	3	bd	3	17	132	bd	bd	bd	59	26	44	28	bd	bd	14	45	167	29	431	1
Nch 9	2	bd	5	18	42	bd	bd	bd	57	12	43	26	bd	bd	12	29	60	24	29	1
Nch 10.a	bd	bd	5	12	91	bd	bd	bd	55	18	44	26	bd	bd	9	45	77	45	1134	1
Nch 10.b	3	bd	9	15	35	bd	bd	bd	50	15	41	36	bd	bd	7	32	58	28	49	2
Nch 11	bd	bd	5	12	68	bd	bd	bd	30	13	41	21	bd	bd	6	76	108	32	109	2
Nch 12.a	4	3	10	11	49	bd	bd	bd	66	13	45	28	bd	bd	6	42	92	29	112	2
Nch 12.b	bd	bd	10	19	86	bd	bd	bd	112	14	51	29	bd	bd	9	13	87	16	170	3
Nch 13	6	bd	10	16	35	bd	bd	bd	249	20	75	38	12	9	18	bd	98	9	60	3
Nch 14	3	bd	9	13	35	bd	bd	bd	69	BD	70	48	13	7	10	bd	26	bd	284	bd
Nch 15	3	bd	6	20	19	bd	bd	bd	23	23	84	23	bd	9	11	14	27	9	34	3
Nch 16	3	bd	6	bd	19	bd	bd	bd	17	11	76	23	bd	bd	bd	bd	23	8	40	2
Nch 17	2	bd	4	11	16	bd	bd	bd	16										12	2

Appendix IV: Fe and Mn Speciation data

This appendix contains the tabulated data of total Fe and total Mn content per mineral fraction as determined by the sequential mineral extraction (speciation) process. The reported data sets comprise of Fe and Mn abundances for the following mineral groups:

- Total carbonate
- Oxides excluding magnetite (in this case hematite)
- Magnetite
- Silicates

All data is reported in weight percent (wt. %) and separated into two groups, comprising the Lower (Kuruman/Griquatown BIFs) and Upper (Hotazel BIF) Transvaal Supergroup respectively.

Lower Transvaal Supergroup											
Sample	FeCarbonate	FeOxide	FeMagnetite	FeSilicate		Sample	MnCarbonate	MnOxide	MnMagnetite	MnSilicate	
Gas 1	11.07	2.40	7.03	17.55		Gas 1	0.25	0.02	0.05	0.09	
Gas 2	13.68	1.64	6.63	21.99		Gas 2	0.44	0.02	0.07	0.12	
Gas 3	8.47	2.30	11.90	12.90		Gas 3	0.40	0.02	0.03	0.08	
Gas 4	2.45	0.28	0.28	9.40		Gas 4	0.13	0.02	bd	bd	
Gas 5	10.86	2.17	6.60	14.35		Gas 5	0.23	0.02	0.02	0.02	
Gas 6	2.42	2.49	10.14	6.60		Gas 6	0.15	0.02	bd	0.02	
Gas 7	5.00	3.38	11.08	11.39		Gas 7	0.15	0.02	bd	0.01	
Gas 8.a	8.16	3.23	13.41	22.08		Gas 8.a	0.35	0.03	0.05	0.09	
Gas 8.b	14.31	0.81	3.04	5.49		Gas 8.b	0.55	bd	0.03	0.04	
Gas 9	4.79	6.02	15.03	11.42		Gas 9	0.43	bd	bd	0.06	
Gas 10	9.75	3.10	9.24	20.79		Gas 10	0.09	bd	bd	0.05	
Gas 11	15.21	2.57	9.62	4.22		Gas 11	0.40	bd	bd	0.03	
Gas 12	2.62	4.52	9.32	5.51		Gas 12	0.16	bd	bd	bd	
Gas 13	9.48	1.56	1.93	5.36		Gas 13	0.14	bd	bd	bd	
Gas 14	12.74	4.67	13.01	12.68		Gas 14	0.46	bd	bd	0.06	
Gas 15	11.44	1.38	4.97	19.37		Gas 15	0.44	bd	0.04	0.07	
Gas 16	16.29	1.08	3.55	18.03		Gas 16	0.34	bd	0.04	0.08	
Gas 17	1.58	4.10	11.66	23.87		Gas 17	0.05	bd	bd	0.08	
Gas 18	9.89	3.92	10.37	4.89		Gas 18	0.38	bd	bd	0.03	
Gas 19	7.89	5.00	10.98	9.91		Gas 19	0.06	bd	bd	0.03	
Gas 20	0.88	6.66	15.67	4.53		Gas 20	0.03	bd	bd	bd	
Gas 21	1.55	5.47	12.78	14.85		Gas 21	0.02	bd	bd	0.06	

Gas 22	1.40	6.66	15.57	9.02	Gas 22	0.03	bd	bd	0.01
Gas 23	13.93	0.69	1.37	24.58	Gas 23	0.33	bd	bd	0.08
Gas 24	1.18	9.94	16.66	11.41	Gas 24	0.03	bd	bd	0.01
Gas 25	1.23	8.76	13.93	16.76	Gas 25	0.03	bd	bd	bd
Gas 26	9.86	3.16	5.97	14.15	Gas 26	0.06	bd	bd	0.01
Sample	FeCarbonate	FeOxide	FeMagnetite	FeSilicate	Sample	MnCarbonate	MnOxide	MnMagnetite	MnSilicate
Nel 1	8.86	1.62	7.43	2.76	Nel 1	0.46	0.01	bd	0.02
Nel 2	14.67	1.05	6.79	9.80	Nel 2	0.37	0.01	0.08	0.11
Nel 3	17.55	0.87	3.73	16.81	Nel 3	0.48	0.02	0.13	0.05
Nel 4	17.52	0.43	1.00	5.47	Nel 4	2.04	0.03	0.16	0.05
Hex 1.a	17.23	0.52	1.71	7.87	Hex 1.a	2.46	0.03	bd	0.11
Hex 1.b	3.24	3.63	11.20	7.07	Hex 1.b	0.26	0.01	bd	0.03
Hex 2	3.32	2.42	10.10	13.61	Hex 2	0.40	0.02	bd	0.08
Hex 3	4.60	1.63	7.11	17.46	Hex 3	0.39	0.02	0.02	0.22
Hex 4	6.16	1.55	8.38	20.32	Hex 4	0.51	0.02	bd	0.08
Hex 5	11.52	0.34	0.62	5.95	Hex 5	0.54	0.02	0.01	0.02
Hex 6	21.99	0.50	1.52	5.48	Hex 6	2.64	0.05	0.02	0.12
Hex 7	16.51	1.14	2.93	15.76	Hex 7	0.25	0.02	0.03	0.03
Hex 8	13.71	0.30	2.10	14.98	Hex 8	0.39	0.01	bd	0.09
Hex 9	13.03	1.24	3.13	15.12	Hex 9	0.27	0.01	0.02	0.05
Hex 10	12.03	0.69	3.78	13.68	Hex 10	1.81	0.03	0.18	0.39
Hex 11	6.87	2.13	11.50	11.45	Hex 11	0.34	0.08	bd	0.07
Hex 12	12.71	2.40	7.85	5.30	Hex 12	0.33	0.01	bd	0.02
Hex 13	7.45	4.62	13.76	13.00	Hex 13	0.41	0.02	bd	0.08
Hex 14	1.03	0.78	1.18	27.64	Hex 14	0.02	0.01	bd	0.04
Hex 15	0.50	0.21	0.98	1.19	Hex 15	0.01	bd	bd	bd

Hex 16	10.67	2.05	9.64	12.92	Hex 16	0.13	0.01	0.01	0.03
Hex 17	11.00	4.67	12.50	8.87	Hex 17	0.35	0.02	0.01	0.03
Hex 18	8.10	2.54	12.58	10.43	Hex 18	0.05	0.01	bd	0.01
Hex 19	8.99	1.63	8.09	12.93	Hex 19	0.07	0.01	bd	0.01
Hex 20	5.49	2.59	11.91	9.22	Hex 20	0.29	0.01	bd	0.03
Hex 21	2.84	1.67	10.41	19.55	Hex 21	0.06	0.01	bd	0.06
Hex 23	8.86	1.32	7.46	5.91	Hex 23	0.26	0.02	bd	0.01
Hex 24	4.17	3.85	10.13	4.26	Hex 24	0.20	0.02	bd	bd
Upper Transva	aal Supergroup								
Sample	FeCarbonate	FeOxide	FeMagnetite	FeSilicate	Sample	MnCarbonate	MnOxide	MnMagnetite	MnSilicate
G 1	0.76	8.22	16.28	1.26	G 1	0.12	0.03	bd	0.08
G 2.a	0.86	7.70	16.41	0.22	G 2.a	0.31	0.03	bd	0.06
G 2.b	0.79	12.08	20.73	0.16	G 2.b	0.29	0.05	bd	0.04
G 3	0.24	8.71	15.62	0.21	G 3	2.46	0.29	0.11	0.21
G 4	0.17	6.13	11.66	0.41	G 4	3.67	0.49	0.22	0.74
G 5	0.10	5.68	9.35	0.25	G 5	4.78	0.87	0.33	0.66
G 6	0.11	6.36	8.19	0.17	G 6	4.88	0.95	0.37	0.54
G 7	0.07	6.33	2.53	0.49	G 7	5.15	0.29	0.02	0.10
G 8	0.10	5.45	1.00	0.73	G 8	5.09	1.48	0.64	1.09
G 9	0.14	9.05	1.88	0.51	G 9	4.11	0.85	0.31	1.39
G 10.a	0.21	7.22	4.51	0.53	G 10.a	4.25	0.73	0.28	1.25
G 10.b	0.25	6.56	7.63	0.64	G 10.b	4.22	0.58	0.28	1.10
G 11	0.25	6.44	7.41	0.73	G 11	2.93	0.46	0.22	0.97
G 12	0.31	11.57	6.78	0.84	G 12	2.02	0.34	0.13	0.71
G 13	0.23	2.65	13.32	0.77	G 13	1.48	0.09	0.01	0.39
G 14	0.31	7.86	20.13	0.77	G 14	0.48	0.08	bd	0.18

G 15.a	0.54	8.30	10.97	0.54	G 15.a	1.69	0.77	0.33	0.78
G 15.b	0.57	6.60	10.18	0.86	G 15.b	1.89	1.03	0.46	1.38
G 16.a	0.31	7.82	15.72	0.90	G 16.a	0.77	0.35	0.12	0.78
G 16.b	0.34	6.76	17.04	0.67	G 16.b	0.90	0.41	0.14	0.75
G 17	0.41	6.29	18.23	2.23	G 17	0.30	0.10	0.02	0.57
G 18	0.34	6.51	18.70	2.68	G 18	0.09	0.06	bd	0.48
G 19	0.33	5.28	11.44	2.27	G 19	0.57	0.43	0.18	1.01
G 20	0.60	5.16	4.17	2.73	G 20	1.35	0.96	0.37	1.57
G 21	0.13	9.57	7.03	5.45	G 21	5.47	1.83	1.22	1.62
G 22	0.13	5.85	0.79	0.78	G 22	6.74	2.54	1.59	0.94
G 23	0.46	7.02	1.32	0.34	G 23	11.95	3.36	1.91	1.40
G 24	0.15	6.01	0.90	0.65	G 24	6.56	3.24	2.04	3.70
G 25	0.22	8.96	1.22	5.27	G 25	7.17	3.38	1.90	2.93
G 26	0.10	8.40	1.02	1.79	G 26	10.98	2.79	1.36	1.56
G 27.a	0.17	14.77	1.57	1.13	G 27.a	11.78	1.22	0.20	0.28
G 27.b	0.06	19.74	1.86	1.12	G 27.b	9.59	0.47	bd	0.14
G 28	0.04	28.28	1.66	1.22	G 28	6.06	0.25	bd	0.14
G 29	0.05	28.71	1.68	0.46	G 29	5.22	0.21	bd	0.12
G 30	0.05	22.42	1.35	16.04	G 30	0.72	0.64	0.15	0.84
G 31	0.17	21.85	1.26	12.77	G 31	0.14	0.42	0.10	0.58
G 32	0.64	14.16	4.26	6.12	G 32	0.10	0.05	bd	0.08
G 33	0.56	15.78	6.26	6.77	G 33	0.24	0.09	bd	0.12
G 34	0.42	7.33	10.09	2.86	G 34	0.87	0.06	bd	0.13
G 35	0.20	3.28	5.44	2.11	G 35	0.81	0.06	bd	0.26

Appendix IV: Total Carbon and Carbon Isotope Data

Samples from the GL 81 core section was analysed in detail for total carbon and respective carbon isotope values. This appendix contains the tabulated data, and includes:

- Total Carbonate Carbon (TC) in weight %
- Total Organic Carbon (TOC) in weight %
- 2¹³C Bulk Carbonate Carbon
- 2¹³C Bulk Organic Carbon

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Sample	TC %	TOC %	¹³ C Bulk Carbonate C	¹³ C Bulk Organic C
G 1	0.21	0.05	-4.54	-27.75
G 2.a	1.19	0.06	-4.82	-27.40
G 2.b	1.1	0.07	-4.70	-27.81
G 3	4.43	0.12	-5.25	-27.08
G 4	4.47	0.18	-5.73	-28.26
G 5	5.06	0.14	-5.77	-28.38
G 6	5.09	0.24	-4.64	-28.72
G 7	7.32	0.24	-3.95	-28.46
G 8	6.92	0.20	-4.24	-28.45
G 9	5.85	0.13	-4.69	-28.15
G 10.a	5.72	0.12	-5.14	-27.77
G 10.b	5.08	0.13	-4.54	-28.02
G 11	4.53	0.16	-4.98	-28.77
G 12	5.61	0.15	-5.09	-28.30
G 13	4.53	0.12	-5.15	-27.63
G 14	4.82	0.13	-6.21	-28.05
G 15.a	1.71	0.58	-6.24	-28.48
G 15.b	3.62	0.15	-6.68	-27.93
G 16.a	2.66	0.11	-6.71	-28.50
G 16.b	3.04	0.10	-6.78	-27.79
G 17	0.82	0.06	-7.8	-28.08
G 18	0.36	0.06	-5.33	-28.06

G 19	0.72	0.11	-4.82	-28.27
G 20	1.2	0.13	-7.94	-27.64
G 21	4.25	0.10	-8.66	-27.99
G 22	6.33	0.19	-8.68	-28.31
G 23	4.98	0.22	-8.80	-26.54
G 24	4.67	0.13	-9.79	-28.27
G 25	3.04	0.12	-8.64	-28.01
G 26	4.16	0.12	-7.66	-28.89
G 27.a	4.75	0.10	-8.04	-28.80
G 27.b	3.62	0.09	-10.46	-29.05
G 28	2.73	0.07	-10.14	-28.34
G 29	2.55	0.08	-9.65	-28.31
G 30	0.67	0.05	-7.04	-28.60
G 31	0.05	0.06	-11.2	-28.49
G 32	0.42	0.04	-8.40	-28.39
G 33	0.56	0.06	-7.17	-28.42
G 34	2.46	0.07	-5.22	-27.83
G 35	2.06	0.08	-4.53	-28.52