INTERPRETATION OF MINERALOGICAL, CHEMICAL AND MORPHOLOGICAL FEATURES OF DURICRUSTS AND ITS APPLICATION TO MINERAL EXPLORATION

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INTRODUCTION

The object of mineral exploration is to locate economic deposits with minimum expenditure in time and money. In order to achieve this goal it is essential to select the most favourable environment and to design the search procedures for the environment in question.

Duricrusts are a striking feature of tropical and subtropical landscapes where they occur as extensive, resistant horizons which form a surface or near-surface caprock and are best seen in incised landscapes. Since they cover many potentially rich mineral provinces of the world, it is important to question what effect they have on mineral exploration. Duricrusts are defined as specific soil types formed by near-surface processes associated with weathering.

In spite of the sheer aerial extent of soils over the landsurfaces of the earth, Levinson (1974) expressed surprise at how little exploration geologists know about this surficial environment. Weathering and pedogenetic processes therefore, require discussion in this text. However, in order to adhere to the scope of this dissertation only a brief description of the factors and characteristics of soil formation are given in the first chapter.

In the second part, duricrusts are differentiated on the basis of composition into laterite, silcrete and calcrete. Beginning with a concise description of both natural and experimental investigations concerned with mineral decomposition and neomineralisation during weathering, the morphological, physical and chemical characters of each type are described. Environmental factors are then discussed in an attempt to identify specific duricrust types in terms of climate, geographic location, age and formation process. Once duricrust structure and texture are related to topography, specific types may be used to assess the significance of suspected markers in the landscape and permit identification of individual weathering surfaces on which mineralisation may give rise to gossans of widely different physical and chemical characteristics. The interpretation of photogeological, geochemical and geophysical data acquired during mineral exploration in duricrust terrains is problematical and some of the limitations to these search procedures are discussed in the final chapter.

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2. PEDOGENIC AND GEOCHEMICAL DIFFERENTIATION DURING WEATHERING

2.1 EVOLUTIONARY PROCESSES

The classical conception of the exogenous geochemical cycle describes the earth's crust as a complicated dynamic system which consists of a number of subsystems (reservoirs) continuously changing matter and energy with one another. Within this environment, Erhart (1965, In Millot, 1970) applies the term "biostasy" to periods of soil formation and "rhexistasy" to phases of denudation. Periods of biostasy are represented by normal vegetation while phases of rhexistasy are characterised by the dying out or lack of vegetation due to soil erosion resulting from climatic change or tectonic disturbance. The loss of vegetation initiates degradation and denudation of soils and weathering zones.

Geologists use the term "soil" in a broader sense than the agriculturalists to refer to all materials produced by weathering 'in situ', regardless of their depth or utilization by plants. Thus, residual deposits such as duricrusts (laterite, silcrete, calcrete) are considered soil. Weathering processes also govern indirectly the distribution of these deposits since evidence of unconformities in the geological record are used to infer prolonged periods of continental erosion and the lithological sequences encountered in sedimentary basins are really correlative formations of the weathering sequences which occur in the neighbouring landscape. For these reasons 4 main geomorphic processes are distinguished within the exogenous environment. They are considered conveniently as follows :

(i) Weathering is defined as "the total effect of all the subaerial processes that co-operate in bringing about the decay and disintegration of rocks provided that no large scale transport of the loosened product is involved" (Holmes, 1965). It is traditional to distinguish among the weathering factors, the physical, chemical and biological mechanisms (Table 1). Temperature variations are not considered to be directly involved in the granular disintegration of rocks but the main role is an indirect one governing the moisture and also the solubility of gases or salts in rock pores. Moreover, the rates of chemical reactions are increased with increasing temperature.

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In this dissertation the role of chemical weathering will be principally considered.

TYPE OF WEATHERING	EXAMPLES	SUMMARY		
Physical	Unloading (expansion of rock during erosion) Thermal expansion Frost action (ice wedges) Colloid plucking (pulling effect of gels)	Generally of secondary impor- tance. Net effect is particle size reduction; increased surface area; no change in chemical composi- tion.		
Chemical	Solution Hydration, hydrolysis Oxidation (with or without va- lence increase) Reduction Carbonation (exchange reactions in part)	Complete change of chemical and physical properties; net increase in volume.		
Biological	Wedge work of roots Plant acids	Combination of chemical and physical effects.		

TABLE 1. WEATHERING PROCESSES

(From : Krumbein & Sloss, 1963)

(ii) Pedogenesis pertains to the formation of soil profiles. Most soils are a combination of one or more of 4 basic ingredients, viz. organic material, residual minerals or rock fragments, secondary minerals formed during weathering and soluble material either in solution or temporarily precipitated. A characteristic feature of soils is the distribution of the various components into sequential layers or horizons. It is generally agreed that in residual soils the horizons reflect successive phases or stages in the transformation of bedrock and to differentiation of the mineral mass during its redeposition from aqueous solutions (i.e. the stadial hypothesis of Smirnov, 1976). The significance of the origin of different horizons within the soil profile cannot be overemphasized.

(iii) Erosion implies the removal and displacement of weathered material either by the mechanical work of meteoric forces (rainfall, water, wind etc.) or by the chemical dissolving action of waters under the influence of gravity. Erosion promotes denudation (lowering) of the landscape and flattening of the landform as transported material is moved from higher or lower surfaces. (iv) Sedimentation. "Burial in the sea is the ultimate fate of most sediments" (Ordway, 1972). However, transitory deposits of weathered debris (detrital sedimentation) or reprecipitated material (chemical sedimentation) may be moved and transported by erosional forces into favourable low lying continental sites. If there is complete redeposition of soils in terrestrial areas, Valeton (1972) envisages the cyclic episodes of soil formation - polygenetic transformation erosion and denudation in high level areas developing at the same time as the cyclic episodes of sedimentation - soil formation and polygenetic transformation in basins.

The geochemical differentiations occurring during these supergene processes are produced by two opposing mechanisms. The mechanism of subtraction (i.e. leaching of the more mobile constituents) is dominant during the period of biostasy whereas the mechanism of addition (i.e. absolute, lateral accumulation of mobile constituents) proceeds through the period of rhexistasy.

2.2 FACTORS OF DIFFERENTIATION

2.2.1 Weathering balance of equatorial and temperate pedogeneses

One of the basic principles of chemistry is that all substances tend towards a condition of equilibrium with their surrounding environment. The weathering environment is characterised by relatively low temperature and pressure, and high concentrations of water, free oxygen and carbon dioxide. It is an attempt to achieve this equilibrium that rocks undergo weathering. The rock forming minerals can be arranged in generalised order of decreasing weatherability. As might have been suspected this configuration parallels Bowen's reaction series (Fig. 1).



(From : Levinson, 1974)

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Fig. 1 Bowen's reaction series.

Empirically, a general pattern of increasing stability among different classes of minerals is sulphide, carbonate, silicate, oxide (Joyce, 1976).

The relict minerals are both chemical and mechanical weathering resistant with a relatively high specific gravity (S.G.), e.g.

Mineral	S.G.	Mineral	S.G.	Mineral	S.G.
wolframite	7.2-7.7	magnetite	5.2	rutile	4.2-4.3
cassiterite	6.8-7.1	ilmenite	5.0-5.0	garnet	3.6-4.3
scheelite	5.9-6.1	zircon	4.7	topaz	3.5-3.6
monazite	4.9-5.3	corundum	3.9-4.1	quartz	2.65-2.66

The relict minerals are therefore found by panning or jigging soil material and can be used as guides to local and regional geology (Techniques based on detrital resistant heavy minerals. In : Proc. 2nd Sem. on Geochem. Prosp. Techniques, UNESCO Pub. No. 38, 1970, 115-163). Relict minerals are also used as a reference in the quantitative determination of mineralogical and geochemical differentiations during weathering. Since quartz is the only constituent to show a progressive increase from bottom to top (except in illuvial horizons) of intensely weathered profiles, Lelong and Souchier (1972, in Lelong et al., 1976) have used the isoquartz method to illustrate and compare complete geochemical trends in sedentary profiles of temperate ("acid brown soils") and equatorial ("ferrallitic") soils that have developed on granitic rocks. The chemical balances are expressed as a percentage of each element compared with the amount originally present in the parent rock, i.e. rate of variation. A variation rate of 100% marks the boudary between losses (<100%) and gains (>100%). The bases, Na₂O, K₂O and CaO are treated collectively for the sake of simplicity. Mineralogical and geochemical balances are depicted in Fig. 2 and Table 2.

The results, as summarised from Lelong et al. (1976), indicate that the decomposition of primary weatherable minerals is only partial (40-50%) in temperate soils but almost total in the equatorial soils. The chemically weathered fraction comprising secondary clay minerals and amorphous inorganic products is only about 10% for temperate soils but very great (30-40%) for equatorial soils. These facts conform with the characteristically low silt/clay ratios obtained by granulometric analyses for equatorial soils (Fig. 3).



Fig. 2. Mineralogical (left) and chemical (right) balances in soil profiles of temperate and equatorial soils, on granitic rocks, referring to a constant weight of quartz

(From : Lelong et al., 1976)

TABLE 2. Abbreviations used in Fig. 2

- Qu = quartz
- Fk = potassic feldspars
- Pl = plagioclases
- Ph = phyllites
- Ar = clay minerals
- Fa = inorganic amorphous matter
 (mainly oxides and hydroxides of Al and Fe)
- Gi = gibbsite

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(From : Mohr and Von Baren, 1954)

- Red andesitic lateritic soil; Priangan, West Java; stage 5 No. 2 FIG. 3 SUCCESSIVE STAGES OF WEATHERING OF INDONESIAN LATERITIC

No. 19650 - Red andesitic tuff lateritic soil; Ibid. stage 4-5

KEY				
	Gravel	> 2 mm		
Fraction 1	Very coarse sand	2-1 mm		
2	Coarse sand	1-0.5 mm		
3	Medium sand	0.5-0.2 mm		
4	Fine sand	0.2-0.1 mm		
5	Very fine sand	0.1 mm-50µ		
6	Coarse silt	50-20µ		
7	Silt	20-5µ		
8	Fine silt	5-2 <i>µ</i>		
9	Clay	2-0.5µ		
10	Colloidal clay	$< 0.5 \mu$		

SOILS AS DEMONSTRATED BY TEXTURE

Losses of the chemically weathered fraction do not exceed 25% of the amount initially present in the parent rock under temperate climates but are considerable (40-50%) in equatorial soils. Disparities in the intensity of chemical weathering as discussed above are accompanied by differences in the nature of the secondary minerals formed. Temperate soils are characterised by the presence of 2:1 clay minerals (illite, vermiculite, montmorillonite) whereas equatorial soils contain 1:1 clay minerals (kaolinite, halloysite) predominantly or even Al-hydroxides (gibbsite).

In addition to the marked differences, certain geochemical similarities are seen to exist between the two pedogeneses. Elements are released and removed in the same order : bases<combined silica<Al<Fe. The majority of the alkaline and alkaline earths (mainly Na and Ca which do not enter into secondary minerals) are removed by solutions percolating through the weathering profile. Some elements, mainly Fe, Al and Si, are retained in part and join together.in the profiles to form a significant

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fraction of the saprolite. The Fe and Al metallic elements are mainly fixed in oxyhydroxides or enter into clay minerals; but they are partially leached or translocated from the A to the B horizon (illuviation). The concentration of these accumulations is maximum in the most weathered soil profiles, i.e. equatorial soils, where even kaolinite, $Al_2Si_2O_5(OH)_4$, is finally decomposed to yield gibbsite, $Al(OH)_3$, and dissolved silica, H_ASiO_A .

No similar balances for the other pedogeneses are available. However, if it is assumed that the formation of pedogeneses is simply a chemical weathering process which, in the end, is controlled only by physico-chemical conditions it follows also that the geologic, topographic, climatic and morphologic field factors are directly related to the physico-chemical conditions. Therefore, weathering balances may be extrapolated from consideration of environmental factors that affect weathering and soil formation.

2.2.2 Physico-chemical processes and related environmental factors

Hydrolysis. The hydrogen ion concentration (pH) of groundwater is important in weathering because hydrolysis is facilitated by the acidity of the solution. Hydrolysis is linked with exchange reactions between the bases of the silicate minerals and the H^+ ions of the electrolytically dissociated parts of the water, e.g. :

Silicate +
$$H_2O$$
 + H_2CO_3 = Cations + OH + HCO_3 + H_4SiO_4 (1)

The primary source of H^+ ions in water is from the dissociation of weak carbonic acid, (H_2CO_3) formed by dissolving CO_2 from the atmosphere. The initial pH of rainwater varies from 5.5 to 6.5 (Norton, 1973). More important sources are CO_2 dissolved from the soil atmosphere as well as some clay minerals, roots of plants and chelating agents (humic acids, plant excretions) which provide H^+ ions on reaction.

The organic portion of a soil is a manifestation of the biological reactions involved in the soil forming process. Since the main portion of organic matter is derived from surface vegetation it is almost always concentrated near the upper parts (O and A horizons) of soil profiles. Micro-organisms are entirely responsible for the oxidative decay of organic material to humus during which large amounts of carbon dioxide, methane, hydrogen and oxygen (as water) are liberated to the soil atmosphere, e.g. :

 ${}^{2C}_{6}{}^{H}_{10}{}^{O}_{5} + {}^{2O}_{2} = {}^{C}_{6}{}^{H}_{10}{}^{O}_{5} + {}^{H}_{2}{}^{O} + {}^{4CO}_{2} + {}^{2CH}_{4} \qquad (2)$ (plant cellulose) (humus)

Humus comprises three components : humic acid, fulvic acid, and insoluble humins, which are all part of an extremely heterogenous organic polymer system (Jackson et al., 1978). The ability of humic acids to weather silicate minerals is considered uncertain by Krauskopf (1967) and Loughnan (1969) but the work of Schalasca et al. (1967), Jackson and Keller (1970) and Baker (1973) provide strong evidence for increased silicate weathering in the presence of humic compounds by their control on soil acidity.

Abrasion pH is the pH at which rocks and minerals are first attacked by groundwater. In situ measurements at the fresh rock/ weathered rock interface are practically impossible and are therefore simulated by measuring the pH of pulps resulting from grinding (abrasion) small rock or mineral samples in distilled water (Table 3). The reactions are not very acid because the effect of hydrolysis is to consume H⁺ ions and produce OH⁻ ions (equation 1).

FORMULA	FORMULA	ABRASION pH
Silicates	THE STREET	
Olivine	(Mg.Fe),SiO,	10.11
Augite	Ca(Mg,Fe,Al)(Al,Si),O.	10
Hornblende	Ca ₂ Na(Mg,Fe) ₄ (Al,Fe,Ti) ₃ Si ₂ O ₂₂ (O,OH) ₂	10
Albite	NaAlSi O.	9.10
Oligoclase*	Ab, 70 An, 10-20	9
Labradorite*	AbenensAncours	89
Biotite	K(Mg Fe) AISi O (OH)	80
Microcline	KAISi_O.	0,9
Anorthite	CaAl.Si.O.	0, 0
Hypersthene	(Mg,Fe) Si O.	8
Muscovite	KAl Si O. (OH)	7.8
Orthoclase	KAISi.O.	8
Montmorillonite	(Al, Mg)Si,O, (OH), nH,O	67
Halloysite	Al Si O. (OH).	6
Kaolinite	Al ₂ Si ₂ O ₅ (OH)	5-7
Oxides		
Boehmite	A10(OH)	67
Gibbsite	Al(OH).	67
Quartz	SiO	67
Hematite	Fe ₂ Ô ₃	6
Carbonates		
Dolomite	CaMg(CO _a) _a	9 10
Calcite	CaCO.	8

Table 3				
Abrasion pH	values for	some	common	minerals

(From : Birkeland, 1974)

The reaction of soil normally ranges from pH4 to pH8 (Fig. 4). The pH of 8 at the base of the profile is high because the bedrock is ultrabasic. On acid to intermediate rock, values of only 6 or 7 might be reached. In equatorial soils the pH is lower than in temperate climates because the abundance of rain combined with good permeabilities tends to keep them close to the pH of rainwater as the basic cations are leached out from the median and upper parts of the profiles (Maignien, 1966).



Fig. 4 Weathering profile on ultramafic rock (Kouaoua Plateau, New Caledonia), after Trescases, 1973b. A = ferruginous crust; B = gravelly ferruginous horizon; C = fine saprolite; D = coarse saprolite; E = weathering front; F = quartz and garnierite in diaclases; G = parent rock.

(From : Lelong et al., 1976)

 H^{\dagger} ions are chemically active because their small size enables them to penetrate many crystal structures and their large charge to size ratio facilitates polarisation and substitution of large metal cations. The most resistant minerals are those formed exclusively of interlocking silica tetrahedra (tectosilicates) which are both geometrically compact and chemically efficient structures. The less the interlocking and the greater the inclusion of other metal cations (Al³⁺, Fe²⁺, Ca²⁺, Mg²⁺, K⁺, Na⁺, etc.) which form weak bonds in the silicate lattice (neosilicates), the more readily the mineral will break down under the action of hydrolysis (Loughnan, 1969).

During hydrolysis water first attacks the ions having large diameters and weak ionic potentials (Fig. 5). Thus, the voids created by the substitution are invaded by more water and the process is selfperpetuating if the outside water is replenished by abundant rainfall and groundwater circulation. Such circulation prevents cation saturation at the crystal interface. Eventually the silicate layers become isolated.



Under tropical and sub-tropical climates where rainfall is seasonal, the soil solutions are not so highly diluted and the removal of bases not so total but temperatures are nevertheless sufficiently high to cause intense hydrolysis. Under wet climates the decay of organic matter is retarded but accumulation enhances slow, intense hydrolysis and leaching under the influence of very acid organic compounds. Under the contrasting hot, dry, climatic conditions of desert and subdesert areas, organic matter is much less abundant but that which is present undergoes an intense humification. Hydrolysis and leaching processes are therefore limited and only the more mobile elements, such as the bases, undergo a certain migration; the soil pH remains alkaline.

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Oxidation. In aerated environments such as weathering, oxidation affects chiefly the iron which goes from Fe²⁺ to Fe³⁺ (Norton, 1973). Oxidation may act as a process in mineral decomposition by disrupting the electrostatic neutrality of a crystal, e.g. in the transformation of biotite to vermiculite. Alternatively, the oxidation of iron may occur after its release by other weathering processes, e.g. :

The hematite/geothite reaction is reversible and the oxidation products give the tropical soils their typical yellow-brown to red colour (Mohr and Van Baren, 1954).

Cheluviation. Lambrechts (1975, in Macvicar, 1978) states that it is still not certain what causes the translocation and precipitation of the oxhydroxides (sesquioxides) in the B-horizon under aerobic conditions. Evidence is accumulating to suggest that Fe- and Al- sesquioxides probably move in the soil as organo-metallic chelating complexes formed from humic acids (Jackson et al., 1978). Because the chelates are soluble they move downward with the percolating groundwater and upward in the presence of an oscillating water table or where capillarity and evapotranspiration are important. Precipitation has been ascribed to various causes : higher exchangeable Ca and Mg, microbiological decomposition of chelate and Eh-pH variations (Wright et al., 1963; Schnitzer, 1969; Norton, 1973). Therefore, in dry desert and subdesert areas where Fe and Al are not released, the profiles show a poor, immature development by comparison to the leached podzolic profiles with a well-developed B-horizon under wet climates (Fig. 6).

Clay mineral transformations and neoformations. Rocks or minerals of varying composition weathering in the same environment can produce different clay minerals of which only 7 types are important in soils (Fitzpatrick, 1971). These compounds differ considerably among themselves in physical, chemical and structural properties (Table 4). It is beyond the scope of this dissertation to discuss in any detail the large literature on soil clays. A review of some of this work is Table 4. Clay Minerals : composition and structure (Data from : Fitzpatrick, 1971)

- <u>Kaolinite</u>: Al₂Si₂O₅(OH)₄. The simplest of the clay mineral structures referred to as 1:1 layering. Comprises one octahedral gibbsite sheet, Al(OH)₃, and one silica tetrahedral sheet, SiO₄, in which each apical oxygen of the silica sheet replaces one hydroxyl group of the gibbsite sheet.
- <u>Halloysite</u>: Al₂Si₂O₅(OH)₄ nH₂O. Structure comprises kaolinite layers separated from each other by sheets of hydrogen bonded water molecules.
- 3. <u>Montmorillonite</u>: (AI,FeMg)₂₋₃ (Na,Ca)₁₋₃ (Si,Al)₄O₁₀ (OH)₂. A 2:1 layered clay mineral formed of 3 sheets: two sheets of silica tetrahedra joined to a central aluminium sheet in the planes of the apices of silica tetrahedra. Adjoining threesomes are loosely bonded by a few basic cations, Na,K,Ca⁺, etc.
- 4. <u>Illite</u>: Al₂Si₄(Al,K) O₁₀(OH). The 2:1 layering is like that in montmorillonite but some Al³⁺²ions substitute for Si⁴⁺ ions in the tetrahedral layers. The resulting increase in negative charge is neutralised by basic cations. Consequently, compositions are less definite than 1:1 layered clay minerals.
 - 5. <u>Vermiculite</u>: Mg_{0.5}(Al_{2.3},Si_{5.7})(Al_{0.5},Fe_{0.7}, Mg_{4.8}) O₂₀(OH)₄.nH₂O. A 2:1 clay mineral that exists in both di- and tri-octahedral forms and can be regarded as hydrated mica in which the K⁺ ions are replaced by Mg²⁺ and Ca²⁺ ions.
 - 6. <u>Chlorite</u>: Al,Mg₅(OH)₁₂(Al₂Si)₆AlMg₅O₂₀(OH)₄. A 2:2 or 2:1:1 type of layered silicate in which a brucite like sheet, Mg(OH)₂, is sandwiched between 2 mica layers and replaces the K⁺ in the mica structure. The composition is variable with Mg, Fe and other cations replacing Al³⁺ to varying degrees.
 - 7. <u>Allophane</u> : Amorphous. Sometimes regarded as a clay mineral and at other times considered as a mixture of silica gel and Al- hydroxide.
 - Note : Mixed-layer clays : Clay minerals scarcely ever occur in a pure form in soils. Interlayering of 2:1 and 2:1:1 layer clay minerals is possible because many of the species are structurally similar and because some expand readily in water.



Fig. 6 . Diagrammatic representation of soil profiles. (A) A typical mature podzol soil profile in a temperate zone showing all the important horizons of interest in exploration geochemistry. (B) Variations in soil profile in four climatic environments. Note that all horizons are not present in every profile, but that every profile has some horizons.

(From : Levinson, 1974)

given in Loughnan (1969), Millot (1970) and Birkeland (1974). It suffices to mention only that 3 principal processes have been invoked to account for their genesis :

(i) detrital inheritance - clay minerals present in the rock (biotite, chlorite, etc.) remain intact because of their stability

(ii) transformations - unstable clay minerals are modified by the environment (e.g. oxidation) without altering their 3-layered structure, e.g. :

(iii) neoformation - clay minerals are formed as entirely new species (like the sesquioxides) through the chemical interchange of mineral constituents.

Although kaolin is commonly an end clay product in chemical weathering, Millot (1970) dispels the often quoted myth of the direct kaolinization of feldspars, e.g. :

 $2KAlSi_{3}O_{8} + 2H^{+} + 9H_{2}O = Al_{2}Si_{2}O_{5}(OH)_{4} + 2K^{+} + 4H_{4}SiO_{4} \dots \dots (4)$ (Orthoclase) (Kaolin)

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By minute observations, Millot followed the changes taking place during weathering of basic rocks and maintains that "the initial factor of chemical weathering is hydrolysis which releases elements of the crystal into solution Kaolinization is a later and facultative phenomenon. It is a further neoformation from the ion released by hydrolysis". The evolutionary sequence of soil clays reflecting their stability in the zone of weathering is as follows :

Feldspar Fe-Mg minerals Fe-Mg minerals Hillite hixed illite-vermiculite hixed chlorite-vermiculite hixed chlorite hixed chlorite

(a) with good drainage : kaolinite
(b) with poor drainage : montmorillonite

Generally, the distribution of clays in soils is marked by relatively low contents in the A and C horizons with the maximum amount in the upper part of the B horizon (Birkeland, 1974). Several mechanisms acting together have been invoked to account for this distribution : (i) clay particle translocation by percolating groundwater facilitated by the small grain size (<0,002 mm), (ii) clay formation 'in situ' and (iii) neomineralisation with constituents derived by weathering higher in the profile and moving downward in solution to crystallize as illuvial clay. Conditions for clay migration can very with depth in the soil profile or even seasonally and the distribution of clay mineral species can be related to conditions of leaching and erosion (Fig. 7).

In intertropical regions, abundant rainfall and high average temperatures promote the formation of ferrallitic soils in which kaolinite is the main clay component whereas under temperate climates the clay fraction of fersiallitic soils is dominated by 2/1 clay minerals, mainly illite, vermiculite montmorillonite (Van Niekerk and Lambrechts, 1977). Partridge (1975, in Corbett, 1978) has found that prolonged weathering under humid conditions (annual water surplus) followed by extensive leaching of the clayey matrix (kaolinite) from ferrallitic pedogeneses produces soils with a high voids ratio and hence "collapsible" grain structure.



Time (younger)

Fig. 7 Vertical distribution of clay minerals as a function of leaching conditions within the soil. (A) Leaching conditions favor the formation of kaolinite and montmorillonite; each forms at different levels in the soil profile. (B) Rapid lowering of the surface by erosion results in the montmorillonite residing in a soil environment of high leaching. (C) With time, the montmorillonite in the surface becomes desilicated and alters to kaolinite. Rates of ground-surface lowering, mineral alteration, and amount of leaching are important to stable end-product clay mineral formation. With slow groundsurface lowering, alteration may proceed at the same rate, and the claymineral distribution may always appear as in (A). If the rate of erosion far exceeds the rate at which the clay mineral can change, a distribution like (B) occurs temporarily.

(From : Birkeland, 1974)

Carbonation. The origin of pedogenic carbonate horizons involves carbonate-bicarbonate equilibria as discussed for calcium by Krauskopf (1967) and shown by the following equilibrium reaction :

$$ca^{2+} + 2HCO_{3} \leftrightarrow CaCO_{3} + H_{2}CO_{3} \qquad (5)$$

Soluble Ca⁺⁺ ions released by weathering and their precipitation as CaCO3 within the soil profile occurs under conditions which drive the reaction to the right, i.e. a lowering of CO2 pressure, a rise in pH, or an increase in the ionic concentration of reactants to the point where saturation is reached. Temperature and pressure are the most important parameters governing CO, solubility which is likely to be the chief factor with which the solution is in equilibrium through its effect on the pH (Netterburg, 1969). CaCO, solubility relations in terms of pH and temperature are shown in Fig. 8. It is apparent that if the temperature is increased the solubility of CO, and CaCO, are decreased causing precipitation of the latter.



Fig. 8 Some factors affecting CaCO₃ solubility.

CaCO₃ with varying pH in an equilibrium solution of $CaCO_3 - CO_2 - H_2O$ at 25°C. (B) Relationship between temperature and $CaCO_3$ solubility.

(From : Birkeland, 1974).

In humic environments the pCO_2 of soil moisture is greater than atmospheric and $CaCO_3$ solubility is therefore greater under vegetated surfaces than under surfaces that lack vegetation. All of the above-mentioned conditions which favour $CaCO_3$ precipitation are enhanced under hot, dry desert or semi-desert climates due to the combined effects of low rainfall, limited hydrolysis, evapotranspiration, paucity of vegetation and temperature gradients in the soil moisture.

In brief, the climate directly or indirectly, through the vegetation and biological activity, controls the pedogenesis.

Climate. The warmer and wetter the climate, the more intense are the hydrolytic processes and the higher the degree of release of elements. The rainfall and temperature also govern the subsequent behaviour of the released chemical species in the soil solutions. Mobility is controlled, in part, by pH which depends on the abundance of rainfall and groundwater circulation; the solubilities are influenced by the temperature which also controls the evapotranspiration and concentration of solutions.

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It is commonly stated that chemical weathering is nil in arid regions. However, the soils of desert and semi-arid regions have been found to contain smectites and mixed layer mica-vermiculite clay minerals (Van der Merwe, 1962). Van der Merwe and Weber (1963) and Purves (1976) found that granite in the arid regions also gave some kaolinite. The red Kalahari sands on lime in southern Africa were found to contain smectites and mixed layer clays with some kaolinite in some profiles (van der Merwe, 1962). It has been suggested (Birkeland, 1974) that the reason many workers envisage little chemical weathering in these dry arid regions is because many of the landscapes are eroding and therefore the products of chemical weathering are being continually swept away.

Vegetation and biological activity are closely related to climate and are generally fairly uniform over a given climatic zone. They influence soil formation by their control on soil acidity from the humus they produce and by the role they play in the formation of organometallic complexes which solubilize relatively immobile heavy cations.

2.2.3 Zonal soils concept

It is apparent from the above discussion that on a global scale the distribution of major soil groups ("zonal soils" or soil orders) can be related to essentially four bioclimatic zones distributed between the high latitude regions where the climate is cold and wet and the low latitudes where the climate is hot and wet or dry (Fig. 9).

Grossly, two major pedogeneses may be distinguished on the basis of pedogenic and geochemical differentiations within the zonal soils (Hunt, 1972) :

(i) Pedalfers - a name chosen to emphasize the leaching of aluminium (in the form of silicates, e.g. clays) and iron (in the form of ferric oxides) from the eluvial A horizon and their accumulation in the illuvial B horizon. These are pedogeneses of wet, well-drained regions, giving acid soils where the bases, and to a lesser extent the silica, released are more or less removed, i.e. an open chemical system defining subtractive geochemical differentiations. The higher the temperature the more rapid and intense is the differentiation they induce.









(From : Birkeland, 1974)

"Intrazonal soils" have more or less well-developed soil characteristics that reflect the dominating influence of some local factor, e.g. parent material and/or topography over the more normal effect of the climate and vegetation.

Parent materials interfere essentially through the susceptibility to alteration of their minerals. Rocks do not always follow the order of weatherability expected of their constituent minerals owing to such factors as texture and structure. As an example, Van der Merwe (1962) has drawn attention to black smectitic (montmorillonite) and red kaolinitic clays occurring adjacent to each other on basic igneous rocks of the Bushveld Complex such that the soil forming factors for both, with the exception of parent material, are the same. The red clays correspond to magnetite bands in the norite; the latter being overlain by "black turf" (vertisols). The differences in pedogeneses are attributed to differences in permeability of the weathered rock with magnetite derived soils being more porous thereby increasing their water absorbing capacity which facilitates leaching as well as aeration (oxidation).

It is also well known that fine-grained rocks will weather much faster than coarse-grained rocks of the same composition because of their greater exposed surface per unit volume (Fig. 10). According to Millot (1970) chemical weathering results from "the parallel effects of fragmentation and hydrolysis of rock minerals, each of these mechanisms leading to the other". Complete weathering of the small crystals therefore explains the low silt/clay ratio of tropical soils.



FIG. 10 Particle size classes used in pedology and some of their properties

(From : Birkeland, 1974)

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Topography is an important factor inasmuchas the drainage and depth to the water table depends on topography and by its control on microclimate. Concerning the distribution of the normal annual rainfall and climate of South Africa, Van der Merwe (1962) remarks on the marked influence of mountain barriers which give rise to changes from subhumid to arid conditions within a short distance.

As a general principal it may be stated that the surface of the water table constitutes a subdued replica of the surface topography and that subdued surfaces of low relief favour shallow water tables while dissected topography of high relief is usually characterised by deep water tables (Partridge, 1967).

There is little need to emphasize the significance of slope in the mode of weathering of rock and in the development of the soil profile as this has been adequately dealt with by Corbett (1978). In brief, topography (and vegetation) influences runoff and thus can increase or decrease the effective rainfall and hence influence the depth of leaching. Lateral sorting of soils by water and gravity is widely found on slopes. The combined effects of creep and wash result in the segregation of soil according to particle size. In general, finer particles are moved further down the slope than coarser particles. Thus, on the upper slope the truncated soil profile is characteristically thin, stoney and coarse-textured being formed of residual materials left by these slope processes. At the slope foot erosion gives way to deposition, unless the streams are in the process of active degradation, and the soils are deep, fine-textured and cumulative often showing buried horizons resulting from incursion of debris washed from upslope. If little removal occurs from the footslope the soil particles remain in position long enough to become intensely weathered encouraging the development of deep clayey soils. Moreover, footslope soils tend to be poorly drained for the high clay contents retard water movement through the profile. Hydromorphic soil profiles with characteristic bleached gley horizons or mottled pseudogley horizons are developed. Mottling is considered to reflect intermittent wet and dry conditions during which reduction of ferric oxides and hydroxides, as well as manganese, takes place in wet poorly aerated soils (van Niekerk and Lambrechts, 1978). These compounds are soluble and mobile. During subsequent drying, oxygen enters the soil and ferrous oxides are oxidised and precipitated.

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Hydromorphic environments are therefore characterised by a low pH and strong development of colloids in which many chemical elements are likely to be accumulated.

This relationship between soil and slope is known as 'catena' or 'facies'. Widespread throughout the African sub-continent in intertropical catenae is the occurrence of a layer of gravel which has been designated the "stone-line". From the geologists point of view the stone-line is of great importance in the information it conveys regarding the development and origin of the soil material. It is commonly taken to mark the boundary between residual and overlying transported soil. It is stressed, however, that it is not a regular stratigraphic stratum and may even be a biotic stone-line formed by termites which have carried the finer particles of soil up to the surface to form the 'transported zone' and leaving a concentration of gravels at some depth below the surface resting directly on residual soil (see Corbett, 1978).

Under extreme topographic conditions (mountainous reliefs and steep slopes) the erosion rate is higher than the chemical weathering rate and the soils that remain immature or non-existent, whatever the climatic conditions may be, are termed "azonal soils".

Correct interpretation of morphological, mineralogical and chemical soil properties is the first step towards making meaningful predictions regarding the origin and properties of a soil horizon for exploration purposes. A relatively new empirical system (binomial) for classifying the soils of South Africa has been evolved, based on the above properties and has overshadowed and terminated Van der Merwe's (1962) zonal approach (Van der Eyk et al., 1969; Macvicar, 1978). An apparent shortcoming (from the viewpoint of the geological profession) of pedological soil classification systems, including the South African binomial system ("form" and "series"), is the omission of the nature and origin of deep materials below the genetic soil or solum. These materials and other geomorphic factors such as slope are catered for by a mapping device known as the soil phase which is applied as a qualification to the series. In its present form, however, it can be adapted to geology.

2.2.4 Time of Evolution

This factor may also explain very important pedogenic and geochemical differentiations. The time required for soil to reach a steady state condition has been considered by Birkeland (1974). 'A' horizons form rapidly and are easily altered in less than 1000 years whereas 'B' horizons are much slower. From simple calculations the time required to form a ferrallitic soil profile 100m thick leached of silicon and bases in equatorial regions has been estimated to be 10⁷ years or more (Kronberg et al., 1978). In wet temperate zones the silicon content of subsurface waters and the intensity of drainage are not much lower (Davis, 1964), which suggests that the unit of weathering time should not be much longer. However, the equatorial pedogeneses are much thicker than those of temperate climates. This difference is probably due to the time factor. On old, stable basements of equatorial regions such as West Africa and Brazil, chemical weathering might have been going on for a long period without being really impeded by any intense erosion, in as much as the saprolites and soils were preserved by a thick vegetal cover. In fact some of the ferrallitic soils in Brazil may well have been in the process of formation since the Atlantic opened up (Kronberg et al., 1978). In temperate regions on the other hand, successive episodes of erosion brought about by climatic change (Pleistocene glaciation) swept away the major part of the saprolites formed during more ancient periods (Maignien, 1966).

Thus, some disparities between pedogeneses may result rather from differences in the duration of chemical weathering than from differences in the nature of the processes.

3. DURICRUSTS

The terms laterite, silcrete and calcrete refer specifically to soil or surface deposits which have become cemented or replaced by iron oxides, silica and calcium carbonate respectively. Appropriate descriptive terms are used to describe the physical nature and degree of development of these materials. The problem of how duricrusts formed can be approached by determining whether there are any modern analogues of the material. An alternative method is to determine fairly accurately the age of the duricrust under consideration and then from geological, geomorphological and other evidence deduce the environmental conditions under which they formed.

3.1 LATERITE

3.1.1 Generalities

Definition. Ferricrete is applied as a general term for a near surface ferruginous accretion of which laterite is the major type. It appears increasingly difficult to give a pure morphological, physical or chemical definition to the word 'laterite', it having evolved through the geological into the pedological field. The broad grouping of soils described at various times as Tropical Red Earths, Ferrisols, Ferrallitic Latosols, Oxisols and Ultisols are all used to describe Laterite. This usage is considered to be too general and Alexander and Cady (1962) give the following narrower definition :

> "Laterite is a highly weathered material rich in secondary oxides of iron, aluminium or both. It is nearly void of bases and primary silicates but it may contain large amounts of quartz and kaolinite. It is either hard or capable of hardening on exposure to wetting and drying".

Emphasis is placed on the characteristic property of induration (hardening) defined in this context by Maignien (1966) as "a state in which the hard brittle consistency of the medium is not affected by humidity".

Geochemical properties of iron and aluminium. With a content of 5,0%, iron is the fourth most common element in the lithosphere after oxygen (47,5%), silicon (28,8%) and aluminium (8,1%). It is relatively concentrated in igneous rocks and shales but relatively scarce in sandstones and limestones. Aluminium is well represented in eruptive feldspathic rocks and argillaceous or schistose rocks but relatively scarce in carbonates and sandstones as well as in ultrabasic rocks (Clarke, 1924).

Iron and aluminium are rather similar elements being classified in the group of 'hydrolysates' of Goldschmidt (Fig. 5). They are both oxyphile elements in the upper lithosphere and give rise to amphoteric hydroxides. But Fe can occur in two oxidation states which gives its aspects of chemical behaviour that are sometimes similar and in other cases dissimilar to Al. The problem with respect to the genesis of laterites is basically one of how to effect a chemical separation of Fe, Al, Mn and Si, four normally relative immobile elements. Numerous writers have called upon variations in (a) the rates of reaction (Wollast, 1967), (b) the relative solubility of these elements due to variations in Eh and pH (Norton, 1973) and (c) complexing organic agents (Huang and Keller, 1970).

Figure 11 illustrates graphically the differences in the stability fields of Fe, Al and Mn oxides as a function of Eh-pH and Figure 12 superposes the solubility curves of alumina, iron and silica in terms of pH as unanimously accepted today.





Fig. 12 Relationship between pH and solubility of Al, Fe, amorphous silica and quartz (From : Birkeland, 1974).

Fig.11 Eh pH diagram showing the solubility limits (10^{-6} mole/l) of Al, Fe and Mn, in the systems Al₂O₃-H₂O, Fe₂O₃-H₂O and MnO-H₂O, at 25°C and 1 atm. The lines of equal solubility of Fe -Al and Mn-Al are dashed. Norton, 1973.

On examination of Figures 11 and 12, the relative behaviours of the four oxides are immediately apparent. They are considered conveniently as follows :

(a) In an acid medium, Al and Fe are more soluble than silica. Under low pH conditions (pH<4), Al is more soluble than Fe when the environment is oxidising enough (Eh>0,4) giving rise to 'laterisation' if Fe is available in the parent material (protore).

(b) In a neutral medium, Al and Fe are insoluble whereas Si retains its solubility. At low to intermediate pH, under reducing conditions, Fe is more soluble than Al giving rise to 'bauxitisation' if Al is available in the protore.

(c) In an alkaline environment (pH>9) the solubility of Al andSi meet and increase together.

(d) Under no reasonable conditions of Eh-pH are the oxides of Fe and Mn of equal solubility and would therefore not be dissolved or precipitated in equal amounts.

(e) Manganese behaves in a manner similar to Fe but is more soluble (mobile) than Fe for any given Eh-pH.

Thus it appears that under most conditions normally encountered in soils, i.e., groundwater pH ranging from 4 to 8, Al and Fe are far less mobile than Si. Huang and Keller (1970) were able to reduce and even reverse the difference in mobility between Al and Si using organic acids in their leaching experiments. By taking their results a step further, Huang and Keller (1972) suggested that the complexing properties of fulvic acid on Al³⁺ (a hexacordinate chelate) are such that it may be possible to form kaolin if there is an interaction between soluble (or colloidal) organic complexes of both Al or Si, or between Al complexes and dissolved silica (H_ASiO_A).

It would seem to be reasonable to conclude, in the light of the above studies, that some dissociation of these elements is plausible in the environment of weathering. Furthermore, that soluble organic acids are not only capable of promoting the dissolution of silicate minerals but can also yield intermediary species which may eventually lead to the formation of new minerals. Such processes are clearly important in the concentration of Fe and Al sesquioxides during laterization and related deep leaching phenomena.

3.1.2 Analytical Study

Physical and chemical characters. Essentially three structural types of laterite are distinguished :

- a free concretionary or nodular structure (in an earthy matrix)
- a continuous skeletal structure
- a cemented structure

MacFarlane (1971) distinguishes colitic (<2mm ϕ), pisolithic (2-20mm ϕ) and concretionary (>20mm ϕ) textures formed by concentrated precipitation or deposition of sesquioxides around various nuclei such as quartz grains and mineral debris.

A useful, descriptive, partially evolutionary classification is that developed by Pullan (1967) which shows a progressive development of laterite through various stages of increasing ferruginization. Laterite formed within millimetre distances of the rock surfaces by selective ferruginisation and segregation of secondary minerals produces a multicoloured *vermicular ironstone* which refers, specifically, to an internal wormlike structure or tubes, 20-30 mm in diameter, that are often filled with white kaolin. Increasing ferruginisation decreases the number of vermicules and the presence of vesicules or blister-like cavities, 5mm in diameter, gives rise to a *vesicular lateritic ironstone* with a much harder aspect. Vesicules may be filled with a pink earthy material (iron-stained kaolinite?). This is synonomous with MacFarlane's (1971) vermiform laterite. Progressive development leads to a more uniform structure and if the earthy fill is removed from vesicules by washing or solution a *cellular* or *scoriaceous ironstone* is produced.

The erosion of laterite leads to the formation of detrital materials. Resolution of *detrital laterite* is widely recognised (Nye, 1955; De Swardt, 1964; MacFarlane, 1971). Rolled nodules become recemented at the point of nodule contact to give an open structure whereas vesicular laterite breaks down into coarse fragments providing material for a recemented ironstone breccia or conglomerate. High contents of the sesquioxides of Fe and/or Al and an Al_2O_3 : SiO₂ ratio of less than 2 are features of indurated laterite (Maignien, 1966). If iron predominates they are called ferruginous laterites and if aluminium predominates they are called bauxites. Mineralogically, the major components of ferruginous laterite, geothite/ hematite, and bauxite, gibbsite/boehmite, are mixed in variable proportions to yield grades ranging from a few percent Fe_2O_3 to >80% and a few percent Al_2O_3 up to 60%. A combined water content, determined by loss on ignition, varies from 5% to 35% (i.e. pure gibbsite : $Al_2O \cdot 3H_2O$) increasing linearly, at the expense of iron, as the Al_2O_3 content increases (Fig. 13).



Fig. 13Al₂O₃ content and ignition loss of lateritic samples collected from above various parent rocks in many countries (From Schellmann, 1975)

The combined silica content of laterite is predominantly in the form of clay minerals especially kaolinite. Traces of illite and vermiculite are reported from some young laterites (van der Merwe and Heystek, 1952).

Bauxites commonly develop over undersaturated aluminous rocks such as synetite, dolerite, etc., whereas laterites are formed over a much wider variety of parent materials. Pseudomorphs of gibbsite after feldspars and goethite after ferromagnesian minerals retain the structures of the replaced minerals particularly in recent or immature laterites while the older ones tend to be concretionary or pisolitic in form (Alexander et al., 1956). Chemical compositions of the discrete components of laterite are scarce. Alexander et al. (1956) who studied samples from Africa stated that the nodules examined had a high sesquioxide content and low silica content. Maignien (1966) reports that the pisolitic crusts of Guinea are composed of pure alumina or the oxides or iron. Schellmann (1975) states that bauxite tends to develop pisolitic structure more than laterite does, however, Prescott and Pendleton (1952) were of the opinion that nodules contained less free alumina than massive forms and that their Mn content was lower.

Colour and density (2.5-3.6) vary considerably in relation to overall bulk composition, level of development and formation conditions. In an oxidising environment iron yields ochre, red or black colours whereas alumina, white in the pure form, is often mixed with iron to give reddish tints (Schellmann, 1975). The manganese minerals, lithophorite and birnessite, occur as thin purplish black coatings on concretions (Goudie, 1973). Density increases with increasing ferruginization so that older crusts are more dense than recent ones and cemented formations are denser than those of scoriaceous structure. Consequently, physical definitions of hardness and colour are unsatisfactory.

The minor components of laterite, although contributing to the morphology and composition of the latter, do not actually play a role in their genesis. However, a study of these may throw considerable light on the history of laterites and especially on their relationships with subjacent or superjacent horizons. Quartz is usually present in only small amounts being poorly represented in bauxites but is more abundant in ferruginous laterites where it occurs as residual grains randomly distributed throughout the groundmass. Fine-grained gibbsite and quartz of colloidal or even sub-colloidal size commonly occur filling fissures and pores of the matrix of lateritic crusts (Schellmann, 1975). Quartz of apparently external origin (alluvial, aeolian, etc.) is reported in aluminous laterite formed from quartz free parent material (Maignien, 1966). Residual grains of magnetite, chromite and ilmenite, among others, may be present in considerable properties in addition to Co and neoformed Ni silicates. It must be remembered that they themselves constitute ore types in some cases, viz. lateritic nickel, manganese oxides, etc.

The chemical and mineralogical data of laterite indicate extreme variabilities between ferruginous and aluminous and members. Disparaties may be attributed to differences in the factors of soil formation, viz. parent material, climate, topography, vegetation and time. Therefore, chemical classifications of laterite based on Fe-Al

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content and various oxide ratios are largely unsuccessful.

Types of laterite deposits

These types are specified by the topographic levels at which these deposits were largely formed (see Grubb, 1973). Ferricretes and laterites occupy the following physiographic environments :

- High level peneplains (uplands)
- Low level peneplains (terraces)
- Valley or low level basins with high water table
- Talus slopes.

(1) Peneplain deposits. Bauxites and ferruginous laterites occur most commonly as concretionary layers or crusts in more or less indurated 'blankets' which cap hills (mesas) and plateaus (tablelands) and which offer protection against erosion. These topographically high levels are fairly widespread in the humid and sub-humid inter-tropical zones of Africa, South America, Indonesia, Asia and Australia where they are considered as well-planed planation surfaces, mostly of Tertiary age, described in Africa as "African surface", in Australia as "Old Plateau" and in India as "high level laterite" (King. 1962; De Swardt, 1964; Stephens, 1971; Mulcahy, 1960, 1963; Grubb, 1973). However, they are not confined to humid inter-tropical regions of the world. Occurrences of laterite in temperate regions are well documented (Maignien, 1966; Grubb, 1973) and their extension into drier climates such as the Australian and African deserts indicate that many of the accumulations are fossil and that conditions were favourable to their formation and/or preservation at some time or other in the history of the earth.

The deepest known lateritic profiles are 80-120m thick with indurated crusts of 10-30m, whereas many profiles are 15-30m in total thickness (Goudie, 1973). Significant differences in profile development are recorded from different topographic levels. These are conveniently considered in terms of 'high level' and 'low level' deposits.

(a) '<u>High-level' deposits</u>. These are generally found in undulating forested terrain capping high plateaus in tropical or sub-tropical climatic zones, e.g. : Deccan Trap in India, S. Queensland,
 Hawaii, N.W. Oregon and Washington, Arkanas, Central Africa, Mitchell
 Plateau (Australia), Ghana and Guinea (Grubb, 1973). They are commonly

bauxitic or highly ferruginous forming thick blankets of up to 23mand are generally developed on volcanic or igneous source rocks. The vertical sequence from top to bottom through a typical bauxitic profile developed over nepheline syenite is illustrated and described in Figure 14. Chemical compositions indicate a high grade bauxite deposit with 62,0% Al_2O_3 and 0.9% Fe_2O_3 . The contact between granular bauxite and parent material is often very sharp and irregular with only a thin horizon of basal saprolite (underclay) when present.

The tropical nickeliferous laterite described by Chetalat (1947, in : Park and McDiarmid, 1975) over ultramafic rocks in New Caledonia is a good example of a ferruginous laterite of this type (Fig. 15).







Fig. 15. Typical section and zones through ferruginous laterite deposit (From : Park and MacDiarmid, 1975).

(b) 'Low level' deposits. These more frequent deposits are commonly associated with low relief planation surfaces, e.g. northern South America, Malaysia, northern Australia. Unlike their high level counterparts, these deposits are generally less than 9m thick, are of aluminoferruginous composition and have a thick underlying kaolinitic horizon. The main levels from top to bottom over basic igneous and granitic parent materials are shown in Figure 16.



Fig 16 Lithology and mineralogy of bauxitic laterite profiles over meta-quartz dolerite (A) and gneissic granite (B). Diff.—difference between total mineralogy by XRD/chemical analysis and 100%, qz.—quartz; gib.—gibbsite; kao.—kuolin; goe.—guechtic; hm.—hemalite; mgh.-- mmghemite; ats.—analase; hb.—hornblende; pfs.—plagioclase; lcz.—leucoxenized illmenite; or., orthoclase; mp.-- microperthile; mcl.—microcline; bio.—blotte; acc.--accessory minerals (zircon, magnetite, ratile, epidote).

(From : Sadlier & Gilkes, 1976)

There is a tendency for iron to be associated with the black pisolitic material in the upper parts of the crusts whereas the lower part is relatively enriched in Al. These laterites are generally considered impure bauxites. They generally lack an inherited parent rock structure, unlike the high level deposits, and whereas the latter are commonly vesicular or scoriaceous, alumino-ferruginous varieties tend to be pisolitic or concretionary. Relations with tropical soils. The example described by Aubert (1954, in : Maignien, 1966) is chosen as a typical ferrallitic soil profile :

Lateritic soil on granite

Dakpadou forest in the west of the Lower Ivory Coast, 50 km. north of Sassandra; slightly degraded ombrophil forest.

Sub-equatorial climate without a distinct dry season, annual precipitation 1,700 mm., mean temperature 27° C.

Gently rolling topography, section on top of low plateau.

Parent rock: syntectonic granite with a high content of ferromagnesian minerals.

0 cm. Forest litter-bed of decomposing leaves, twigs and branches apparently lying on the soil.

- 0-110 cm. Grey-brown horizon, slightly humic down to 35 cm., thereafter beige; fine sand and gravel; high content of very hard, round, dark ferruginous concretions, especially in the first 40-50 cm.; below approximately 80 cm. the horizon becomes more compact, the concretions less hard and the colour brick-red.
- 110-175 cm. Fairly abrupt transition to a hardened horizon which can be broken by hand fairly dull-brown to red bands joining up and outlining cavities containing an ochreous to beige earth.
- 175-650 cm. A non-hardened horizon, more compact at the base; brick-red with welldelineated beige, ochre or grey spots; still some hard nodules, especially in the upper part of the horizon; riddled by small channels. The quartz grains are less pulverized in the upper horizons.
- 650-340 cm. Transition to mottled clay, with poorly delineated mottles of a clearer beige or grey colour; quartz grains more abundant; some whitened, friable elements at the base bave retained the felspathic habit.
- 840-1100 cm. An ochreous-brown horizon with a high content of quartz and white, powdery elements, which contains nodules of less decomposed rocks exhibiting altered pyroxines. Gneissose gruss towards 9 m.; white, friable, felspathic materials, quartz grains and greatly altered coloured elements.

Towards 1,200 cm. Gneissose parent rock with a high content of ferromagnesian minerals.

The ferrallitic soil profile described above shows some features resembling the 'high level' and 'low level' deposits which are conveniently compared as follows :

Ferrallitic soil profile	Lateritic bauxite profile		
 (1m) leached upper, weakly humic horizon (A) 	- residual soil		
 (6m) eluvial horizon of Fe- and Al- accumulation (B) 	- alumino-ferruginous laterite		
- a horizon of mottled clay	- mottled clay		
- a horizon of initial decomposition	- bauxite or ferruginous laterite		
- fresh parent rock	- fresh parent rock		

The development of ferrallitic soils and their relationship to laterite ('ferrallitic cuirasse') are well illustrated in Fig. 17.


Fig. 17. Development of ferrallitic soils and laterite ('ferrallitic cuirasse')

The massive and thick accumulation of Fe and Al in laterites and bauxites can be considered as due to a prolonged ferrallitic evolution during which the B-horizon develops progressively as the profile goes deeper, migrating downward as the topographic surface is lowered by erosion. Concretions start to form when there is 12% Fe₂O₃ (Meillon, 1978) and they are commonly regarded as an advanced state of mottling indicating alternate wetting and drying.

It is generally accepted, therefore, that laterite represents an ultimate term in pedalfer development derived by exposure of the classical 'B-horizon' following erosion of the softer, superjacent formations (Fig.17). Once the sesquioxides are exposed they can have a history dating back to the Tertiary or even Cretaceous periods (Stephens, 1971; Grubb, 1973) and tend to become indurated. Induration appears, therefore, to be the sole specific characteristic of laterite. It is a secondary pedological phenomenon district from primary lateritic weathering.

This hardening process has been discussed at length by Maignien (1966). Ancient laterite commonly supports present day grassland which may have been forested originally. During periods of rhexistasy, often explained by the existence of a climatic change with marked trend toward aridity, the grassy vegetation which succeeds deforestation is considered to bring about once again a mobilization or iron in the upper portions of exposed lateritic crusts. Iron, so released, descends to fill the interstices of the lower levels during recrystallization of the hydroxides in the form of successive ferruginous films, i.e. platy texture. Exposure to lower relative humidities would also tend to cause the dehydration of goethite (FeO-OH) into hematite (Fe_2O_3). Maignien concludes that hardening is related to the iron content, specifically to the state of crystallization of goethite or hematite or to a more or less continuous arrangement of the constituents implying some degree of migration. The causes are connected with the conditions of immobilization of materials in solution and with the environmental conditions in which the processes occur. The essential characteristics of laterite remain when the climate has changed to a drier regime.

Genesis of bauxites and laterites

'High-level' bauxites and laterites. During the initial phases of lateritic weathering the texture of parent rocks is commonly preserved. This implies that weathering took place without volume change and forms the basis of the isovolumetric method described by Millot (1970) in order to study the geochemistry of weathering. Bonifas (1959, in Millot, 1970) studied the 'weathering balance' of a lateritic profile developed over dunite from Conakry (Guinea) using this method by comparing a 1cm³ sample of fresh dunite with a 1cm³ sample of its saprolite (see Table 5).

Table 5 : 'Weathering balance' of dunite from Conakry by the isovolumetric method.

sio2 TiO2 A1203 Cr203 Fe CaO MgO H2O S.G. 95 4,5 32,8 1.4 0,25 0,22 Fresh dunite 103 29,7 2,8 Weathered dunite 2,5 2,5 93,5 0 0,57 0,24 0,25 17,7 1,58 Differences -92,5 -2,0 +60,7 -1,4 -102,5 -0,01 +0,03 -12,0 (absolute) Differences -97,5 -44,5 +185 -100 199 -4 +13,5 -40 -(in % of the (components of dunite)

Numerous such isovolumetric studies over different parent materials are published (Millot, 1970; Valeton, 1972). A striking feature is the intensity of alterations reflected by a high increase in

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Fe (in this case ± 185 %) or Al_2O_3 if Al is available in the parent rock. As reported above during weathering and leaching within the more common pH range (4-8), bases are removed first and then combined silica whereas Fe and Al are relatively insoluble. During the initial phases of lateritic weathering, pseudomorphs of gibbsite after felsapars and goethite after ferromagnesian minerals retain the structures of the replaced minerals (Alexander et al., 1956). Bauxite and ferruginous laterite are thus considered as strictly residual accumulations derived by leaching of the more mobile constituents (bases, SiO₂). Such deposits are essentially primary ones even if re-dissolution and re-precipitation processes in the exposed crustal layer progressively destroy the inherited parent rock structures.

'Low level' laterite. The Fe203/Al203 ratio of this type of laterite is greatly increased relative to the parent material; unlike 'high level' deposits where the ratio is essentially constant. According to Maignien (1966), this is best explained by lateral import of iron leached from areas up the hydraulic gradient. Based on evidence from studies of tropical soil catenae, this interpretation implies selective chemical leaching and a hydrological control. The effect of groundwater is important since the mobilisation, migration and deposition of Fe, Al, Mn and Si are affected by variations in Eh, pH, vegetation and biological activity, all largely dependent on the level of water saturation and on the water regime of the soils. Mn is most mobile, then Fe and finally Al whose solubility is very limited under the reducing (Eh<0,4) and pH conditions of subsurface water. The forest equatorial pedegenesis normally corresponds to a peneplain landscape, with convex hills cut by a dense network of valleys, and in which groundwater circulates laterally and obliquely at various shallow (a few metres) depths (Fig. 18).



Water at A will divide itself into proportions directly related to the ease of movement. In the three directions illustrated, the largest amount will take the shortest and least resistant route, path 1, and the smallest amount path 3.

Fig. 18. Flow of subsurface water (From : Williamson, 1969)

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Lateral flow may be appreciable through coarse grained porous pediment gravels and talus cones, under terraces and in alluvial groundwater which function as oxidising reception zones to dissolved Fe and Mn selectively leached from upland sites. The tendency, therefore, is for Fe and Mn to accumulate in relatively low, sub-horizontal layers which are capable of becoming encrusted (Figs. 19-21).



FIG. 19 — Catena of soils showing a denuded ironpan (1), a colluvial ironpan (2) and ironpan formation in the terrace above the ravine (3).' Neighborhood of Labé, Guinea. Western Africa FromMAIGNIEN, 1966.



FIG. 20 — Catena of soils in the neighborhood of Kankan, Milo river valley, Guinea, West Africa. Three levels of terraces with crusts and concretionnement of iron in the modern alluvial plain by hydromorphy FromMAIGNIEN, 1966.



FIG. 21 — Catena of soils in the neighborhood of Kankan, Milo river valley. Guinea, Western Africa. Encrusted alluvial terraces of the Milo river. The loose superficial horizons are partially croded From MAIGNIEN, 1966.

Schellmann (1975), however, considers that an absolute accumulation of iron by precipitation of laterally moved, dissolved Fe is a highly unlikely source of extensive laterite surfaces. Rather, the increase in the Fe_2O_3/Al_2O_3 ratio is attributed to a loss of Al_2O_3 . The reasons for the behaviour of the Al, which concentrates or does not concentrate during lateritic weathering, is discussed in terms of kaolinite solubility. Although recognising the controls of Eh-pH on Fe and Al solubilities, Schellmann notes that greatly differing acidities and redox potentials, particularly very low values, are normally not developed during lateritic weathering.

Alumino-ferruginous laterite derived from feldspathic rocks, either quartz rich or not, generally lie on a thick kaolinitic saprolite in which the feldspars have been completely altered while the quartz persists. Gibbsite formation seems to proceed in two steps :

> Step 1 = feldspar \longrightarrow kaolinite Step 2 = kaolinite \longrightarrow gibbsite

Kaolinite dissolves incongruently to give gibbsite only if the soil solutions contain a very low concentration of dissolved silica (less than 1 ppm) and an intermediate range of pH (4 to 7) in which gibbsite is stable. At higher concentrations in very acid or alkaline conditions, kaolinite dissolves congruently and gives Al³⁺ (acid solution) or Al(OH)₄ (alkaline solution) ions and the precipitation of gibbsite does not occur. Removable of soluble Al ions by soil solutions would substantially increase the Fe_2O_3/Al_2O_3 ratio giving rise to aluminoferruginous laterite of the 'low level' type. This interpretation implies that laterite or bauxite development is a function of the amount of dissolved silica in the weathering solution in addition to being a function of the Fe_2O_3/Al_2O_3 ratio of the parent rock.

The concept of topographic level explains fairly well the formation of bauxites and ferruginous laterite in 'high level' upland regions characterised by high rainfall, good drainage and a deep permanent water table, particularly those areas underlain by silicate rocks free of quartz and high in Al and Fe respectively. During the leaching process of silicate minerals in the common pH range (4-8) of upland areas, bases are removed first and then combined silica, whereas Fe and Al (gibbsite) accumulate residually as crystallized products. Grubb (1973) envisages downward percolation of soil solutions with little or no fluctuation within the weathering zone as the main factor in their formation. Consequently they retain inherited parent structures and may be described as 'eluvial deposits' of 'relative accumulation'.

The same concept explains the formation and characteristics of alumino-ferruginous laterite in low-level peneplains where water table fluctuations within the profile probably account for the thick mottled underclay and in which inherited parent structures progressively. disappear. The thick underclay in turn reflects impeded drainage which means that in the wet season soil solutions are likely to contain a high concentration of dissolved silica. In the ferrallitic soil profiles Fe is seen to accumulate more easily than Al at the level of the B horizon but it is relatively depleted at the level of the hydromorphic underclay as is attested by the mottling and frequent bleaching (pallid zone) of this formation. In this way one could explain, with improved drainage conditions and less of Si (i.e. low water-table) the presence of a bauxitic zone intercelated between a superficial ferruginous crust and deeper clayey horizons. Since the Al-accumulations likely result from vertical and lateral redistribution of this element they cannot be considered as strictly residual and are best termed 'illuvial-eluvial' deposits.

(2) Valleys or low level basin laterites. The evolution of lateritic crusts by lateral migration of iron as envisaged by Maignien (1966) is probably more applicable to these types of deposit which are usually of limited extent (Figs. 19-21). In order to illustrate the importance of geomorphic factors in their distribution, a few examples may be cited from the Land Pattern occurring in the area of the Pretoria-Johannesburg granite dome after Partridge (1975). In addition to old erosion surfaces, Partridge^{*} distinguishes lateritic development in the following geomorphic environments :

- Gully heads and pan side slopes
- Hillslope-pediment junctions.

Laterites occurring on hillslope-pediment junctions ('lateral ferricretes') are formed through reduction in the velocity and trans-

*For a more complete summary of this work, see Corbett (1978).

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porting power of episodic sheet wash from the convex hillslope as it debouches on the pediment. Dissolved iron salts are deposited at the head of the pediment as the discharge infiltrates through the hillwash soils. Notable examples occur in the Bankenveld of the Transvaal and in the Cape Fold Mountains at the junction of dip slopes in quartzitic rocks with subjacent pediments.

Gully head and pan side slope deposits occur on gentle slopes and are commonly located beneath transported soil. Other examples of this type of deposit occur in Zambia and are described by Dr. A.G. Smith (In : Discussions, MacFarlain, 1971), who recognises their occurrence on well plained pediplain surfaces that are drained by spaced marshy hollows known as 'dambos'. A considerable amount of rainfall drains to the dambos by lateral seepage through strongly-leached soil and each dambo is fringed by hardened outcrops of laterite.

In his study of tropical soil catenae, Maignien (1966) notes that the morphology of encrusted laterites is determined by the physico-chemical conditions at the site of their accumulation. In acid soils encrusted forms are diffuse and produced by impregnation giving rise to fairly complete cementation of soft material. This is analagous to MacFarlane's (1971) 'pedogenetic laterite' which comprise irregular pisoliths or are cellular to platy. In argillaceous and silted media, i.e. hydromorphic soils containing high contents of the basic cations, the oxides of iron and manganese tend to accumulate as well rounded and regular pisoliths. These have been termed 'groundwater laterite' by MacFarlane (1971) who suggests, from her studies in Uganda, that pisolithic structures reflect immaturity in the laterite. Downslope they thicken and grade into a mature vermiform variety indicative of a more stable water table.

Partridge (1975) emphasizes the importance of a fluctuating water table within all geomorphic environments in which laterites develop (including old erosion surfaces) and stresses that their formation is always dependent on the presence of suitable sources of iron salts as well as the appropriate climatic circumstances.

(3) Talus slope deposits. The occurrence of laterite on slopes of up to 10° is often recorded (Mulcahy, 1960, 1961; Trendall,

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1962) and more rarely up to 20° (De Swardt, 1964). As reported previously, one of the most conspicuous features of peneplain type deposits is their frequent association with flat-topped mesa and butte assemblages. The characteristic slope form of the mesa is fairly constant and consists of a flattened upper slope and summit separated sharply by a band of hard laterite from a concave or straight middle slope which passes into a fairly straight lower slope of low inclination (Moss, 1968). Talus slope deposits are in theory detrital crusts at the foot of formerly encrusted mesas and are formed by the consolidation of laterite fragments derived from erosion at higher levels. Pallister (1956) has shown that the lack of diminution downslope in the size of lateritic detritus once it is reduced to the size of a pea may be a factor in the maintenance of essentially straight, as opposed to the more normal concave, pediment profiles. Owing to subsequent leaching and reprecipitation (Fig. 22), the distinction between detrital and in-situ residual laterite is not always apparent, for as an end-product both give rise to a uniform pisolotic or vermiform structure.



Fig. 22 Multi-process formation of ferricrete in a pediment environment. (Bedrock 1 may be a rock susceptible to *in situ* ferricrete formation with all the characteristic features (including the pallid zone), but in some circumstances the new laterite may form over a less susceptible rock, for example, a quartzite.)

(From : Goudie, 1973.

It is in fact, quite possible, that a significant proportion of some peneplain laterites were originally products of downwasting from regions of active laterization. Such a sequence of events appears to have been effective in Nigeria where De Swardt (1964) describes most of the present landscape as having formed by a second, younger laterite on slopes of up to 20° , which contains much detrital material from the older primary, higher level peneplain deposit (Fig. 23).



Fig. 23 A typical Nigerian valley profile with preserved remnants of the older laterite. The aeolian layer occurring in the north of the country is not shown. Vertical scale exaggerated. A = older laterite; B = younger laterite; C = soil; D = alluvial deposits; E = recent incision of valleys; F = mottled and pallid zones; G = bedrock.

(From : De Swardt, 1964)

Other occurrences of this type are reported from Arkansas (Gordon et al., 1958). Guiana (Moses and Mitchell, 1963), Gove, N. Australia (Grubb, 1970) and the Darling Range (Mulcahy, 1960).

Laterization and geomorphology

The physiographic relations of laterite are well documented and shown to occur principally on high level planation surfaces of subdued relief. For example, Stephens (1971) infers that the major regional occurrences of laterite in Australia once had a sub-continental distribution extending continuously in the form of a huge crescent from the southwestern part of arid W. Australia, across the northern and central regions to the eastern and south-eastern coastal areas of Queensland and New South Wales (Fig. 30). Predominantly the laterite was a relative accumulation of alumino-ferruginous composition and though place to place differences in the age of laterite have been recorded, dating from the Cretaceous, Stephens concluded that "the great upper sub-continental laterized surface seem to have been both chronologically and geomorphically accordant with widespread continental planation" to which he assigns an age of Late Tertiary (Pliocene). This closely parallels conditions in India and Africa where the chief duricrusts lie upon early- or mid-Cainozoic landsurfaces of extreme planation (King, 1962). In Africa, laterite occurs patchily in the south with other duricrusts (Fig.29) but is more abundant in central Africa (Nile-Congo watershed zone) extending across the Sahel and Sudan zone and locally is found within arid and semi-arid areas (Goudie, 1973). It is best developed in most of the west and parts of eastern Africa where De Swardt (1964) has traced the existence of two laterite horizons upon upper (older) and lower (younger) level Cainozoic landsurfaces (Fig. 23). Laterite overlies basalts of the Deccan Plateau in India and occurs at lower levels on the eastern side of the peninsular. The lower duricrusts as in Africa and Australia are younger formations and of relatively limited extent (King, 1962; Stephens, 1971; Grubb, 1973).

If, as many authors contend, the characteristic laterite cappings or subsurface laterites occurring within these landscapes are essentially of pedological origin then their present occurrence as an ultimate stage in pedalfer development represents a level which corresponds fairly closely to the original planation surface on which they were formed. According to King (1962) the "accepted mode of origin for the duricrust is that the constituents were leached from the bedrock by groundwater, were carried upwards to the surface of capillarity and have been deposited in and above the soil as the water evaporated". Therefore, laterite formation and pallid zone (bleached underclay) formation are believed to be synchronous and complementary processes reflecting concentration and leaching respectively. King (1962) has also mentioned that duricrusts of this type "afford proof positive of the absence of Davisian downwearing, for they are invariably accumulative upon flat, weakly drained landsurfaces of great age".

Although possibly exclusive to laterites, mottled and pallid zones are not always present (Mulcahy, 1960; De Swardt, 1964; Nye, 1955). Furthermore, even where deep pallid zones occur the depletion in Fe is often inadequate to account for the concentrations in the encrusted horizons (Oertel, 1956; Trendall, 1962). Therefore, if the origin is purely a weathering process related directly to groundwater and its fluctuation then the present occurrence of hard laterite is not the fossilized remnant of an old surface but the relic of a certain level more or less deep in the regolith. The danger of assuming the conformity of laterites with old planation surfaces has been argued by Trendall (1962) who asserts that the characteristic flat-topped laterite hills of parts of tropical Africa are the results of subsequent erosion. Trendall's theory of 'apparent peneplanation' is apparently a compromise between residual concentration from an overhead source and upward movement of solutions while the entire profile moves downward.

MacFarlane (1971), however, considers that both theories are untenable in that they invoke an incredible range of water-table movement, "a movement apparently unable to bring about the desired transfer of the concentrates from lower to higher levels in the profile". In

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her study of the relations between 'spaced' and 'packed' pisolithic laterite on high level planation surfaces ("Buganda surface") in Uganda, MacFarlane (1971) considers that the overlying, closely packed, pisolithic sheet is not an entirely 'in-situ' formation but is due to downwasting and progressive soil encroachment on spaced pisolithic bearing substrata. The latter are believed to represent an advanced state of mottling formed as the water table commences lowering upon initiation of the succeeding cycle of erosion. A factor in the geomorphic importance of laterite lies in its high infiltration capacity (Goudie, 1973) and MacFarlane (1971) attributes the formation of the thick, underlying pallid zone to post-incision modification by leaching through the crust.

Maignien (1966) has noted that the thickness of ferruginous crusts is not always a function of topographic level but relates to the proximity of drainage axes. In favourable localities, such as along fault zones and valley edges, the crusts and weathering profiles are always thicker. Furthermore, the lowering of base level has the effect of deepening the alteration front of ferrallitic soils and gives rise to a characteristic bevelled form in cross-section (Fig. 24).



FIG. 20. — Diagram of the emplacement of lateritic crust and of the formation of relief by lowering of base level

(From : Maignien, 1966)

On a more regional scale, Mulcahy (1960) reports that the depth of the pallid zone in W. Australia decreases towards the dry continental interior. These features appear to substantiate MacFarlane's (1971) belief that pallid zone development is largely a later modification of the original profile and she suggests that "pallid zones only occur beneath protective but impermeable carapaces where they are susceptible to leaching without being washed away".

A further factor in the geomorphic importance of laterite lies in its strength (Goudie, 1973). Indurated crusts as a consequence offer considerable resistance to erosion and fossilize the forms where they occur even if only in the form of mesas. Therefore, not only is the mesa due to the existence of the lateritic crust but also the formation and survival of the pallid zone (MacFarlane, 1971). De Swardt (1964) maintains that over vast areas in Nigeria laterization on two surfaces (Fig.23), corresponding to King's (1962) early-Cainozoic ("African) and late-Cainozoic ("post-African") planation surfaces "froze" the "uneven landscape being lowered by erosion under humid tropical conditions and which already possessed the main topographic features of the present day". The intersection of multiple weathering surfaces, whether on peneplains, pediments or river terraces may produce a complex landscape following incision (Fig. 25).



Fig. ²⁵ Sombroek's model of ferricrete surface development in Sokoto (Nigeria).

(From : Goudie, 1973).

Since the hardening mechanism of laterite described by Maignien (1966) relates to iron content, the simple distribution in topographic level between 'high-' and 'low-level' peneplain deposits and between peneplain and detrital deposits is not universally applicable. Indurated crusts of lower level containing a higher iron content would tend to protect the zones in which they formed while erosion lowers the surrounding softer formations. Older crusts or less indurated aluminous crusts occupying the highest positions would then be gradually reduced by scarp retreat and this may give rise to lateritic relief inversion whereby remnants of younger levels of laterization occur topographically higher in the landscape. Different interpretations are plausible, and Fig. 26 schematizes the possible history of some lateritic deposits in West Africa as envisaged by Lelong et al. (1976). The former peneplain has become a highland covered with alumino-ferruginous laterite.

Environmental factors of laterite formation

The wide variety of laterite types from according to one or more of the following individual models :

-	Residuum		accumulation is residual
-	Precipitate	•	<pre>precipitates form in soil ('pedogenetic laterite') or in the zone of water table movement ('ground- water laterite')</pre>
-	Detrital	:	absolute accumulation from older laterite
_	Residual	4	downwasting surfaces.

The principal mechanism causing the immobilization of iron dissolved in subsurface water is oxidation. This applies to free ferrous ions as well as ferro-organic complexes, where the iron, no longer protected, is oxidised and precipitated (Jackson et al., 1978). Oxidation occurs on approach to the soil surface where the groundwater table crops out, in the zone of oscillation of the water table, during circulation through coarse material or older cavernous crusts, on cutting off the supplies of complexing organic matter and during increase of natural drainage by accelerated aeration of the percolating water.

Rainfall is generally more important than temperature in controlling laterite distribution but rates of reactions and solubilities of the major elements are closely related to temperature and solution pH. Moderate to high temperatures in intertropical zones are an important factor in accelerating lateritic weathering and alternating conditions of wetting and drying appear essential for sesquioxide precipitation. In particular this accounts for the lack of crusts



Fig.26 The possible stages of the formation of West African bauxites and laterites. The stages (1)-(5) are described

EXPLANATION

(1) Period of tectonic calm (Cretaceous, Tertiary?), equatorial climate with forest vegetation; a thick lateritic blanket developed, exhibiting a relatively superficial accumulation of Fe and Al (primary alumino-ferruginous laterite) in surface layers and a lithomarge in deeper poorly drained zones.

(2) Deeper penetration of weathering and slow erosion, under steady climatic conditions; Fe and Al may be progressively dissociated, either by a preferential leaching of superficial Al or by the mobilization of Fe in deeper hydromorphic layers. The mobilized elements redeposited more deeply and laterally in illuvial lateritic crusts developed on slopes or above the groundwater table.

(3) Occurrence of erosion due to a drier climatic phase: formation of a crust of primary laterite on the massifs, wearing away of the peneplain, and formation of pediplain with vast plane surface ("glacis") rich in lateritic debris (Pliocene, Lower Quarternary).

(4) Reappearance of a humid-forest pedogenesis, resulting in re-deepening of weathering profiles and lateritization of the glacis (forming secondary ferrugino - aluminous laterites).

(5) Erosion of tectonic or climatic origin leading to incision, dismantling of residual massifs and breaking up of the lateritized glacis, becoming lateritic crusts of plateaus. The present evolution in West Africa is approximately at this stage.

(From : Lelong et al., 1976)

within profiles that are always humid; as in the equatorial zones where leaching prevails over immobilization. In regions presently arid to semi-arid, laterite is related to deep weathering and certain workers believe they formed under hot, wet, tropical conditions orginally.

Tropical forest cover facilities the formation of lateritic alteration soils but inhibits their exposure, dehydration and induration. Deforestation encourages the precipitation of sesquioxides within the soil and development of pedogenetic laterite above an indurated groundwater laterite horizon.

Geological and geomorphological evidence shows that laterite is associated with graded surfaces of low relief that have developed through long periods undisturbed by major tectonic activity.

3.2 SILCRETE

Definition. Silcrete is regarded as a useful lithological term for extremely hard indurated duricrust of silceous composition. The terms 'surface quartzite' and 'grey billy' have also been used extensively in South African and Australian literature, respectively. All workers who have discussed the petrology of silcretes have drawn attention to the absence of feldspars and other easily weathered minerals and to the presence of up to 90% of allogenic quartz set in an amorphous siliceous matrix. Silcrete and laterite can be regarded as complementary forms of duricrust since the process of laterisation involves desilication and leaching of bases.

3.2.1 Generalities

Abundance in the different rocks. Silicon (Si) is the main cationic constituent of the upper lithosphere and its average concentration in igneous rocks is 27,8% (or 59,14% SiO_2). The average for sedimentary rocks (57,95% SiO_2) is not much lower except that a wide range of values occur with high contents in sandstone (78,33% SiO_2) and very low contents (5.19% SiO_2) in limestone (Clarke, 1924).

Supergene behaviour of silica. The solubilities of the natural forms of silica vary according to their degree of crystallization.

It is noted by Wey and Siffert (1961 in : Millot, 1970) that the solubility of opal, cristobalite and quartz and very much lower than the solubility of amorphous silica (Fig. 27).



Fig. 27. Solubility of amorphous silica, opal, cristobalite and quartz (From : Millot, 1970).

In water, silica may (a) polymerize to colloidal silica, (b) form dispersed molecules of silicic acid, (c) occur as ions (Valeton, 1972). A depolymerization equilibrium is established in water which can be represented by the following reaction :

 $(SiO_2)_n + 2n H_2O \implies nH_4SiO_4$ (6) (natural silica) (silicic acid)

Equilibrium between amorphous silica and silicic acid is attained at 20 to 25° C for a concentration of 120 to 140 ppm SiO₂. At concentrations less than this silica is dispersed as a true solution in the form of monomolecules of silicic acid (H₄SiO₄). All measurements on the concentration of silica in natural waters (streamwater and groundwater : 10-60 ppm; seawater : 1-2 ppm) give values lower than 120 ppm at 25°C but near hot springs the concentration may be high (Krauskopf, 1967; Davis, 1964).

The solubility of silica is strongly dependent on temperatures as demonstrated by Okamoto et al. (1957). A rise in temperature from 0 to 73° C causes the solubility of H_4SiO_4 to increase by a factor of four.

Okamoto et al. (1957) also proved that metallic cations have no effect on the solubility of silica except Al $^{3+}$, and, under particular conditions Mg²⁺. With increasing Al³⁺ concentration, the solubility of colloidal and molecular dispersed silica decrease. However, Al³⁺ has very low solubility for ordinary values of pH.

The solubility of silica in water is practically independent of pH, as long as the pH remains lower than 9. Above pH9 monosilicic acid dissociates and the true solubility of silica increases (Fig. 28).



(From : Millot, 1970)

From the above studies it can be deduced that silica dissolves fastest and most easily in tropical climates where its normal state in natural waters will be in true solution. Under the pH conditions encountered in soils (pH 4 to 8), silica will have a constant solubility and variations in pH are unlikely to play a role in the solution or precipitation of silica in natural environments. The difference between the solubility of amorphous silica and of the crystalline forms of silica is such that a solution saturated with $H_A SiO_A$ silica (120-140 ppm SiO, at 20-25°C) will be supersaturated with respect to the crystalline forms of silica. Moreover, every solution containing 40, 60 or 80 ppm SiO, in true solution is undersaturated relative to amorphous silica but supersaturated relative to quartz and silicates. Since soil solutions do not contain concentrations of silica higher than the limit of solubility, it is highly unlikely that dissolved silica could polymerize and give rise to true silica gels through flocculation, i.e. amorphous silica.

Silicification and growth of crystals. Silicification occurs in a variety of cryptocrystalline forms, viz. quartz, opal and chalcedony (Goudie, 1973). It is important in surficial geochemistry to recognise that the small size of crystals reflects disorder in their lattice (Millot, 1970).

Microcrystalline quartz (1µ) comprises an assemblage of many small quartz crystallites that are arranged into regular polyhedra.

The majority of opals are not amorphous but partially organised structures commonly grouped into aggregates in which the arrangement of silica tetrahedra resemble that of cristobalite with partial disorder. The disorder favours the presence of water and foreign ions (cations) and limits the size of particles.

Chalcedony can be considered an intermediate structure represented by an alternating association of quartz fibres with opal. The quartz crystallites are characterised by major boundary irregularities in the lattices between fibres where silica is apparently disorganised in the presence of water and mineral cations to represent opal.

Experimental work on the growth of crystals is reviewed by Millot (1970) and Stephens (1971). Slightly supersaturated solutions poor in impurities are capable of nourishing the growth of crystals by adding step by step the ions necessary for regular lattice stacking. Spontaneous nucleation ensures the growth of monocrystals rather than overgrowths on existing larger grains. More concentrated solutions induce an abundance of nuclei rapidly and give rise to twinned and polycrystalline structures. Places in which the dissolved products can accumulate are necessary and evaporation can be one of the principal factors controlling supersaturation and the direct precipitation of silica from solutions. Sudden changes in temperature and concentration and the presence of foreign ions disturb the regularity of the growing structure, i.e. accentuate lattice disorder. If suitable cations are present and in sufficient proportions, they are no longer tolerated but neoformed into clay minerals. The restricted development of silicification will lead either to the microcrystalline quartz facies or to the chalcedonic facies that is typical of a first mode of disorder in crystals. Very restricted and imperfect cryptocrystalline growth is represented by opal, a still more disordered stage, where entrapped water and cations lead to the development of only crystalline outlines, similar to cristobalite, but of very small size $(+ 100 \text{\AA})$.

Thus, the nature of the environment of accumulation will determine to a large extent what silicifications are formed and the compositions of their associated clay minerals, if any. It is not excluded that, at the limits of solubility, solutions highly enriched in silica could polymerise and give rise to true silica gels through flocculation though this is considered to be more common in the interpretation of silification of deepseated origin : volcanic emanations, hydrothermal veins, hot springs, etc.

3.2.2 Analytical study

Physical and chemical characteristics. From information assembled by numerous workers, the gross characteristics of silcrete are well presented by Goudie (1973).

Silcrete forms an extremely dense and resistant duricrust with the greatest consolidation in the surface layer. They are commonly coloured yellowish brown or grey (Australian 'grey billy') but can display patches of two or more colours (red, white, yellow, brown). Silcretes display a characteristic and distinctive texture due to the presence of quartz clasts set in a microcrystalline matrix of quartz, opal and/or chalcedony. There is usually a good conchoidal fracture, a vitreous texture and greasy feel. Silcretes form massive, concretionary, nodular and conglomeratic types generally described by the nature of the incorporated clasts.

The more massive, finer textured white forms of silcrete are usually termed porcellanite. Some massive or sheet silcrete, typical examples of which occur over much of central Australia, displays a columnar structure with the columns exhibiting grooves in their vertical faces. It is frequently whorled in places and has a ropey form (Stephens, 1971). At other sites the silcrete may be vesicular and not have a good conchoidal fracture. Normally there is only one silcrete horizon in a profile but multiple silcrete beds have been recorded from a number of localities (Stephens, 1971; Goudie, 1973; Senior and Senior, 1972). In addition to quartz clasts of sand size, many species of sheet silcrete contain rock fragments ranging in size from pebbles to boulders. The composition of the clastic components vary with the underlying lithology but commonly consist of quartzite (including vein quartz), carbonate and clayey material as well as abraded silcrete. Individual indurated crusts (5-10m thick) with a great hardness (7 on Mohs's scale) are often underlain by soft, kaolinitic, mottled and pallid zones up to 50m thick which is separated from bedrock by a weathered or ferruginous zone of variable thickness. The hardening mechanism in silcrete may be similar to the hardening of laterite, as described by Maignien (1966), whereby iron enrichment, in the case of laterite, may arise from either removal of other constituents or accumulation from outside sources, and then hardening is brought about by crystallisation and dehydration. The quantity of silica required to cement a silcrete effectively is probably less than the amount of goethite required for a laterite. As little as 10% of Si can cement a soil horizon effectively (Flatch et al., 1969). Consequently it is a factor in the great strength of even relatively poorly cemented silcrete. The compositional forms of silicification vary according to the stage of development. Wey and Siefert (1961 in : Valeton, 1972) established the stability of mineral phases as follows :

amorphous opal -> cristobalite(chalcedony) -> quartz silica montmorillonite -> kaolinite

decreasing disorder; increasing dehydration; increasing stability

The occurrence of evaporitic minerals (salts, lime, gypsum, alunite) in discrete bands up to several inches in thickness and horizontally or subhorizontally disposed immediately below the silcrete (quartz, chalcedony) capping have been recorded, along with opal, from some Australian profiles (Stephens, 1971) and are an important factor in considering their genesis as well as in mineral evaporation, i.e. conductive overburden. Goudie's (1973) compilation of some South African and Australian silcrete chemistry (Table 6) confirms the high levels of silica (<u>+</u> 95% SiO₂), relatively low levels of alumina and ferric oxide (1-2%) and the virtual absence of alkaline and alkaline earth elements. In some cases, samples of extreme purity have been recorded.

	South Africa			Australia		
	%	Sample size	Range	%	Range	Sample size
SiO2	93.75	14	86.32-97.14	95.63	58.70-99.50	26
Fe2O3	1.65	14	0.11- 5.04	2.66	0.03-31.60	15
MgO	0.46	8	- 1.63	0.06	- 0.10	5
CaO	0.45	8	- 1.10	0.29	0.06- 1.90	15
TiO ₂	1.62	14	0.23- 2.77	0.57	0.10- 1.80	14
Al ₂ O ₃	1.17	14	0.09- 3.78	1.63	0.10-18.40	25

Table 6 (From : Goudie, 1978) South African and Australian silcrete chemistry

The presence and relative distribution of resistate minerals (anatase, zircon, etc.) are also important in considering the genesis of silcretes. Relatively recent detailed petrographic and chemical studies of silcrete from South Australia, not recorded by Goudie (1973), have led Hutton and co-workers (1972) to recognise a range of silcretes between two end members with distinct chemical and textural characteristics. At one end of the continuum there are the titanium-poor sheet silcretes, similar to those described above, that contain rounded waterworn quartz clasts cemented by microcrystalline quartz or chalcedonic silica and which form part of a weathering profile. At the other end of the continuum there are titanium-rich (up to 25% TiO2) skin silcretes found in direct contact with the host material. The presence of titania in some Australian and South African silcretes has been noted and discussed previously (Williamson, 1957; Frankel and Kent, 1938" Frankel, 1952; Mountain, 1952) but in none of the analyses does the titania content exceed 3%. Williamson (1957) regarded a TiO2/SiO2 ratio in excess of 0.01 as high but Hutton et al. (1972) record ratios in the skin silcretes from the Beda River/Lake Torrens area (South Australia) of more than ten times this value. The skin silcretes vary in thickness from 1mm to 20cm and the boundary between the skin silcrete and the host quartzite is generally very sharp. In some samples the skin may parallel the bedding in the underlying sandstone but in many instances skins are developed along surfaces at a high angle to bedding, along vertical joint surfaces and may even

follow the curved surfaces of outcrops. The skins show gross features similar to those described above for sheet silcretes particularly the porphyroclastic texture and yellow brown colour. The skin silcrete consists ofstrongly etched and pitted, angular residual quartz grains of variable size (up to that of the quartz grains in the host) cemented together by a browhish aphanitic matrix (anatase). This is often gradational outwards into a granule rich matrix consisting of finegrained quartz shards, cryptocrystalline silica cementing material and a large number of very fine-grained rutile and/or anatase and zircon granules. The skin silcretes are also high in zirconium content (0,05 to 0,25% Zr) by comparison to the sheet silcretes (<0.04% Zr).

Age and distribution of the major occurrences of silcrete. Silcrete is most common in southern and Saharan Africa and in central and southern Australia where it occurs mainly as cappings on plateau remnants and river terraces, in valley floors and as depression (basin) deposits.

In southern Africa silcrete is prevalent in the coastal zone of South Africa and in the Namib Desert near Luderitz extending patchily north to Angola (Fig. 29). On the south coast silcrete extends locally from Bellville near Cape Town to Mt. Frere in the Transkei (Frankel and Kent, 1937; Mountain, 1946; Stephens, 1971). Silcretes are widespread in the area of the Kalahari Basin (including Etosha Pan) where they occur in association with calcrete.

Only isolated occurrences of silcrete are found in central and East Africa (Goudie, 1973) but become intensive once again in the Saharan zone of North and West Africa, of which the literature, mainly French, has been reviewed by Millot (1970).

In Australia the silcrete deposits are very extensive and occur in more inland and drier areas than does laterite (Fig. 30) though it does occur in association with laterite in the north and with calcrete in the south and west (Stephens, 1971).

Stephens (1971) has postulated a Pliocene age for the major regional occurrences of silcrete in Australia quoting the following points in support of this view : (i) quartzose silcrete containing a



Fig. 29. Silcrete, ferricrete and calcrete distribution in southern Africa (From : Goudie, 1973)

Fig. 30. Silcrete and ferricrete distribution in Australia (From : Goudie, 1973)

matrix of chalcedonic silica and microcrystalline quartz occurs in massive sheet like form encapping rocks which range in age from Precambrian to Cretaceous; (ii) silicification of widely distant Miocene formations (Plantagenet Beds in the SW and at Lake Cowan south of Kalgoorile, in W. Australia and at Lake Pidinga east of the Nullabor Plain in S. Australia); (iii) Late Tertiary and Quaternary diastrophism has been responsible for minor folding of the silicified surfaces. However, a number of minor occurrences in eastern Australia situated marginal to or in the beds of streams are of Quaternary age. Opaline silcrete in Australia occurs consistently on the gypsiferous surface of Late Pleistocene age in the area west and south of Lake Eyre (Wopfner and Twidale, 1967).

Similarly, in southern Africa, silcretes occur locally on a mature planation surface of the "Post African" cycle in the Grahamstown area (Corbett, 1978). Mountain (1946) records, in addition, isolated ledges and flat-topped hills with silcrete at lower levels than the Grahamstown pediplain which he regards not as outliers of the Grahamstown silcrete, but rather as connected with that of the coastal plain. This data taken in conjunction with the terrace deposits in the Mossel Bay-Oudtshoorn-George area, the multiple silcretes on the Grahamstown pediplain and the abundance of abraded silcrete fragments as inclusions in the silcrete testify to repeated formation during the Tertiary, probably continuing into Quaternary times.

Silicification and geomorphology. Interesting examples of silcrete from the Beda Valley, near the southern extremity of Lake Torrens in S. Australia, have been studied by Hutton et al. (1972) who treat of the chemical and physical processes involved in solution, migration and deposition of silica. As discussed previously, the authors suggested a range of material between two end members. The first type, skin silcrete with markedly angular quartz grains, has a comparatively high content of the elements (Ti, Zr) usually associated with very resistant minerals (rutile, anatase, ilmenite, zircon, etc.) and is well developed in scarp foot situations where it occurs in direct contact with the underlying host (Fig. 28). The second type, massive sheet silcrete with rounded waterworn grains, has a low content of Ti and Zr and is well-developed in pediment toes where it forms part of a weathering profile. The gross features of the sheet silcretes described by Hutton et al. (1972) from Ellis Gully (Fig. 31) are remarkably similar to those of regional occurrence in Australia described by Stephens (1971). These include more massive silcrete of quartz/chalcedony composition, about 4m thick, in which the upper part shows marked columnar structure while the lower part grades into highly weathered kaolinised shale.





The two end members are described, but the full range of intermediate types showing a combination of the textural and chemical properties of the end members occur along the pediments (Beda Surface) that slope at $3^{\circ}-4^{\circ}$ from the base of the scarps which delimit the Arcoona plateau to just above the present drainage lines (Torrens Surface).

From thin-section, chemical and electron probe studies on skin silcrete, Hutton et al. (1972) established that silicon was essentially absent from some areas and suggested that titania (anatase) might be acting as the cementing phase. Furthermore, they drew attention to the following facts : (i) Ti and Zr contents vary inversely with the thickness of the skin; (ii) Ti and Zr are concentrated in the skin relative to the host rock and (iii) there is a high degree of correlation (r = 0,92) to the extent to which Ti and Zr have been concentrated. This evidence taken in conjunction with the solution etch features of angular quartz grains indicates to the authors that the increase in the amount of relatively immobile elements, Ti and Zr, in the skins is due to the loss of silica. Concentration by loss is supported by some of the South African data of Frankel and Kent (1937) who were able to determine the parent rocks for the Grahamstown silcrete, which overlies several formations, from the heavy residues and the grain sizes of quartz. These authors show that the silcrete overlying the Witteberg Quartzite had 0,103% heavy minerals whereas the quartzite itself had 0,045%. The silcrete overlying the Lower Dwyka Shale had 0,043% heavy minerals and the shale itself 0,009%.

On the other hand, the massive sheet silcretes display a dilution of these immobile elements and since they occur in the lower part of the landscape, Hutton et al. (1972) postulate two forms of silcrete : one produced by extensive leaching of the rocks to such an extent that even the quartz is being attacked, the other by the accumulation of silicon from some outside source.

Silica minerals are hard and stable and so silcrete is resistant to weathering and erosion. The highly durable silcrete may, like laterite, extensively preserve a surface of planation and give rise to the widespread plateau or mesa and butte assemblages so typical in arid central Australia and in many parts of southern and northern Africa. Where the silcrete has been folded, as in SW Queensland marginal to the Flinders Range, it again acts as a resistant stratum and gives rise to cuesta, homoclinal or hogback forms (Goudie, 1973).

A detailed Australian profile from S.W. Queensland can be taken as an example to illustrate the stratigraphic relations of silcrete (Fig. 32).



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Figure ³² Diagrammatic cross section of a multiple silcrete profile from the southern limb of the Innamincka Dome and a comparison with a section from the northern limb.

(From Senior & Senior, 1972)

A striking feature is the lenticular bedding of the multiple Tertiary silcretes which rest unconformably on deeply weathered kaolinitic sandstone and mudstone of the Cretaceous Winton Formation. Similar features have been described for the Grahamstown silcretes by Mountain (1946) and Stephens (1971) who recognise at least three superimposed horizons. Stephens states that "these horizons of silcrete appear to have been formed successively upwards in bodies of aggrading sedimentary materials. The companion material beneath the uppermost silcrete horizon has a juvenile weathering appearance compared to the minerals below the lower two horizons. The lowermost horizon of silcrete, which is also the thickest, shows marked fluting of some of the vertical surfaces of the silcrete blocks". Reconstruction of the original Grahamstown silcrete horizon from the heights of scattered residuals suggest a surface of moderate (>70 feet) to low relief (Mountain, 1946).

The lenticular characteristics of the silcrete beds imply that they are not necessarily the product of surface silicification of a pediplain and consequently cannot be correlated over large areas as envisaged by King (1962). It is noteworthy that Corbett (1978), in his recent review of landscape evolution and erosion cycles in southern Africa, arrives at the same conclusion and continues De Swardt and Bennett's (1974) campaign for the reform of the geomorphological classification of South Africa. Senior and Senior (1972) interpret that the silcrete in S.W. Queensland formed by movement of silica charged groundwater into fluviatile argillaceous beds or lenticular sand bodies bounded by less permeable sediments. With regard to the Grahamstown silcrete, Mountain (1946) records the presence of a fossilized "stone-line" in silcrete resting on Dwyka tillite and suggests that the silcrete is to be regarded as a silicified soil or subsoil, supporting the theory of Frankel and Kent (1937). It is considered that the differences in interpretation may merely reflect proximal-distal relations to drainage axes on the pediment surface. However, the fact that the silcretes appear to have formed as a widespread veneer on a planation surface of low relief, where the distance between silcrete bands is small, means that they can be used as structural markers on a regional scale. In this regard Corbett (1978) comments : "Features such as the Grahamstown pediplain can be correlated with the (lateritic) Richmond Dalton surface (in Natal) only in the sense that they both represent mature landforms of the Post-African cycle between the great escarpment and the coast. They do not represent remnants of an original surface extending from Natal to the S.E. Cape".

Evidence of breakup and redevelopment of Tertiary landsurfaces in coastal southern Africa is afforded by the descriptions of Frankel and Kent (1937), Mountain (1946) and Smale (1973) of multiple silcretes, abraded silcrete fragments as epiclastic material and by related occurrences of brecciated silcrete in a matrix of laterite from the Grahamstown pediplain. It is significant that the many minor occurrences of silcrete in South Africa occur in the general lateritic zone parallel to the coastline which is considered to have formed by rifting involving monoclinal downwarping of the original Gondwana surface and accompanying graben formation (see Corbett, 1978). These local occurrences may be considered genetically parallel to those formed in the more elevated Hamersley region of W. Australia where Stephens (1971) recognises considerable tectonic uplift, rejuvenation of the stream pattern and an ensuing erosion that has almost completely destroyed the original lateritic surface replacing it by a number of lower surface silcrete deposits particularly where there is some evidence of former restriction of drainage. It is noteworthy that Corbett (1978) remarks on the resistant quartzite ridges which surround the Grahamstown pediplain in the west and suggests that drainage off these quartzite ridges might be an important factor in forming the well developed silcrete capping common to this and other mature pediplains of the Post African cycle in the S.E. Cape interior.

With regard to the effects of silcrete in subsequent slope from evolution, Ollier and Tuddenham (1962) have indicated that the hard band acts as a datum for slope development by controlling scarp (breakaway) retreat. All outlying hills have a characteristic form so long as they retain a duricrust capping, i.e. flat-topped mesas with concave slopes as described by Moss (1968) for lateritic crusts. Slopes are envisaged as being rapidly reduced once the silcrete is eventually removed owing to the presence of a soft underlying clayey formation. The silcrete capping overlying the characteristic undercut slopes breaks up into large blocks and falls to produce steep scree slopes (18-25°) (Driscoll, 1964). The debris leads to a pavement of fractured, abraded and polished silcrete blocks, boulders and pebbles on the pediment below the residual surface effectively protecting the underlying finer fractions. For example, the 'gibber plains' of arid and semi-arid Australia consist of silcrete fragments, up to 0,6 metres in diameter, produced by the destruction of silcrete capped mesas to give stoney desert tableland soils (Aitchison and Grant, 1967). Slope movement effects often cause a redistribution of the surface stoney pavement into distinctive sub-parallel linear patterns readily observed from the air.

Review of theories on silcrete formation. Experimental evidence supported by studies in France and Saharan Africa led Millot (1970) to conclude that silicification is controlled essentially by two interdependent factors :

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- the nature of the circulating solutions
- the nature of the material replaced.

The variety of silicifications appear to be interpretable in terms of the growth of crystals. If the host material is a carbonate, calcareous or dolomitic, chalcedony develops preferentially and attapulgite or sepiolite (fibrous Mg-clay minerals) are the common, neoformed, associated clay minerals. If the material is a sand or clean sandstone, quartz develops except if the cement is calcareous giving rise again to chalcedony. Opal is characteristic of silceous impregnations in clayey material.

Several theories have been proposed in explanation of the source of the silica for the cementation that has produced silcrete. From a genetic aspect silcretes show the following main features :

- a complementary zonal distribution to laterite
- a high clastic component including abraded silcrete
- occurrence of evaporite minerals in the sub-crustal profile
- an association with geomorphically related fossil and existing drainage patterns.

King (1962) hypothesises that the duricrusts (including silcrete) occurring on ancient planation surfaces of regional extent in Australia are residual accumulations. Short distance translocation has been proposed and the following quotation from King is an example of the suggestion for the source, concentration and precipitation of silica : "The accepted mode of origin for the duricrust is that the constituents were leached from the bedrock by groundwater, were carried upwards to the surface by capillarity and have been deposited in and above the soil as water evaporated".

Frankel and Kent (1937) suggest as an alternative to evaporation that silica, "derived by quiescent leaching of the underlying rocks," precipitated in upper soil layers after capillary rise because of atmospherically derived sodium chloride which aided the coagulation of "colloidal solutions of silica".

Goudie (1973) makes reference to the concentration of silica by primitive accumulator plants and aeolian dust. Hutton et al. (1972) have suggested that the weathering of some minerals in areas of strong leaching and flushing such as the scarp foot zone may result in the concentration of more stable minerals such a silica. A mechanism apparently envisaged by Corbett (1978) for the Grahamstown silcretes.

Long distance translocation has been proposed by Stephens (1971) who concluded that silcrete is an absolute accumulation introduced by the lateral movement of discharge from groundwater in areas of desilication and deposited by precipitation and crystallization induced by evapotranspiration. That laterite and silcrete are coeval and cogenetic has been questioned by Smale (1973) who emphasizes the need for a much more arid climate to generate silcrete.

The prevailing view appears to recognise considerable lithological and geomorphic control, i.e. flat areas and sluggish drainage. The configuration of silicrete surfaces suggests a sequence of flood plain and lacustrine conditions during deposition. These features would indicate that silcretes are slightly younger than laterites and an origin by 'absolute accumulation' is widely favoured.

3.3 CALCRETE

3.3.1 Generalities

Terminology. A number of terms for calcrete and differing usages of the same terms have developed over the past few years. The widely used terms caliche (American terminology) and kankar (Australian and Indian terminology) are normally regarded as synonomous with calcrete (South African terminology). However, Goudie (1973) and Carlisle (1978) indicate preference for the retention of calcrete as a term of general utility since it has few local connotations and it has so far been less misused and less subject to confusion than the other above-mentioned terms. Calcretes may be defined as mobile heterogenous mixtures of host material and an authigenic cementing phase composed predominantly of calcium or calcium-magnesium carbonate (Netterburg, 1978). Authigenic means deposition from solution in place after the host sediment has been deposited. Geochemistry of calcium and magnesium. Ca and Mg are two of the major, strongly lithophile, cationic constituents of the earth's crust. They are, however, very irregularly distributed in the lithosphere and hydrosphere. As shown by Table 7, Mg, which is the scarcest of the 8 elements of the upper lithosphere, is well represented only in limestones and to a lesser extent in igneous rocks where it is concentrated in carbonate and femic minerals respectively. Ca is nearly twice as abundant by weight as is Mg in igneous rocks occurring in both femic constituents and plagioclase feldspar and is very abundant in limestone.

Table 7. Average Ca and Mg contents in igneous and sedimentary rocks

		Igneous rocks	Sandstones, etc.	Shales, etc.	Limestones
8	MgO	3,49	1,16	2,44	7,89
\$	CaO	5,08	5,50	3,11	42,57

(Data from : Clarke, 1924)

Ca and Mg are, in addition, invariably constituents of all plants.

Ca- and Mg-minerals are rather susceptible to decomposition by weathering and form soluble simple or hydrated cations in the full range of pH of groundwater solutions (Fig. 5 : ionic potention below 3). The behaviour of Ca and Mg under supergene conditions is illustrated by the summary of their contents in the accompanying tabulation :

Material	% MgO	% CaO
Igneous rocks	3.49	5,08
Salts of lakes and river water	5,65	28,55
Salts of seawater	6,12	1,61
Argillaceous sediments	2,44	3,11

(Data calculated from : Rankama & Sahama, 1952)

The cycle of Mg differs rather pronouncedly from that of Ca. Mg is nearly as abundant in riverwater as in seawater whereas Ca exceeds all other cations in solution in riverwater but in the sea by far the greatest part is removed from solution by precipitation in the form of CaCO₂. The origin of carbonate horizons in soils and surface deposits involves carbonate-bicarbonate equilibria as discussed in section 2.2.2. If CaCO₃ (calcite) is dissolved in pure, CO₂ free, water at 25°C the solubility is only 12-14 ppm. Aragonite at 15 ppm is slightly more soluble and MgCO₃ (Magnesite) at 106 ppm (at 20°C) even more so. The solubility of CaCO₃ is governed by five essentially independent variables :

- pCO₂ During dessication and a loss of CO₂, the solubility is decreased due to a reduction in the amount of soluble bicarbonate.
- T^OC The effect of increasing temperature is to decrease CaCO₃ solubility. It is practically independent of pCO₂.
- pH The effect of pH is very marked. At pH<7, the solubility increases 100 fold for every decrease of 1 pH unit. Above pH7 the effect diminishes and a solubility of ± 10 ppm is reached at pH 10. In practice, however, addition of CO₂ decreases the pH causing increased solubility.
- Ph Hydrostatic pressure under normal conditions increases the solubility of gaseous CO₂ thereby increasing carbonate solubility.
- Salts The presence of salts such as CaSO₄, Na₂CO₃, MgCO₃, (Ca,Mg)CO₃, etc., yield a common iron (to CaCO₃) in solution thereby decreasing the solubility of CaCO₃.

(Netterburg, 1969).

The authigenic cement in calcretes may come from several sources : Ca^{2+} released by weathering could combine with HCO_3^- and deposit CaCO₃ within the soil profile. In many places an external source of Ca⁺⁺ seems likely because the high concentrations indicate far too much CaCO₃ for the amount of weathering of the assumed parent material (Birkeland, 1974), plus the fact that many thick accumulations are elongated along drainage patterns, fossil or present (Carlisle, 1978). The CO₂ is predominantly of oganic or inorganic origin within the soil.

3.3.2 Analytical Study

Physical and chemical characters. Nearly all of the comprehensive classifications of calcrete are based on the level of evolution or degree of induration of calcrete (see Goudie, 1973). A useful sequential model proposed by Netterburg (1978) envisages six stages of calcrete development each possessing a significantly different range of physical properties (Fig. 33).



(From : Netterburg, 1978)

<u>Calcified soil</u> refers to soft friable carbonated soil with an inherited structure and little or no nodular development. <u>Powder</u> <u>calcrete</u> is also soft, friable and free from nodular development but, unlike the former, the silt fraction is high with very little trace of sand size particles. <u>Nodular calcrete</u> consists of distinct, hard concretions some of which attain sizes of more than 7 cm in diameter. Coalescence of the nodules gives rise to <u>honeycomb calcrete</u> which consists of soil-filled voids between rounded masses of calcrete. The peak of calcrete development wherein all the nodules have become cemented together is represented by <u>hardpan calcrete</u>. Weathering and solutional alteration (reworking) of the hardpan causes it to break

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down to give <u>boulder calcrete</u>. Soil, in which the boulders invariably occur, is almost always non-calcareous and when covered the boulders are always rounded on their upper surface (Netterburg, 1969). Hardpan and boulder calcrete are the oldest in that they represent a mature and reworked stage but, paradoxically, they are "younger" in that they attained their stage of development more recently than say nodular calcrete (Netterburg, 1978). Normal calcrete profiles are 5-10m thick with a hardpan of up to 1,5m though on the southern edge of the Kalahari Basin, calcrete profiles attain thicknesses of 60m with an indurated crust of 10m (Goudie, 1973).

Mineralogical and chemical properties of calcrete are given by Netterburg (1969, 1978) and Goudie (1972, 1973). The average composition of 300 calcretes worldwide (Goudie, 1972) is as follows :

Calcium carbonate	•	80%
Sílica	*	12%
Al-Mg-Fe oxides	:	78

The world mean value of 42,62% CaO for calcrete corresponds very closely to the Clarke value of 42,57% CaO for limestone. A figure of 50% by weight of combined Ca-Mg carbonate is used by Netterburg (1969) to distinguish calcified soil (<50%) from calcrete (>50%). This figure coincides with the lower limit set for limestones and accounts for the usage of 'surface limestone' as a term for calcrete. The low contents of MgCO, (+ 3,0%) are attributed by Goudie (1973) to the fact that Mg- is more soluble than Ca- carbonate and therefore susceptible to leaching from the profiles. In addition, Mg++ may have been selectively removed from the soil pore moisture by cation exchange on clay minerals, particularly where montmorillonite is present. In special cases, however, the MgCO2 and CaSO4 contents may rise quite high and as such are referred to as 'dolocrete' and 'gypcrete' respectively. Values of up to 40% MgCO₃ are recorded from the Etosha Pan dolocretes in S.W.A. (Goudie, 1973) and an interesting occurrence of gypcrete with up to 90% CaSO4 has been discribed by Martin (1963) and Carlisle (1978) from the Namib Plain of coastal S.W.A.

The host phase of calcrete comprises mainly allogenic quartz, feldspar and clay minerals though kernels or inclusions of rock fragments of any type, including calcrete, may be present. Smectites, attapulgite[#], micaceous minerals and sepiolite (in that order) are the commonest clay minerals in calcretes. Glauconite and analcime are responsible for the green colour of much of the Kalahari Beds. The authigenic phase usually consists of various generations of calcite, occasionally dolomite and rarely aragonite, gypsum and barite; amorphous silica is common. A reasonable amount of chemical data is available on major oxide contents (SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO) of calcrete but information is very scarce on minor elements (Na, K, Ti, P, Mn, S, Fe) and, according to Netterburg (1969), the field of trace elements remains virtually untouched (Table 8).

Variation in composition during calcrete development (Table 8). Analyses are unfortunately not available for honeycomb and boulder calcretes but the general increase of carbonate components (CaO, MgO, BaO, CO2) in relation to the non-carbonate (SiO2, total Fe, Fe₂O₃, FeO, K₂O, TiO₂ and H₂O+) components through nodular calcrete to both types of hardpans is marked (Table 7) and indicates that some form of differentiation takes place during calcrete formation. Similarly, Goudie (1973) has recorded a highly significant inverse correlation (r=-0,91) between the CaCO2 and SiO2 contents of calcrete. Netterburg (1969) has also shown that the composition of nodular calcretes varies with size fraction. For example, the plus 40-mesh fractions tend to be higher in carbonate components and lower in noncarbonate components (mainly clay mineral constituents) than the minus 40-mesh fractions. These features verify Du Toit's (1956) suggestion that clay is slectively excluded from calcrete during its formation and conforms with observations in profle, where calcrete is seen to invade the planes of weakness in the bedrock causing fragmentation of the lithology at the interface. The tensile strength of quartz is exceeded by the force of calcite crystallization and a transitional, brecciated zone commonly occurs at the base of the profile with progressive 'ingestion' of bedrock towards the surface. The process is therefore envisaged as a mechanical and chemical replacement by carbonate of the host soil grains leading to a selective elimination of the fine clay fraction and a progressive dispersal of coarse soil grains so that they eventually appear to 'float' and do not occur in point-to-point contact as they would in the host material (Brown, 1956).

*Attapulgite is a fibrous clay mineral sometimes called polygorskite.

Component	Calcified sand	Nodular calcrete	Hardpan	Tufaceous Hardpan	Limestone
SiO2	40.44	21.08	13.96	12.40	5.19
Al ₂ O ₃	2.26	4.09	1.66	1.31	0.81
Total Fe	0.60	2.43	1.89	0.63	0.54
Fe ₂ O ₃	0.44	1.22	0.69	-	-
FeO	0.14	1.30	0.49	-	-
MgO	1.76	3.13	3.59	2.10	7.90
CaO	27.90	36.43	42.85	44.25	42.61
Na ₂ O	0.44	0.48	0.89	1.20	0.05
к ₂ 0	0.17	0.50	0.21	-	0.33
TiO2	0.07	0.40	0.06	0.10	0.06
P205	nil	0.05	0.007	0.035	0.04
MnO	0.07	0.12	0.10	0.20	0.05
BaO	0.85	0.02	0.62	-	nil
so3	-	0.04	0.18	-	0.05
co2	21.33	24.00	34.89	33.35	41.58
Loss on ignition	127	31.63	38.33	40.00	2.
н_0+	2,00	2.98	2.17	2.50	0.56
н_0-	0.86	0.84	0.98	1.59	0.21
MgCO 2	3.7	6.50	7.50	4.40	14.1
CaCO3	44.1	65.10	76.50	79.00	-
Organic Mat.	1.12	0.05	0.06	0.06	-
Al ₂ 0 ₃ +Fe ₂ 0 ₃	3.01	4.97	2.29	1,53	
H ₂ 0 [±]	2.86	3.78	2.53	3.71	-
Opal. SiO		-	1.01	11.01	-

Table 8.	Chemical composition	of some South African calcrete types
	and carbonate rocks.	(From : Netterburg, 1969)

Cr	B	V	Cu	Sn	Ag
(ppm)	(ppm)	(<u>ppm</u>)	(<u>ppm</u>)	(<u>ppm</u>)	(ppm)
ni1-1000	100-1000	100-3000	30-300	nil-1000	3-30
The cement to grain ratio is thus a useful guide to relative age and a ratio of coarse (plus 40-mesh) to fine (minus 40-mesh) carbonate of more than about 2.0, or the presence of kaolinite in the fines, appears to indicate a fossil calcrete (Netterburg, 1969). Immature calcretes have a high content of residual quartz whereas ancient calcretes may contain appreciable introduced silica.

An important property of calcretes, from the stratigraphic point of view, is that they exhibit facies changes, i.e. nodular calcretes may grade laterally into scattered nodules or a calcareous soil or it may coalesce into honeycomb calcrete and ultimately hardpan. This is considered to be due to the dominating influence of some local factor over the more important environmental factor controlling calcrete formation (Netterburg, 1978).

Types of calcrete deposits. These types, like laterite, are specified by distinctive morphological characteristics. Most calcretes occupy low angle pediments, alluvial plains, river terraces and valleys together with major basins of terrestrial aggradation. Contrary to the usage of Hunt (1972), lakeshore tufa, spring tufa, travertine or sinter are specifically excluded from calcrete sensuo-stricto.

(1) <u>Surficial sheet calcrete</u>. These are relative accumulations of Ca- or Ca-Mg-carbonate layers resulting from weathering of igneous, metamorphic or sedimentary rocks. In the U.S.A. the word 'caliche' is used most commonly in place of sheet calcrete whereas in W. Australia 'kunkar' is the term applied (Carlisle, 1978). It is essentially synonomous with a well developed calcic horizon, Cca or K in the terminology of soil scientists, and analagous to Netterburg's (1969) 'pedogenic calcrete'. All six stages of calcrete development from calcified soil through to boulder calcrete may be present within any level of the soil profile. Hardpan ("petrocalcic horizon") may vary considerably in structure and may occur as a solid sheet or caprock over which has been deposited laminar calcrete or it may be breciated,

fissured or even conglomeratic (Netterburg, 1969). These features are considered to indicate several phases of calcification, solution, recementation and expansion under the influence of a perched water table that has formed as a consequence of the continous and cemented nature and low infiltration capacity of hardpan calcrete. In one example from southern Africa, Netterburg (1978) recognises at least 12 ages of authigenic cement (Fig. 34).



(From : Netterburg, 1978)

Multiple hardpans are, like silcrete, the result of an aggrading profile, each hardpan representing an unconformity or diastem.

Surficial sheet calcrete is most commonly thought to develop in arid or semi-arid climatic regions such as the western part of southern Africa, southwestern Australia and the High Plains of the U.S.A. In southern Africa, surficial sheet calcrete is widespread occurring extensively in parts of the Karoo, in the N.W. Cape region, on the Namib margins and around Etosha Pan, near Mafeking, in the Springbok Flats and in the Limpopo Mobile Belt near Messina (Fig. 35). The relationship between sheet calcrete distribution and climate in southern Africa is close. Netterburg (1969) has demonstrated that the eastern (wet) boundary of calcrete (and the dry western boundary of laterite) correlates well with the 500mm annual isohyet (Fig. 35) except for individual deposits at Lichtenburg and north of Bloemfontein which may owe their origin to localised, shallow water tables. He suggests that at Lichtenburg the deposits are due to Ca-bicarbonate charged groundwater draining from the Transvaal dolomite into weathered Dwyka shales. Similarly, in the winter rainfall region of Western



(From : Carlisle, 1978)

Australia, surficial sheet calcrete is confined to an area receiving between 250mm and 500m rainfall per annum. An aridic to xeric soil moisture regime is characteristic (Carlisle, 1978). Goudie (1973) presents numerous plots of climatic indices against calcrete distribution worldwide and the 1250mm contour of the average free surface evaporation is also an important boundary. Goudie concludes that on a macro-scale, climate is the major factor controlling calcrete distribution. It must be appreciated, however, that the above parameters refer to present day climate and calcretes, especially hardpan calcrete, commonly relate more to paleoclimates as far back as the Carboniferous in certain cases (Netterburg, 1978).

An interesting example of the action of climate is the occurrence of calcrete in the Namib Desert of S.W.A. which have been partly or wholly converted to gypsum. The crusts of gypcrete lie up to 60 km inland within the fog belt of the west coast and are only up to 1m thick in places. Martin (1963) ascribes their origin to reaction between pre-existing Tertiary and Pleistocene calcretes and H2S blown inland from azoic areas off the coast and precipitated with dew or mist. Carlisle (1978) records sulphur isotope studies (δ^{34} S) which do not confirm Martin's hypothesis and suggests that mist transport of marine salts (sulphates) followed by illuviation of both halite and gypsum is more plausible. This particular variety of pedogenetic gypcrete (or calcrete) developing on the surface of older calcrete is referred to as reconstituted gypcrete (or calcrete) by Carlisle. Pedogenic calcrete may also develop by in situ dissolution and reprecipitation of CaCO, on outcropping limestone such as the calcrete described by Netterburg (1969) on the limestones and dolomites of the Otavi Mountainland in northern S.W.A. The local effects of topography, altitude and vegetation on climate are well exemplified in this region whereby calcrete occurs on the northern slopes in preference to the southern slopes of the Otavi Mountainland. The source of authigenic cement in surficial pedogenic calcrete is thus deemed to be from the soil itself, from organic debris or from airborne material including dust and loess. Gardner (1972) ascribes a caliche, 2,6m thick in Nevada, U.S.A., to aeolian aggradation and suggests that 25% of the Ca^{++} and HCO_3^{-} have been derived from rainwater and the remainder from dust.

Two mechanisms for pedogenic carbonate accumulation are proposed :

- simple translocation of CO₃ from the upper soil horizons and its deposition in a lower horizon at about the limit of meteoric infiltration (per descensum)
- capillary rise of infiltrated meteoric water under the influence of evaporation, CO₂ loss, and precipitation of CaCO₃ above the maximum depth of penetration (per ascensum).

(Netterburg, 1969).

Netterburg (1969) in his study of southern Africa calcretes conclude that most are of the surficial sheet type, with hardpans averaging 1.5m in thickness, and owe their origin to pedogenesis. Van der Merwe (1962) accepts both mechanisms and invokes the former for the origin of normal illuviated carbonate horizons in soils and uses the second to explain the occurrence of calcrete under noncalcareous Kalahari sand. Carlisle (1978) considers that only under favourable circumstances, i.e., on very flat terrain where Cabicarbonate rich groundwater is fairly close to surface (<3m), can capillarity coupled with evapotranspiration cause precipitation of a large amount of lime at shallow depths, though the rate may be slow. Pure evaporation is thus thought to be of minor importance in the role of calcrete formation and CO, loss and evapotranspiration induced by dessication are considered to play the major role (Netterburg, 1969). Carbonate precipitation requires long periods of soil moisture deficiency between short rainy seasons and the development of laminated hardpan takes place only if the groundsurface is neither rapidly eroded nor alluviated for a substantial period of time. Rates of calcrete formation in the range 50-500mm/1000 years are comparable with erosion rates (Netterburg, 1978). Calcic and K-horizons may require 1000-1 000 000 years to reach a steady state and are slowly adjusting, relatively persistent features while petrocalcic (hardpan) horizons are very persistent (Birkeland, 1974). Therefore, calcretes which have developed close to an aggradational surface are likely to be younger than that surface especially if they follow its contours and appear to be pedogenic in origin. On the other hand, calcretes which crop out on an erosional landsurface are fossil and probably largely older than that surface. A case in point is the Pliocene age

attributed by Mabbut (1955, see Corbett, 1978) to the "African" erosion surface in Bushmanland, N.W. Cape, following identification of the early Pliocene 'horse' in calcrete. Netterburg (1978) points out that this must not be taken too literally though it does provide an order-of-magnitude estimate. Calcretes tend also to increase both in thickness and level of evolution with the apparent age of the landsurface with which they are associated. In this regard, Netterburg (1978) remarks on the good correlation between his calcrete map (Fig. 35) and Partridge's (1975) landsurface map of southern Africa (see also Partridge in Corbett, 1978). Most calcretes range in age from Upper Tertiary to Recent but most of the world's thick and massive calcretes, such as occur on the "African" erosion surface of the Urinanib Plateau, S.W.A. and Bushmanland, N.W. Cape, appear to be of Tertiary age. Netterburg (1978) refers to well-developed honeycomb calcrete on small remnants of the Post African dicyclic (Oligocene and Miocene) erosional surface between Luderitz and Aus in S.W.A., whereas calcareous soils containing only scattered nodules are the usual forms of the Recent aggradational surface in Okavangoland and in Bushmanland in S.W.A.

(2) <u>Valley calcrete</u>. These calcretes comprise thick carbonate cemented surface deposits or soils in bodies elongated along paleodrainages and are analagous to Netterburg's (1969) 'groundwater calcrete' which he used to describe calcified Tertiary sands and gravels on terraces of the Vaal and other rivers in southern Africa. Valley calcretes are particularly well represented in Bushmanland and the Northern Cape, in the Namib Plain of coastal S.W.A. and in the Kalahari of Botswana. Typically, valley gravels are calcified throughout and massive, retaining only primary sedimentary structures. Any pedogenic profile or specific hardpan, honeycomb or laminated horizons such as may be found in pedogenic sheet calcrete are distinctly lacking and Netterburg (1969) believes that valley calcrete does not develop beyond the second stage of nodular calcrete.

Netterburg (1978) points out that the age of a terrace deposit will only provide a maximum age for any calcrete in it, so by calculating the rates at which carbonate can be precipitated by evapotranspiration, he has arrived at a time period of 70 000-110 000 years for calcification of some of the terrace deposits (±7m thick) of the Vaal River. From archaeological and other evidence Netterburg (1969b) concluded that the '60m Gravels' and their calcification are of Pliocene age and the calcification of the 'Current Gravels' is of middle Pleistocene age confirming the above calculated time period. The older river terraces tend to be more heavily calcified than the younger ones though reconstituted calcrete of the same age could occur on all terraces as in the Namib Plain.

Relatively recent detailed studies of the Namib valley calcretes have been documented following the discovery of numerous carnotite occurrences in the region (Von Backstrom and Jacob, 1979; Carlisle, 1978; Hambleton-Jomes, 1978). The calcrete hosts are crudely lenticular masses of alluvium and soil cemented by Ca or Ca-Mg carbonate which are up to tens of metres thick, several hundred to a few kilometres wide and tens of kilometres in length and occupy the axial portions of palaeostreams. The valley calcretes are characterised by a relatively clean and pure authigenic cement composed dominantly of sparry calcite, with neither dolomite nor opal, and an abundance of coarse detrital, waterworm fragments resembling concrete in texture. Reasons given by Carlisle (1978) for the coarseness of the fluvial detritus are the rapid change in relief from 2000m in the Khomas Hockland above the Great Western Escarpment to the low lying broad coastal platform of the central Namib Desert and the relatively limited degree of chemical weathering. Mabbut (1952) presents evidence for Tertiary calcification of the "Main Terrace" gravels on the Ugab River and Netterburg (1969b) also assigns a Pliocene age to calcification of the gravels and a probable correlation with the Kalahari Limestone deposits of the Kalk Plateau. The previously deep weathered and eroded "African" surface was apparently formed by earliest Tertiary times (Mabbut, 1952). Tertiary climates ranging from periods of rainfall greater than today became more arid presumably as a result of the cold currents off the west coast of Africa as the Atlantic opened up (Netterburg, 1978). Great volumes of sediment accumulated on the "African" surface as a result and thicknesses of >100m of calcified alluvium have been reported from paleoriver channels midway between the Escarpment and the coast (Carlisle, 1978). Evidence suggests that the thick alluvial sediments were calcified by the end of the Tertiary because pronounced pluviation in the Pleistocene, corresponding with interglacial periods in the Northern Hemisphere, resulted in intense rejuvenation of major rivers and deep inclusion of the calcrete. Various pluvial periods

during the Pleistocene are considered to be responsible for the aggrading profiles during which lesser terraces formed within incised valleys and several of these can be approximately dated as Middle and Upper Pleistocene cultural units (Netterburg, 1969b). As arid climates returned new thin calcretes, and within the fog belt, gypcretes have formed. They are purely surficial and pedogenic in origin overlying the older calcreted gravels unconformably.

Very similar compositional and morphological features as discussed above for valley calcrete in southern Africa have been described for uraniferous occurrences in W.Australia though some significant differences do exist (Carlisle, 1978). Unlike the palaeodrainages of the Namib, the valley calcretes are developed entirely within the "New Plateau" (corresponding to the "post-African" cycle of erosion in southern Africa) and occupy the uppermost parts of valley fills which trend mainly S.E. to the Nullabor Plain. Present day streams are short ephemeral rivulets on the shallow-sloping valley flanks disappearing on the alluvial plains before reaching the valley floor. Thickest and widest calcrete bodies occur where bedrock morphology or some other feature has caused a decrease in slope gradient and where the groundwater table approaches surface. Shrinkage cracks and open solution cavities are common and the calcrete is a good aquifer unlike the Namib valley calcrete. Carlisle (1978) presents evidence for a late-Pleistocene to Recent age for the valley calcrete. This contrasts with the Pliocene age of the Namib valley calcretes. Since they occupy a region of internal drainage, deltaic calcrete and lacustrine calcrete are distinguished in valley regions where the palaeodrainages enter salt lakes and clay pans (playas), i.e. where subsurface water has encountered hypersaline pore waters and lacustrine clays. Most W. Australian valley, deltaic and lacustrine calcretes are, as a consequence, weakly to strongly dolomitic and opaline silica is a fairly common accessory, as is sepiolite (a hydrated Mg rich clay mineral). Carlisle (1978) notes that hardpan valley calcrete does occur in W.Australia and describes dense, rock-like, porcellaneous varieties from the uraniferous occurrence at Yeelirrie. He suggests the reason that groundwater calcrete in the Namib Valley does not develop beyond the nodular stage may be due to it retaining some of its permeability permitting continued escape of CO2 and H2O vap.

It is noteworthy that in W. Australia pedogenic and valley calcrete are mutually exclusive (Carlisle, 1978). Valley calcrete and its associated groundwater types are confined to particularly arid areas such as the interior of W. Australia, a region characterised by highly variable and episodic summer rains (170-250mm) and a strongly aridic soil moisture regime. The wet and dry boundary (250mm) marking the distribution between groundwater and pedogenic calcrete respectively is referred to as the Menzies Line (Carlisle, 1978) or Soufoulis' Line (Goudie, 1973). Besides marking the boundary between distinctive climatic and soil moisture regimes, Carlisle (1978) suggests that other reasons for the existence of the Menzies Line may be : (1) the large and continuing supply to the southerly 'pedogenic' region of calcareous dust from exposed limestones and calcareous soils on and around the Nullabor Plain, or (2) the known presence of Cretaceous to Eocene marine limestones deposited on a submerged 'Old Plateau' surface almost as far north as Kalgoorlie.

Similar morphological relations have been described by Goudie (1973) and Netterburg (1969) from the Kalahari where all types of calcrete are present (Fig.35). TheKalahari Plains are believed to be constructional surfaces developed by aggrading fluvial agencies operating from the upwarped margins within the interior of the southern African subcontinent following the breakup of Gondwanaland in late-Jurassic/early-Cretaceous time (Corbett, 1978). The Kalahari sediments, which exceed 50m in thickness, consist of clays, marls, gravels and limestone overlain by ubiquitous aeolian sand (Boocock and van Straten, 1962). Kalahari Limestone (calcrete) is widespread, and owes its origin to the drying up of the Kalahari basin largely brought about by the capture of streams feeding it during crustal movements at the close of the Tertiary (Pliocene) (Corbett, 1978). A change from a wetter to drier climate also seems to be indicated and was possibly brought about by the appearance of the cold Benquella current off the west coast of Namaqualand and SWA around this time (Netterburg, 1969). Thus the position of the Kalahari calcrete may mark the position of the 500mm isohyet in Pliocene and pre-Pliocene times. In eastern Botswana, Goudie (1973) remarks on the fact that palaeodrainage lines such as the Serurume Valley, on the "African" surface, have marked calcrete development whilst the interfluves, underlain by iron-rich shale, have a strong development of lateritic hardpan. A pan or lacustrine

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origin is indicated by the presence of fossiliferous (shelly and diatomaceous) calcrete along drainage courses and around old lake shorelines such as the Makarikari depression (Goudie, 1973). In N.W. Botswana between the Okavango swamps and Angolan border, calcrete hosting fresh water gastropods have been described from the parallel depressions between dunes but are absent from the dunes themselves (Netterburg, 1969, 1978).

All of these characteristics as well as the terrain, the size of the catchment areas and their occurrence along the axes and gathering points of groundwater drainages suggest that valley calcrete and its associated types (deltaic and lacustrine) have formed through nonpedogenic processes by laterally flowing groundwater (Netterburg, 1969; Carlisle, 1978), i.e. they mark previous water levels.

The mechanism of 'groundwater calcrete' formation postulated by Netterburg (1969) to explain the calcification of thick alluvial sands and gravels in the Vaal and other southern African rivers proposes a fluctuating water table which progressively declines through the entire section during which carbonate is dissolved and reprecipitated in groundwaters of varying pCO2. This mechanism is at variance with that proposed by Carlisle (1978) who envisages periods of strong evapotranspiration over a moderately deep water table during which pore spaces above the capillary fringe become filled with soil air. The capillary fringe marks the zone through which groundwater can rise above the water table under the influence of surface tension or cohesive forces between water and soil particles. This tendency for materials to retain water is known as 'water potential', moisture tension' or 'soil suction' and exerts a controlling influence on carbonate deposition because it determines the position at which open pore spaces will appear in the soil and the tendency with which $H_2^0_{vap}$ or C_2^0 will escape into them. In highly saline soils and fluvial sediments, e.g. W. Australia and the Namib Desert, pCO, and pH2O are likely to show a progressive decrease upward in the profile during intense dessication throughout most of the year. Therefore, Carlisle (1978) envisages loss of CO, from Ca-bicarbonate charged groundwater into the soil air in the upper parts of the capillary fringe and consequent precipitation of CaCO, down to appreciable depths, though the rate may be slow. Gravelly deposits are more quickly calcified than non-gravelly deposits, other things being equal.

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In W. Australia where carbonate charged groundwater is shallow enough in alluviated valleys of low relief, loss of CO₂ during periods of strong dessication (evapotranspiration) from the capillary fringe to a level within the soil moisture zone could be expected to cause carbonate precipitation in the latter. A noteworthy feature of groundwater calcrete that are unrelated to a soil profile is pointed out by Carlisle (1978) in the Namib occurrences. The carbonate is often coarsely crystalline, clean and clear, and lacks the illuvial clay so typical of those in W. Australia.

A genetic and morphological classification of calcretes, dolocrete and gypcretes has been developed by Carlisle (1978) with emphasis on the source of the authigenic cement (Table 8). Although developed specifically for the determination of uranium favourability, since carnotite mineralisation occurs only in economic amounts in groundwater calcrete, it may be successfully applied to problems of base-metal prospecting in areas covered by calcrete. The fundamental genetic difference between the two calcrete types is that pedogenic calcretes are the products of vertical redistribution within the soil, i.e., a relative accumulation, whereas the non-pedogenic calcretes are products of lateral transport and therefore an absolute accumulation.

A GENETIC AND MORPHOLOGICAL CLASSIFICATION OF CALCRETES (DOLOCRETES AND GYPCRETES) WITH EMPHASIS ON THE SOURCES OF AUTHIGENIC CEMENT AND THEIR URANIUM FAVORABILITY

TABLE 8

CATEGORY	PROCESS	URANIUN FAVORABILITY ASSUMTNG A SOURCE TERRANE
I, PEDOGENIC CALCRETES, CALICHES, AND CARBONATE HORIZONS Caliches, Surficial-sheet Calcretes, Kunkars (Dolocretes, Gypcretes)	The authigenic cement has been concentrated vertically within a soil profile (i.e., by "relative" accumulation).	
A. Illuvial Calcrete, Caliche, or Kunkar	Precipitation of cement within the soil moisture zone after downward transport and evapotranspiration. Equivalent to a well developed calcic horizon or petrocalcic horizon in U.S. soils terminology.	Very low to negligible. Trace amounts of uranium may occur in lower parts of carbonate horizons in contact with clay or other materials.
B. In Situ Calcrete	A less common variety of pedogenic calcrete. The cement is derived from subjacent rock or sediment by weathering in place.	Low unless developed on a rich substrate.
C. Capillary Rise Pedogenic Calcrete	A probably rare variety of pedogenic čalcrete (cf. II.A.1.). The cement is derived by capillary rise from stagmant ground- water sufficiently shallow over a wide area that the capillary fringe intersects the soil moisture zone, but without signifi- cant lateral transport.	Same -
II. NONPEDOGENIC CALCRETES	The authigenic cement has been introduced into the host soil or sediment by non-soil-forming processes (i.e., by "absolute" accumulation).	
A. Groundwater Calcretes	Concentration of authigenic cement externally derived from laterally moving groundwater; fluvial contributions may be appreciable.	
1. VALLEY CALCRETE a. Western Australian Variety	Precipitation of cement within the soil moisture zone and/or capillary fringe by capillary rise from a shallow groundwater table influenced by bedrock morphology.	High in areas of constriction and upwelling of groundwater. Destroyed by dissection and leaching.
b. Namib Desert Variety	Precipitation of cement within the capillary fringe or gravitational-water zone from a changing water table.	Same
2. DELTAIC CALCRETE	Precipitation as in Valley Calcrete, 1.a. above, but with lacustrine clays and hypersaline pore water causing ground- water to slow and approach the surface. The downdrainage equivalent of Valley Calcrete.	Low in mature, elevated calcrete deltas. High in recent calcrete deltas with zones of upwelling.
3. GROUNDWATER LACUSTRINE CALCRETE	Precipitation by a variety of processes. May be related to deltaic calcretes. Not to be confused with normal lacustrine limestones, nor with lake shore tufa or "beachrock" formed by surf action in hypersaline lakes.	Same
4. OTHER GROUNDWATER CALCRETE	e.g., "Cienega" calcrete from groundwater seeps.	Unknown
B. Gravitational Water Calcrete	Deposition of authigenic cement from waters descending through the intermediate (gravitational water) vadose zone with warying amounts of lateral transport.	Low in patchy carbonate derived from descending waters. Moderate in carbonate fanglomerate depending upon amount of lateral concentration. May facilitate reconcentration of carnotite. Moderate in weathered bedrock.
C. Fluvial Calcretes I. Gully Bed Cementation 2. Case Hardening 3. Fluvial Laminar Crusts	Concentration of authigenic coment from sheat-flood or streams. (See text; Lattman, 1975; Goudie, 1973.)	Very low to negligible
III. RECONSTITUTED AND DETRITAL CALCRETES		
A. Brecciated and Recemented Calcrete	Mainly a surficial process associated with weathering, erosion, or solution and collapse of pre-existing calcrete and commonly producing "rockhouse structure."	Negligible in itself but may occur above mineralized nonpedogenic calcrete.
B. Loose Detrital Calcrete	Boulder calcrete, gibbers (Australia), calcrete dobris.	Negligible

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4. MINERAL EXPLORATION ON TROPICAL AND SUBTROPICAL LANDSURFACES

4.1 SURFACE EXPRESSION OF OREBODIES AND DURICRUSTS

In order to take full advantage of the surface expression of orebodies in mineral exploration it is necessary to understand their genesis and field relations. Sulphide weathering and gossan formation have been well documented (Blanchard, 1968; Blain and Andrew, 1977; Andrew, 1978) and only the salient features related to the foregoing account are noted here.

Sulphide minerals are unstable in the near surface environment in the presence of water-dissolved oxygen. The decreasing oxidation potential of groundwater with depth and a corresponding increase in pH are the major factors controlling the corrosive decomposition of sulphides to yield gossan at or near the water table. Under the influence of electro-chemical processes, sulphide minerals are oxidised to hydrous iron oxides <u>+</u> silica assemblages. Carbonates (malachite, azurite, cerrusite, smithsonite, etc.) are the predominant oxides of the ore minerals in gossans followed by silicates (e.g. chrysocolla). The more soluble sulphates, phosphates and halides are generally preserved only in arid climates. Of the geological factors which influence the mechanisms of sulphide oxidation, the depth and stability of the water table are of prime importance. Other factors include : climate, the physicochemical nature of ore and host rock and geomorphology.

The mineralogical assemblages of gossan are in stable equilibrium with their individual surface environments and their refractory nature is reflected in many cases by their surface expression in the form of resistant spiry ridges e.g. Namib Pb deposit, S.W.A. However, water table movements produce unstable assemblages, and associated deep penetrative weathering and/or the development of thick duricrust profiles can effectively destroy the classic gossan ridge form leaving residual boulders or scattered gossan rubble at or near surface. Consequently, exposure of an ancient weathering surface commonly fails to reveal clear surface expression of gossans on that surface. Added field complications occur in cases of ancient glaciated surfaces where transported detrital gossan fragments resemble ferricrete. The Bushmanland Plateau, N.W. Cape, is approximately at this stage of development where Karoo cover has been stripped off by erosion to reveal the glaciated surface of the Namaqua metamorphic complex - an important base metal province. Proximal-distal relations are reflected in the mineralogical, textural and geochemical features of transported gossan. Proximal gossans range from a closely packed accretionary crust (transported limonite) whereas distal gossans comprise rock and gossan clasts in an exotic limonite matrix precipitated from solutions which have been leached from the primary gossan. The geochemical contrast of transported gossan decreases away from the source with progressive dilution by extraneous limonite and/or silica.

Mineral exploration is really a search for and evaluation of features which may indicate mineral deposits (Leuder, 1959). Many of these features, e.g. structural controls, ferruginous oxidation zones, etc., which could have a bearing on the localisation of mineral deposits can be seen on aerial photographs in areas of good outcrop. The techniques of the photogeologist, using both black and white (panchromatic) as well as coloured photos has become a well developed art (Avery, 1977). However, the main points to be observed in a photogeological study of a particular lithology are relatively few and simple. These are considered as follows :

 the photographic tone ('greyness') or colour of the lithology in contrast to that of the surrounding areas,

 the resistance to erosion of the lithology relative to that of adjacent areas,

3) the topographic form of the whole lithological unit,

4) the boundaries of the individual outcrops,

5) the joint and fault patterns,

6) the drainage pattern and vegetation cover,

7) the bedding, foliation or gneissossity and thus the fold patterns,

8) the regional geological environment.

From such a list of salient features most geologists would be able to deduce the broad lithology (igneous, metamorphic, sedimentary) and hopefully, the surface expression of possible orebodies, even if inexperienced in photogeological interpretation. Probably the greatest advantage of colour photography lies in its ability to establish clearly, evidence of primary and supergene mineralisation at surface. Gossan, ferruginous oxidation zones, alteration haloes, etc., are all features in which colour is the primary recognition aspect. The obvious disadvantages of colour over the more normal panchromatic method appears to be its added cost and scale limitation. Optimum scales for colour photography are 1:10 000 - 1:30 000. Above 1:30 000, the flying height is such that colour definition is lost. Large scale panchromatic and colour photography flown at low altitudes or enlarged from existing photographs are often useful for detailed geological mapping and as an aid to geochemical (drainage and soil surveys) and geophysical (interpretation of surficial features) prospecting and to mineral development.

Relatively new developments in the field of photogeology include thermal infra-red imagery which does not record differences in light and shade but rather differences in temperature within an area being scanned. Perhaps the most revealing new development, for a broad overview, are the pictures produced by scanning the earth's surface from satellites (ERTS Imagery) using radiation sensors of various types (Avery, 1977). ERTS imagery may possibly provide new insights into the tectonic causes for the regional distribution of mineral deposits and hence be useful as a guide (Grootenboer et al., 1975) but for more detailed target selection it is difficult to understand how recording temperature differences or using photographs at such a scale can be of any practical application. Perhaps bodies of oxidising sulphide in some desert or forested region might be located because their heat of oxidation makes them differ thermally from the surrounding rock, but if exposed these are just as likely to be located from panchromatic or colour photography at lower cost. In areas of poor outcrop the applicability of infra-red thermal imagery to lithological mapping is dubious since the natural emissivity of soil cover, moisture variation and vegetation often exceed that of varying rock type (Kyle, 1974). In this environment panchromatic photos are best and where gossans are poorly exposed or expressed as forms other than resistant ironstones, geobotanical anomalies often mappable on airphotos, may be characteristic (Cole and le Roex, 1978). Thus, the use of infra-red or ERTS imagery is restricted and constitutes only a preliminary guide to the reconnaissance and regional mapping of large areas; more particularly in the interpretation of large scale structures which could have a bearing on the localisation of mineral deposits.

Owing to their sheer aerial extent and blanket effect over the surface of the earth, in addition to their destructive capabilities on the surface expressions of orebodies, the recognition and interpretation of duricrusts is important in mineral exploration. Duricrusts reduce definition on airphotos of the underlying formations and where fully developed they obliterate any expression from below. When duricrust cover is only thin, however, it is often possible to "see through" the cover and identify trends on photos from rocks below. Rapid visual scanning of ERTS imagery or aerial photography picks out duricrust covered regions very well. From work assembled by numerous authors, Goudie (1973) discusses the importance of duricrusts in the landscape. The following indicators, extracted from this work, may constitute significant keys to duricrust location and type on aerial photographs :

- 1. Flat tops to plateaux.
- 2. A mottled, spotty grey tone where calcrete is exposed at the surface.
- A major break in slope flanking drainage axes due to the indurated capping (Fig. 36).
- 4. A distinct light tone at breaks of slope in calcrete terrain.
- Cliff sections display darker photo tones when laterite is exposed.
- Crenulated steep slopes with deep linear gully forms. Broad, flat gully floors with near vertical heads due to spring sapping (Fig. 36).
- A lack of surface drainage lines due to their high infiltration capacity.
- The presence of pseudokarstic features (swallow holes, sink holes, grottos) and associated lacunate drainage pattern (Fig. 37).
- The localised distribution of pans may indicate calcrete terrain, e.g. the Kalahari; Delaryville-Vryburg area; Krans Pan, Vogelstruis Pan, Vogel Pan (Hopetown).

- 10. Calcrete pseudo-anticlines (Fig. 38) and heiroglyphic surface patterns (Fig. 39); the latter related to joint systems in the underlying bedrock.
- Stunted or almost no vegetation indicates intensive weathering and hardening of the soil (c.f. 'bowals' or extensive vegetation clearings, Fig. 20).
- 12. Characteristic vegetation types.



Fig. 36. Calcrete slope forms from South Africa



A Cross-section of caliche buckle



Fig. 38 Caliche structures and anticlines.



Fig. 37. Lacunate drainage pattern From Kalkrand, S.W.A.





(Note : All figures, 36-39, from Goudie, 1973)

4.2 GEOCHEMISTRY

Generalities. In considering soil as an important sampling medium in areas of little or no outcrop, it is noteworthy that Mitchell (1965) in his treatise on "Trace Elements in Soils" contends that the trace-element content of a soil is dependent almost entirely on the parent material from which the soil was derived and on the nature of the weathering and soil forming processes operating on these parent materials. Thus it becomes apparent that an insight into this relationship between duricrust and parent material is of considerable practical importance recognising the effectiveness of soil trace-element analyses in discovering base-metal deposits where the concentrations either intersect the surface or are shallowly buried (Table 9).

Table 9 : Some examples of ore discoveries in tropical and subtropical landscapes in which geochemical exploration played a major role.

Deposit	Type of Survey	Reference
Shangani Cu-Ni,Rhodesia	Soil	Phillpott, 1975
Otjihase Cu, S.W.A.	Soil	Scott, 1975
Selibi Ni-Cu,Botswana	Regional soil	Baldock, 1976
Kalengwa Cu,Zambia	(Stream sediment) soil	Ellis & McGregor, 1967
Mombezhi Dome, Cu,Zambia	(Stream sediment) soil	Benham et al., 1976
Yandera Porphyry Cu, N.Guinea	(Stream sediment) soil	Fleming & Neale, 1979

Geochemical soil surveys normally give rise to numerous anomalies which require elucidation as to whether they are related to a deposit of ore grade, or to mineralisation not of ore grade, or to some enrichment process entirely unrelated to mineralisation. The interpretation of geochemical data must take into account numerous factors of which most applied geochemists are well aware. Interpretation is the real art of geochemical prospecting, however, its effectiveness requires that the samples have been collected in the right place and that they have been prepared and analysed by the correct method for the environment in question. Yet, Levinson (1974) points out how surprisingly little exploration geologists do know about the surficial environment and stresses that "it is impossible to know too much about soil forming processes ..., because the dispersion (or lack of dispersion) of metals in soils forms the basis of many exploration programmes". Only a brief outline of the characteristics and distribution of soils in relation to the foregoing account can be given here. A considerable amount of further information within this framework may be extracted from numerous publications on soil science. The main difficulties arising in soil surveys are enumerated by Joyce (1976) and include the following :

(i) Failure to take into account changes in soil type within the survey area.

(ii) Failure to interpret correctly the origin of the soils.

(iii) Failure to sample consistently from one horizon.

In the design of geochemical base metal prospecting programmes on tropical and subtropical landsurfaces of great absolute age, it is important to recognise that these surfaces have been subjected to appreciable chemical weathering where sulphide deposits characteristically develop gossanous cappings. The difficulties posed in geochemical interpretation by soils subject to intense weathering and leaching of the more mobile heavy metals are exemplified in a paper by Scott (1975) who discussed the investigations made into Cu and Zn distribution in the soils overlying the Otjihase orebody exposed some 20 km north-east of The discovery area of the Otjihase Cu-Zn massive Windhoek, S.W.A. sulphide deposit lies at a height of 2000m. above sea-level, just below the ancient 'Owambo' landsurface of Tertiary age. As a result of this elevation, the area receives an annual rainfall of 37 cm. The basal zone of sulphide oxidation lies 20-25m vertically below surface and 100-179m downdip from the gossan outcrop. Soils show some profile development and have neutral to midly acidic reactions (pH=6.0-7.0). Under alkaline conditions Zn is more mobile than Cu and Scott was able to calculate that 92.9% of the original copper and 93.1% of the original zinc had been leached from the oxidised reef zone. Furthermore, only 30% of the Cu (between 4 x background limits) and 27% of the Zn (between 2 x background limits) in the overlying soil was contributed directly from gossanous reef material at surface. Consequently, background metal values in soils are extremely low and Scott concludes that "in the case of zinc, a very subdued profile, or possibly no detectable anomaly at all may be present at surface". The 'Owambo surface' represents an ancient pediplain over which outcropping duricrust (calcrete) is a feature (Corbett, 1978). Thus, the appearance of the Cu and Zn deficiency may also be attributed to extensive surface erosion and loss of the

A-horizons and organic matter; the former being the principal soil reservoir of heavy metals and the latter being necessary for the periodic reduction of the hydrous iron oxides to release the occluded heavy metals.

The phenomenon of heavy metal leaching from upper soil layers and their redistribution and concentration at depth within the weathered profile may explain some false anomalies ('high backgrounds') in truncated soil profiles along break-aways which delimit landsurfaces of different age.

Exploration in lateritic terrain. The relationship between lateritic duricrusts and the soils associated with them is best exemplified in many of the major, tectonically stable, shield areas of the world particularly those falling within unglaciated or arid tropical climatic zones where extensive areas of low relief, least affected by later modifications, are preserved.

The importance of geomorphological factors in controlling soil characteristics is well established (Mulcahy, 1961; Bettenay, 1976; Maud, 1965). For example, large tracts of W. Australia are commonly weathered to depths of 80m or more and some of the difficulties in soil surveys mentioned above are well illustrated in the lateritic terrain of the S.W. region extending from Perth on the coast for about 110 miles inland to near Kalqoorlie on the Yilgarn Shield (Fig. 40).



Fig. 40. Variation in the drainage and soil pattern inland from the coast near Perth, Western Australia. Zones A to D are described in text.

(From : Mulcahy, 1961)

Erosional modification of the lateritic mantle on the 'Old Plateau' has been the dominant influence in the present pattern of soils (Mulcahy, 1961). With reference to Figure ⁴⁰ the following salient features are noted :

Zone A : a region of residual laterite on the 'Old Plateau'. Owing to the low intensity of drainage, lateritic mantles are well preserved on drainage divides and the sand plains flanking these are deposits formed from the decomposition of the ferruginous lateritic zones.

Zone B : a region of incision into the 'Old Plateau'. Younger lateritic profiles are developed on the valley sides and floors and weathered clays are exposed on the pediments below the truncated laterite profiles.

Zone C : a region of intense incision leading to the complete removal of pre-weathered materials to expose relatively fresh bedrock.

Zone D : a region sharply dissected in response to tectonic uplift of the Darling Range. Recemented detrital laterite is stable on steep slopes due to the influence of higher rainfall.

Parent materials range from ferruginous duricrust, through mottled and pallid zone clays to weathered rock and relatively unweathered basement. Since second generation soils are likely to inherit the geochemical characteristics of the parent materials, two aspects must be considered : enrichment and depletion. Most of the information which is available on the distribution of trace elements in soils can be found in the soil science literature where agriculturalists refer to fertility in terms of toxicity (enrichment) and deficiency (depletion). It is difficult to simply list the enriched and depleted trace elements in laterite because of their variation in parent material and the effect of many interactions which control their fixation (Jenne, 1968). Mn, for example, is sometimes depleted and at other times present in amounts toxic to plant growth (Maignien, 1966). Generally, Cr, Cu, Ga and Nb are strongly concentrated in amounts more than even insoluble Al. Some elements (Zn, Ti, Sc, V, Be, Mn, Y, Pb) are enriched in amounts less than Al whereas Sr, La, Ba, Ca and Mg are essentially completely leached (Levinson, 1974).

Since deep weathering planation surfaces which favour gossan development also favour laterite development, the geochemical enrichment

in laterite of heavy metals (Cu, Ni, Pb, Zn, Co, etc.) poses problems in base mineral exploration. The so-called 'Ironstone Problem' discussed at length by Blain and Andrew (1977) refers to the difficulty in distinguishing petrographically, texturally and geochemically, 'true gossan' from lateritic ironstone (false gossan'). Summarising briefly, true gossans formed from weathering sulphides of Fe, Ni, Cu, Pb, Zn, etc., represent a residual silicified material composed largely of goethite and/or limonite from which most of the ore metals have, to a lesser or greater degree, been leached under relatively acid conditions; brought about by decomposition mainly of pyrite. On the other hand, laterites represent residual limonite goethite accumulations from barren rocks and the presence of secondary silica in cherty and opaline form is also relatively common (Stephens, 1971). Limonite, and Mn-oxides when present in laterite, are notorious scavengers of the mobile heavy metal cations such as Cu, Ni, Zn, Co, etc.

Jenne (1968) provides convincing evidence that the fixation of heavy metals (Co, Ni, Cu, Zn) in clays, soils and sediments is not related primarily to the cation exchange capacity of clay minerals, as previously thought, but to the sorption effects of ubiquitous hydrous oxides of Mn and Fe. The common occurrence of these oxides as coatings allows the oxides to exert chemical activity far out of proportion to their total concentrations. Sorption or desorption of heavy metal cations occurs in response to their aqueous concentration, to pH and to the amount and strength of organic and inorganic complex ion formers in solution. However, the hydrous Fe-oxides are invariably admixed with silica in lateritic ironstones as well as in gossan where, in addition, fine laminae of limonite in boxworks or colloform textures commonly comprise silica rich and silica poor layers (Blain and Andrew, 1977). The critical soil pH of 6 for Mn, Zn, Cu, and Ni deficiency suggests that some more soluble form of iron predominates in soils below this value.

In discussing how trace elements occur in ironstones it is pertinent to review briefly the applicability of three analytical extraction techniques discussed by Gedeon et al. (1977) for multi-element analysis of laterized rocks by atomic absorption spectrometry. The elements considered include Cr, Cu, Co, Fe, Mn, Ni, V, Zn and Pb. These authors found that of the three single acid digestions tested, hydrofluoric-perchloric (HF) was the best with extractions close to 100%

followed by nitric-perchloric (NP) and finally pechloric (PE). All three digestions were found to be unsatisfactory for Cr and V. NP and PE digestions as 'partial extraction' techniques, are comparable to the classical 'cold extraction' described by Hawkes and Webb (1962) which theoretically releases metals present as sulphides or sorbed loosely on other minerals. Occluded material and substituted atoms in relatively insoluble materials are therefore inaccessible. Since the residues of the partial extraction techniques include such minerals as hematite, goethite, limonite, etc., secondarily dispersed heavy metals (Cu, Ni, Zn, etc.) held within these minerals are not being released. Therefore, where geochemical abundances are being used to distinguish between true and false gossans, total attack following milling to minus 200-mesh is the most applicable analytical method to break down the silica in the limonites and release the Fe-oxides. Partial or selective attacks may be applied to enhance the contrast of certain elements in weathered sulphides, e.g. sodium dithionite extraction to distinguish sulphide and silicate nickel (Smith, 1977).

A classical example of the geochemical exploration problems in lateritic terrain is afforded by the reported investigation of a pseudo-gossan ('false-gossan') at Killara, W. Australia (Butt, 1979). The pseudo-gossan, containing up to 1850 ppm Cu or up to 690 ppm Zn in chip samples, lies on the pediment of a topographically inverted laterite (pisolitic) capped hill. The lateritic ironstones of Tertiary age overlie a residual weathering profile 35-45m deep which comprises an upper zone (15m thick) of silicified kaolinite-quartz with goethite mottling and carbonate in depth; this in turn overlies a soft ferruginous clay zone which passes into saprolite below the water table at 30m (Fig. 41).



Fig. 41. Geology and weathering profile determined by percussion drilling. Cu and Mn values (ppm) are maximum values found. Drill section on pediment slope below laterite outcrop,Killara. (From Butt, 1979)

Closely spaced percussion drilling along the Cu anomaly indicated that the pseudo-gossan is developed along a carbonaceous shale/intrusive dolerite contact. The fresh rocks contain only trace quantities of sulphide (py after po, and cpy) and it appears that optimum redox conditions for the co-precipitation of Cu with goethite, and to a lesser extent with Mn-oxides, occurred along the contact between the two environments during weathering.

Since lateritic soils commonly represent colluvia and a redistribution of iron- and manganese-hydroxides, the distribution of heavy metals in them is likely to be complex making the recognition of significant anomalies in soil surveys difficult. If gossan recognition in a soil survey is to be attempted on the basis of mobile, scavengeable elements such as Cu, Ni or Zn, then an additional factor, like the abundance of Fe- (limonite) and Mn-oxides, need to be considered. For example, a high Cu/Fe+Mn ratio is much more likely to indicate a true gossan than is simply a high abundance of Cu (Viewing, 1979).

Mazzuchelli and James (1966) discussed in detail the distribution pattern of arsenic in the Eastern Goldfields region near Kalgoorlie in terms of soil horizons, mineralogy, size fractions and bedrock mineralogy. They observed that As was concentrated with iron in the nodules of laterite and concluded that the coarse fraction gave better indications of an underlying As source, and possibly gold, than did the minus 80-mesh fraction which is conventionally taken in many surveys. Similar conclusions were reached by Zeissink (1971) who suggested that the coarser pisolithic fraction of laterite be analysed for the immobile pathfinder elements, Pt and Te, in the search for sulphide nickel in W. Australia. Like Pt and Te in nickel sulphide deposits, Se and Au are commonly associated with massive volcanogenic base metal deposits where they occur in sulphide minerals and not in silicates. Owing to the limited mobility of these pathfinder elements under supergene conditions, they would be expected to remain behind as immobile indicators of sulphide in leached gossanous material (Viewing, 1979). Apart from establishing that the highest Cu contents are found in the coarse fractions (plus 8-mesh and 8- to 36-mesh) of all lateritic soils, it is significant that Butt (1979) reports the absence of the common pathfinder elements (Ag, Bi, Cd, Ga, In, Mo, Sb, Sn, As) and the lack of a hydromorphic dispersion halo around the ironstones, indicating pseudo-gossan.

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That surface soil sampling is inappropriate over much lateritic terrain is afforded by the studies of Smith (1977) in the Kalgoorlie nickel area of W. Australia. Mineralisation at Ora Banda consists of extensive disseminated pentlandite in altered metabasalt and overburden consists of complete and truncated laterites which comprise part of a weathering zone extending to a depth of more than 90m. Metal distribution (Cu, Ni, Fe) in the laterized residuum over mineralised and barren ultrabasic rocks is both complex and overlapping in value (Fig 42).



Fig. 42. Ni, Cu and Fe concentrations through a laterite profile developed on : (A) barren ultrabasic rocks, (B) mineralised ultrabasic rocks. (From : Smith, 1977)

The published profile results do indicate, however, that over mineralised bedrock Ni and Cu values increase with depth whereas over unmineralised bedrock they decrease with depth. This is consistent with downward migration of ore-elements during oxidation and with surface enrichment of laterite by migrating surface and groundwaters. Thus, a distinction could be made by collecting additional samples at depth. Lateritic weathering, however, reportedly extends to depths of 90m and from a practical viewpoint indicates that drilling is still the primary method of discrimination. Other approaches associated with gossan interpretation include statistical techniques such as the empirical scattergram method of Clema and Stevens-Hoare (1973) based on various combinations of six of the most useful elements (Cu, Ni, Zn, Pb, Mn, Cr) capable of distinguishing Ni gossans from other ironstones. The more sophisticated multi-variate technique involving discriminant analysis is dealt with in detail by Bull and Mazzuchelli (1975). Basically, chemical variables are chosen to include both mobile and immobile elements, some of which belong within ore and some of which are more representative of silicate rocks.

Exploration in calcrete terrain. Widespread calcrete forming under arid to semi-arid climates is, like laterite, invariably accumulative upon ancient planation surfaces of low relief that have survived erosion and modification by glacial, tectonic and other processes. As the surfaces are often old the present climate does not always suggest deep chemical weathering. However, the pre-Tertiary age of the "African" and "Australian" (Old Plateau) surfaces is widely recognised as are climatic changes since their inception (Flint, 1959). During the later stages of their evolution, a prolonged period or periods of deep weathering under a humid climate and very likely fluctuating water table produced a lateritic weathering surface. Although without counterpart in coastal S.W.A. and the N.W. Cape (probably due to the early change to arid conditions under the influence of the cold offshore currents) it is significant that in the N.W. Cape, accordance between the calcrete covered 'African surface' and pre-weathered glacial Karroo surface is widely recognised (Corbett, 1978). As described above, the development of calcrete around gossanous cappings to orebodies which extend to great depths under the influence of pre-weathering during more humid or wetter (glacial) conditions, may have a profound effect on the surface expression of the latter.

Elemental mobility depends on an interplay between hydromorphic and mechanical dispersion processes (Hawkes and Webb, 1962). The unavailability of chemically dispersed Cu and Zn in calcareous soils has been ascribed to sorption of these metals by CaCO₃ though sorptiondesorption phenomena is a function primarily of pH and secondarily an effect of Ca-bicarbonate ions on heavy metal solubility (Jenne, 1968). In calcrete terrain, where pH lies in the range 8.0-8.5 (Carlisle, 1978) chemical dispersion of the ore forming elements is restricted and in this environment mechanical dispersion effects are most important. Consequently geochemical soil surveys involve locating significant metal values associated with variously dispersed gossan fragments in calcrete. The size and distribution ofgossan fragments, like included bedrock, depends on the level of evolution of the calcrete.

An example of metal dispersion in an arid region underlain by widespread calcrete is provided by Wheatley (1978) regarding exploration in the vicinity of the Aggeneyes and Gamsberg base metal deposits, Bushmanland, N.W. Cape. The climate is semi-arid with sporadic rainfall amounting to 100mm p.a. High summer temperatures cause high rates of evaporation to exceed precipitation. The skeletal soils are strongly alkaline (mean, pH = 8.5) 'Red desert soils' made up 2-10 cm of dry sandy loam topsoil grading down into rubbly nodular calcrete or bedrock. The main aim of the geochemical orientation study was to establish metal dispersion criteria in various calcrete types because these control interpretation of regional ('blanket soil') grid sampling (Fig. 43).



Fig. 43. Endogenous and exogenous soil-metal profiles (-80 mesh fraction) over schistose amphibolite rock with disseminated Cu mineralisation. Note the lack of relation between surface and bedrock values when the surficial material is exogenous (non-pedogenic)

(From : Wheatley, 1978)

Endogenous or typical pedogenic residual calcrete is sheetlike, friable and nodular (< 5cm ϕ) carrying fragments of bedrock progressively dispersed upward in the profile with development of calcrete. Most profiles over mineralised schist in the minus 80-mesh fraction of calcrete increase in depth indicating that calcrete has impeded their dispersion. Nevertheless, samples at the top of the calcrete provide a dilute reflection of metal content related to bedrock mineralisation. In the case of exogenous or transported ('valley') calcrete which may have a similar concretionary profile, soil metal values have no relationship to bedrock.

Similar conclusions were reached by Cox (1975) who presented geochemical assay results in a calcrete profile over a Ni prospect at Pioneer, W. Australia. Ni, Cu, Co and Cr values in the minus 80-mesh fraction were found to decrease progressively upwards over ultramafic rocks whilst Zn values show an erratic vertical distribution.

It is clear from these two examples, therefore, that the existence of a pedogenic calcrete soil horizon does not impede geochemical soil surveys (Fig. 44). However, anamalous metal values located in non-pedogenic calcrete need to be traced to source by follow-up work.



Fig.44 Geochemical orientation survey, JH prospect, showing nickel content of topsoil, calcrete and weathered bedrock from horizontal groove samples taken on north wall of costean No.10.

(From : Cox, 1975)

Exploration in silcrete terrain

Stephens (1971) notes that the stratified soils of local origin laid down on the extensive pedimented 'gibber plains' in Australia are calcareous, gypsiferous and somewhat saline suggesting that they are not related in origin to those formed in association with laterite, i.e. by redevelopment of silcrete itself. Generally they contain much aeolian material and a coating of desert varnish (up to 500µm thick) commonly occurs on exposed silcrete fragments. Birnessite and hematite have been identified as the Mn- and Fe-oxide phases in desert varnish. These occur in association with illitemontmorillonite mixed-layer clays (Potter & Rossman, 1979). According to these authors the origin of the material in the varnish is external to the rock on which it forms and they suggest that the clays are transported in particulate form, probably by wind and water. Apart from certain transport in water, the form in which Fe and Mn reach the varnish surface is unknown, however, their scavenging effect on heavy metals by Mn- and Fe-oxides has already been stressed. Consequently,

geochemical exploration techniques applicable to prospecting in hot dry desert regions are equally applicable to geochemical exploration on the 'gibber plains' of Australia. What should be taken into account in determining optimum size fractions for geochemical enhancement in soil surveys, is the very fine grain size (minus 200-mesh) of much aeolian material and the coarse grain size of silcrete (and other rock fragments) which are host to such scavenger materials.

4.3 GEOPHYSICS

Generalities. The bases of the various geophysical methods employed in mineral exploration are determined by difference in physical properties between the target (e.g. sulphide mineralisation) and host formations (e.g. country rock or overburden) :

- Magnetic methods thus depend on the precence of a susceptibility or remanance factor difference.
- Gravity methods rest on specific gravity differences present.
- Resistivity methods detect differences in impedance (i.e. specific resistisity), or, inversely, the electrical conductivity.

- Induced polarisation (I.P.) depends on the difference in charging effects at dispersed metallic conductors versus other surfaces and the resulting changes in capacitative decay.
- Electromagnetic methods (E.M.) depend primarily on the conductivity difference and on the induction parameter.
- Radiometric methods detect differences in radiation (α, γ) .

It is customary to call the target response 'signal' and the response from other unwanted formations 'geological noise'. Other sources, termed 'random noise', may be instrumental, operational or may arise from external sources. A target is detectable when the signal is clearly distinguishable from the prevailing noise, i.e. a favourable signal to noise ratio (Bosschart, 1979).

Since the oxidation of sulphides has the effect of moving the target far below surface, penetration is an important consideration for the uses of geophysics in duricrust terrain characterized by a deep weathering. Unfortunately this is far from being the only restriction imposed by the environment. There are two types of electrical conductivity important in geophysical prospecting :

- metallic or electronic conduction which occurs when electrons move along current paths as in metals, metal sulphides, graphite and clays with a high cation exchange capacity.
 - electrolytic conductivity where positively or negatively charged ions are transported under the influence of an electric field. Ions originate by the dissociation of salts or acids in aqueous solutions.

Duricrust profiles are characterised by a thick underclay horizon and, in many instances, soluble salts which occur more abundantly in association with calcrete soils in arid environments. The occurrence of salts (NaCl) in lateritic profiles in W. Australia has been noted by Mulcahy (1960). This is surprising in view of the intense leaching of alkali and alkali earths during lateritic weathering, however, Mulcahy considers the salts to be of recent marine origin transported inland on rain clouds whereas Carlisle (1978) attributes their origin to dry salt lake dust redistributed by illuviation through the profile. The point emphasized here is that duricrusts constitute a thick and conductive overburden which present particular problems for geophysicists employing electrical prospecting methods (I.P. and E.M.) since low resistivity layers tend to 'short circuit' transmitted energy from reaching and energizing the underlying fresh rock which contain the target sulphide mineralization; this results in a low signal/noise ratio.

Induced Polarization surveys. An excellent review of the I.P. method has been prepared by Hallof (1972). The approach is essentially non-mathematical and is aimed at geologists and exploration people rather than geophysicists to demonstrate, through practical examples, the applicability of the method and various electrode configurations that are in common use. The two major problems encountered in applying I.P. in duricrust terrain where low resistivity layers occur are termed 'electromagnetic coupling' and 'masking' (Baird et al., 1979).

(a) Electromagnetic coupling arises from eddy currents induced in a low resistivity near-surface zone by the time varying current flowing in the transmitting dipole cable and in the ground. These eddy currents set up electromagnetic fields which are detected at the measuring dipole and cannot always be separated from polarization effects arising from the underlying bedrock. The relative effect of coupling increases as the electrode separations increase and as the conductivity increases (resistivity decreases). Thus, the least coupling would occur for a survey using the lowest frequencies (i.e. time domain in preference to frequency domain) and shortest useful electrode separations.

(b) Masking occurs when there is a great contrast in resistivity between a near surface layer and the underlying bedrock. If the thickness of the weathered zone is sufficiently large in comparison to the electrode spacing and if its resistivity is sufficiently low with respect to the bedrock, then a high percentage of the transmitted current will be concentrated in the upper layer. If the geological noise due to overburden increases above a certain level then the target may be undetectable.

Electrode array configurations are extremely important in attempting to minimize geological noise due to overburden. There are

numerous electrode configurations that can be used in making I.P. measurements, however, most of the surveys now done use one of three electrode configurations as shown in Fig. 45.



Fig. 45. Three electrode configurations of common use in I.P.

(From : Hallof, 1972)

Scale model I.P. and resistivity data for vertical and horizontal sources (targets), without and with overburden, and for the three various arrays are compared in Figures 46 - 51. A concise explanation follows :

(i) Vertical source without overburden (Fig. 46-47).

The profile results show in Fig. 46 that the gradient array gives no resistivity anomaly and a relatively small apparent frequency effect anomaly (2%) by comparison to the pole-dipole and dipole-dipole electrode configuration. In figure 47 the anomalous dipole-dipole data for n = 1-5 are plotted in pseudo-section form. Because of the depth of the source and its depth extent (i.e. dyke-like), the maximum I.P. effects are measured for the largest electrode separations (n = 5).

(ii) Vertical source with overburden (Fig. 48 and 49).

As would be expected due to coupling, the presence of the conductive layer has reduced the magnitude of the apparent resistivity and apparent fequency effect anomalies for all three configurations (Fig. 48). It is significant that the apparent resistivity level measured for the gradient array is 50% higher than for the other two arrays and that the corresponding I.P. anomaly has almost disappeared. This reflects that the gradient array, characterised by large current electrode separations, gives the most coupling. Comparing the dipoledipole data plotted in Fig. 49 with Fig. 47, the apparent resistivity values show the nearly horizontal contours expected for a horizontal surface layer with a slight resistivity low over the source. The maximum value of the apparent metal factor anomaly remains the same in both cases indicating the advantage of this parameter inasmuch as











1 2

(A/2+13+25

]รุ่งและ

Nr == 1075

+

+units

(1+12+23% 115% (non-uniform)

(Mf) 2*4700+1000

FIGURE 51

120

it is practically independent of non-polarizable, conductive zones such as conductive overburden.

(iii) Horizontal source (Figs. 50 and 51).

Because a large volume of the source is close to the surface, the anomalous values measured for all electrode configurations are greater in magnitude. For wide relatively shallow sources the anomalous effects for the gradient array appear to be more distinct though they are much the same for all three configurations.

Electromagnetic surveys. Concentrated (massive) sulphide deposits which are targets of EM surveys have much higher conductivities than their host rocks and will usually cause detectable anomalies. However, high conductivity surface formations that commonly occur in areas covered by duricrust present masking problems to EM surveys which may be even more considerable than found in I.P. surveys.

Certain operating factors in E.M. prospecting methods can be varied within limits to maximize the signal/noise ratio. These include the frequency of the applied current (ω) and the measuring geometry (ρ), i.e. transmitter-receiver separation, coil orientation, traverse direction. The product of these two factors is called the 'operating parameter' ($\omega \rho$) of a given E.M. system. The relations between signal, noise and operating parameters are illustrated schematically in Fig. 52.

The effect of conductive overburden (W. Australia situation) in reducing the signal to noise ratio, i.e. T_1/N_1 to T_2/N_2 , for a given operating parameter by comparison to a poor conductive situation (e.g. Canadian Shield) is apparent. A lowering of the operating parameter $(\omega_2 \rho_2)$, i.e. by lowering the frequency or reducing the transmitter-receiver separation, in areas of conductive overburden may perhaps sufficiently improve the signal/noise ratio (T_3/N_3) to again render the target discernible. However, the transmitter-receiver separation can only be varied in moving source and receiver (ground) systems, where the effects of shortening this separation is to decrease penetration. On the other hand, the effect of lowering the frequency of E.M. systems leads to increased instrumental noise and other technical difficulties (Baird et al., 1979).



A point to note is that in areas of extensive surface conductivity it is frequently useful, for example, in an airborne E.M. Input system, to contour amplitude of one of the early channels to show distribution of this surface material. In areas of residual soils, such a surface conductivity map can be a geologic reflection of the underlying lithology. Apart from a conductive overburden, however, duricrust terrain is characterised by a deep weathering so that shears and faults become foci of more intense alteration. As the groundwater is usually saline in arid regions, these deeply and intensely weathered zones often give strong conductive indications which cannot be distinguished from those of orebodies.

Gravity surveying. Gravity metre surveying is probably one of the most under rated geophysical methods in mineral exploration. Of significance to exploration in areas underlain by duricrusts is the probability that a buried sulphide deposit, itself a dense mineral mass, will be characterised by a dense siliceous gossan within the zone of weathering. This is likely to provide a strong contrasting density within relatively low density near-surface layers giving rise to recognizable and interpretable gravity anomalies.

The Bouguer anomaly map is the result of the gravity meter integrating all the gravity effects of all the mass distribution. The sum effect shown on the map is usually listed as the combined regional and residual effects. The residual is determined in order to eliminate the deep seated and resolve the shallow or economic effects. The residual anomaly map alone is of little value unless a knowledge of the method of arriving at it is known. The residual anomaly map must be interpreted based on probability factors, and a knowledge of the geology of the area, combined with the regional and Bouguer control (Campbell, 1979).

That gravity techniques have found little application in potentially mineralised provinces of regional extent for direct location of orebodies is probably due to a number of factors, the most important of which include :

(i) being a ground method, the relatively slow speed of coverage.

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(ii) the large exercise in computing the reading value to the terrestrial vertical gravity gradient taking into account instrument drift, latitude, free-air and terrain corrections.

(iii) the susceptibility of gravity measurements to extreme variations in profile relief, i.e. variations in residual soil cover and differential weathering.

In certain circumstances, however, where quality is not all important, it is an extremely useful tool to discriminate a very precise and local target such as a conductor found by electrical methods which may be due either to massive sulphides or to graphite or to ionic conduction. Under these conditions, where only one line of gravity readings is taken over the target, a quantitative interpretation based on terrain corrected data would not be necessary. Of practical significance is the fact that the depth to the causative body may be simply calculated as twice the half-width of a gravity anomaly. Furthermore, the area under any anomaly profile is proportional to the mass of the causative body which means that the gravity method is directly applicable to tonnage estimation. Peripheral control, however, should extend beyond the area of interest for a distance at least equal to the depth to economic depths, and preferably to twice this depth.

Magnetic surveys. Measurements of the earth's magnetic field are useful in prospecting in that some minerals become magnetized when they are situated in a magnetic field. The degree to which a material becomes magnetic when a field is applied is measured in terms of magnetic susceptibility. In most rocks the magnetic susceptibility is determined by the amount of magnetite present, with the susceptibility being roughly 10 to 20 times the weight percent of magnetite for contents of a few percent. The thicker the overburden or, conversely, the deeper the source, the broader and less definite the magnetic anomaly will be. However, the magnetic method is not subject to the same severe limitations imposed by the duricrust environment on electrical prospecting methods. It not only utilizes a natural earth field, but for a buried pole source (monopole) the intensity of the magnetic anomaly varies under a comparatively mild inverse square law relative to depth (Breiner, 1973). Furthermore, this already minor limitation is partly offset by the fact that magnetite, being among the most resistant minerals, will tend to be

present in residual soils in higher proportion than other more soluble minerals. Thus, the pattern of magnetic anomalies recorded over an area of deep weathering and thick overburden typified by duricrusts, reflects broadly the magnetic properties of the underlying rocks.

Aeromagnetic surveys permit rapid and economic coverage of duricrust terrain. The aeromagnetic contour plan may be correlated with geological trends and boundaries of concealed lithological units. Certain lithologies produce characteristic anomaly forms and anomaly intensities are indicative of the degree of basicity of the rocks. In quantitative methods of interpretation, a detailed analysis of an anomaly leads to a determination of the depth, configuration and magnetic susceptibility of the causative body. Thus, aeromagnetic surveys will aid the search for mineral deposits in duricrust environments by adding to the knowledge and understanding of the regional geology where surface mapping is difficult because of sparse outcrops.

A more direct application of the aeromagnetic method to mineral exploration is possible if the ore deposits include,or are spatially associated with,appreciable quantities of magnetite. For example : (1) Placers may be found in stream beds because magnetite, being heavy, may become concentrated in detectable amounts. (2) Magnetic iron ores may be located with considerable reliability. (3) Massive volcanogenic base metal deposits frequently contain magnetite as a significant accessory mineral or are closely associated with a prominent magnetite quartzite (Campbell and Mason, 1977). (4) Basic igneous rocks carrying nickel and/or other economic minerals may be located if they have a significant magnetite content.

In such areas the airborne results are usually not adequate to define drilling targets and a ground magnetic survey is usually a pre-requisite to any drilling programme. However, ground magnetic surveys are more susceptible to background noise arising from surface concentrations of magnetite. In addition, organic action particularly in high humas soils, is thought to be responsible for the formation of the magnetic mineral, maghemite, from other non-magnetic forms of iron oxide (Breiner, 1978). Valeton (1972) reports up to 15% maghemite in some laterites - a phenomenon of importance in quantitative methods of precision ground magnetic survey interpretation. Radiometric methods. The radiation field at any point consists of two parts, namely ; (1) cosmic radiation, and (2) alpha, beta and gamma radiation emitted by solids, liquids or gases close enough to the point to affect the detector used.

For purposes of this discussion, cosmic radiation (gamma) may be approximated as constant and uniform. Because alpha (helium nuclei) and beta (electrons) rays possess both a mass and charge, their penetration through earth materials is a few millimetres or less. Therefore, the detection of alpha or beta rays does not lend itself to remote sensing applications as does the detection of gamma rays (electromagnetic radiation) which have their origin in a nuclear decay process (U-238; Th-232; K-40) and which are capable of penetrating a foot or more of earth type materials.

In the weathering zone, U is very soluble under most oxidizing conditions (Hambleton-Jones, 1978). Uraninite and related reduced (U^{4+}) oxides limit the mobility of U under reducing conditions, but in aerated waters, U in the 6⁺ valence state dissolves as UO_2^{2+} (uranyl ion), UO_2OH^+ , and uranyl carbonate complexes. Because of this solubility in oxidizing media, uranium released by oxidation of uraninite and other reduced U minerals, or by breakdown of apatite, sphene, and other accessories moves with the water until it encounters a reducing environment, an adsorbent, or a precipitant (vanadate, phosphate).

Among the adsorbents are freshly precipitated Fe³⁺ oxyhydroxides which tend to release the U as they become better crystallized (Van Der Weijden et al., 1976). Similarly, organic acids are strong adsorbents of U (Szalay, 1964). For these reasons it is very likely, especially in areas of ancient laterite, that much uranium has been leached from surface horizons where background levels of gamma radiation will be very low. In addition, thick leached profiles over Bedrock would suffice to block radioactivity.

Higher levels of background radioactivity ('false anomalies') may be expected to occur on breakaway slopes in association with truncated lateritic profiles where the deeper, reducing horizons are exposed. The high solubility of uranium thus imposes severe limitations on the effectiveness of airborne radiometric surveys to detect U orebodies beneath lateritic cover. The solubility coupled with the strong affinity of U for organic matter and Fe-sesquioxides suggests that false anomalies may occur over sites of 'hydromorphic' laterite (i.e. 'groundwater' type).

Because of strong complexing by carbonate ions, a high content of carbonate promotes the solubility of uranium in waters of intermediate oxidation state. Many insoluble uranyl minerals are known and carnotite $(K_2(UO_2)_2(VO_4)_2 \cdot 8H_20)$, requiring unusually high concentrations of UO_2^{2+} and VO_4^{3-} ions, commonly occurs, therefore, in exogenous calcrete (transported) where economic concentrations are spatially associated with some restriction in subsurface drainage (Carlisle, 1978). Photogeological interpretation and airborne radiometric surveying are suitable methods for the exploration of uraniferous calcrete deposits.

5. CONCLUSION

Materials which are recognised as having been formed by pedogenic or non-pedogenic processes but which have not undergone any degree of cementation (induration) are not classified as duricrusts.

The genesis of duricrusts, particularly those well represented in Africa, Australia and Asia, is related to the persistent stability of these emergent Precambrian shields and to a geological setting that began to take shape at least as early as the Mid-Mesosoic (Tertiary period).

The occurrence of duricrusts worldwide cannot be related simply to any single factor of soil formation (viz. parent material, climate, topography, vegetation and biological activity) age or formation process. Rather, they form in response to a variable combination of physico-chemical processes, the most important of which are climate and a favourable regime of groundwater fluctuation. As the deposits formed by weathering are often old, the present climate does not always suggest duricrust development. The essential characteristics of duricrust remain when the climate has changed to a drier regime. Fossil duricrusts retain a close relationship with relief and perpetuate old landsurfaces. Although generally associated with low relief they are by no means restricted to planation surfaces. Duricrusts may also develop on slopes of up to 20° and indurated horizons, at low topographic levels, have caused well documented cases of relief inversion. Consequently, the occurrence of such material cannot be accepted uncritically as an indication of old, nearly level, residual landsurfaces of great absolute age (Mulcahy, 1960). The location, shape and internal structure are commonly sufficient to recognise multiple genesis, if any, and fit the wide variety of duricrust deposits into the following genetic classification:

- Fluvial (Valley channel (Sheet flood
- Lacustrine
- In-situ
- Capillary rise (uncommon)
- Pedogenic (per descensum (per ascensum
- Detrital types of secondary origin

(Goudie, 1973)

In mineral exploration over duricrust environments of regional extent, one of the greatest needs is increased speed of coverage coupled with a method of discriminating 'true anomalies' related to mineralisation from 'false anomalies' related to background noise. Interpretation of small-scale ERTS imagery is a cost-effective method for rapid delineation of duricrusts over large areas. The various surface expressions of duricrust that can be detected by photogeology are classified into the four interrelated fields of structural, topographical, vegetational and mineralogical features, which have a combination of tonal, textural and spatial characteristics. The potentials and limitations of the different available sensing techniques are made clear. Once duricrust structure and texture are related to topography and individual models of genesis, duricrust type may be used to assess the significance of suspected marker horizons in the landscape and permit identification of individual weathering surfaces on which similar sulphide mineralisation may give rise to gossans of widely different physical and chemical characteristics.

No successful routine geochemical method of prospecting for bedrock mineralisation in lateritic terrain has yet been publicised although attempts have been made to discover suitable pathfinder elements. In calcrete terrain, on the other hand, available data does indicate that geochemical soil surveys are not impeded by the presence of pedogenic calcrete. Nevertheless, attention must be paid to orientation surveys to determine which soil horizon, size fraction and analytical technique to adopt for each specific geochemical problem. These conditions can be established on the basis of samples from selected trenches or pits over known mineralisation and over barren areas. A point to note is that orientation surveys represent only a fraction of the cost of any regional (blanket) soil survey.

The circumstances of a deep weathering, a conducting overburden and a widespread incidence of saline groundwaters (salt filled pores and fractures) all combine to render electrical prospecting methods highly susceptible to an abundance of unwanted and strong surficial effects. This appears true no matter what operational technique, coil configuration or field geometry, air or ground is resorted to. In practical terms, electrical surveying in duricrust environments is severely limited in its effectiveness and emphasizes the fact that no electrical method is to be relied upon as a primary survey tool for widespread coverages of virgin ground. On the other hand, carefully interpreted aeromagnetic data over potentially mineralised areas underlain by extensive duricrust provides the most reliable guide to subsurface lithological mapping and permits the direct or indirect selection of targets for ground follow-up utilizing a variety of techniques to suit particular situations. As with any sampling programme, orientation surveys involving 'in-line' or 'expander' resistivity tests should be undertaken to determine whether the surface layer has a sufficiently low resistivity as to give rise to coupling or even masking during electrical prospecting. The results of these tests can often be used to determine the resistivities and thicknesses of horizontal layers and the depth to bedrock.

In order to justify the use of prospecting methods which are more direct in the search for mineral deposits in duricrust environments, it is necessary to predict the maximum depth of cover to remain of economic interest in the design stage of any mineral exploration programme. This factor is dependent on the economic considerations of value of the element and grade and size of the deposit sought.

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BIBLIOGRAPHY

- AITCHISON, G.D. and GRANT, K. (1967). A preliminary appraisal of the engineering significance of silcretes and ferricretes in Australia. Proc., 4th Reg. Conf. for Africa on Soil Mechanics and Found. Engng., C.T., 1, 53-56.
- ALEXANDER, L.T. and CADY, J.G. (1962). Genesis and hardening of laterite in soils. Tech. Bulletin, United States Dept. of Agriculture, 1282.
- ANDREW, R.L. (1978). The evaluation of gossans in mineral exploration. A short course held at Rhodes University, Grahamstown, 56p.
- AVERY, T.E. (1977). Interpretation of aerial photographs. Burgess Publ. Co., U.S.A., 392p.
- BAIRD, J.G., BOSSCHART, R.A. and SEIGEL, H.O. (1979). Geoelectrical techniques in areas with conductive near-surface formations. Applications Brief, Scintrex Ltd., Canada, 16p.
- BAKER, W.E. (1973). The role of humic acids from Tasmanian Podzolic soils in mineral degradation and metal mobilization. Geoch. et Cosmochim. Acta, 73, 269-281.
- BALDOCK, J.W., HEPWORTH, J.V. and MARENGWA, B.S. (1976). Gold, base metals and diamonds in Botswana. Econ. Geol., 71, 143.
- BENHAM, D.G., GREIG, D.D. and VINK, B.W. (1976). Copper occurrences of the Mombezhi dome area, N.W. Zambia. Econ. Geol., <u>71</u> 433-442.
- BETTENAY, E. (1976). The geomorphological control of soil distribution in S.W. Australia. 9th Int. Congr. of Soil Science, Trans., 4, paper 64.
- BIRKELAND, P.W. (1974). Pedology, Weathering, and Geomorphological Research. Oxford Univ. Press, U.S.A. 285p.
- BLAIN, C.F. and ANDREW, R.L. (1977). Sulphide weathering and the evaluation of gossans in mineral exploration. Minerals. Sci. Engng., 9, No. 3, 119-150.
- BLANCHARD, R. (1968). Interpretation of leached outcrops, Nevada State Bureau Mines, Bulletin 66.
- BOOCOCK, C. and VAN STRATEN, O.J. (1962). Notes on the geology and hydrogeo'logy of the central Kalahari Region, Bechuanaland Protectorate. Trans. Geol. Soc. S.A., 65, Part 1, 125-176.
- BOSSCHART, R. (1979). A short course in exploration geophysics (lecture notes), Rhodes University, Grahamstown.
- BREINER, S. (1973). Applications manual for portable magnetometers. Geometrics, U.S.A.

- BROWN, C.N. (1956). The origin of caliche on the N.E. Llano Estacado, Texas, J. Geol., 64 (1), 1-15.
- BULL, A.J. and MAZZUCCHELLI, R.H. (1975). Application of discriminant analysis to the geochemical evaluation of gossans in Elliot, I.L. & Fletcher, W.K. (Eds.) Geochemical Exploration 1974. Elsevier, 219-226.
- BUTT, C.R.M. (1979). Geochemistry of a pseudo-gossan developed on a black-shale dolerite contact, Killara, W. Austr. Jour. Geoch. Explorn. 11, No. 2, 131-156.
- CAMPBELL, G. (1979). A short course in exploration geophysics (lecture notes). Rhodes University, Grahamstown.
- CAMPBELL, G. and MASON, R. (1977). The application of airborne and ground geophysical techniques to the search for magnetite-quartzite associated base metal deposits in southern Africa (in press).
- CARLISLE, D. (1978). The distribution of calcretes and gypcretes in SW United States and their favourability based on a study of deposits in W. Australia and S.W.A. U.S. Energy Resour. Dev. Admin. Subcontract 76-022-E.
- CLARKE, F.W. (1924). Data of Geochemistry. U.S. Geol. Survey Bull. 770.
- CLEMA, J.M. and STEVENS-HOARE, N.P. (1973). A method of distinguishing nickel gossans from other ironstones on the Yilgarn Shield, W. Australia. J. Geochem. Explor., 2, 393-402.
- COLE, M.M. and LE ROEX, H.D. (1978). The role of Geobotany, Biogeochemistry and Geochemistry in Mineral Exploration in S.W.A. and Botswana - a case history. Trans. Geol. Soc. S.A., 81, No. 3, 277-318.
- CORBETT, D. (1978). A review of landscape development and the erosion cycles in southern Africa. M.Sc. (Min. Exp) dissertation, Rhodes University, Grahamstown.
- COX, R. (1975). Geochemical soil surveys in exploration for nickelcopper sulphides at Pioneer, near Norseman, W. Australia, in Elliot, I.L. & Fletcher, W.K. (Eds) Geochemical Exploration 1974. Elsevier, 437-460.
- DAVIES, G. (1964). Silica in streams and groundwater. Am. Jour. Sci., 262, 870-891.
- DE SWART, A.M.J. and BENNETT, G. (1974). Structural and physiographic development of Natal since the late Jurassic. Trans. Geol. Soc. S.A., 77, 309-322.
- DRISCOLL, E.M. (1964). Landforms in the N. Territory of Australia. In Geographers in the Tropics : Liverpool Essays, (Ed) Steel, R.W. and Prothero, R.M., London, 57-80.

DU TOIT, A.L. (1956). The Geology of South Africa. Oliver & Boyd.

- FITZPATRICK, E.A. (1971). Pedology a systematic approach to soil science. Oliver & Boyd.
- FLEMING, A.W. and NEALE, T.I. (1979). Geochemical exploration at Yandera porphyry copper prospect, Papua New Guinea. J. Geochem. Expl., 11, No. 1, 33-52.
- FLINT, R.F. (1959). Pleistocene climates in eastern and southern Africa. Geol. Soc. Am. Bull., 70, 343-374.
- FRANKEL, J.J. (1952). Silcrete near Albertina, Cape Province. South African Journal of Sci., 49, 173-182.
- FRANKEL, J.J. and KENT, L.E. (1937/8). Grahamstown surface quartzites (silcretes). Trans. Geol. Soc. of South Africa, 40, 1-42.
- GARDNER, L.R. (1972). Origin of the Mormon Mesa caliche, Clark County, Nevada. Geol. Soc. Am. Bull., 83, No. 1, 143-156.
- GEDEON, A.Z., BUTT, C.R.M., GARDNER, K.A. and HART, M.K. (1977). The applicability of some geochemical analytical techniques in determining "total" compositions of some laterized rocks. Jour. Geochem. Explor., 8, 283-303.
- GORDON, M., TRACEY, J.I. and ELLIS, M.W. (1958). Geology of the Arkansas bauxite region. U.S. Geol. Survey Prof. Paper 299, 268p.
- GOUDIE, A. (1972). The chemistry of world calcrete deposits. J. Geol., 80, 449-463.
- GOUDIE, A. (1973). Duricrusts in Tropical and Subtropical landscapes. Clarendon Press, Oxford, 174p.
- GROOTENBOER, J., VILJOEN, R.P., VILJOEN, M.J., LONGSHAW, T.G. (1975). ERTS Imagery : An appraisal of applications in geology and mineral exploration. Min. Sci. Engng., 7, No. 2, 132-168.
- GRUBB, P.L.C. (1970). Mineralogy, geochemistry and genesis of the bauxite deposits on the Gove and Mitchell Plateaux, N. Australia. Miner. Deposita, 5, 248-272.
- GRUBB, P.L.C. (1973). High level and Low Level Bauxitization : a criterion for classification. Min. Sci. Engng., 5, No. 3, 219-231.
- HALLOF, P.G. (1972). The Induced polarization method. 24th Int. Geol. Cong., Sect. 9, 64-81.
- HAMBLETON-JOMES, B.B. (1978). Theory and practice of geochemical prospecting for uranium. Minerals. Sci. Engng., <u>10</u>, No. 3, 182-197.
- HAWKES, H.E. and WEBB, J.S (1962). Geochemistry in Mineral Exploration. Harper & Row, N.Y., 415p.

HOLMES, A. (1965). Principles of physical geology. Nelson, 386-306.

- HUANG, W.H. and KELLER, W.D. (1970). Dissolution of rock forming minerals in organic acids : simulated first stage weathering of fresh mineral surfaces. Am. Mineral., 55, 2076-2094.
- HUANG, W.H. and KELLER, W.D. (1972). Organic acids as agents of chemical weathering of silicate minerals. Nature, Phys. Sci., 239, 96, 149-151.
- HUNT, C.B. (1972). Geology of soils. W.H. Freeman & Co., San Francisco, 345p.
- HUTTON, J.T., TWIDALE, C.R., MILNES, A.R. & ROSSER, H. (1972). Composition and genesis of silcretes and silcrete skins from the Beda Valley, S. Australia. Jour. Geol. Soc. Australia, <u>19</u>, Pt. 1, 31-39.
- JACKSON, K.S., JONASSON, I.R. and SKIPPEN, G.B. (1978). The nature of metals-sediment-water interactions in freshwater bodies, with emphasis on the role of organic matter. Earth Sci. Rev., 14, No. 2, 97-146.
- JACKSON, T.A. and KELLER, W.D. (1970). A comparative study of the role of lichens and "inorganic" processes in the chemical wtrg. of recent Hawaiian lava flows. Am. Jour. Sci., 269, 446-466.
- JENNE, E.A. (1968). Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water; the significant role of hydrous Mn + Feoxides. Adv. Chem. Ser., 67, 337-387.
- JOYCE, A.S. (1976). Exploration Geochemistry. Austr. Min. Found. 220p.
- KING, L.C. (1962). Morphology of the Earth. Oliver & Boyd.
- KRAUSKOPF, K.B. (1967). Introduction to Geochemistry. McGraw Hill, N.Y., 706p.
- KRONBERG, B.I., FYFE, W.S., LEONARDOS, O.H. & SANTOS, A.M. (1979). The chemistry of some Brazilian soils : Element mobility during intense weathering. Chem. Geol., 24, 211-229.
- KRUMBEIN, W. and SLOSS, L.L. (1963). Stratigraphy and sedimentation. San Fransisco, Freeman.
- KYLE, D.L. (1974). The application of airborne line scan sensing to mineral exploration, in : Seminar-geological applications of Remote Sensing Techniques held at Rhodes University, Grahamstown, 11-13.
- LELONG, F., TARDY, Y., GRANDIN, G., TRESCASES, J.J. and BOULANGE, B. (1976). Pedogenesis, chemical weathering and processes of formation of some supergene ore deposits. In : Wolfe, K. (Ed), Handbook of Stratiform and Stratabound Ore Deposits, 3, 93-166.

LEUDER, D.R. (1959). Aerial photographic interpretation. McGraw-Hill, N.Y.

- LEVINSON, A.A. (1974). Introduction to Exploration Geochemistry. Appl. Publ. Ltd., Alberta, 612p.
- LOUGHNAN, F.C. (1969). Chemical weathering of the silicate minerals. New York, Elsevier.
- MABBUTT, J.A. (1952). The evolution of the middle Ugab Valley, Damaraland, S.W.A. Trans. Roy Soc. S. Afr., 33, 333-365.
- MABBUTT, J.A. (1955). Erosion surfaces in Namaqualand and the ages of surface deposits in the S.W. Kalahari. Trans. Geol. Soc. S.A. 58, 13-30.
- MACFARLANE, M.J. (1971). Laterization and landscape development in Kyagwe, Uganda. Qtly. Jour. Geol. Soc. Lond., No. 54, <u>126</u>, Part 4, 501-539.
- MACVICAR, C.N. (1978). Advances in soil classification and genesis in southern Africa. Paper read at the 8th Congress of the Soil Science Soc. of southern Africa, Pietermaritzburg, 18p.
- MAIGNIEN, R. (1966). Review of research on laterites. Nat. Res. Research 4, UNESCO Publ.
- MARTIN, H. (1963). A suggested theory for the origin and brief description of some gypsum deposits of S.W.A. Trans. Geol. Soc. S.A., <u>66</u>, 34-352.
- MAUD, R.R. (1965). The application of geomorphology to pedology. Proc. S. Afr. Sugar Technol. Assoc., 39, 266-269.
- MAZZUCCHELLI, R.H. and JAMES, C.H. (1966). Arsenic as a guide to gold mineralization in laterite covered areas of W. Australia. TIMM (Sect. B) 75, 286-294; discussion, 76, 127-129.
- MEILLON, J.J. (1978). Economic Geology and Tropical Weathering. CIM Bull., 71, No. 795, 61-70.
- MILLOT, G. (1970). The geology of clays. Springer Verlag, N.Y. 429p.
- MITCHELL, R.L. (1972). Trace elements in soils and factors that affect their availability. Geol. Soc. Am. Bull. 83, No. 4, 1069-1076.
- MOHR, E.C.J. and VAN BAREN, F.A. (1954). Tropical soils. Van Hoeve, The Hague.
- MOSES, J.H. and MITCHELL, W.D. (1963). Bauxite deposits of British Guiana and Surinam. Econ. Geol., 58, 250-262.
- MOSS, R.P. (1968). Soils, slopes and surfaces in tropical Africa, in : The Soil Resources of Tropical Africa, A symposium of the African Studies Assocn. of the U.K., Moss, R.P. (ed), Camb. Univ. Press, 29-60.
- MOUNTAIN, E.D. (1946). The geology of an area east of Grahamstown. Geol. Surv. S.A., Explan. of sheet 136 (Grahamstown).

- MOUNTAIN, E.D. (1952). The origin of silcrete. S.A. Jour. Sci., <u>48</u>, 201-204.
- MULCAHY, M.J. (1960). Laterites and lateritic soils in S.W. Australia. J. Soil Sci., <u>11</u>, 206-226.
- MULCAHY, M.J. (1961). Soil distribution in relation to landscape development. Z. Geom. 5, 211-225.
- MULCAHY, M.J. (1973). Landforms and soils of southwestern Australia Jour. Roy. Soc. of W. Austr., 56, Pts 1 & 2, 16-22.
- NETTERBURG, F. (1969). The geology and engineering properties of S.A. calcretes. Unpub. Ph.D. thesis, Univ. of Wits., Jhb (4 vols).

1.00

- NETTERBURG, F. (1969b). Ages of calcretes in southern Africa. S. Afr. Archaeol. Bull., 24, 88-92.
- NETTERBURG, F. (1978). Dating and correlation of calcretes and other pedocretes. Trans. Geol. Soc. S.A., 81, 3, 379-392.
- NORTON, S.A. (1973). Laterite and bauxite formation. Econ. Geol., <u>68</u>, 353-361.
- NYE, P.H. (1955). Some soil forming processes in the humid tropics. Jour. Soil Sci., <u>6</u>, 51-72.
- OERTEL, G. (1956). Cited in MacFarlane (1971).
- OKAMOTO, G., OKURA, T. and GOTO, K. (1957). Properties of silica in water. Geochim. et Cosmochim. Acta, 12, 123-132.

OLLIER, C.D. and TUDDENHAM, W.G. (1962). Slope development at Coober Pedy, S. Australia. Jour. Geol. Soc. Austr., <u>9</u>, No. 1, 91-105.

- ORDWAY, R.J. (1972). Earth Sciences. Van Nostrand/Reinhold, N.Y., 788p.
- PALLISTER, J.W.(1956). Slope development in Uganda. Geogr. Jour., 122, 80-87.
- PARK, C.F. and McDIARMID, R.A. (1975). Ore deposits. Freeman & Co., San Francisco.
- PARTRIDGE, T.C. (1967). Some aspects of the water table in South Africa. 4th Reg. Confer. for Africa on Soil Mech. and Found. Engng., C.T., 41-44.
- PARTRIDGE, T.C. (1975). Some geomorphic factors influencing the formation and engineering properties of soil materials in South Africa. Soil Mech. and Found. Engng., Proc. 6th regional confer. for Africa, 37-42.
- PHILLPOT, D.E. (1975). Shangani a geochemical discovery of a nickelcopper sulphide deposit. In : Elliot, I.L. & Fletcher, W.K. (eds.) Geochemical Exploration 1974. Assocn. of Explor. Geochem., Spec. Pub. 2, 503-510.

- POTTER, R.M. and ROSSMAN, G.R. (1979). The Mn- and Fe-oxide mineralogy of desert varnish. Chem. Geol., 25, No. 1/2, 79-94.
- PRESCOTT, J.A. and PENDLETON, R.L. (1952). Laterites and lateritic soils. Tech. Communicat. Commonw. Bureau of Soil Science, 47.
- PULLAN, R.A. (1967). A morphological classification of lateritic ironstones and ferruginized rocks in N. Nigeria. Nigerian Jour. Sci., 1 No. 2, 161-174.
- PURVES, W.D. (1976). A detailed investigation into the genesis of granite derived soils. Ph.D. thesis. Univ. of Rhod. Cited in Macvicar, 1978.
- RANKAMA, K. and SAHAMA, T.G. (1952). Geochemistry. Univ. of Chicago Press.
- SADLEIR, S.B. and GILKES, R.J. (1976) Development of bauxite in relation to parent material near Jarrahdale, W. Australia. Jour. Geol. Soc. Austr., 23, Pt. 4, 333-344.
- SCHALASCHA, E.B., APPELT, H. and SCHATZ, A. (1967). Chelation as a weathering mechanism. Geoch. et Cosmoch. Acta, <u>31</u>, 587-596.
- SCHELLMANN, W. (1975). Formation of and prospecting for tropical bauxite above silicate rocks. Min. Mag. (July), 33-39.
- SCHNITZER, M. (1969). Reactions between fluvic acid, a soil humic conpound, and inorganic soil constituents. Soil. Sci. Amer. Proc. 33, 75-81.
- SOCTT, M.J. (1975). Case histories from a geochemical exploration programme - Windhoek District, S.W.A. In : Elliot, I.L. & Fletcher, W.K. Geochemical Exploration 1974. Assocn. of Explor. Geochem. Spec. Publ. No. 2, 481-492.
- SENIOR, B.R. and SENIOR, D.A. (1972). Silcrete in S.W. Queensland. Extract No. 4, from Bulletin No. 125, Bur. of Min. Res. (Geol. and Geophys), Canberra.
- SMALE, D. (1973). Silcretes and associated silica diagenesis in South Africa and Australia. Jour. Sed. Petrol., <u>43</u>, No. 4, 1077-1089.
- SMIRNOV, V. (1976). Geology of Mineral Deposits, Moscow, MIR Publishers, 520p.
- SMITH, B.H. (1977). Some aspects of the use of geochemistry in the search for nickel sulphides in lateritic terrain in W. Australia. In : Butt, C.R.M. & Wilding, I.G.P. (Eds), Geochemical Exploration 1976. Assocn. of Explor. Geochem. Spec. Vol. No. 6, 259-282.
- STEPHENS, C.G. (1971). Laterite and silcrete in Australia. Geoderma, 5, 5-52.
- SZALAY, A. (1964). Cation exchange properties of humic acids and their importance in geochemical enrichment of UO₂²⁺ and other cations. Geoch. et Cosmoch. Acta, 28, 1605-1614.

- TRENDALL, A.F. (1962). The formation of 'apparent peneplains' by a process of combined laterisation and surface wash. Zeits. fur Geomorph. 6, 183-197.
- VALETON, I. (1972). Bauxites. Developments in soil science, No. 1, Elsevier, Amsterdam, 226p.
- VAN DER EYK, J.J. & DE VILLIERS, J.M. (1969). Soils of the Tugela Basin. A study in subtropical Africa. Natal Town and Regional Planning Comm., Pietermaritzburg.
- VAN DER MERWE, C.R. (1962). Soil groups and subgroups of South Africa. Science Bull. 356. Chemistry Series No. 165. Dept. Agric. Tech. Serv., Pta.
- VAN DER MERWE, C.R. and HEYSTEK, H. (1952). Clay minerals of South African Soil Groups. I. Laterites and related soils. Soil Sci., 74, 383-401.
- VAN DER MERWE, C.R. and WEBER, H.W. (1963). The clay minerals of South African soils developed from granite under different climatic conditions. S. Afr. J. Agric. Sci., 6, 411-454.

1

- VAN DER WEIJDEN, C.H., ARTHUR, R.C. and LANGMUIR, D. (1976). Sorption of uranyl by hematite : theoretical and geochemical implications. Geol. Soc. Am. Abstr. with Program, 8, 1152.
 - VAN NIEKERK, B.J. and LAMBRECHTS, J.J.N. (1977). Morphological criteria and their interpretation for agriculture in terms of soil behaviour and land quality. Proc. 7th Nat. Cong. Soil Science, Dept. of Agric. Tech. Services, 1-5.
 - VIEWING, K. (1979). A short course in Exploration Geochemistry, Rhodes University, Grahamstown.
 - VON BACKSTROM, J.W. and JACOB, R.E. (1979). Uranium in south Africa and S.W.A. Phil. Trans. Roy. Soc. Lond., A291, 307-319.
 - WHEATLEY, C.J.V. (1978). Aspects of geochemical exploration in the Bushmanland Region, N.W. Cape, in Mineralization in Metamorphic Terranes. Geol. Soc. S. Afr., Spec. Publ. 4, 205-214.
 - WILLIAMSON, W.O. (1957). Silicified sedimentary rocks in Australia. Amer. Jour. Sci., 255, 23-42.
 - WILLIAMS, P.W. (1969). The geomorphic effects of groundwater. In : Chorley, R.J. (Ed), Introduction to Fluvial Processes. Methuen & Co. Ltd., 108-122.
 - WOLLAST, R. (1967). Kinetics of the alteration of K-feldspar in buffered solutions at low temperatures. Geoch. et Cosmoch. Acta, <u>31</u>, 635-648.
 - WOPFNER, H. and TWIDALE, C.R. (1967). Geomorphological history of the Lake Eyre Basin. In : Landform studies from Australia and New Guinea. Jennings, J.N. and Mabbutt, J.A. (eds), Cambridge, 119-144.

WRIGHT, J.R. and SCHNITZER, M. (1963). Metallo-organic interactions associated with podzolization. Soil Sci. Amer. Proc., 27, 171-176.

ZEISSINK, H.E. (1971). Trace element behaviour in two nickeliferous laterite profiles. Chem. Geol., 7, 25-36.