

# **GEOCHEMICAL EXPLORATION IN CALCRETE TERRAINS**

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## 1. INTRODUCTION

Calcretes are widespread in the drier parts of the world and may underlie up to 13% of the total land surface (Yaalon, 1981 *in* Goudie, 1983). The earliest references to calcrete (by whatever name) date back to 1840 after Renou's work in Algeria (in Goudie, 1973) and Charles Darwin's observations of the Pampas of South America in 1890. Calcrete has been used to build churches, houses and roads and from the engineers point of view may be a desirable feature. In Australia valley calcrete is a useful aquifer for potable water used for domestic, farming and mining purposes. From the mineral explorationist's point of view, however, they form physical and chemical barriers to the surface expression of sub-cropping mineralisation and as a result hide potential mineral deposits from discovery by geochemical means. In some instances calcrete actually hosts mineralisation which may be in economic concentrations (e.g. uranium) or possibly in concentrations that, although not economic, are high enough to make calcrete a reservoir or storage facility for later reconcentration (e.g. gold at Eldorado Valley, Nevada).

The problem of detecting the geochemical signature of mineralisation below calcrete has prompted some workers to say that in certain situations geochemical exploration in calcrete terrains may be futile (e.g. Danchin, 1971).

In 1977 Bradshaw and Thomson reported that calcretes had "generally been ignored or avoided as media for geochemical sampling and its use is virtually unreported in the literature". There have been some small advances since then and calcrete does get passing mention in the exploration literature, but the number of works dedicated to the problem of mineral exploration in calcrete terrains are few and far between. Workers who have delved into this field include Butt (1992), Carlisle (1978, 1980, 1980), Garnett (1983), Guedria et al. (1989), Kilham (1985) and Vermaak (1984). At this point it should be noted that there appears to be a sizeable French school involved with exploration in the calcrete terrains of north Africa, but due to the language barrier they have not been reviewed here (with the exception of Leduc, 1986).

This work takes a look at some of the literature on calcretes and especially the problem of geochemical exploration in calcrete terrains. The conclusion that will be reached is that exploration in calcrete terrains is not futile and that provided the explorationist is aware of the types of calcrete and their genetic implications calcrete can be used as a sampling medium and anomalies can be detected through calcrete.

### 1.1. EXPLORATION SIGNIFICANCE OF CALCRETE DEVELOPMENT

The presence of calcrete has both advantages and disadvantages for mineral exploration. The major disadvantages are (Butt, 1992):-

1. Many pedogenic calcretes represent absolute additions to the soil which may be developed over pre-existing deeply weathered profiles; this profile may have been partly truncated prior to soil and calcrete formation. The concentration of mobile metals associated with economic mineralisation are depressed due to leaching of the pre-existing profile and the absolute addition of calcium carbonate to the soil profile dilutes and depresses the anomaly contrasts even further. The replacement of primary and secondary minerals by carbonates may lead to the mobilisation and loss of some elements such as Pb and Zn.



2. The high pH prevailing in the regolith of calcrete terrains (pH commonly 8.4 in mature calcrete profiles, but may rise to 10 or 11 (Kilham, 1985)) reduces the chemical mobility of many elements and so restricts the development of epigenetic anomalies.

Calcrete formation may be advantageous to exploration in the following circumstances (Butt, 1992):-

1. In some environments the calcrete represents a pH contrast to underlying neutral to acid regolith and may cause the precipitation and concentration of leached metals so forming epigenetic anomalies (e.g. Kadina).
2. Gold can be enriched in calcareous horizons of soils and may give rise to, or enhance, a near surface expression of concealed mineralisation (e.g. Bounty, Mount Pleasant).
3. Groundwater calcretes may form the host rock and aquifer for the transport and deposition of economic concentrations of uranium.

## 2. CALCRETE

### 2.1. DEFINITION AND TERMINOLOGY OF CALCRETES

The word "calcrete" was first used by Lamplugh in 1902 to describe lime-cemented Pleistocene gravels in the Bay of Dublin ("sand-and-gravel beds are cemented sporadically into hard masses by solution and redeposition of lime through the agency of infiltrating waters"). At about the same time he also coined the words "ferricrete" and "silcrete", so providing the basic terminology for duricrusts as used today.

Goudie (1973) synthesised various definitions in the literature and defined duricrusts as follows:-

"A product of terrestrial processes within the zone of weathering in which either iron and aluminium sesquioxides (in the cases of ferricretes and alcretes) or silica ( in the case of silcrete) or calcium carbonate ( in the case of calcrete) or other compounds in the case of magnesicrete and the like have dominantly accumulated in and/or replaced a pre-existing soil, rock, or weathered material, to give a substance which may ultimately develop into an indurated mass."

Watts (1977) suggested the following definition for calcretes in particular:-

"A term for terrestrial materials composed dominantly, but not exclusively, of calcium carbonate, which occur in states ranging from powdery and nodular to highly indurated, and are the result of displacive and/or replacive introduction of vadose carbonates into greater or lesser quantities of soil, rock or sediment within a weathering profile."

Goudie (1983) further commented on this definition saying that cementation may also be an important process, that usage of the phrase "weathering profile" may not be fully appropriate, and that restriction of formation to the vadose zone may be unduly restrictive.

Since Lamplugh's initial usage of "calcrete" Netterberg (1980) has noted that modern usage has formally or informally extended the term to include almost any material of almost any consistency and carbonate content formed within the regolith by the *in situ* cementation and/or replacement of a pre-existing material by carbonate precipitated from the soil water or groundwater. Indeed, even rocks with carbonate contents as low as 5-10% have been called calcretes.

Although they may have been formed in a similar fashion, materials such as speleothems, spring tufas, aeolianites and beachrocks are usually excluded from a definition of calcrete (Netterberg, 1980). The mechanism of calcification is not restricted and calcretes may be of pedogenic or non-pedogenic origin, or both (Netterberg, 1969b).

Calcrete terminology has, in the past, been somewhat confusing. For instance, caliche, which is the common usage in the United States has also been used in South America to describe nitrate accumulations in the west coast deserts

and for gypsum deposits in the Death Valley of California (Hunt and Mabey, 1966 in Goudie, 1973). However, usage of the word "calcrete" has few local connotations and is less subject to confusion than other synonyms. Listed below are some of the calcrete descriptors used in the literature:-

Table 1  
Local Terminology of Calcrete

Caliche (USA)	Natural concrete (India)
Calcicrete (Britain)	Giglin, Jijilin (Nigeria)
Croûte calcaire (France)	Steppenalk (German E. Africa)
Carapace calcaire (France)	Soil travertine (Australia)
Caprock (USA)	Calcareous laterite (Australia)
Travertine / travertine crust (Australia)	Canto Blanco (Canary Islands)
Sheet limestone (E. Africa)	Chebi-chebi (central Africa)
Vlei limestone (S. Africa)	Cornstone (England)
Kafkalla and Havara (Cyprus)	Gatch (Kuwait)
Caatinga limestone (Brazil)	Calcareous duricrust (Australia)
Tosca, Tosca, Tosca Blanca (Spain, Argentina)	Deckkalk (German SWA)
Torba beda (Libya, Tunisia)	Lime crust yerma (Kubiena)
Tafezza/ Trab/ Tifkert (N. Africa)	Nari (Israel)
Rimrock (USA)	Kankar, kunkur, kunker, cancar (India)
Bhata (India)	Tufa (southern Africa)
Dhandla (India)	Mbuga limestone (E. Africa)
Taparas (Provence)	Tepetate (Mexico and Texas)

## 2.2. CALCRETE CLASSIFICATION

Netterberg's revised classification (1980) is the system most commonly used in southern Africa. It is a descriptive classification based largely on the secondary (chemical) structure and sequence of development. Netterberg's classification is applied only to those materials containing more than about 50%  $\text{CaCO}_3$  by mass or more than about 50% K-fabric by volume. K-fabric is defined by Gile *et al.* (1965) as a "fabric in which fine grained authigenic carbonate occurs as an essentially continuous medium". No minimum strength or degree of cementation is required. Table 2 illustrates the stages in the development of calcretes based on Netterberg's (1980) classification.

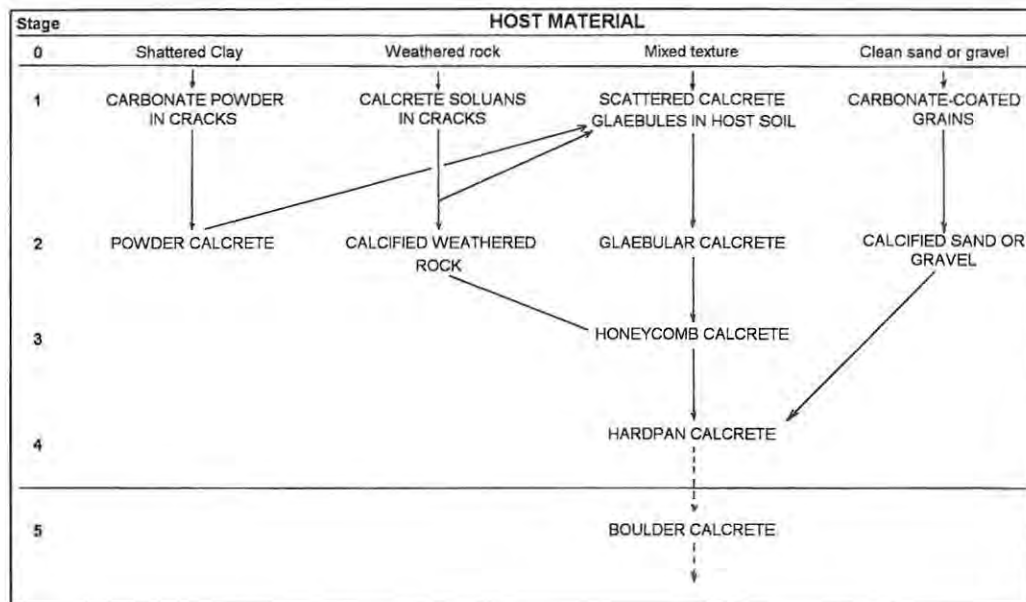
### 2.2.1. Calcareous Soil

"Calcareous" is used to suggest little or no cementation, and such soils are usually soft, loose and very weakly or completely uncemented by the low carbonate content, which occurs mostly as grain coatings and patches of powdery carbonate. Total carbonate content lies between 1 and 10%.

### 2.2.2. Calcified Soil

A calcified soil would be cemented by carbonate to a firm or stiff consistency. It possesses little or no nodular development. The carbonate may be evenly distributed throughout the horizon, as in calcified sands and gravels, or it may be confined to fissures which produces a fabric transitional to honeycomb calcrete. "Calcified" is used in preference to "calcareous" to imply cementation of the **whole** horizon. The amount of carbonate present is usually in the range 10-50%.

Table 2  
Stages in the development of calcretes (after Netterberg, 1980)



### 2.2.3. Powder Calcrete

Netterberg (1980) defines powder calcrete as "a fine, usually loose, but sometimes up to stiff, *in situ*, intact powder, high in silt-sized calcium carbonate with few visible host particles and little or no nodular development". They seldom exceed 500mm in thickness.

### 2.2.4. Honeycomb Calcrete

Honeycomb calcrete forms when the nodules in a nodular calcrete grow larger and more numerous until they partly coalesce and/or some of the fines become cemented. The interstitial voids will be filled with what appears to be original host material and are seldom greater than about 30mm in diameter. In the less well developed varieties the voids may be connected. Honeycomb calcretes seldom exceed 500mm in thickness. Honeycomb calcretes are highly regarded as good road material.

### 2.2.5. Hardpan Calcrete

A hardpan calcrete is formed when most of the larger voids in honeycomb calcretes become filled by carbonate and the host grains in calcified soils begin to float in the carbonate cement. They are very hard (up to Mohs hardness = 5), often outcropping, relatively impervious, sheetlike layer of calcrete normally overlying softer or looser material. The bottom contact may be sharp or gradational while the top contact is almost always sharp. Individual layers of hardpan are seldom more than 500mm thick although accumulations of several metres thick are known (e.g. Mariental area) (Netterberg, 1980). Hardpans may be intact and massive or they may possess a number of mechanical and chemical structures and textural features which are briefly described below:-

1. *Pseudo-bedding*: bedding or laminae inherited from the host material.
2. *Inclusions*: host gravel, quartz sand particles, previously formed nodules, fossils, stone artefacts.
3. *Voids, Pedodes, Pipes and Birdseye*: Voids are common in all calcretes and porosities up to 75% have been recorded, but 30-50% is typical; termitary channelling; decayed roots; pedodes are the pedological equivalent of geodes; voids after diatoms and gastropods.
4. *Tufa*: tuffaceous hardpan calcretes of low density ( $1-2\text{g/cm}^3$ ) and high porosity (30-75%) are often associated with pans, vleis and water courses; upper portions of tuffaceous calcretes may be coated with a hard, impervious rind of opaline silica or laminar calcrete.
5. *Plates*: Platy hardpan capping massive or other hardpan; very hard (Mohs hardness of 6 common)
6. *Laminae*: Thin wavy rinds of very hard, silicified calcrete frequently found coating and sealing the surface of mature hardpans; also occurring as stalactitic rinds below calcrete boulders; seldom greater than 25mm thick.
7. *Joints and Faults*: fissuring and shattering due to weathering and due to deformation on crystallisation.
8. *Solution Hollows and Pinnacles*: Hollows of centimetres to metres common in calcretes covered by soil, especially in higher rainfall areas; they represent a stage of weathering between hardpan and boulder calcrete.
9. *Solution Channels and Pipes*: Vertical solutionally enlarged joints and root or stem holes from a few millimetres to 500mm in diameter.
10. *Veins, Recalcified Voids and Stalactites*: Voids and joints or any other opening may become recalcified; a process of solutional weathering.
11. *Breccia*: Several cycles of fracturing and recementation may produce a calcrete breccia; usually confined to the older calcretes.

### 2.2.6. Calcrete Boulders and Cobbles

Weathering of calcrete hardpans forms discrete boulders and cobbles. They are commonly hard to very hard and when covered by soil have rounded upper surfaces formed due to solution by infiltrating groundwaters. In higher rainfall areas cobbles and boulders may occur as the only form of calcrete in the profile. Commonly this form of calcrete has laminated rinds which enables sizes smaller than cobbles to be distinguished from calcrete nodules/glaebules.



## 2.3. CALCRETE DISTRIBUTION

The best developed calcretes in the world are to be found on the High Plains of the USA, the Pampas and intermontane basins of Argentina, the semi-arid coastal lowlands of Venezuela, the Kalahari of southern Africa, the plains of East Africa, the hamadas of North Africa, parts of eastern Spain and southern France, the Bekaa of Lebanon, Cyprus, the deserts of southern C.I.S., parts of Rajasthan (India) and arid Australia.

Calcretes are widespread in the drier parts of the world and may underlie up to 13% of the total land surface (Yaalon, 1981 *in* Goudie, 1983). Calcretes are known from polar regions (Swett, 1974 *in* Garnett, 1983), but are more typical of warm regions with limited precipitation - generally forming in areas with 400 to 600mm of rain per year (Goudie, 1983). In very arid parts of the world gypcretes and evaporites tend to predominate although gypcrete and calcrete may occur together in the same profile as on the west coast of Namibia (although gypcrete is replacing calcrete here).

The biota of an area also influences the formation of calcretes; species of mopane in southern Africa concentrate calcium in their leaves which is then available to the near surface environment upon decay of the leaves.

Although climate plays an important role in the formation of calcrete it is not the only factor and on a local scale factors other than climate influence calcrete formation.

### 2.3.1. Calcrete Distribution and Geomorphology

Calcrete is known to form on steep slopes, but tends to develop preferentially on low angle slopes with slopes in the order of 2 to 4m per km (1:500 to 1:250) being most favoured (Goudie, 1983). Most calcretes have developed on low-angle pediments, glacis<sup>1</sup> or alluvial plains, and on river terraces and valley fills. The Pampas, the Kalahari, the American High Plains, and the Wajir Basin are all major basins of slow terrestrial aggradation (Goudie, 1973). Other than valley fills calcrete is known to form preferentially around low lying areas where the groundwater is close to surface such as at Lichtenburg, Etosha and Makgadigadi. North of Etosha calcretes are known to form in the "straats" between dunes, but not on the dunes themselves. This may be a function of closer proximity to calcareous source rock, increased flow of water or dense undergrowth development with its evapotranspirational capabilities (Goudie, 1973).

Furthermore, it can be generally stated that the upslope parts of a terrain are areas of carbonate solution while the lower portions of the sloped terrain are areas of carbonate accumulation (Van Zuidam, 1975 *in* Goudie, 1983).

### 2.3.2. Calcrete Distribution and Groundwater Chemistry

Goudie (1973) does not dwell on the issue of groundwater chemistry, but only mentions it in order to refute vague claims by Strakhov (1979, *in* Goudie, 1973) that carbonate-rich groundwaters are associated with calcretes. Dominance of carbonate or bi-carbonate in groundwater is not necessary for calcrete formation.

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<sup>1</sup>Glacis: A gently inclined slope or bank, less steep than talus e.g. a piedmont slope (Bates and Jackson, 1987)

### 2.3.3. Calcrete Distribution and Climate

Geomorphology, host rock and biota are local controls on calcrete distribution, but on the macro scale climate is the major determinant. Many different climatic indicators have been used to study the distribution of calcretes and, in particular, southern Africa has proved to show good correlation between climate and calcrete distribution (Fig 2). In southern Africa the eastern boundary of calcrete distribution corresponds well with the 500mm annual precipitation isohyet, the 1250mm average free surface evaporation loss and the 30-50 Regenfaktor<sup>2</sup> (Goudie, 1973). Weinert's N-values also show a very close correspondence with calcrete distribution where:-

$$N = 12 \frac{E_j}{P_a}$$

where  $E_j$  = Evaporation during the warmest month (January)

$P_a$  = Annual Precipitation

An N-value of 5 corresponds well with the eastern boundary of hardpan calcrete in southern Africa.

Australia is problematical in that it does not respond well to a climatic analysis of calcrete distribution. In Western Australia there is little calcrete in areas more humid than 250mm annual precipitation, while in the Adelaide area of South Australia and parts of northern Australia calcrete extends into areas approaching 500mm annual precipitation, a more normal situation in terms of world calcrete distribution.

In the USA there is a relationship between calcrete, rainfall and evapotranspiration with a Thornthwaite index of 0 being applicable. The boundary between "lime-accumulating and non-lime-accumulating soils in the United states..follows more closely the line dividing the sub-humid zones of Thornthwaite into moisture-deficient and moisture-abundant sub-zones (Moisture Index = 0) than it does the limits of any rainfall zone" (Price, 1933 in Goudie, 1973). Figure 1 shows the position of this zero moisture index line in the USA. Below is a brief

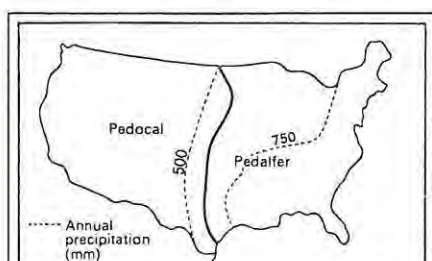


Fig 1: Distribution of calcrete in the U.S.A The bold line defines a moisture index of 0 (after Thornthwaite) to the west of which calcrete is accumulating (from Goudie, 1973)

description of Thornthwaites Moisture Index ( $I_m$ ) (Schulze, 1958):-

$$I_m = (100s - 60d)/n$$

where  $s$  = water surplus; an excess of precipitation over potential evapotranspiration

$d$  = water deficit; a deficiency of precipitation over potential evapotranspiration

$n$  = potential evapotranspiration; the amount of moisture that would be transferred from a vegetation-covered soil to the atmosphere by evaporation and transpiration, if it were consistently available in optimum quantity. (a calculated quantity)

Elsewhere in the world the 500mm isohyet seems to be a fairly consistent

<sup>2</sup>The Regenfaktor is the ratio of the mean annual rainfall (mm) to the mean annual temperature (°C). A ratio of less than 40 is taken indicate aridity.

humid boundary to calcrete formation although in the Pampas of South America calcrete extends into zones of 1200mm precipitation per annum and in Angola and northern Namibia the 850mm isohyet forms the humid limit. The discussion so far has revolved around the humid limit of calcrete formation, but there does also tend to be a dry limit. For example calcretes are rare in areas of Tunisia where rainfall is less than 400mm per annum (Despois, 1955 in Goudie, 1973). Calcrete is also known from localities in north Africa where the rainfall is about 100mm/yr.

At this stage it is important to note that some calcretes are fossil, i.e. they are not forming today and may therefore have been formed in times of a different climatic regime. A climatological interpretation in terms of modern climates will then not be valid. South Africa is just such a case according to Carlisle (1980). The most intensive development of pedogenic calcrete in South Africa is found in the extremely aridic soil moisture regime. In Australia the non-pedogenic valley calcretes occur in an identical soil moisture regime, but whereas the S.African calcretes are fossil the Australian valley calcretes are forming today. Carlisle's (1980) conclusion is that the most intensive pedogenic calcrete formation in southern Africa occurs within an area where pedogenic calcretes should not be forming today. In Western Australia the non-pedogenic valley calcretes and pedogenic calcretes form in areas that are mutually exclusive - the soil moisture regime being the discriminant factor with the valley calcretes forming in the more aridic regime.

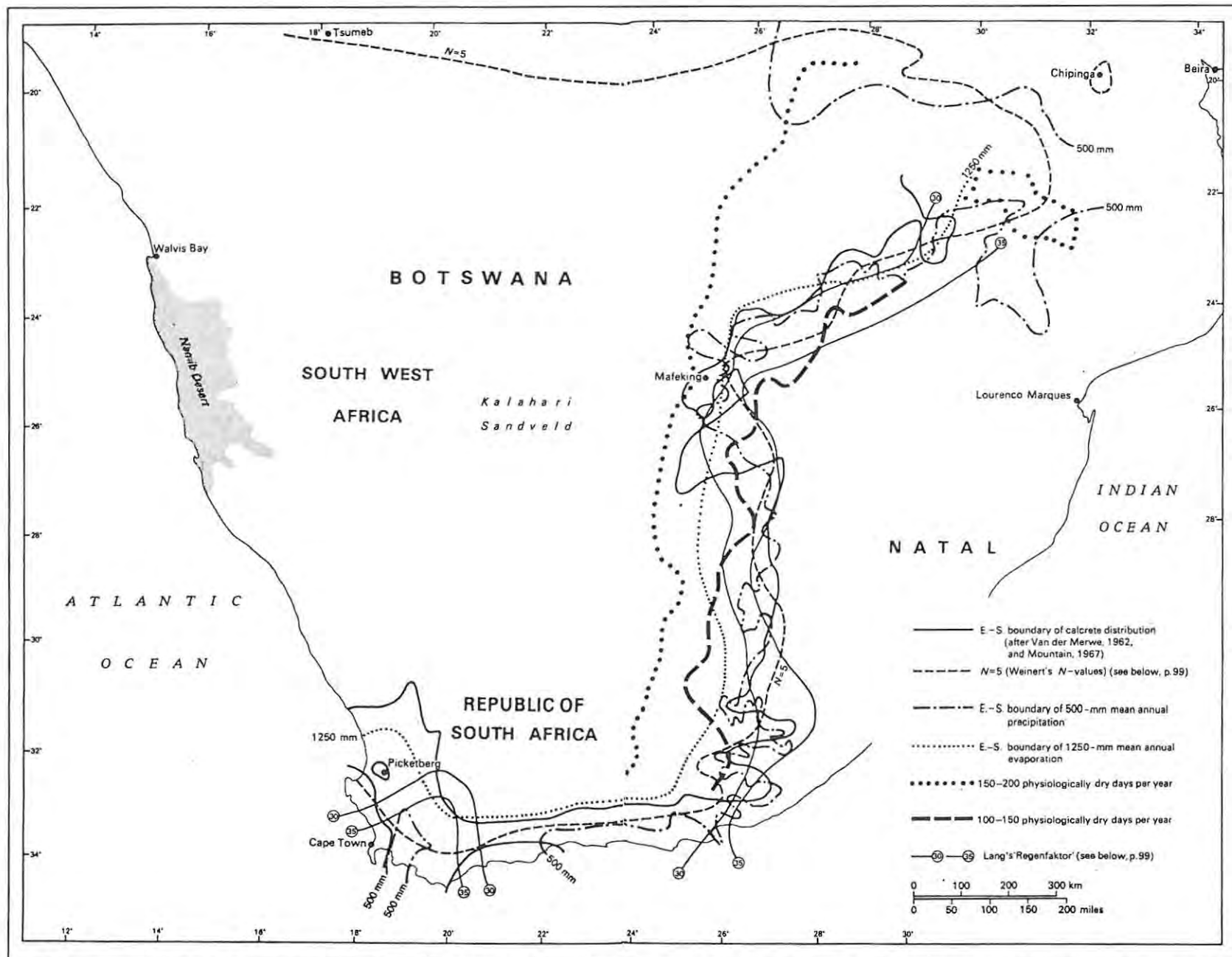


Fig 2: Climatic indices and the calcrete boundary in southern Africa (from Goudie, 1973). West of the boundary of calcrete distribution (after Van der Merwe, 1962 and Mountain, 1967) is the area that Netterberg (1971) describes as "all types of calcrete common". East of the boundary no well developed hardpan is found, although dispersed nodules may be found where conditions are favourable.



### 2.3.4. Calcrete Distribution and Host Rock Lithology

Woolnough (1930, in Goudie, 1973) proposed a model of calcrete formation based on bedrock lithology and dismissed the idea that climate had anything to do with duricrust formation. It is now recognised that calcretes can develop in any host material; calcrete is, for instance, recorded from host lithologies as diverse as granite, shale, laterite, sand, gneiss, schist, mudstone, marl, limestone and kimberlite. Calcrete does, nevertheless, show a predilection for calcium or carbonate rich lithologies; Kilham (1985) for instance has noted the preferential formation of calcrete over kimberlite in comparison to the surrounding shales and Goudie (1973) notes the importance of basic volcanic rocks (with their calcic minerals) as a substratum for calcrete.

### 2.3.5. Calcrete Distribution in Southern Africa

Figure 3 shows the distribution of calcretes in southern Africa. See also Figure 2 which shows the distribution of southern African calcretes with respect to climatic indices. Calcretes are most common on the western two thirds of the sub-continent south of latitude 17°S (Netterberg, 1980) and, as stated earlier, climate is the major, though not the only controlling influence. Also mentioned was the fact that, strictly speaking it is the soil climate that is important. Carlisle (1978) takes the soil moisture regime into consideration and it can be seen from his figure 5.3 that the aridic (A) and sub-aridic (A<sub>s</sub>) soil moisture regimes correspond very closely with the distribution of calcrete as shown in Fig 2. The most intense calcretisation occurs within the aridic (A) regime.

- A Aridic Regime: Hot dry climate; soil never moist for long periods. Mean monthly precipitation never exceeds evaporation (E) or  $E^{0.75}$ .

$$E_a/P_a > 13 \quad E_a = \text{Annual evaporation; } P_a = \text{Annual precipitation.}$$

$$E_w/P_w > 9 \quad E_w = \text{Evaporation in wettest month; } P_w = \text{Precipitation in wettest month.}$$

$$E_a - P_a = 3000 \quad \text{Annual water loss}$$

- As Subaridic Regime: Episodic isolated convective storms in late summer and autumn. Precipitation exceeds  $E^{0.75}$  in one to five summer months.

$$E_a/P_a > 5 \text{ to } 10$$

$$E_w/P_w > 2 \text{ to } 4$$

$$E_a - P_a = 2000 \text{ to } 3000$$

A further consideration of the soil moisture regime is that of Thornthwaite (Schulze, 1958)(see section 2.3.3) and in South Africa calcretes occur where  $I_m$  (moisture index) < -20 or where the water deficiency is > 200mm (Netterberg, 1971).



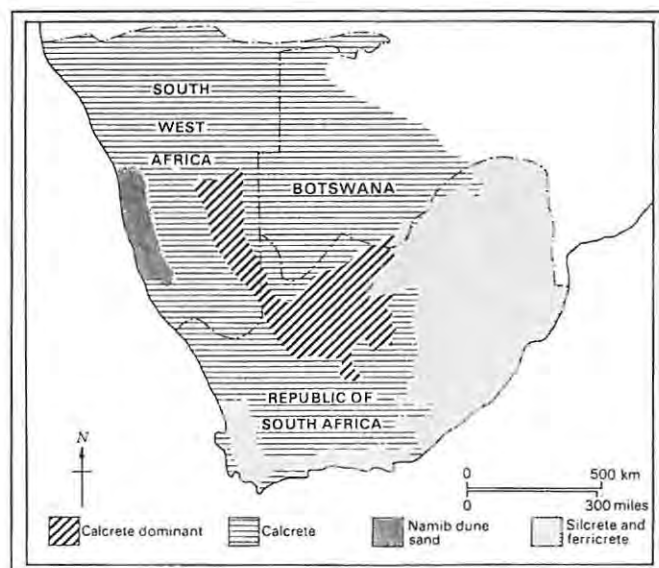


Fig 3: Generalised representation of calcrete distribution in southern Africa, with ferricrete and silcrete zones (from Goudie, 1973 after Mountain, 1967)

## 2.4. CHEMICAL COMPOSITION AND MINERALOGY OF CALCRETE

Goudie (1972) reviewed 300 analyses of calcrete the results of which are shown in the table below:-

Table 3  
Regional and world calcrete chemistry (from Goudie, 1972)

	North Africa	East Africa	South Africa	India	Australia	Cyprus	World
CaCO <sub>3</sub> %	74.81		79.13	61.02	87.97	83.62	<b>79.28</b>
SiO <sub>2</sub> %	11.33	14.26	11.83	17.92	6.49		<b>12.30</b>
Al <sub>2</sub> O <sub>3</sub> %	0.70	2.48	2.38	3.13	1.58		<b>2.12</b>
Fe <sub>2</sub> O <sub>3</sub> %	0.95	1.82	1.51	3.62	2.26		<b>2.03</b>
MgCO <sub>3</sub> %			8.72		6.28	4.56	
Al <sub>2</sub> O <sub>3</sub> /Fe <sub>2</sub> O <sub>3</sub> %			1.89	2.70		1.92	
CaO %		41.79	43.19	40.19		46.68	<b>42.62</b>
MgO %		2.50	3.66	1.66		3.47	<b>3.05</b>

*Carbonate:* Calcium carbonate (79% of average world calcrete) is predominantly in the form of microcrystalline calcite with Goudie (1972) only reporting two known occurrences of aragonitic calcrete. The mean world value for CaO of 42.62% compares almost exactly with the mean world figure for limestone in general (Clarke, 1924 in Goudie, 1972).

Generally MgCO<sub>3</sub> contents are low, but may locally be high (e.g. 34.9% and 40.21% MgCO<sub>3</sub> reported from Keimoes and Etosha)(Von Backstrom, 1964 and Gevers, 1930 in Goudie, 1972). Depending on the author the

distinction between high- and low-Mg calcites is taken as 4 or 8 mol%  $\text{MgCO}_3$  (Watts, 1980). The low  $\text{MgCO}_3$  content is attributed to the higher solubility of  $\text{MgCO}_3$  over  $\text{CaCO}_3$  and the supposition that it may therefore be preferentially leached from a profile under conditions of good drainage. Under situations of poor drainage  $\text{MgCO}_3$  and other soluble salts may accumulate along with  $\text{CaCO}_3$ . Indeed, in Libya there appears to be a significant +0.62 correlation between water soluble salt content of a calcrete (as determined by dissolution of powdered calcrete in deionised water) and its  $\text{MgCO}_3$  content (Goudie, 1972).

Early work by Goudie (1972) indicates that there is no correlation between the groundwater geochemistry and the calcrete composition. As a simplistic analogy Bond (1946 in Goudie, 1972) compares calcrete formation to the formation of nearly pure  $\text{CaCO}_3$  scale in water cooling plants (and kettles) whatever the quality of the untreated water. In contrast, later work by Mann and Horwitz (1979) suggests that dolomite is more prevalent in areas where groundwater salinities are elevated.

*Silica:* After calcium carbonate the second most abundant constituent of calcrete is silica in the form of clastic quartz grains and as authigenic opaline or chalcedonic silica cement. Authigenic silica is a common feature of southern African calcretes and sufficient silica in a calcrete may warrant the name sil-calcrete. The source of the authigenic silica in calcrete has been variously attributed to: fluctuating groundwater, kaolinization of feldspars, serpentinisation, proximity to basalts, upward migrating silica rich solutions and downward percolating alkaline water (various authors in Watts, 1980). Watts (1980) discusses the preferred alternative of silica release on replacement of silicates by calcite. Silica shows an inverse solubility relationship with calcite; high pH's favouring calcite precipitation and silica solution and at low pH's the reverse being true. As calcrete formation proceeds, under fairly high pH conditions (pH~8 - 8.3, Goudie, 1972; pH=8.4, Kilham, 1985), silicates are replaced by calcite and the, now silica rich, pore fluids may migrate to areas of high salinity or free  $\text{CO}_2$ . Under conditions of high salinity or high free  $\text{CO}_2$  the corresponding decrease in pH will cause silica precipitation. Silicification is usually only a feature of the more mature calcretes and tends to occur in the lower levels of these calcretes.

There is some relationship between the stage of calcrete development and its silica content: Young calcretes have a high silica/calcite ratio due to the high percentage of sand and rock fragments; in more mature calcretes the ratio is more equated as a result of calcite accumulation and replacement; in old calcretes the silica/calcite ratio may again be high due to the deposition of amorphous silica and weathering/solution of the carbonate fraction of the calcretes.

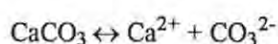
*Clay Minerals:* Clay minerals detected in calcretes include palygorskite, sepiolite, montmorillonite, illite and chlorite. Palygorskite and sepiolite are the most common and may account for in excess of 80% of the total clay mineral content; these two clay minerals are also most commonly found in the more mature calcretes while montmorillonite occurs in the immature calcretes (Watts, 1980). The presence of montmorillonite is important to exploration because of its high cation exchange capacity and its ability, therefore, to carry ore related metals. The calcrete environment is especially conducive to higher cation exchange capacity since the ability of montmorillonite to adsorb cations rises with pH (Levinson, 1974). There seems to be consensus that palygorskite and sepiolite are neoformational minerals and their almost ubiquitous presence suggests that they play an integral role in the formation of calcretes. Illite and chlorite are thought to be dominantly detrital, whereas kaolinite may be authigenic after feldspar. Montmorillonite may be detrital or authigenic after illite or glauconite (Watts, 1980).

## 2.5. PHYSICAL CHEMISTRY OF CARBONATE AND METAL MOBILITY

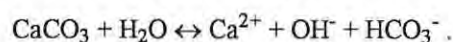
Calcrete is formed by the precipitation of  $\text{CaCO}_3$ ; the following section discusses the solubility  $\text{CaCO}_3$  of and expected metal mobility in the calcrete environment. Deposition of calcium carbonate is controlled primarily by equilibrium in the reaction (Krauskopf, 1979)



Factors influencing this equilibrium are pressure, pH, temperature and concentration which will be considered below. Before considering the effects of pH, temperature etc. let's look at the solubility of calcium carbonate in *pure* water where  $\text{CaCO}_3$  dissociates according to



Tables given by Krauskopf (1979) show that the solubility product of calcite, the most common carbonate in calcretes, is  $10^{-8.3}$  from which one can easily calculate the solubility of  $\text{CaCO}_3$  \*. However,  $\text{CO}_3^{2-}$  hydrolyzes in water and the situation is complicated by the following reaction :-



Solving for this equation reveals that, at temperatures near  $25^\circ\text{C}$ , the solubility of calcite ranges from about 10 to 50 mg/l depending on the degree of saturation with  $\text{CO}_2$ . The pH calculated for the above situation would be 8.4.

### 2.5.1. Effect of pH

Consider, firstly, equation 1 above and Figure 4 which illustrates the concentrations of the various carbonate species at differing pH's.

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\*  $K_{sp} = 10^{-8.3} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = [\text{Ca}^{2+}]^2$

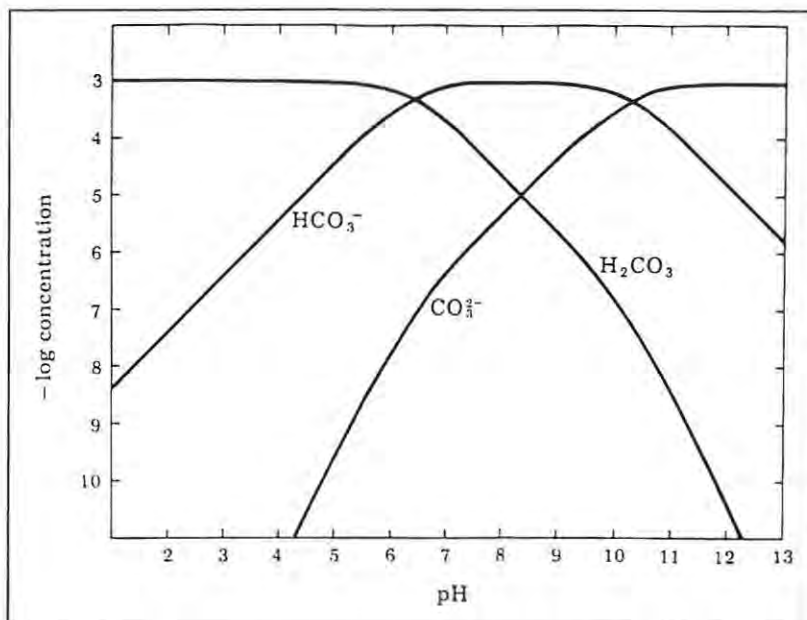


Fig 4: Concentrations of carbonate species at 25°C, in solutions with total dissolved carbonate = 0.001M (from Krauskopf, 1979).

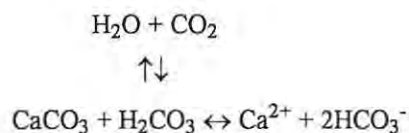
At low pH, where most dissolved carbonate exists as  $\text{H}_2\text{CO}_3$ , the forward reaction in equation 1 is favoured and carbonate is dissolved. At high pH the reverse reaction is favoured and calcium carbonate is precipitated. This reverse reaction is a result of the preferred reaction of the  $\text{OH}^-$  with the stronger acid,  $\text{H}_2\text{CO}_3$ , rather than the weak acid  $\text{HCO}_3^-$ .

### 2.5.2. Effect of Temperature

Most salts are more soluble at higher temperatures, but some carbonates and sulphates display the opposite behaviour viz. decreasing solubility with increasing temperature. In addition to this effect is the effect that temperature has on  $\text{CO}_2$  solubility. Gases are more soluble in cold water than in warm water and the increased solubility of  $\text{CO}_2$  at lower temperatures drives equation 1 to the right (because  $\text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{H}_2\text{CO}_3$ ) and calcium carbonate dissolves. In general, the solubility of carbonates is much more influenced by the change in the solubility of  $\text{CO}_2$  than by the temperature coefficient of the solubility itself.

### 2.5.3. Effect of $\text{CO}_2$ Partial Pressure

The partial pressure of  $\text{CO}_2$  plays an important role in calcium carbonate solubility and equation 1 is very sensitive to changes in the amount of dissolved  $\text{CO}_2$ . As already discussed above temperature affects  $\text{CO}_2$  solubility and hence its partial pressure in solution. Any process that increases the amount of  $\text{CO}_2$  available to the solution makes more  $\text{CaCO}_3$  dissolve; anything that decreases the amount of  $\text{CO}_2$  causes  $\text{CaCO}_3$  to precipitate. Equation 1 is affected by  $\text{CO}_2$  partial pressure in the following manner:-



In the process of photosynthesis plants may remove  $\text{CO}_2$  from the soil and so reduce the solubility of calcium carbonate. Some roots may also create a micro-environment of high  $\text{CO}_2$  partial pressures around their roots resulting in calcite solution. Decay of organic matter in the presence of air or aerated water gives  $\text{CO}_2$  in large amounts and hence makes  $\text{CaCO}_3$  in the vicinity more soluble.

#### 2.5.4. Calculated Metal Mobility

Theoretical considerations of the mobility of metals in the geochemical environment are many, but none offer a final solution. The diversity of these environments and the factors affecting them means that there will always be disparities between theoretical estimations of relative mobility and observed mobilities. Probably one of the most widely used works on element mobility is that of Andrews-Jones (1968, in Levinson, 1974) which is an empirical estimation, but based upon theoretical considerations of Eh and pH. The calcrete environment is an alkaline one (pH typically 8.4) and therefore the fourth column of Table 4 is relevant here.



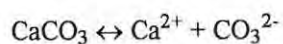
Table 4

Relative mobilities of the elements in the secondary environment (from Levinson, 1974  
after Andrews-Jones, 1968)

RELATIVE MOBILITIES	ENVIRONMENTAL CONDITIONS			
	Oxidizing	Acid	Neutral to Alkaline	Reducing
VERY HIGH	Cl, I, Br S, B	Cl, I, Br S, B	Cl, I, Br S, B Mo, V, U, Se, Re	Cl, I, Br
HIGH	Mo, V, U, Se, Re Ca, Na, Mg, F, Sr, Ra Zn	Mo, V, U, Se, Re Ca, Na, Mg, F, Sr, Ra Zn Cu, Co, Ni, Hg, Ag, Au	Ca, Na, Mg, F, Sr, Ra	Ca, Na, Mg, F, Sr, Ra
MEDIUM	Cu, Co, Ni, Hg, Ag, Au As, Cd	As, Cd	As, Cd	
LOW	Si, P, K Pb, Li, Rb, Ba, Be Bi, Sb, Ge, Cs, Tl	Si, P, K Pb, Li, Rb, Ba, Be Bi, Sb, Ge, Cs, Tl Fe, Mn	Si, P, K Pb, Li, Rb, Ba, Be Bi, Sb, Ge, Cs, Tl Fe, Mn	Si, P, K Fe, Mn
VERY LOW TO IMMOBILE	Fe, Mn Al, Ti, Sn, Te, W Nb, Ta, Pt, Cr, Zr Th, Rare Earths	Al, Ti, Sn, Te, W Nb, Ta, Pt, Cr, Zr Th, Rare Earths	Al, Ti, Sn, Te, W Nb, Ta, Pt, Cr, Zr Th, Rare Earths Zn Cu, Co, Ni, Hg, Ag, Au	Al, Ti, Sn, Te, W Nb, Ta, Pt, Cr, Zr Th, Rare Earths S, B Mo, V, U, Se, Re Zn Co, Cu, Ni, Hg, Ag, Au As, Cd Pb, Li, Rb, Ba, Be Bi, Sb, Ge, Cs, Tl

Vermaak (1984) conducted a thermodynamic study of metal mobilities in a carbonate environment, the gist of which is presented here.

The solubility of calcite is governed by the reaction:-



for which

$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 10^{-8.3}$$

The standard free energy of the above reaction is:-

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= [\Delta H(\text{Ca}^{2+}) + \Delta H(\text{CO}_3^{2-}) - \Delta H(\text{CaCO}_3)] - T[S(\text{Ca}^{2+}) + S(\text{CO}_3^{2-}) - S(\text{CaCO}_3)] \\ &= +11\,520.275 \text{ cal/mol}\end{aligned}$$

where

$\Delta G$  = Standard free energy of the reaction

$\Delta H$  = Enthalpy of formation

$\Delta S$  = Entropy

$T$  = Temperature in Kelvin

A chemical reaction is in equilibrium when  $\Delta G = 0$ . Negative values of  $\Delta G$  indicate that reactions tend to the right whilst positive values indicate reactions proceed to the left. The above reaction therefore proceeds to the left at 1 atmosphere and 25°C and calcium carbonate tends to precipitate.

Considering now the situation where calcite is in equilibrium with pure water and the system is open to  $\text{CO}_2$  the following reactions apply:-



Dissolution of calcium carbonate



Dissociation of carbonic acid



Dissociation of bicarbonate ion



Ionic dissociation of water



Equation of hydration

Taking equation 6:-

$$[\text{H}_2\text{CO}_3]/(\text{P}_{\text{CO}_2} * 1) = 10^{-1.5} \quad (7)$$

Using a representative  $\text{P}_{\text{CO}_2}$  of  $10^{-3.5}$  atm equation 6 can be solved for  $[\text{H}_2\text{CO}_3]$ :-

$$[\text{H}_2\text{CO}_3] = 10^{-5.0} \quad (8)$$

Equations 3, 4 and 5 can be re written as:-

$$[\text{HCO}_3^-] = (10^{-6.4} \times 10^{-5})/[\text{H}^+] = 10^{-11.4}/[\text{H}^+] \quad (9)$$

$$[\text{CO}_3^{2-}] = (10^{-10.3} \times [\text{HCO}_3^-])/[\text{H}^+] = 10^{-21.7}/[\text{H}^+]^2 \quad (10)$$

$$[\text{OH}^-] = 10^{-14.0}/[\text{H}^+] \quad (11)$$

and equations 2 and 10 can be combined to solve for  $[\text{Ca}^{2+}]$ :-

$$[\text{Ca}^{2+}] = 10^{13.4}/[\text{H}^+]^2 \quad (12)$$

By substituting a pH of 8.4 into equation 12

$$[\text{Ca}^{2+}] = 10^{-3.4} \quad (\text{see footnote } ^3) \quad (13)$$

Now that the groundwork has been done we can consider ore-related elements dispersed in a soil profile. Carbonate rich solutions coming into contact with such elements will cause the precipitation of metal carbonates at the right pH conditions. Calcrete formation can trap such precipitates and preserve the anomaly from further dispersion. The probability of metal-carbonate precipitation can be viewed in a superficial way by deriving the metal activities in the same manner as was done for  $\text{Ca}^{2+}$  above (equation 13). To do this we use the solubility constants for some of the carbonates at 25°C as given by Krauskopf (1979)

$\text{BaCO}_3$ : $K=10^{-8.3}$	$\text{NiCO}_3$ : $K=10^{-6.9}$
$\text{CoCO}_3$ : $K=10^{-10.0}$	$\text{ZnCO}_3$ : $K=10^{-10.0}$
$\text{PbCO}_3$ : $K=10^{-13.1}$	$\text{CdCO}_3$ : $K=10^{-13.7}$

By using a pH of 8.4, as in the  $\text{Ca}^{2+}$  example the activities can be calculated as:-

$[\text{Ba}^{2+}] = 10^{-3.4}$	$[\text{Ni}^{2+}] = 10^{-2.0}$
$[\text{Co}^{2+}] = 10^{-5.1}$	$[\text{Zn}^{2+}] = 10^{-5.1}$
$[\text{Pb}^{2+}] = 10^{-8.2}$	$[\text{Cd}^{2+}] = 10^{-8.8}$

These activities give some idea of expected relative mobilities in a carbonate environment.

$\text{Ni} > \text{Ca}, \text{Ba} > \text{Zn}, \text{Co} > \text{Pb} > \text{Cd}$	
Mobile	Immobile

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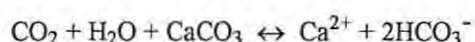
<sup>3</sup>Square brackets thus [ ] denotes activity, but for dilute geological solutions it can be taken to approximate the concentration.

This is somewhat in opposition to mobilities suggested by Andrews-Jones (1968, in Levinson, 1974), Table 4, but it does highlight the immobility of Cd which is exactly what Garnett (1983) observes at Putsberg, but is not suggested by Andrews-Jones (*ibid.*).

## 2.6. MODELS OF CALCRETE FORMATION

In areas where precipitation exceeds evapotranspiration there is a tendency for carbonate to be leached from soils or rock and to ultimately find its way into the oceans. In semi-arid environments, however, such leaching is inadequate for carbonate to be removed from the system and it accumulates in the soil/rock profiles. Models of calcrete formation are dependent upon these translocation and accumulation processes (Goudie, 1983).

Calcrete formation is essentially a function of the solution and precipitation of carbonate according to the following reaction:-



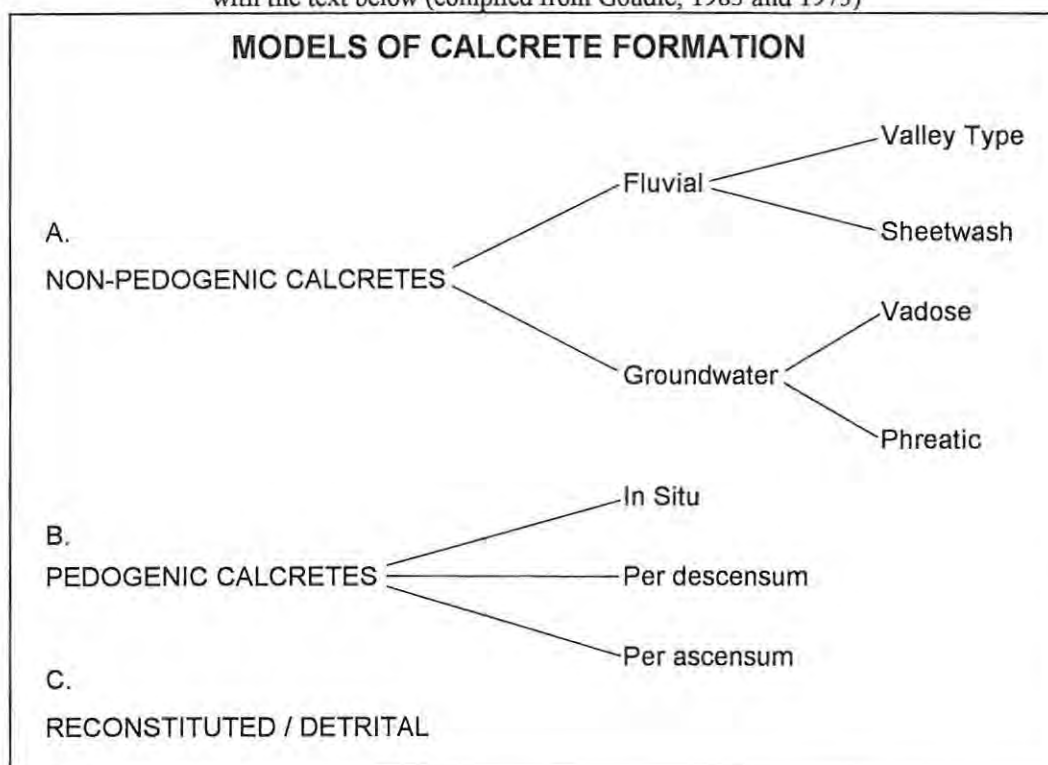
Dissolution of carbonate (reaction proceeds to right) may be caused by increased  $\text{CO}_2$  partial pressure, decreased temperature or low pH. Precipitation (reaction proceeding to the left) may be caused by factors such as a decrease in  $\text{CO}_2$  partial pressure, evaporation, the common ion effect<sup>4</sup>, biological activities or by freezing (Goudie, 1983). Figure 5 is a schematic representation of the various models of calcrete formation that will be discussed in the text.

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<sup>4</sup>The addition to a saturated solution of one salt a quantity of another soluble salt that possesses an ion in common with it leads to the precipitation of the first salt

Figure 5

Schematic representation of the various models of calcrete formation to be read in conjunction with the text below (compiled from Goudie, 1983 and 1973)



#### *A. Non-Pedogenic Calcretes:-*

In this model carbonate cement has been introduced into the host soil or sediment by "absolute" accumulation of carbonate from a source removed from the site of deposition.

*Fluvial:* The formation of calcrete in valleys/drainages is closely associated with uranium favourability (to be discussed in a later section). The sheetwash model envisages the lateral transport of chemically charged surface waters in sheets across low relief geomorphic surfaces to give precipitation in laminae as a result of either infiltration into underlying materials or evaporation at the surface. The sheetwash model has found support in some circles (described in Goudie, 1973), but objections are numerous (Goudie, 1973 pg. 124) and the model is probably no longer seriously regarded.

*Groundwater:* Probably the most common type of non-pedogenic calcrete in which calcite is externally derived from laterally moving groundwater. This type of calcrete also has high uranium favourability. Accumulation of carbonate in the vadose zone may occur through processes such as evaporation at the capillary fringe. Capillary action, once a favoured mechanism for water rise, is no longer considered viable as the force is too weak and would not be able to operate in coarse clastics (e.g. Kalahari sands). The suction force created by evapotranspiration is much stronger and a more likely mechanism.

Mann and Horwitz (1979) proposed a model for the formation of calcretes in the phreatic zone. Their four stage model (Fig 2) deals not so much with how carbonate precipitates in the phreatic zone, but rather with how the calcrete arrives on surface:-



1. Formation of a broad drainage line with an alluvial fill and a shallow groundwater system.
2. Lateral transport of carbonate in the groundwater and precipitation below the water table possibly due common ion effects, mixing or pH changes.
3. Carbonate precipitation in the phreatic zone forms pods and domes which are pushed upwards as further carbonate precipitates below the water table. The pods may coalesce to form larger domes and displace the overlying alluvium and colluvium.
4. A phase of maturation in which older carbonate lifted above the water table is continually displaced upwards, where it may be dissolved, and is replaced by the production of younger carbonate beneath - a steady state equilibrium.

#### *B. Pedogenic Calcretes:-*

Pedogenic calcretes form when authigenic cement is concentrated essentially vertically within the soil profile, primarily by "relative" accumulation.

*In Situ:* The in situ model involves the relative accumulation of carbonate due to the alteration, in place, of suitable bedrock, selective removal of non-carbonate fractions or by solution and reprecipitation causing a reconstitution of the original rock to produce "case-hardening". These duricrusts are therefore residual products of weathering.

*Per Descensum:* Downward concentration of carbonate derived from dust, rainfall, vegetation litter and shells creates an illuvial calcrete (Fig 7). Dust provides a larger input than might be thought possible; for instance 14 sites east of the Rocky Mountains yielded monthly rates of dust deposition of between 17 and 459kg.ha<sup>-1</sup>. The CaCO<sub>3</sub> content of the dust can be as high as 40% in some Israeli examples (Goudie, 1973). Staying in Israel, Yaalon (1964 in Goudie, 1973) has shown that precipitation adds as much as 73kg.ha<sup>-1</sup>.yr<sup>-1</sup> of carbonate to the soil. Vegetation too may yield considerable quantities of carbonate to the soil profile. The leaves of *Colophospermum mopane*, for instance, may have an ash residue of 50% calcium (De Winter et al., 1966 in Goudie, 1973) and litter fall of the steppe vegetation communities may return 20-230kg.ha<sup>-1</sup>.yr<sup>-1</sup> of calcium to the soil (Rodin and Bazilevich, 1967 in Goudie, 1973).

*Per Ascensum:* See Figure 8. Also referred to, by Goudie (1973), as the "capillary rise from soil model". This serves to distinguish this model from that involving carbonate solutions rising from the groundwater. Groundwater plays little or no part in the per ascensum model. The model may be summarised thus (Price, 1933 in Goudie, 1973):-

"Solutions of minerals leached from the soil descend to low levels in cool rainy periods, but ascend by capillarity in dry periods. Evaporation in the soil deposits the minerals. Gradual leaching lowers the zone of accumulation; erosion lowers the top of the soil. Sinking of the water table with progressive entrenchment of streams aids descent of leaching and accumulation of thick caliches."

As mentioned above, a major objection to the use of capillarity is its limited effectiveness in sandy soils.

Klappa (1983) presented a process-response model for the formation of pedogenic calcretes involving both inorganic and organic soil-forming processes. Biological processes are such an important part of his model that he goes so far as to say that "accumulations of calcium carbonate which occur in materials unaffected by biological processes are *not* pedogenic calcretes."

His model involves what he terms a "pedodiagenetic cycle" (Fig 6) in which the formation of pedogenic calcrete involves both pedogenic and diagenetic processes. The reason for coining the hybrid term "pedodiagenesis" is that pedogenesis does not generally include lithification of the soil, and diagenesis usually excludes soil-forming processes as well as weathering by inorganic agencies. The pedodiagenetic cycle is a continuously operating one of six stages; some stages may be repeated or reversed and others omitted:-

1. Preparation of host material: Mechanical and biophysical disintegration, physicochemical dissolution and biochemical weathering of consolidated bedrock.
2. Soil formation: Vertical movement of moisture and biological activity form layered horizons.
3. Accumulation of calcium carbonate:
4. Profile development: from powdery through glaebular to massive sheet calcrete (reflected in a change of the plant species from one with deep vertical tap roots to species with horizontal branching roots).
5. Induration: Accumulation of calcium carbonate reaches a point where biological activity no longer viable - pedogenic processes diminish and diagenesis takes over.
6. Reworking: in which lower plant species (lichen, algae, bacteria) replaced by higher species which penetrate, dissolve and fracture the indurated hardpan eventually forming a reworked, recemented, breccia-conglomeratic calcrete hardpan.

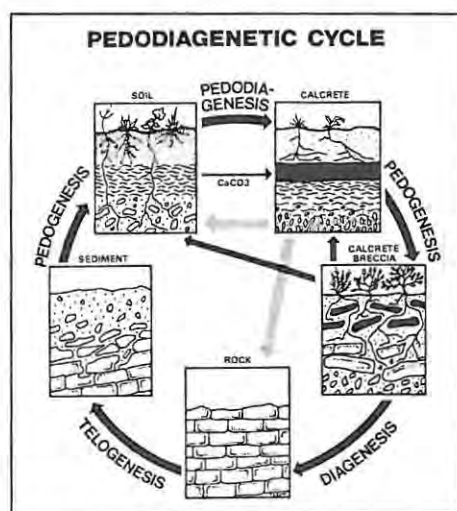


Fig 6: The pedodiagenetic cycle; best visualised beginning at the bottom beginning with "rock" (from Klappa, 1983)

*C. Reconstituted / Detrital Calcretes:-*

The origin of these calcretes involves the lateral transportation and redeposition of weathered fragments of calcrete which are then recalcretised by essentially in situ processes (Fig 9).

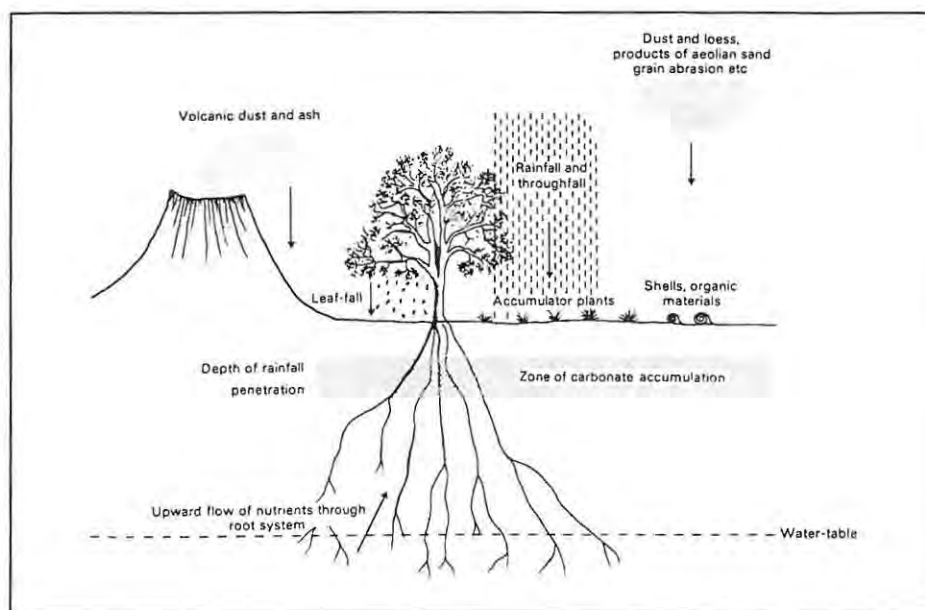


Fig 7: Per descensum model of calcrete formation (from Goudie, 1983)

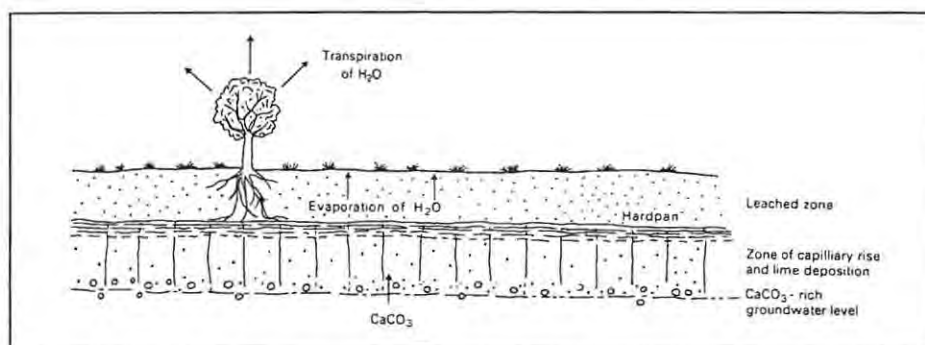


Fig 8: Per ascensum model of calcrete formation (from Goudie, 1983)

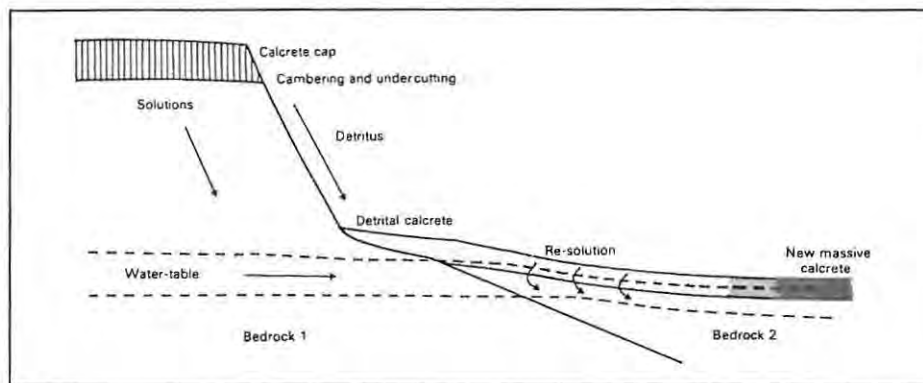


Fig 9: A model of calcrete formation by solution and disintegration of an upper calcrete (from Goudie, 1983)

## 2.7. AGE OF CALCRETES

Most calcretes range in age from upper Tertiary to Recent (Reeves, 1976 in Netterberg, 1978) while most of the world's thick and massive calcretes appear to be of Tertiary age, but are also known from much older deposits such as the Carboniferous Old Red Sandstone (Wright et al., 1993).

Many of the calcretes in southern Africa are associated with artefacts and fossils and can therefore be classified according to their maximum possible age into five categories (Netterberg, 1969b):-

1. Pre-Pliocene
2. Pliocene
3. Lowermost Upper-Pleistocene
4. Uppermost Upper-Pleistocene
5. Recent

Of these the Pliocene (Kalahari Limestone) and the Upper Pleistocene calcretes appear to be the most common (Netterberg, 1978). It should be noted, however, that most S.A. calcretes are considered fossil while some Australian valley calcretes are still forming today.

## 2.8. GEOMORPHIC SIGNIFICANCE OF CALCRETE DEVELOPMENT

### 2.8.1. Calcrete Thickness

As stated before calcretes form a chemical and physical barrier to the surficial expression of underlying mineralisation. The thicker the profile or the more mature it is (higher  $\text{CaCO}_3$  content) the more difficult it is for metal anomalies to attain a surface expression. The thickest recorded calcrete profiles are from the Molopo River valley in South Africa where calcrete attains thicknesses of 60m; clearly there will not be much of an anomaly poking through such thicknesses of calcrete. Table 5 shows the total thickness of some world calcretes while Table 6 shows the maximum recorded thickness of the indurated hardpan portion of the profile.

Table 5  
Maximum thickness of calcrete profiles (from various  
sources listed in Goudie (1973) table 15)

Location	Thickness (m)
Molopo Valley (southern Africa)	60
Millstream (Australia)	47
Llano Estacado (USA)	45
Lichtenburg (South Africa)	38
Uaso Nyiro (Kenya)	35
Gefara (Libya)	20
Argentina	20
Gefara (Tunisia)	15
Channel Islands (Los Angeles)	13
Wajir (Kenya)	12
Australia	10
Algeria	10
Spain	10
Venezuela	10
Puerto Rico	10
Wiluna (Western Australia)	10
Thar Desert (India)	8
Cyrenaica (Libya)	8
Yorke Peninsula (Australia)	7
Scotland (Old Red Sandstone)	5
Nevada (USA)	4.6



Table 6  
Indurated hardpan calcrete thickness (from various sources  
listed in Goudie (1973) table 19)

Location	Thickness
New Mexico	10m
Kalahari	10m
Alicante and Murcia (Spain)	20-30cm
Cyprus	20cm
Tripolitania (Libya)	15-35cm
Valensole Plateau (France)	12cm
Morocco	<10cm
Algeria	5-10cm

Figure 10 shows the distribution of the thickest calcretes in southern Africa (and the world). The association of thick calcrete with drainage is clear. This may be due to the fact that the Kuruman and Molopo Rivers drain carbonate areas and the water table is closer to surface in these drainages.

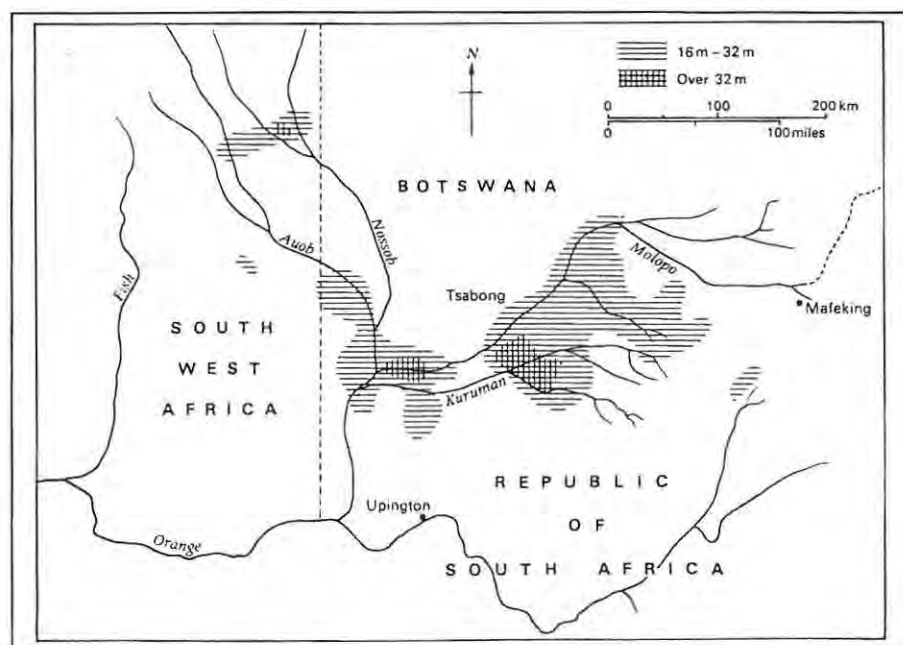


Fig 10: Distribution of the thickest calcrete in southern Africa (from Goudie, 1973)

### 2.8.2. Karstic Features and Drainage

Calcrete, because of its high carbonate content frequently displays a whole series of karstic landforms with unusual drainage patterns, subsurface flow and closed depressions (Goudie, 1973) - factors affecting geochemical exploration by means of stream sediment sampling. The karstic nature (dolines and solution pipes) of some calcrete surfaces has been used to explain the extremely low drainage densities over these areas. In Cyprus, for instance, drainage densities over calcrete are of the order of  $1\text{km.km}^{-2}$ ; whilst other nearby rock types have

drainage densities of  $12.4$  to  $18.6 \text{ km.km}^{-2}$  (Goudie, 1973). Where massive, thick and indurated calcrete overlies less consolidated material sinkholes may form. The Kalkrand area of Namibia for instance shows a pattern of internal drainage into dolines which is in strong contrast to the normal dendritic pattern developed on quartzites in the same area (Fig 11).

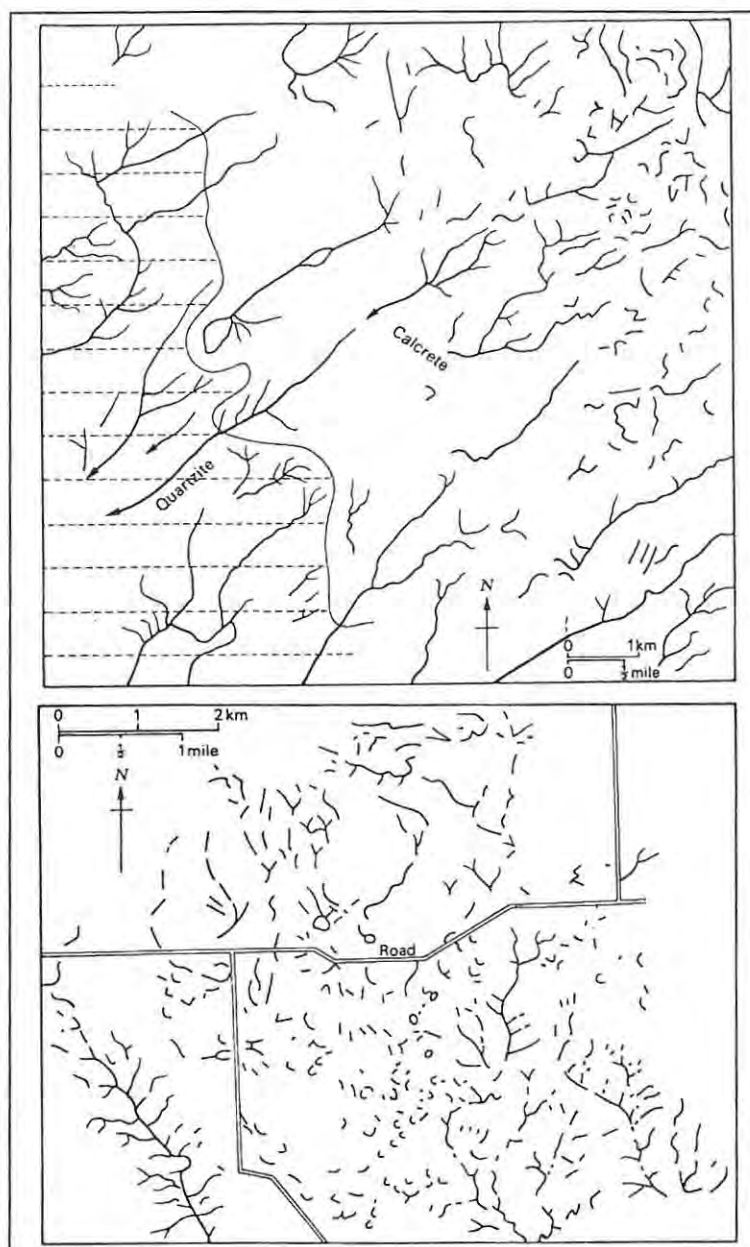


Fig 11: Drainage pattern near Kalkrand, Namibia (top). Note the centripetal drainage pattern towards dolines on the calcrete. Similar patterns are observed on the calcrete overlying the Ogallala Formation of the US High Plains (bottom, Union County, Texas) (from Goudie, 1973).

Goudie (1973) has calculated that on parts of the calcreted High Plains of the USA closed depressions form between 16 and 22% of the surface area at a frequency of about  $0.5/\text{km}^2$ . Between Delareyville and Vryburg (South Africa) the frequency of closed depressions is between  $1.2$  and  $1.6/\text{km}^2$ . Ore related metal dispersion trains are

extremely short in calcrete environments (e.g. Putsberg, see below), but the problem is compounded by the nature of the drainage over calcrete terrains with thick calcrete profiles. It is still possible, however, that the depressions themselves with their centripetal drainage could form loci for the concentration of any ore related metals in the area, or kimberlitic heavy minerals for that matter. Orientation surveys to investigate the possibility of such concentration would need to be conducted and the mode of formation of the depressions established (deflation?, solution?, salt weathering?).

### 2.8.3. Pseudo-Anticlines and Substrate Disruption

The force associated with the volumetric expansion of crystallizing calcite is sufficient to split grains of quartz sand (Rothrock, 1925) which means forces of the order of  $12\ 600$  to  $15\ 100\text{N.cm}^{-2}$  ( $18\ 000$  to  $22\ 000\text{psi}$ ). Displacive calcite growth in calcrete can produce brecciation of the host material and internal buckling of mature calcretes producing structures known as pseudo-anticlines (Fig 12)(or tepee structures on a smaller scale). In some cases the horizontal component of expansion in pseudo-anticlines may be as much as 25 to 30% (Watts, 1978). In the Fitzroy Basin of Western Australia the pseudo-anticlines form groups of low ridges 1.7 to 3.3m high, 10 to 45m across and up to several hundred metres in length; slabs of bedrock on the flanks may be tilted up to angles as great as  $30^\circ$  (Goudie, 1973).

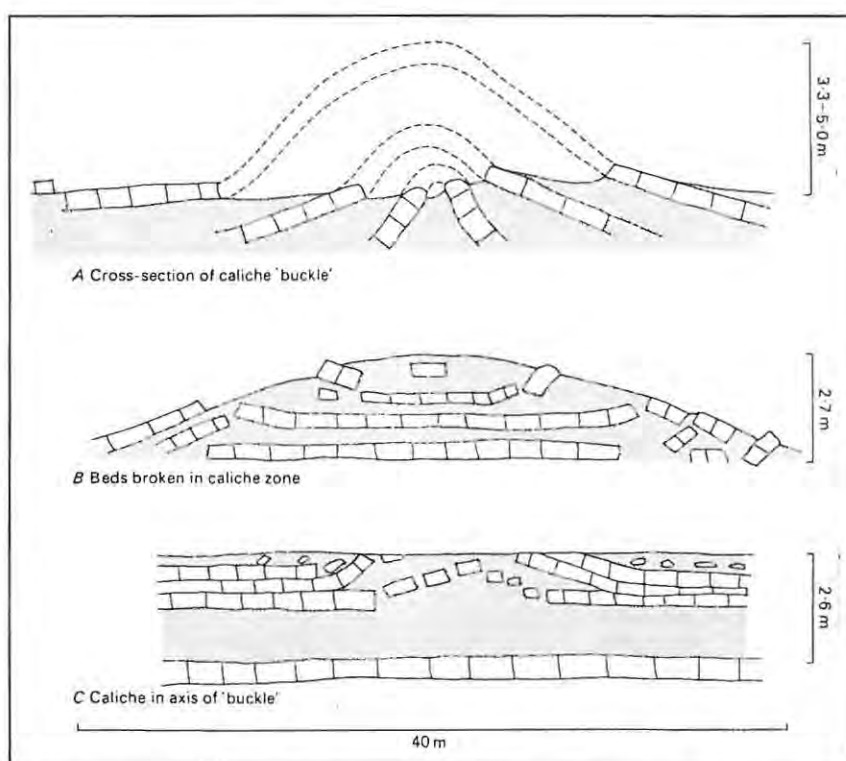


Fig 12: Calcrete buckles and pseudo-anticlines from the USA (from Goudie, 1973 after Price, 1925).

The brecciation and disruption of the host material would be expected to play an important role in the liberation of potentially metal bearing clastic fragments to the dispersive environment (e.g. Surprise Mine, see below). Fragments of brecciated gossan picked from calcrete have proved to be useful in exploration at Putsberg.

### 3. CHEMICAL DISPERSION AND EXPLORATION MODELS

Although geological, geomorphological and environmental conditions are different for each location such that the geochemical response to mineralisation is always unique, there are, nonetheless, many similarities in dispersion characteristics over extensive regions. The purpose of geochemical dispersion and exploration models is to attempt to synthesize these characteristics to illustrate the nature and origin of the surface expression of mineralisation. These models may then be applied in a predictive capacity to anticipate mechanisms of dispersion, select appropriate sampling media and estimate the underlying source and significance of any anomalies (Butt and Zeegers, 1992).

The landscape geochemistry approach of Fortesque (1975) has been modified by Butt and Zeegers (1992) to classify geochemical terrains into areas of similar a) relief, b) climate and c) modification to pre-existing profile. This classification system seems to be becoming more widely recognised and used, not only in academia, but also in industry. Where possible the examples quoted in this work will be assigned coded classifications after Butt and Zeegers (1992).

#### *a) Relief*

Broadly, relief is classified into terrains of i) low to moderate relief and ii) moderate to high relief. Except in extremely arid regions local and regional relief control the degree of preservation of the profile such that areas of low to moderate relief will be dominated by chemical weathering processes while areas of moderate to high relief will be dominated by physical erosion (all other factors being the same).

#### *b) Climate*

The present climate is of fundamental importance in determining the nature of the active geochemical dispersion processes in any given area. Strictly speaking it is the climate of the soil itself that is of importance, but this is so subject to local effects (slope, drainage) that the regional effects of atmospheric climate are considered adequate. The two climatic factors having most influence on the surficial environment are temperature and moisture which are in turn determined by factors such as the relative distribution of the continents and oceans, latitude, altitude, physiography and aspect. Temperature influences the rate of reactions which increase two- or threefold with every 10°C rise in temperature. Moisture is significant both in its involvement in most chemical reactions, either as a reagent itself or as a medium in which reactions can occur, and for its role in physical erosion.

The most widely used climatic classification is that of Köppen (1936, in Butt and Zeegers, 1992) which combines average annual temperature and precipitation characteristics with soil and vegetation distributions which is not always satisfactory for pedological purposes. Five major groups are designated by the capital letters A to E, subgroups are expressed with another letter and a third letter is used to represent temperature and precipitation variations. The Köppen classification system is laid out in Table 7, climatic regions of pedogenetic significance to

tropical and sub-tropical landscapes are illustrated in Table 8 and the distribution of Köppen regions is shown in Figure 9.

Table 7

The Köppen classification system of world climates (from Van Berkel, 1982 after Strahler, 1975).

The 5 major climatic regions	Subgroups	Annual temperature and precipitation quantifiers
<p><i>A Tropical climates:</i> Avg. temp of every month is above 18°C. No winter season. Annual rainfall large and &gt; annual ppt.</p> <p><i>B Dry climates:</i> Potential evap. &gt; ppt on avg. throughout year. No water surplus ∴ no permanent streams.</p> <p><i>C Warm temperate climates:</i> Coldest month has avg temp &lt; 18°C, but &gt; -3°C; at least one month has avg temp &gt; 10°C. Have both summer and winter season.</p> <p><i>D Snow climates:</i> Coldest month avg temp &lt; -3°C; warmest month avg &gt; 10°C.</p> <p><i>E Ice climates:</i> Avg temp. of warmest month &lt; 10°C. No true summer.</p>	<p><i>S Steppe climate:</i> Semi-arid climate with 380-760mm/year rain at low latitudes. Applies only to B group.</p> <p><i>W Desert climate:</i> Arid climate. Most regions &lt; 250mm/year rain. Applies only to B group.</p> <p><i>f Moist:</i> Adequate ppt all months. No dry season. Applied to A, C and D groups.</p> <p><i>w Dry season in winter.</i></p> <p><i>s Dry season in summer.</i></p> <p><i>m Rainforest climate</i> despite short, dry season in monsoon type ppt cycle. Applies only to A climates.</p>	<p><i>a</i> With hot summer; warmest month &gt; 22°C. C and D climates.</p> <p><i>b</i> With warm summer; warmest month &lt; 22°C. C and D climates.</p> <p><i>c</i> With cool, short summer; less than 4 months &gt; 10°C. C and D climates.</p> <p><i>d</i> With very cold winter; coldest month &lt; -38°C. D climates only.</p> <p><i>h</i> Dry-hot; mean annual temp &gt; 18°C. B climates only.</p> <p><i>k</i> Dry-cold; mean annual temp &lt; 18°C. B climates only.</p>

Table 8

Climatic regions of pedogenetic significance in the tropics and subtropics (Young, 1976 in Butt and Zeegers, 1992)

Climatic region	Mean annual rainfall (mm)	Dry season months < 60 mm rain	Köppen equivalent	Natural vegetation	Biomass tonnes/hectare	Zonal soils
Rainforest	> 1800	0-2	Af; Am	Lowland tropical rainforest	300-1000	Leached ferrallitic soils; kaolinitic-gibbsitic; always moist.
Rainforest-savanna transition	1200-1800	2-6	Am	Semi-deciduous forest or forest-savanna mosaic and Asian monsoon forest;	-	Ferrisolic soils on intermediate-basic rocks, less leached than rainforest; top metre may dry out in dry season.
Moist savanna; two wet seasons	900-1200	3-5	Aw	Forest and grasslands	-	Ferrisolic soils on intermediate and basic rocks. Moderately weathered and leached
Moist savanna	900-1200	3-5	Aw, Cwa	Forest and grasslands	67-100	Ferruginous and ferrallitic soils, pH 5-6; kaolinitic some smectite. Base saturation 40-60%. Leached in wet season, dry to 1 m in dry season.
Dry savanna	600-900	6-8	Aw, Cwa	Grasslands with 5-50% tree cover	27-29	Ferruginous and ferrallitic soils, pH 6-7. Base saturation 60-90%. Less intense leaching. Dry to 2 m in dry season.
Semiarid (semi-deserts, steppes)	250-600	8-10	BSh	Xerophytic trees, perennial grasses.	6-10	Brown calcimorphic soils, sierozems, arenosols and lithosols. Carbonate accumulating in profile. Dry most of year.
Arid (deserts)	< 250	10-12	BWh	Bare ground commonly 50%. Xerophytic shrubs, often thorny.	-	Grey and red desert soils on alluvium. Lithosols, detritus on slopes. Dry most of year.
Tropical, high altitude (> 1600 m)	> 600	0-6	Cwb, Cwa	Evergreen forest, merging to grasslands and alpine at high altitudes	-	Humic latosols; podzolic at high altitudes.
Subtropical humid	> 900	0-3	Cfa	Deciduous woodlands	-	Leached ferruginous soils.
Mediterranean	400-800	2-6	Csa	Mixed forests	-	Red and brown earths; lateritic podzolics; terra rossa.



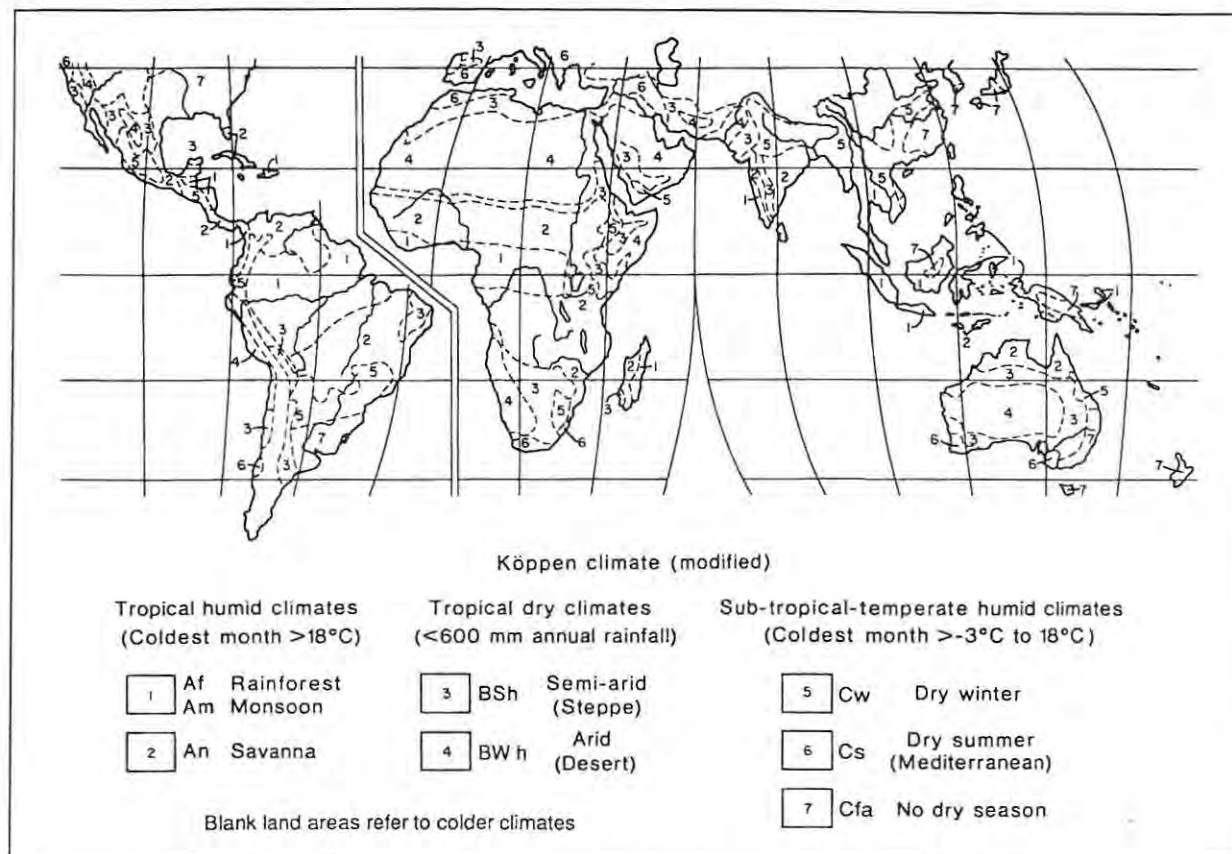


Fig 13: Modified Köppen climate map for the tropics and subtropics (from Butt and Zeeger, 1992)

*c) Modifications to the pre-existing profile*

Butt and Zeegers (1992) have subdivided this aspect of geochemical terrain modelling into 4 further sub-sections viz. i) *degree of preservation of the regolith profile*, ii) *recent alteration*, iii) *neoformation or accumulation of minerals* and iv) *presence and nature of the overburden*. Each of these four sections may be represented by a coded letter or number (Table 9).

- i) Degree of preservation of regolith profile: This determines the importance of geochemical and mineralogical characteristics inherited from previous weathering episodes.
- ii) Recent alteration: The (subjective) degree of alteration described in iii). Chemical alteration of the regolith may have taken place under the present climate or at some time since earlier deep weathering (i.e. after partial truncation of the pre-existing profile). This alteration may take the form of leaching or accumulation or neoformation of secondary minerals described in iii).
- iii) Neoformation or accumulation of minerals: These are consequences of the degree of leaching. This dissertation is concerned with cementation by calcium carbonates (code Ca).
- iv) Presence and nature of the overburden: "Semi-residual" in Table 9 refers to mixtures of residual and transported materials.

Table 9

Classification of geochemical dispersion models: Modifications to pre-existing profile within each climatic and relief zone (from Butt and Zeegers, 1992)

Present climate	Savanna (seasonally humid; Aw, Cwa) Rainforest (humid; Af, Am, Cwb) Warm arid (BSh, BWh) (Köppen classification, Table I.1-1)
<i>Modifications to pre-existing profile within each climatic zone.</i>	
Pre-existing profile	A: Mostly preserved B: Partly truncated C: Fully truncated
Recent alteration	0: Minor 1: Low 2: Moderate 3: Strong
Recent accumulation, cementation or neoformation	0: None Al: Al-oxides AS: Al-silicates Ca: Ca and Mg carbonates (calcrete) Gy: Gypsum Fe: Iron oxides Si: Silica (silcrete) Sm: Smectites
Overburden on pre-existing profile	0: None 1: Residual soil 2: Semi-residual 3: Transported
Examples: A 0 0 [0,1]: lateritic cuirasse, outcropping or beneath residual soil. B 1 Ca [3]: truncated profile, some recent alteration with pedogenic calcrete and transported overburden.	

Since calcrete forms almost exclusively in areas of low to moderate relief in semi-arid (BSh) to arid (BWh) terrains the first two descriptors in the classification of Butt and Zeegers (1992) are the same for all the examples discussed below; it is the modifications to the pre-existing profile that varies between the examples. Figure 4 illustrates, by way of comparison, the classification model of Butt and Zeegers (1989).

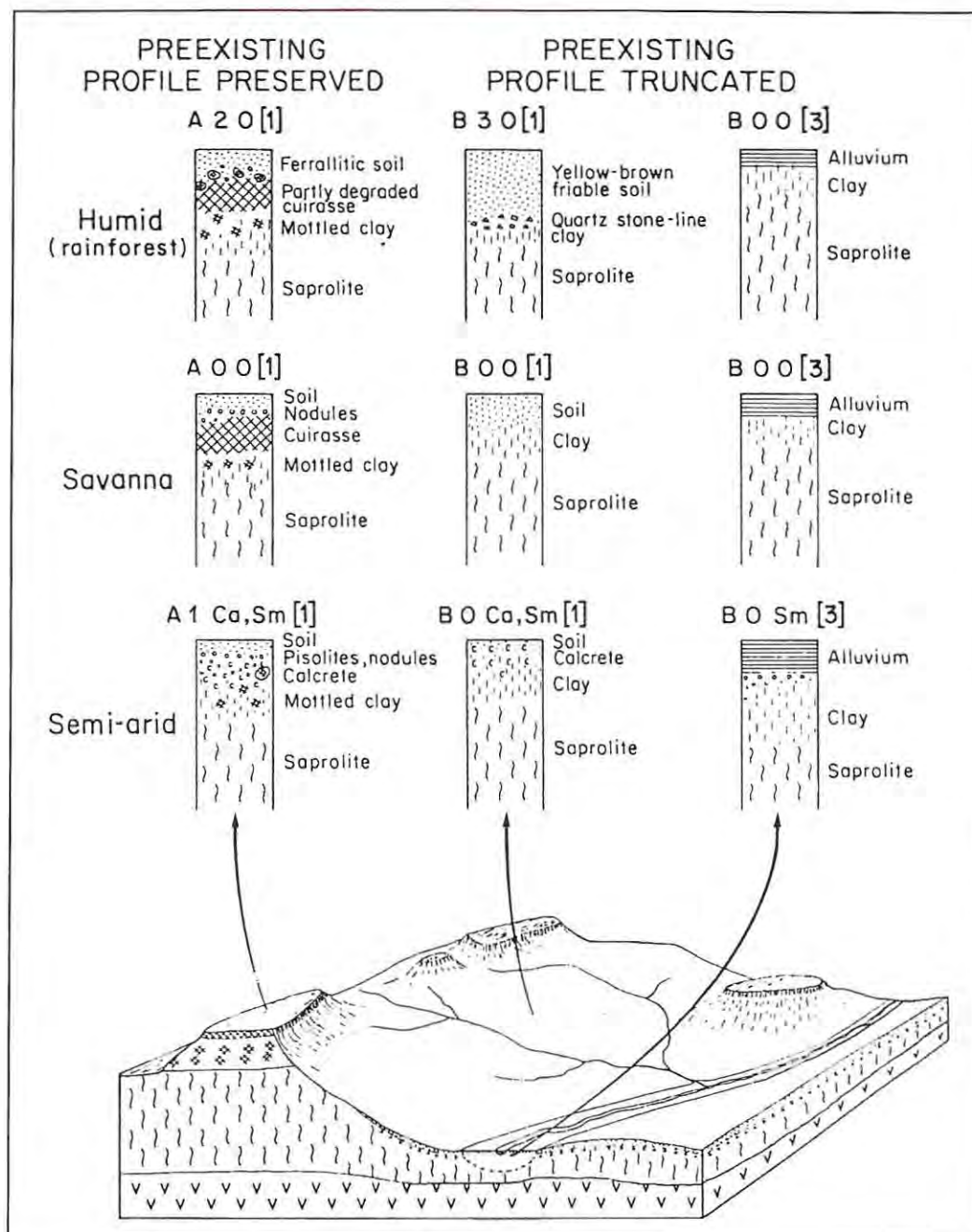


Fig 14: Comparison of some weathering profiles and models in a partly eroded, tropically weathered landscape (from Butt and Zeegers, 1992; Fig I.1-6).

The geomorphology and regolith of a region are the product of its weathering history and thus of the past and present processes of weathering and geochemical dispersion. These are very important parameters in the definition of the dispersion models and therefore in deciding the most effective means of exploring an area (Zeegers and Butt, 1992). Once the weathering and geomorphological environments have been identified the dispersion models and the geochemical response can be anticipated.

The geochemical response can be expressed in terms of the model codes defined earlier:-

$$\Sigma(R,H,M) = A > B > C$$

i.e. the size of the dispersion halo resulting from residual (R), hydromorphic (H) and mechanical (M) dispersion is larger where the pre-existing lateritic profile is preserved (A-type models) and smaller where the profile is truncated (B- and C-type models) (complications to this are the movement of the water table or redox fronts).

$$\Sigma(H,M) \text{ for models } (* 3 * 0,1,2) > (* 2 * 0,1,2) > (* 1 * 0,1,2)$$

i.e. the extent of geochemical dispersion in residual or semi-residual materials is proportional to the degree of leaching of the pre-existing profile under current or recent climatic conditions, although the resulting anomaly contrasts may be so suppressed as to be impractical for exploration. Note that where the recent alteration is one of calcretisation the opposite would be expected to be true; the greater the degree of carbonate accumulation the less the dispersion.

$$\Sigma(R,H,M) \approx 0 \text{ for models } * * * 3$$

i.e. where transported overburden is present above the weathering profile, dispersion haloes are rarely found at surface. Exceptions to this may be found where deep rooted plants tap anomalous metals at depth and deposit them as leaf litter at surface or where animal activity has brought material through the transported overburden. Some calcretes could be considered as "transported overburden" where they have formed by the *Per Descensum* model or where they are accumulations from lateral groundwater flow.

By assigning these codes to exploration areas we are forced to pay attention to the weathering and the geomorphology that govern geochemical dispersion and enable comparisons of areas with like codes.

## 4. SULPHIDE MINERALISATION IN CALCRETE TERRAINS

### 4.1. A-TYPE MODELS: PRE-EXISTING PROFILE MOSTLY PRESERVED

The presence of calcrete on completely preserved lateritic profiles has rarely been documented, but it is known to occur in Mauritania (Nahon et al., 1977 in Butt, 1992) and in south-western Australia.

In the Coolgardie region of south-western Australia calcrete plays an important role in the mechanical fragmentation and release of lateritic fragments to the surface. The abandoned Surprise mine, located 10km east of Coolgardie, is situated in an area of folded ultrabasic rocks with associated sill-like lenses of felsite. Most of the gold production came from mineralised actinolitic shear zones within the ultrabasics and from silicified fracture zones within the felsites (Mazzucchelli and James, 1966). Of interest to Mazzucchelli and James was the observation that analysis of the coarse surficial lateritic material or the coarse soil fraction (+840 $\mu$ m) gave higher As anomaly contrasts than the conventional -80 mesh material. Furthermore they believed that the introduction of calcium carbonate played an important part in the disintegration of the upper indurated laterite. This fragmentary surface horizon was then exposed to erosion and transportation by sheetwash and soil creep which produced a much wider As anomaly than the soil fractions. In this case there was no reported concentration of gold in the calcrete itself - merely the observation that calcrete formation played an important role in the dispersion of the anomaly, but in other areas of Western Australia gold is concentrated in calcrete in preference to the lateritic pisoliths (see section 5.1.3.).

### 4.2. B- AND C-TYPE MODELS: PRE-EXISTING PROFILE PARTLY OR WHOLLY TRUNCATED AND WITHOUT PH CONTRAST

In situations where the pH of soils and saprolite are alkaline throughout the profile, pedogenic calcrete deposited in such profiles will suppress the element concentrations and contrasts even further. However, providing that either the soil or the calcrete are residual, geochemical data is still valid (Butt, 1992).

#### 4.2.1. Pioneer Ni-sulphide Deposits, Western Australia (B 0 Ca 1)

(Cox, 1975).

The Ni-Cu sulphide deposits at Pioneer, Western Australia, 85km SSW of Kambalda occur as small bodies of pyrrhotite-pentlandite-chalcopyrite located at the base of serpentinised ultramafics in the Archæan Kalgoorlie-Norseman greenstone belt. The weathering profile generally consists of 0.1 to 1.0m (avg. 0.2m) residual soils developed over partly truncated 25-100m deep laterite/saprolite profiles. Below about 20cm depth a 0.5 to 1.5m thick calcrete profile is developed across the soil/saprolite boundary. The calcrete is not strongly developed and consists of coatings on weathered bedrock fragments in a groundmass of soft white calcareous clay (powder calcrete). There is no outcrop, but mineralisation subcrops as gossan beneath the residual soils.

Traverses across the mineralised zone showed that metal concentrations in the -80 mesh soil fraction and the calcrete horizon are much lower than in the saprolite and the gossan (Fig 15). The broadest dispersion pattern



(laterally) for Ni, Cu and Co values occurs in the topsoil. The calcrete contains higher metal values, but these show less lateral dispersion than in the topsoil, i.e. the anomalies are sharper. Nevertheless the calcrete does yield anomalous values of Ni, Cu, Co, Zn and Ni/Cr ratios.

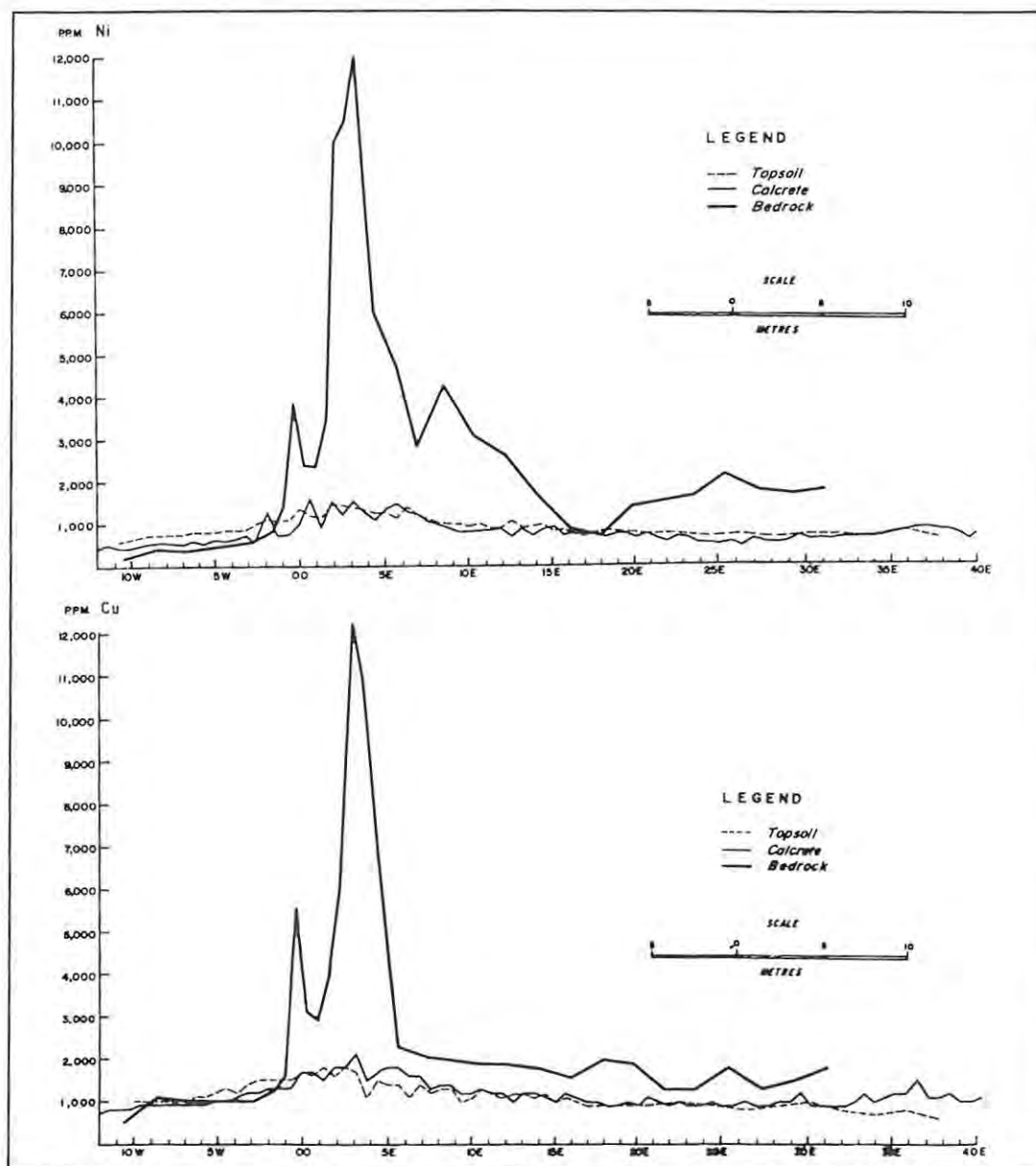


Fig 15: Pioneer prospect, geochemical traverses showing distribution of Ni (top) and Cu (bottom) in topsoils, calcrete and weathered bedrock; Taken from horizontal channel samples in a trench (from Cox, 1975).

The -80 mesh soil fraction was found to contain higher metal values than coarser fractions because Ni and Co are incorporated in Mn-oxides, and Zn and Cu in smectites, which comprise the fine fraction. The coarse fraction consists of clastic diluents such as quartz and feldspar. At Kambalda the opposite is true because gossan fragments on surface increase the metal content of the coarse soil fraction.

Away from the mineralisation the distribution of Ni and Cr in the calcrete horizon accurately reflects the distribution of these elements in the bedrock and helps the delineation of lithologic units, particularly the

ultramafic bodies. The trend of amphibolites, metasediments and cross-cutting granite pegmatites can, likewise, be traced on the basis of their lower Ni and Cr values.

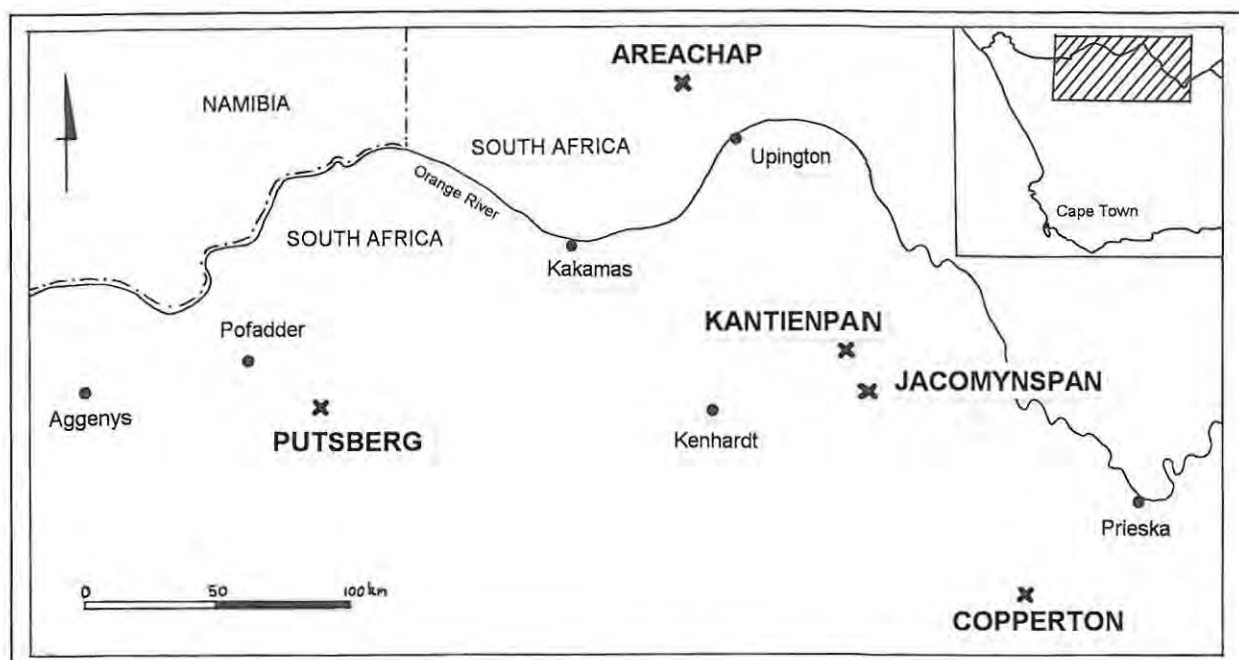


Fig 16: Location of the South African base metal prospects and mines discussed in the text.

#### 4.2.2. Jacomynspan Cu-Ni Prospect, South Africa (B 0 Ca 1,2)

(Tordiffe et al, 1989 and Vermaak, 1984)

The location of Jacomynspan (and Areachap, Copperton, Putsberg and Kantienpan which are discussed later), 110km SSE of Upington, is shown in Figure 16.

The ore body is considered to be an east-west striking, steeply south dipping, chlorite-biotite-tremolite schist containing disseminated chalcopyrite, pyrrhotite and pentlandite (1 to 3% total sulphides). The area is located on the African erosion surface (King, 1962), with a weakly developed northerly drainage. Relief is very low and outcrop poor; country rocks consist of migmatitic, porphyroblastic biotite-garnet gneiss. Late Tertiary/Quaternary calcrete is widespread, but never exceeds 3m in thickness. Texturally it varies from hardpan, nodular, powdery to laminar calcrete and is of pedogenic origin. A thin layer of sand, rarely more than 10cm thick, covers the calcrete.

Vertical dispersion: Vermaak (1984) observed that total MgO content decreases upwards in every calcrete profile. However, relative to a constant  $\text{Fe}_2\text{O}_3$  content (of the mineralised schist) there is often an increase in MgO in calcrete and a relative loss of MgO in the soil. Absolute MnO content of the calcrete is lower than the soils and the soils also display a larger relative increase in MnO. These observations are attributed to the fact that Mg has an affinity for the high pH conditions of calcrete formation (pH of hydrolysis = 10.5 (Levinson, 1974)) and tends to co-precipitate with  $\text{CaCO}_3$ , thus leaving the soil profile relatively depleted in this element. Manganese, on the other hand does not precipitate as readily in the calcareous environment, causing some extent of MnO-enrichment in the soil relative to the calcrete.

Trace element variations in the same profiles are shown in Table 10. Copper, nickel and cobalt commonly show an upwards depletion due to the diluting effect of pedogenic calcrete formation while lead and zinc are often enriched in the soils relative to the calcrete. Lead and zinc are not a feature of the Cu-Ni mineralisation at Jacomynspan and their relative enrichment in the soil is merely a function of higher background values. Of importance is the observation that the top of the calcrete layer (2m above the weathered bedrock) still contains anomalous ore related-element concentrations.

Lateral dispersion: Figures 17, 18 and 19 show the distribution in calcrete and soils of the elements Cu, Ni and Co respectively. Apparent from these figures is the limited lateral dispersion, but higher anomaly to background ratio of the metal anomalies in calcrete. The concentration of Cu in calcrete is virtually always greater than in the soil, which is an illustration of the relative immobility ( $\text{pH of hydrolysis of Cu}^{2+} = 5.3$ ) in the high pH conditions of calcrete genesis and its propensity to precipitate readily as a carbonate. A feature of calcrete is its ability to trap ore-related elements, not only chemically, but also mechanically and so reduce dispersion even further.

The strong correlation between the distribution of the metals in the soils and calcretes is evidence for residual soils and pedogenic calcretes. This situation is ideal for geochemical surveys, but the existence of laterally sourced groundwater calcretes or aeolian soil presents an entirely different situation in which geochemical prospecting may be futile.

On a smaller scale the variations of some elements in calcrete are illustrated in Fig 20. The concentrations of Cu and Ni drop significantly within just 30m of the orebody. Cobalt concentrations are too near the detection limit and too erratic to show any trend. Vermaak (1984) comments that some form of mechanical dispersion is indicated by the downslope tails in Cu and Ni, however similar tails could be formed just as easily by downslope hydromorphic dispersion.

Correlation matrices compiled from whole rock analyses of calcrete show that good correlations exist between  $\text{Fe}_2\text{O}_3$ , MnO, V, Ni and Co indicating a common mode of occurrence for this mafic assemblage. Vermaak's preferred interpretation is one of clastically dispersed Fe- and Mn-hydrous oxides (which scavenge these metals) prior to calcretisation. On the other hand there is no correlation between MgO, Cu and the above mentioned elements (V, Ni, Co) in calcretes indicating a different mode of occurrence, namely that they are precipitated as carbonates (magnesite) and hydrous carbonates (malachite) in the calcrete. Wedepohl (1973, in Tordiffe et al., 1989) points out that at high pH the precipitation of  $\text{Cu(OH)}_2$  may occur rather than adsorption of Cu onto Fe- and Mn-oxides. The moderately good correlation of Cu and MgO with the other ore-related elements in the soil, suggests that in the soil they do not occur as carbonates as in the calcrete.

The relatively low metal values obtained from  $\text{EDTA}^5$  extractions of the Jacomynspan calcretes in comparison with the HCl extractions indicates that very little of the ore-related metal (Cu, Ni) content of the calcrete is weakly bonded or adsorbed on mineral compounds of the sample. On the other hand the low concentrations of the ore-metals obtained by HCl leach in comparison with XRF indicates that very little of the elements are dispersed within the calcite structure.

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<sup>5</sup>EDTA: Ethylene-Diamine-Tetra-Acetic acid

Tordiffe et al. (1989) conclude that "pedogenic calcrete, where the in situ weathering products of a sulphide ore-body are calcretised at a later stage, presents an ideal medium for follow-up and detailed geochemical exploration in the secondary environment".

Table 10

Ore-related trace element variations in different profiles of the Jacomnynspan area (values in ppm; S=soil; C=calcrete; MS=mineralised schist)(from Vermaak, 1984).

SAMPLE NO.	SAMPLE TYPE	Cu	Ni	Co	Pb	Zn
IBC007	C	131	194	19	26	9
IBC008	C	1731	2331	220	29	40
IBC009	C + MS	2745	4356	155	35	58
IBC010	MS + C	4898	23082	1285	22	126
IBC057	S	191	131	18	53	60
IBC058	C	249	217	22	38	19
IBC059	MS	1546	1543	151	40	45
IBC060	S	199	133	20	50	58
IBC061	C	241	349	29	35	32
IBC062	MS	496	450	99	39	129
IBC065	S	135	206	23	62	36
IBC063	C	219	271	27	37	10
IBC064	MS	361	642	81	54	74
IBC093	S	81	109	9	59	89
IBC092	C	121	192	10	47	16
IBC091	MS	1045	1972	111	48	49
IBC111	S	32	43	8	54	36
IBC112	C + S	30	50	5	47	25
IBC113	MS	1360	2236	113	29	44
IBC114	S	51	71	11	54	35
IBC115	C	39	36	19	32	6
IBC116	MS	1586	1815	141	52	62

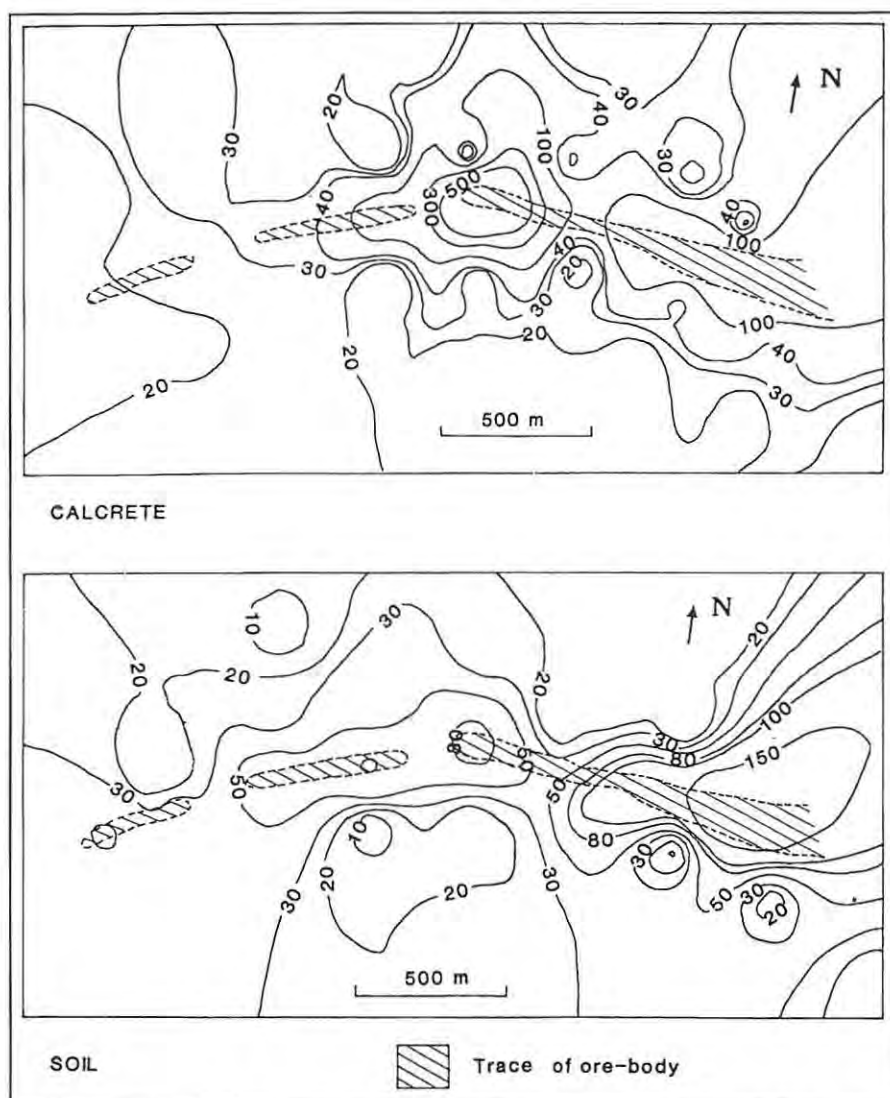


Fig 17: Contour maps of the Cu-values in calcrete and soil samples from the Jacomynspan area (from Tordiffe et al., 1989).



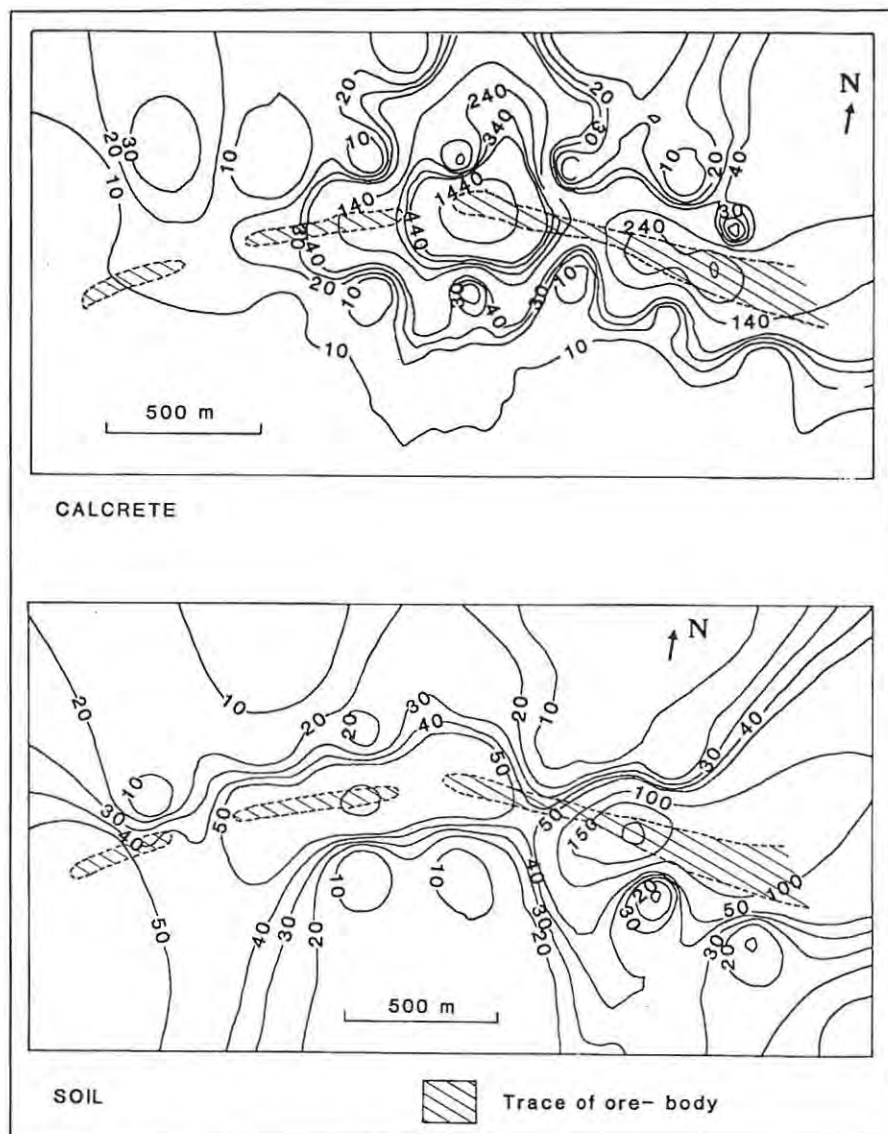


Fig 18: Contour maps of the Ni-values in calcrete and soil samples from the Jacomynspan area (from Tordiffe et al., 1989)

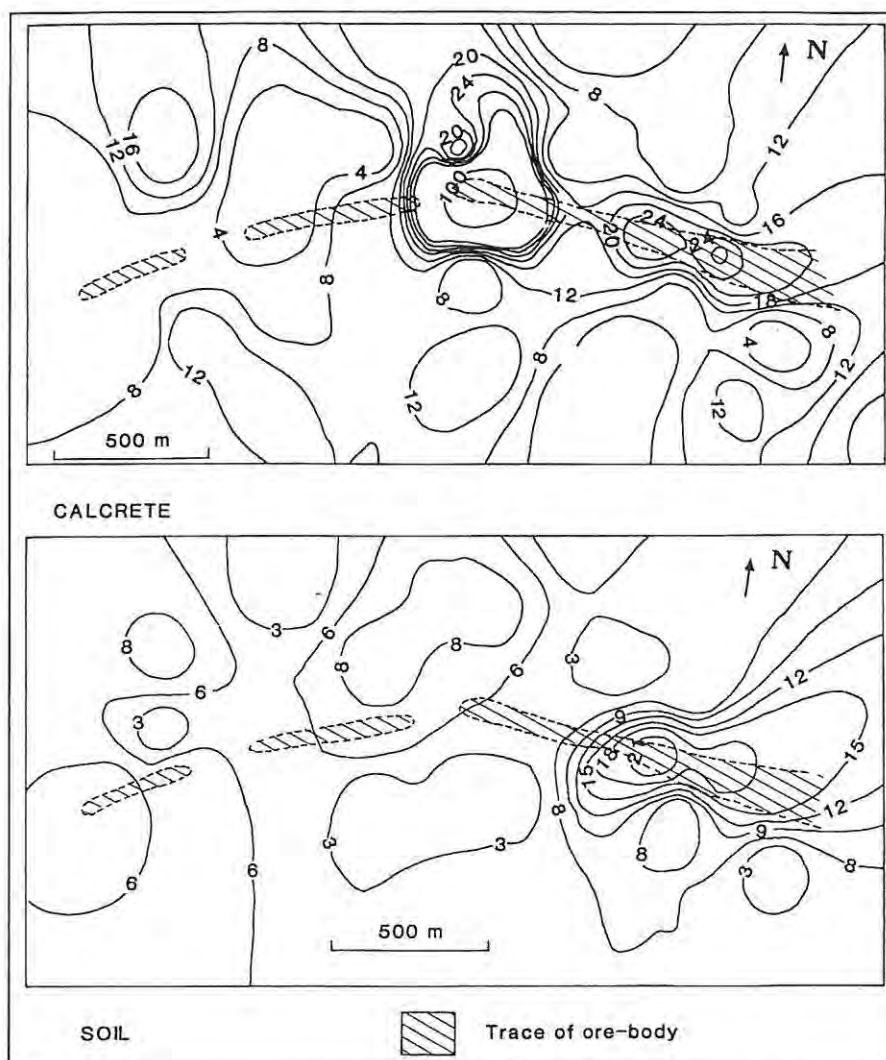


Fig 19: Contour maps of the Co-values in calcrete and soil samples from the Jacomynspan area (from Tordiffe et al., 1989)

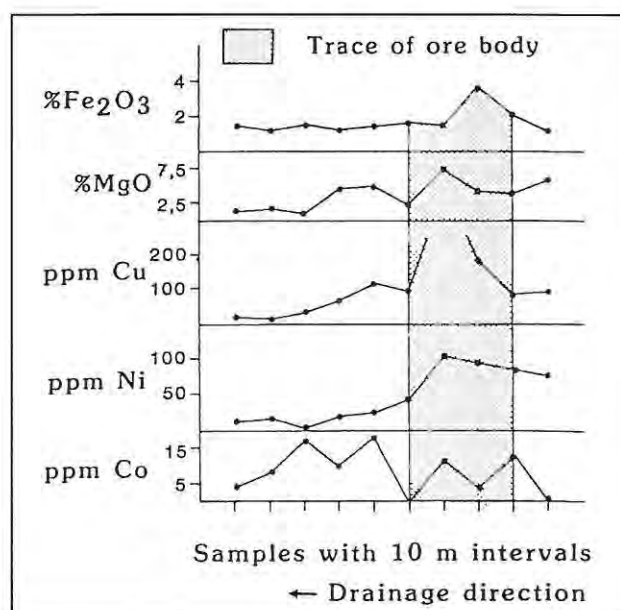


Fig 20: Small scale lateral dispersion of selected elements in calcretes from the Jacomynspan area (from Tordiffe et al., 1989).

### 4.2.3. Areachap Cu-Zn Prospect, South Africa (B 0 Ca 2)

The low grade stratiform Cu-Zn prospect at Areachap is situated about 22km NW of Upington (Fig 16) on an isolated residual of the late-Cretaceous African erosion surface. Host rock to the mineralisation is biotite-garnet schist with associated amphibolites, phlogopite-talc schist and biotite-amphibole feldspathic quartzite (Vermaak, 1984). Mineralisation occurs as massive to disseminated pyrite with subordinate pyrrhotite, chalcopyrite and sphalerite. At surface gossan is well developed and copper carbonates and silicates are commonly found. Pedogenic calcrete is well developed over the gossan (3 to 10m thick) and is usually of the hardpan variety, although laminar, nodular and boulder/cobble types also occur. Gossanous material is commonly included in the calcrete.

Simple histograms of the Cu, Pb and Zn content of calcrete samples from Areachap show a bimodal distribution which is an indication of the ability of the calcrete to hold anomalous metal concentrations (Fig 22).

Vermaak (1984) recognised that certain elements are more strongly depleted (relative to constant  $\text{Fe}_2\text{O}_3$ : assuming  $\text{Fe}_2\text{O}_3$  is the least affected by calcrete formation) during calcretisation:-

Whole rock analyses  
**Mg<Cu<Mn<Ba<Zn<Pb<V<Co,Ni<Mo**  
 least depleted most depleted  
 (ppt as carbonates)

This order of depletions is in contrast to Vermaak's (1984) calculated mobilities (section 2.5.4.) which he attributes to the effects of mixed clastic and hydromorphic dispersion. Clearly, ore-related metals are not all affected in the same way by the chemical conditions of calcrete formation. Elements to the left of the sequence will more readily react with  $\text{CO}_3^{2-}$  to precipitate as carbonates (e.g. Mg and Cu), while elements to the right will tend not to precipitate and so become relatively depleted (Co and Ni). This differentiation Vermaak (1984) attributes to some degree of hydromorphic dispersion and suggests that in an exploration survey using calcrete Cu would be preferred over Ni as an indicator element. On the other hand it could also be argued that if Ni is present in the original material and is most depleted in the calcrete it may also be the most widely dispersed.

Danchin's (1972) study of the Areachap prospect revealed that "considerable amounts of each of these elements (Zn, Cu, Ni, Co and W), with the possible exception of W, can be concentrated by the calcrete. It is also clear that...there is a steady decrease in concentration from the basal mixed zones to the surface or uppermost calcretes. Most important, however, is that the uppermost calcrete samples contain considerably more of the elements under consideration than do the soils sampled... Particularly spectacular are the values for Zn and Cu at Areachap, where the soil values for both elements are of the order of 10-20ppm, whereas even the uppermost calcretes show values in excess of 100ppm." (Fig 21)

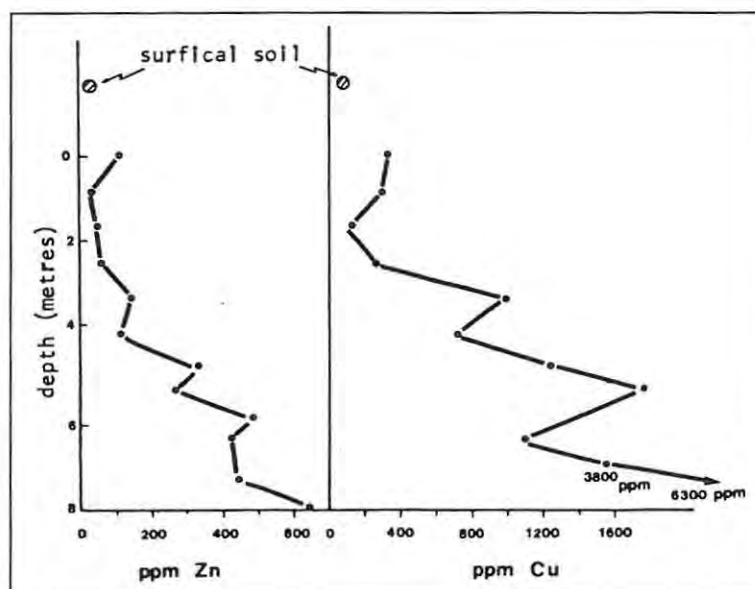


Fig 21: Distribution of Cu and Zn in a soil profile through calcrete over mineralisation at Areachap (from Bradshaw and Thomson, 1979 after Danchin, 1972)

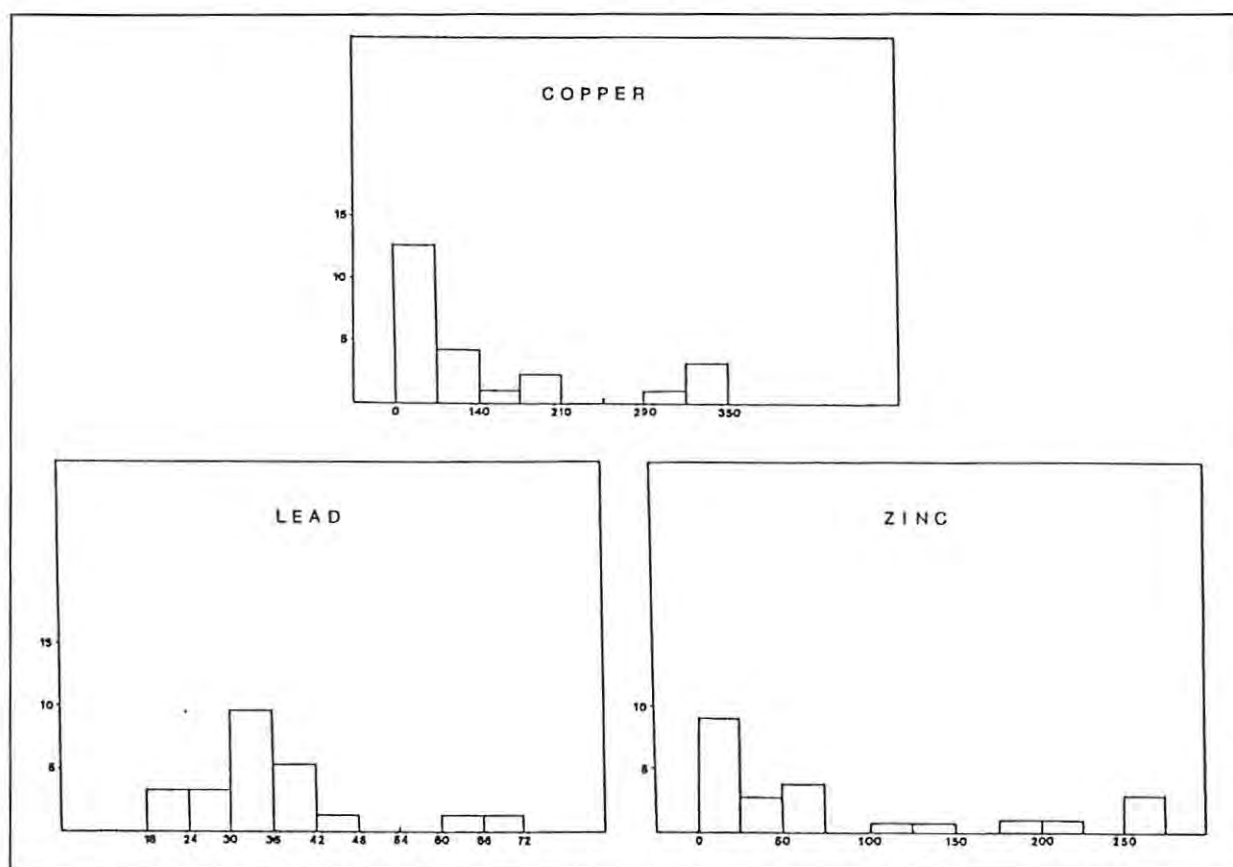


Fig 22: Histograms of Cu, Pb and Zn concentrations (in ppm) in calcrete samples from Areachap (from Vermaak, 1984).

#### 4.2.4. Putsberg, Cu, South Africa (B 0 Ca 1,2)

(Garnett, 1983 and Garnett et al., 1982)

The location of the Putsberg prospect, 30km SE of Pofadder, is shown in Fig 16. Putsberg is located on the late-Cretaceous African erosion surface in the Namaqualand Metamorphic Complex. The host rocks to the Putsberg mineralisation are biotite-sillimanite schists and gneisses, amphibolites and quartzites of the Bushmanland sequence. Mineralisation consists of disseminated pyrite > pyrrhotite > chalcopryrite > sphalerite > galena. The main economic metal is copper (1.5Mt in three ore-bodies @ 1.5% Cu) with some silver and zinc and minor galena (Viljoen et al., 1986).

Calcretisation of the bedrock can penetrate up to 15m, but is typically 2 to 7m. The top of the calcrete is usually well defined, while the base is more gradual. The calcrete is overlain by soil which probably contains a large æolian component. Calcrete boulders up to 50cm across are well developed in the area as are smaller, 1-5cm, nodules set in pinkish-brown subsoil. All forms of calcrete developed over the mineralisation contain some fragments of gossan preserved within them.

Samples at Putsberg were collected from the soil overlying the calcrete, top of the calcrete and the base of the calcrete. Various size fractions were collected including hand-picked, +2mm bedrock chips embedded in calcrete at its base. In order to facilitate interpretation of the results values were expressed in terms of the concentrations in the +2mm rock chips which were taken as 100. This approach enabled percentage depletions and enrichments to be easily observed (Table 11). Copper, lead and zinc are severely depleted in the calcrete, even at the base. There is a progressive depletion in metal values from the finest to the coarsest fractions analysed and from the base of the calcrete through to the soil. Manganese also shows a progressive depletion with increasing particle size, but shows a progressive enrichment in the finest fraction from base of calcrete to soil (the soil is actually enriched in Mn (118%) relative to the rock chips).

Cadmium and silver behave in a similar fashion. At the base of the calcrete the fine fraction yielded the highest values, but the same fraction in the soil had no detectable Cd or Ag. In the top of the calcrete Cd and Ag are preferentially concentrated in the coarser fractions which is in contrast to other elements. Barium is preferentially concentrated in the fine fraction at all three sample sites as is Cr. Synthesizing these element depletions and enrichments into an elemental order of preservation yields the following sequence:-

Top of Calcrete: +2mm fractions	
<b>Cd&lt;Ba,Cr&lt;Ag&lt;Mn&lt;Pb&lt;Zn&lt;Cu</b>	
least depleted	most depleted
Top of Calcrete: -2mm fractions	
<b>Cr&lt;Ba,Mn&lt;Pb&lt;Zn&lt;Cu&lt;(Cd,Ag)</b>	
least depleted	most depleted

These two series are essentially the same bar Cd and Ag in the -2mm fraction which were not detected at all.

Figures 23, 24 and 25 illustrate the lateral dispersion of Cu, Zn and Ba in calcrete at Putsberg. It can be seen that the geochemical response is higher for Cu and Zn in the calcrete than in soil and also that in the case of Cu and Ba





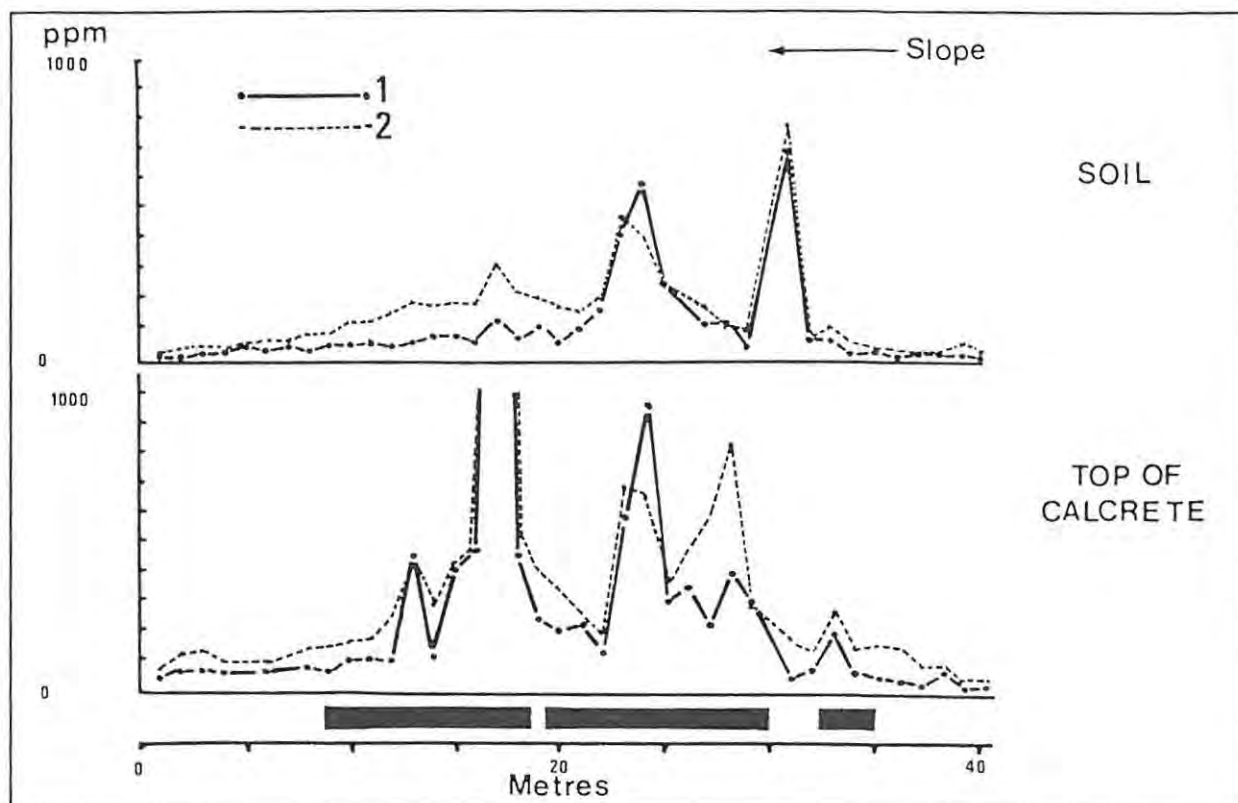


Fig 23: Putsberg Cu response in soil and top of calcrete for the 1-2mm fraction (1) and the 75-180 $\mu$ m fraction (2). Solid black bars represent location of mineralisation below the calcrete. Note the higher response from the calcrete and the finer fractions; also the wider dispersion in the soils. (from Garnett et al., 1982)

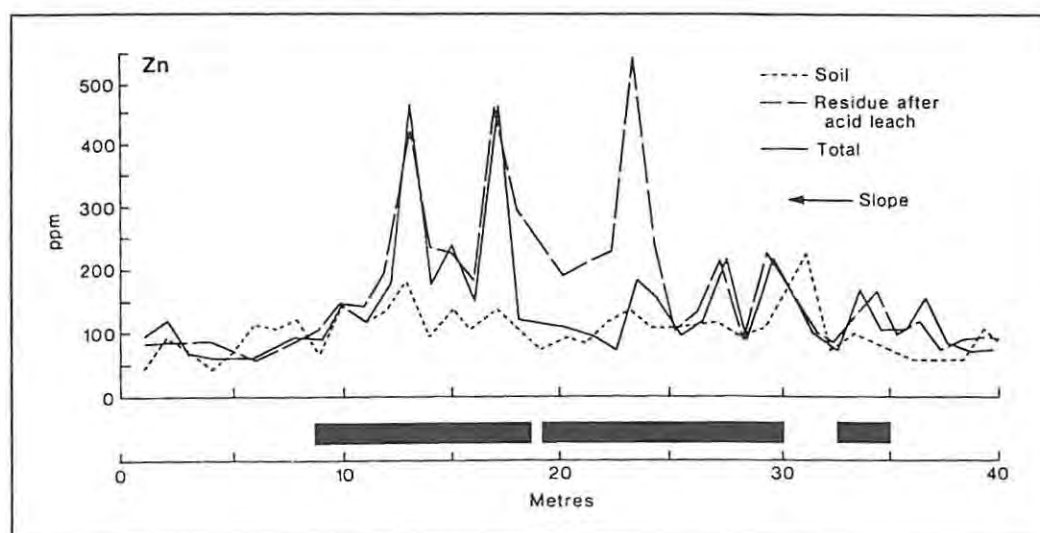


Fig 24: Putsberg Zn in the 75-180 $\mu$ m fraction. Soil is total (hot HCl, AA) analysis. Calcrete was subjected to ammonium acetate leach to remove calcium carbonate and remaining residue analysed by hot HCl, AA. Note how the anomaly can be enhanced by the method of first removing the diluent calcium carbonate. Analysis of the leach liquor yielded very low levels of Zn indicating that Zn is not carried in the calcite structure (from Butt, 1992, Fig III.3-42)

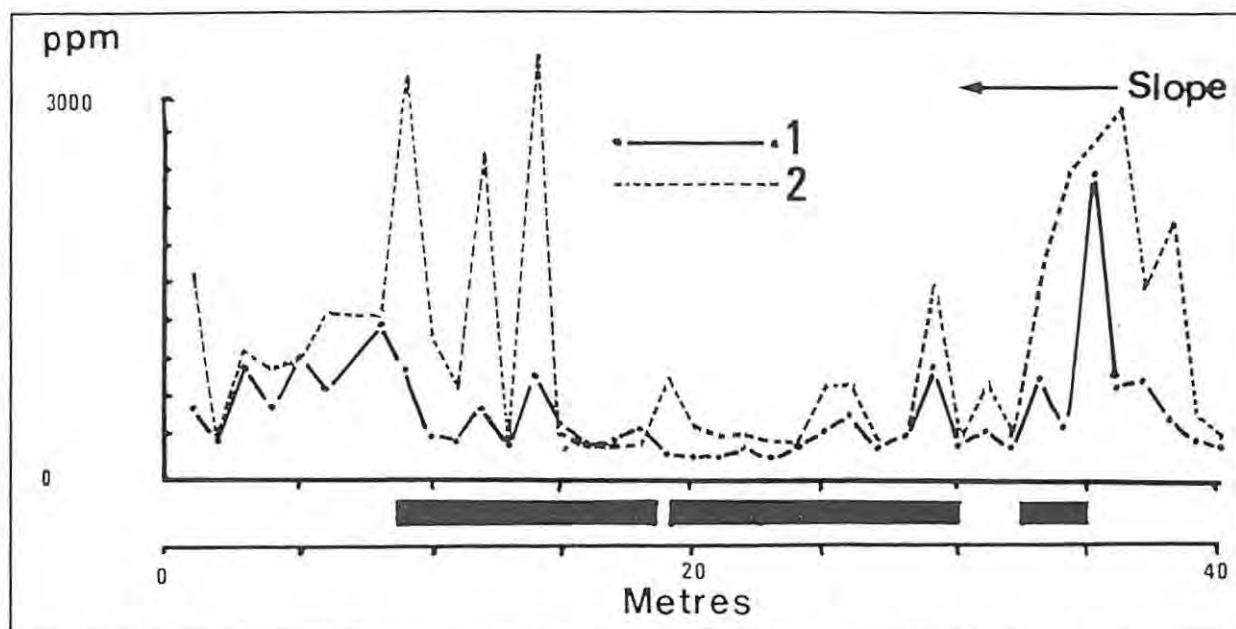


Fig 25: Putsberg Ba geochemistry for the base of the calcrete for the 1-2mm fraction (1) and the 75-180 $\mu$ m fraction (2). Solid black bars show the location of the mineralisation below the calcrete. (from Garnett et al., 1982)

#### 4.2.5. Copperton Cu-Zn-Pb, South Africa (B 0 Ca 1)

Copperton is located about 50km SW of Prieska (Fig 16). The ore deposit consists of sulphides in an amphibolite host covered by thin soils and calcrete of 3 to 8m thickness. The calcrete, formed on the African erosion surface, varies from laminar to nodular and is pedogenic in origin (Vermaak, 1984). Mineralisation consists of pyrite, sphalerite, chalcopryrite, pyrrhotite and galena. Traces of molybdenite, arsenopyrite, Bi-tellurides, graphite and gold are reported (Middleton, 1976 in Vermaak, 1984). Gossan occurs on surface and in the calcrete

Figure 26 shows the distribution of Cu, Pb and Zn in soil and calcrete over the ore zone. It can be seen that calcrete yields a much higher concentration of Cu and Pb than does the soil although the calcrete anomaly is much more restricted than that in the soils. Vermaak (1984) calculated the gains and losses (relative to constant  $\text{Fe}_2\text{O}_3$ ) of various metals that accompany calcrete formation. The sequence is exactly the same as that for Areachap (see relevant section) and bears the same discussion.

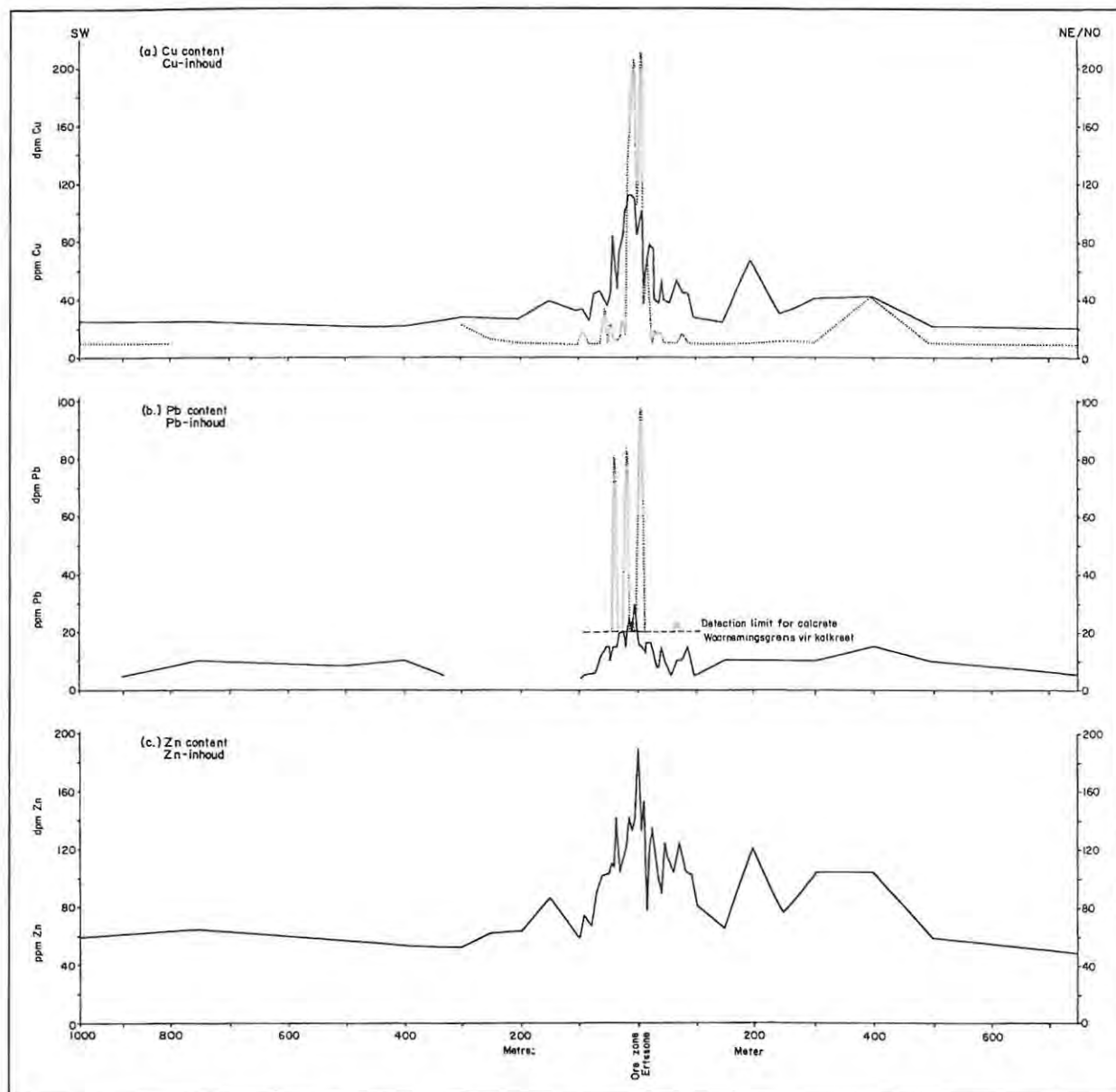


Fig 26: Distribution of Cu, Pb and Zn in soils (-200 mesh) across the Copperton ore zone. No Zn data for calcrete (from Beeson et al., 1975).

#### 4.2.6. Bou-Grine Pb-Zn, Tunisia (C 1 Ca 1)

(Leduc, 1986 and Guedria et al., 1989)

The Bou-Grine Pb-Zn mine is situated about 140km SW of Tunis in Tunisia. Mineralisation consists of stratiform bodies of massive and disseminated sphalerite, galena and pyrite associated with barite and celestite ( $\text{SrSO}_4$ ). Host rocks are Triassic and Cretaceous claystones, sandstones and laminated limestones draped over diapirs of Triassic evaporites. The general geology of the mine area is illustrated in Fig 27.



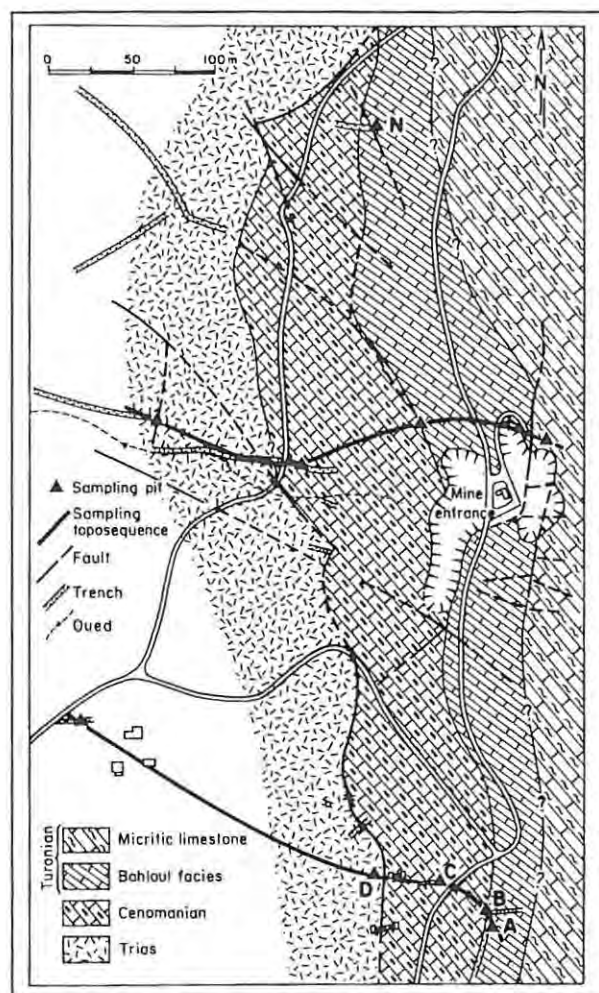


Fig 27: Geological map of the Bou-Grine area. Turonian and Cenomanian ages are late Cretaceous. Triassic rocks are claystones, gypsum, sandstone. Cenomanian lithologies are marl and limestone. Turonian lithologies are clayey limestones and thinly bedded marls; the Bahloul facies is rich in organic matter. Mineralisation occurs as (1) lenticular sulphides (sl, gn, py) associated with sulphates (celestite and barite) which lie at contact between Triassic and Cretaceous rocks; (2) disseminated sulphides (sl, py, gn) in laminated Bahloul limestones and (3) a "semi-massive" body cutting the Cenomanian and Turonian carbonates (>20% Zn). At cut-off 4% Pb+Zn reserves are 7.3Mt at 2.4% Pb, 9.7% Zn (from Guedria et al., 1989).

Soil profiles consist of (from the bottom):-

1. Surficial Horizon (0-0.3m thick): Humic loam, partly colluvial origin, thicker at base of slopes.
2. Calcretes (0.6 to 1.4m thick): (i) Nodular calcrete (0.5-1m thick), (ii) lamellar calcrete intercalated with friable material similar to underlying alterites, (iii) indurated, hard calcrete (ii and iii together 0.1-0.4m thick).
3. Alterites: This term is taken by Guedria et al. (1989) to be synonymous with saprolite and refers to the altered top part of the bedrock (cf. Bates and Jackson (1987) the term "alterite" is "a general term for altered, unrecognizable grains of heavy minerals").



The development of these profiles along a toposequence<sup>6</sup> is shown in Fig 28.

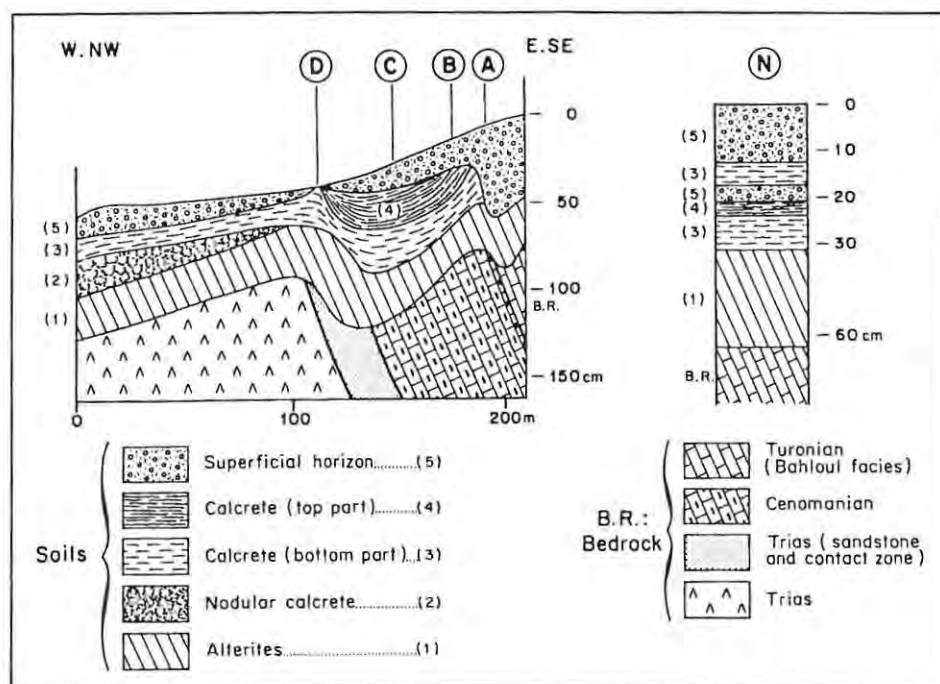


Fig 28: Bou-Grine: Distribution of soil types along the A-D toposequence and isolated profile N used in the Guedria et al. (1989) study. Profile N is significant in that it contains two calcrete horizons separated by a non-calcretised horizon which has a bearing on metal distributions (see below). For location of the profiles see Fig 27. (from Guedria et al., 1989).

The progressive increase of carbonate in calcrete can be explained either by the dilution effect of non-carbonate fractions by massive deposition of  $\text{CaCO}_3$  or by epigenetic replacement of such elements by calcite. In order to determine which of these processes operated at Bou-Grine Guedria et al. (1989) carried out a petrographic examination of calcrete which revealed that calcretisation at Bou-Grine conserves structural or geometrical relationships and is an isovolumetric replacement feature (cf. Watts, 1978 - Displacive calcite in calcretes). Precipitation of calcite thus takes place by dissolution and replacement of pre-existing minerals or biological remains as well as by filling of the pores of the parent rock.

Beginning with the observation that the replacement is isovolumetric Guedria et al. (1989) recalculated the quantities of  $\text{CaCO}_3$ , Pb and Zn in a constant volume ( $1\text{cm}^3$ ) based on the sample densities. Results of this recalculation are plotted in Fig 29. On an isovolumetric basis it can be seen that there is a reduction in Pb and Zn content thus indicating that Pb and Zn are leached from the original host. Even in profile N which has two calcrete horizons separated by a non-calcretised horizon there is reduction of Pb and Zn in the calcrete layers relative to the non-calcretised layer between them. The variation of this loss of Pb and Zn in calcretes (relative to the metal concentration in the bedrock/saprolite) is plotted against  $\text{CaCO}_3$  content in Fig 30.

<sup>6</sup> Toposequence = A sequence of types of soil in relation to position on a slope (Bates and Jackson, 1987).

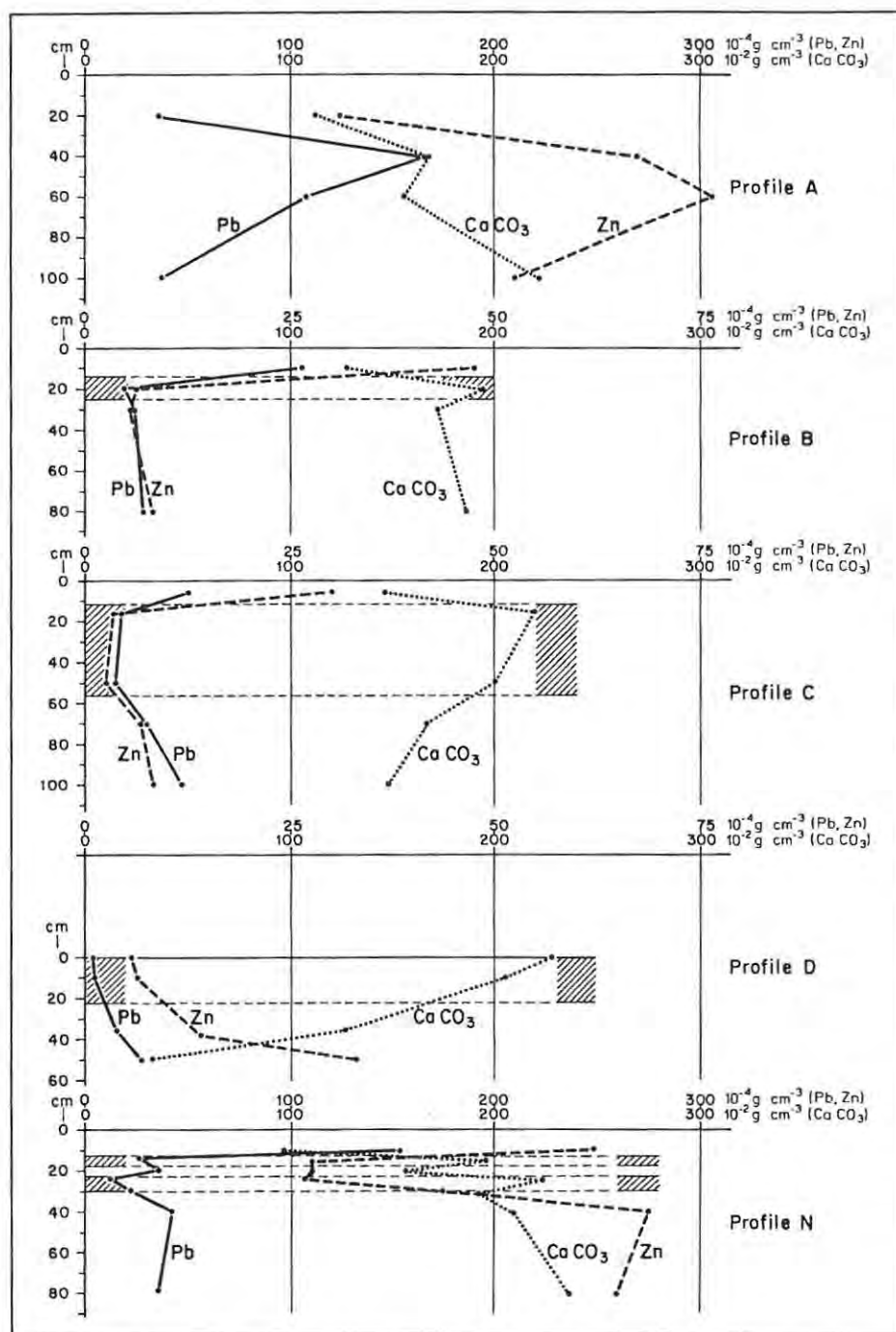


Fig 29: Bou-Grine: Variation in  $\text{CaCO}_3$  ( $10^{-2} \text{ g cm}^{-3}$ ) and Pb-Zn ( $10^{-4} \text{ g cm}^{-3}$ ) on an isovolumetric basis in the four profiles of the A, B, C, D toposequence and also in profile N. Calcrete horizons shown by hatching. See Fig 28 for a section through the toposequence (from Guedria et al., 1989).

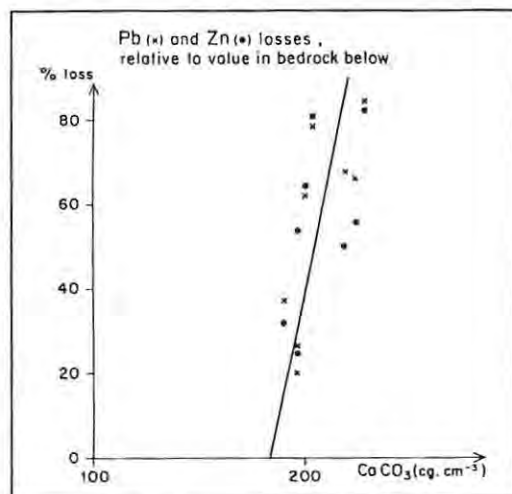


Fig 30: Pb and Zn losses in calcrete horizons as a function of  $\text{CaCO}_3$  content. Values expressed as % of the metal content within the parent rock. The parent rock itself consists mostly of limestones and the problem arises as to whether the carbonate in the calcrete is all neoformed or whether there is an original parental component. Guedria et al. are, however, confident that all the  $\text{CaCO}_3$  is, in fact, newly introduced (from Guedria et al., 1989).

The mineralogical localization of the metals in the soil horizons at Bou-Grine was determined by partial extraction techniques:-

1. HCl (1N) soluble → carbonates, metallic elements loosely bound to iron oxides and clays.
2. Residue of 1. dissolved in Na-tricitrate+Na-bicarbonate+Na-dithionite → Fe-oxides.
3. Residue from 2. dispersed in distilled water and  $\leq 2\mu\text{m}$  fraction separated → clays.
4. Residue from 3. → sand and silt.

As a result of the above investigations it was observed that Pb and Zn are distributed as follows:-

- in the calcreted horizons, the HCl-soluble fraction contains almost all the Pb and 95% of the Zn, at average contents of 610ppm and 3320ppm respectively. Small proportions of each (0.6% Pb and 1.1% Zn) are associated with oxides at average contents of 4ppm and 26ppm respectively;
- in non-calcreted horizons, their affinity is for Fe-oxides and, even though oxides are never abundant ( $\leq 9\%$ ), they can contain up to 86% and 82% of the Pb and Zn respectively at concentrations varying between 20-5000ppm Pb and 40-4462ppm Zn.

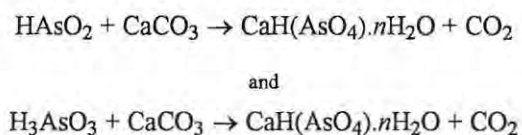
At Bou-Grine, therefore, replacement of the ore minerals by calcite has leached most of the Pb and Zn and that which remains is associated with the carbonate fraction.

#### 4.2.7. Plat Reef PGE's, South Africa (C 0 Ca 3)

(Frick, 1985)

The Platreef is a 200m thick layered succession of mineralised pyroxenites and norites of the ?Main Zone of the Bushveld Complex (Van der Merwe, 1978 in Frick, 1985). It subcrops beneath 1-4m of mostly transported soils on the Potgietersrus Limb of the Bushveld Complex. Mineralisation occurs in the form of sulphides and compounds of the PGE's (pyrrhotite, pentlandite, chalcopyrite, pyrite, cobaltite, gersdorffite, arsenopyrite, Pt-Pd-sulphides, -arsenides and -tellurides and ferro-platinum). Frick (1985) does not give a detailed description of the nature of the calcretes in the area other than to say that calcrete development is "limited".

Anomalous concentrations of the mobile elements Hg and As occur directly over the mineralisation whether the soils are residual or transported - a feature of the active upward migration of these elements. Arsenic gives the more erratic response, apparently because of adsorption to a greater variety of soil components than Hg, but one traverse shows a good correlation with C (as CO<sub>2</sub>). This correlation is thought to be the result of incorporation of As into calcrete. Frick (1985) proposes a reaction between arsenious acid dissolved in groundwater and calcrete according to reactions such as:-



which would yield a stable arsenite of the weilite-group.

#### 4.3. B- AND C-TYPE MODELS: PRE-EXISTING PROFILE PARTLY OR WHOLLY TRUNCATED AND WITH PH CONTRAST

Some calcretes are developed in regoliths that exhibit marked pH contrast between the surface and underlying horizons. If dispersion is active in the underlying horizons, the pH change at the interface may cause the mobilised metals to precipitate, giving surface expression to mineralisation, even where this is concealed by transported overburden (Butt, 1992).

##### 4.3.1. Martins Cu Anomaly, Kadina, South Australia (B 0 Ca 3)

(Mazzucchelli et al., 1980)

Martins Anomaly is located 4km SW of Kadina which is in the Northern Yorke Peninsula about 120km NW of Adelaide.

Kadina and other Cu mining centres in the area (Wallaroo and Moonta) are situated on the eastern margin of the lower to middle Proterozoic Gawler Block which is comprised of low/moderate grade metamorphosed sediments, acid volcanics, intrusive acid porphyries and granitic rocks intruded by later undeformed granite batholiths and small dioritic stocks. Locally, flat-lying undeformed Adelaidean and Cambrian sediments overlie the older basement. Mineralisation is described as a narrow, mainly conformable lode containing chalcopyrite, pyrite and

pyrrhotite in a pegmatitic gangue. Contacts between the lode and schistose metasediment wall rocks are gradational and disseminated sub-ore grade mineralisation generally surrounds the lode.

The area around Kadina is flat lying with a NW-trending system of parallel, low amplitude sand dunes. Overburden varies from 1 to 70m thick. A typical soil profile developed over the aeolian material consists of (top to bottom):-

- grey-brown powdery loam and calcrete rubble (0-0.6m thick)
- calcrete and calcrete-nodules (0.6-2m thick)
- terra-rossa clay (0.3-1.3m thick)
- red, brown and grey clays (2-40m thick)
- fossil residual soil remnants (0-1m thick)
- bedrock

Overburden/bedrock profiles were auger drilled and sampled over 1.5m intervals and analysed for total and cxCu (cold extractable copper) (Fig 31). The distribution of total copper shows the focus of the anomaly in the bedrock with limited dispersion about this focus. The cxCu shows a mushroom shaped dispersion pattern with the strongest part of the anomaly being immediately below the calcrete-clay interface which is the zone of change from acid to alkaline conditions. This distribution pattern is thought to be the result of the upwards migration of Cu from the bedrock with some lateral dispersion taking place before fixation in the zone of higher pH. Lesser enrichments of Cu do penetrate the calcrete and are recovered in the topmost sample (0-1.5m).

Fig 32 shows plan views of the distribution of total Cu in the weathered bedrock and cxCu in the clay immediately below the calcrete horizon. It can be seen that there is a close correspondence between the positions of the anomaly peaks and in the overall dimensions. It would therefore appear that an adequate geochemical response could be obtained by sampling no deeper than the calcrete/clay interface. Such a methodology could save on drilling costs in areas of deep overburden.

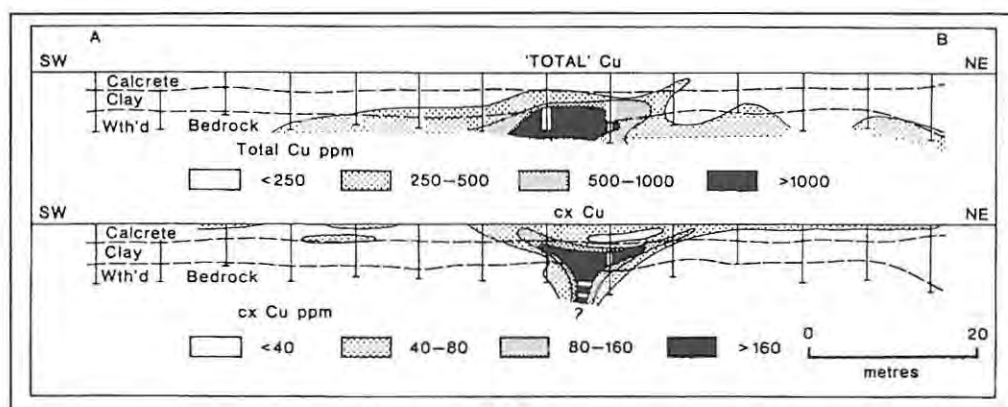


Fig 31: Section view along a drilling traverse showing the distribution of total Cu (top) and cxCu (bottom) at Martin's Anomaly, Kadina (from Mazzucchelli et al., 1980).



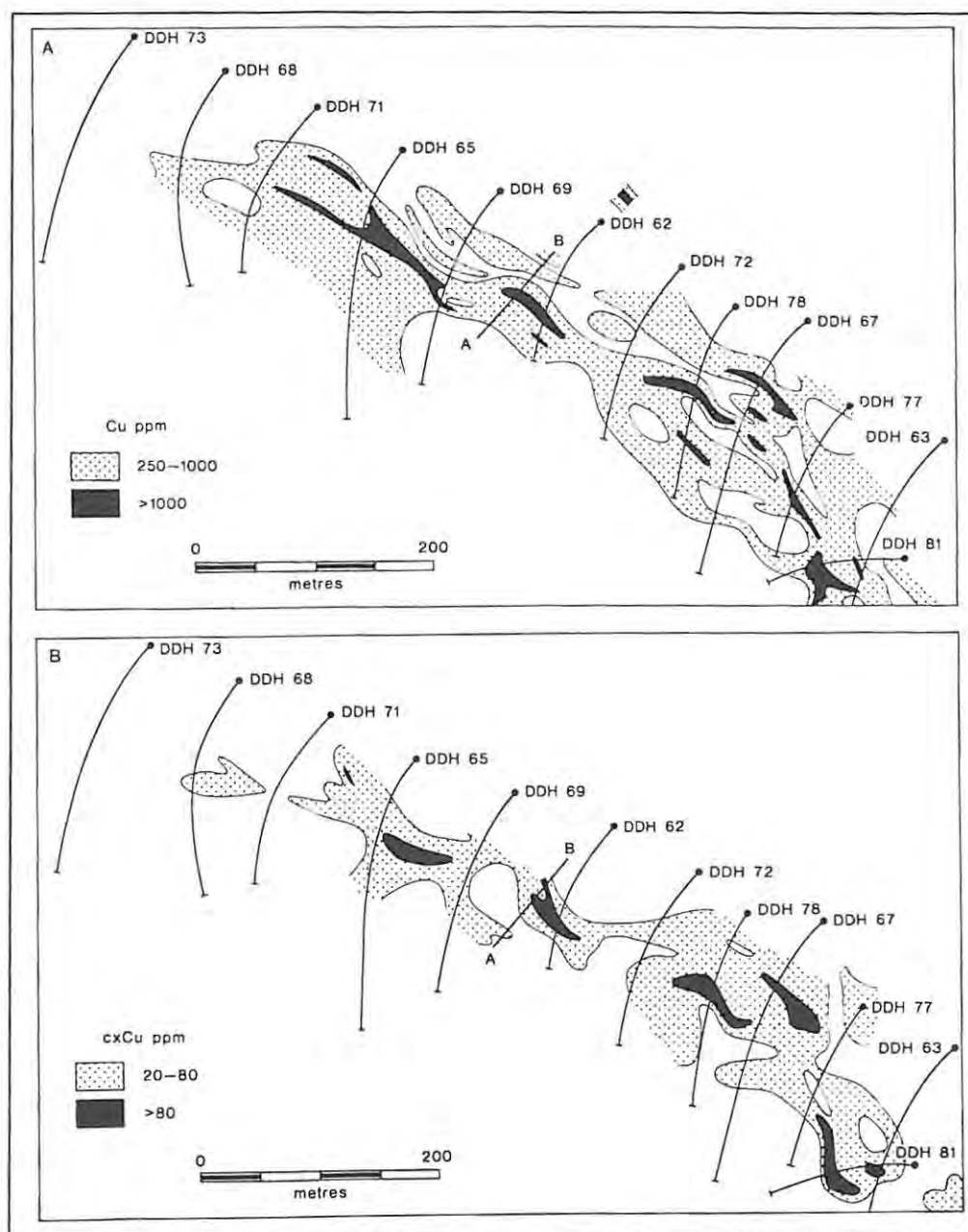


Fig 32: Distribution of total Cu in weathered bedrock (top) and cxCu in clay immediately below calcrete (bottom) (from Mazzucchelli, 1980)

#### 4.3.2. Pima Cu Mining District, Arizona, USA (C 0 Ca 3)

(Huff, 1970)

This case study does not involve surface pedogenic calcrete, but rather deep groundwater accumulations of carbonate in alluvium which Huff (1970) is hesitant to call "caliche". Nevertheless the processes operating in this case are directly applicable to calcrete environments.

The Pima mining district is located about 25km SW of Tucson, Arizona. Mineralisation occurs in the form of Cu-Mo porphyries (Pima open pit) and as Pb-Zn and Au fissure fillings and replacement bodies along faults and breccia zones. The Pima porphyry is covered by 60m of Pleistocene alluvium at the base of which is a distinctive

calcium carbonate cemented conglomerate ranging in thickness from 1.5 to 21m. Locally it is called caliche and rests upon an irregular bedrock surface. It is thickest in valleys cut into the bedrock.

Copper concentrations in the alluvium vary from 5ppm near the surface to 250ppm just above the carbonate cemented conglomerate. In the conglomerate itself, close to the base, where it lies just above the ore zone, values of 4000ppm copper have been recorded. Six metres above the base Cu content is 250ppm. Copper minerals could not be identified in the pebbles of the basal conglomerate, but copper was shown to be distributed through the carbonate matrix. Huff (1970) envisages copper bearing acid (from oxidation of sulphides) groundwater flowing down the water table gradient which precipitates its copper upon encountering the carbonate of the conglomerate.

Conglomerate from a drill hole 2.4km NE of the Mission mine (also a Cu porphyry) contains 1000ppm Cu and overlies rock devoid of copper. An illustration of the effects of pH change on metal mobility. Prospecting for copper by sampling carbonate cemented conglomerates in this case is a viable technique.

#### 4.3.3. Rocky Range Cu, Utah, USA (C 1 Ca 3)

(Erickson and Marranzino, 1960)

This copper deposit is located on a pediment at the foot of the Rocky Range in Beaver County, Utah. Mineralisation occurs in the form of a magnetite-chalcopyrite-garnet-diopside skarn near the contact of limestones with quartz monzonite. The deposit is concealed by 2-20m of alluvium and the pediment slope is about 7°.

The object of the study by Erickson and Marranzino (1960) was to distinguish between metal anomalies caused by mechanical transport from mineralisation upslope and anomalies caused by hydromorphic dispersion from below. The soil profile at a depth of 20 to 30cm contains pebbles and cobbles coated with calcrete. This coating was scraped off, analysed for Cu and compared to analyses of the -80mesh (-175µm) fraction of the soil. Fig 33 shows the distribution of Cu in soils and in calcrete coatings.

It can be seen that the highest Cu values are concentrated in samples from the drainage systems in the eastern part of the area and shows no spatial relationship to the mineralised zone in the mapped area (other than three isolated highs). The copper high in the east is thought to be the result of physical transport of detrital copper minerals from old prospects and pits further upslope. Copper in calcrete on the other hand shows a much closer spatial relationship to the concealed skarn deposit. Significantly, all the core holes in mineralised rock occur within an area in which the ratio of copper in calcrete coatings to copper in soil is 1 or greater (i.e. the copper is preferentially concentrated in the calcrete). Also the strong detrital-copper highs in the east have been eliminated. Copper is considered to have been liberated from the sulphide mineralisation under acid conditions and precipitated in the neutral to alkaline environment of the calcrete (Butt, 1992).

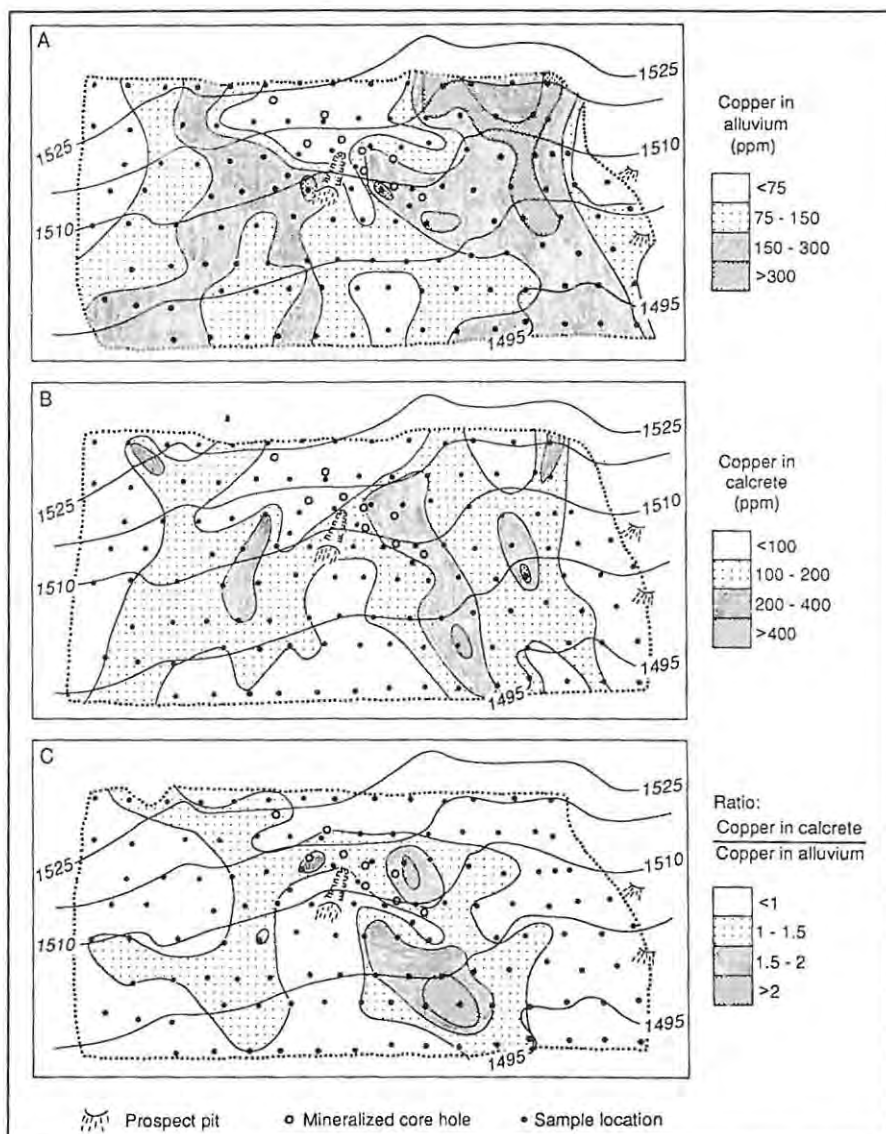


Fig 33: Copper distribution in alluvium; -80mesh (A), calcrete coatings (B) and the ratio between the two (C). For scale: sample points are approximately 100ft apart (from Butt, 1992 after Erickson and Marranzino, 1960).

#### 4.4. GEOBOTANY AND BIOGEOCHEMISTRY IN CALCRETE TERRAINS OF CENTRAL NAMIBIA AND NW BOTSWANA

(Cole and Le Roex, 1978)

Biogeochemistry has proved successful in locating stratiform copper mineralisation in extensions of the Katanga System of Zambia. Exploration on this extension in the Witvlei (140km E of Windhoek) area of Namibia and the Ngwaku Pan (100km SW of Maun) area of Botswana showed that biogeochemical expression of mineralisation can be detected through 30m of calcrete.

Where the soil/calcrete cover is thin or non-existent as over parts of the Witvlei area *Helichrysum leptolepis* (also informally known as the copper flower) proved to be an unfailing indicator of copper mineralisation, but where the

cover is thick *Acacia hereroenses* (Mountain thorn<sup>7</sup>; 14 - 47ppm Cu in a background of 4 - 8ppm Cu) and *Phaeoptilum spinosum* (9 - 78ppm Cu), with their deep tap roots proved to be of more use.

At Ngwaku Pan deeper rooting shrubs such as *Echolium lugardae* indicated copper mineralisation (this species is also present at the Messina and Phalaborwa copper mines).

It also proved possible to distinguish areas of different calcrete development around Witvlei by means of four different plant associations:-

First association: characterising calcrete ridges:-

- Trees: *Acacia giraffae* (Camel thorn), *Acacia mellifera* (Black thorn)
- Shrubs: *Catophractes alexandii* (Trumpet thorn), *Grewia flava* (Climbing raisin)
- Suffrutices<sup>8</sup>: *Leucasphaera bainesii*, *Aptosimum leucorrhizum*
- Grass: *Fingerhuthia africana*

Second association: characterising areas of extensive sheets of calcrete of 10 to >36m thickness overlying shales of the Buschmannsklippe Formation:-

- Trees: *Acacia mellifera*, *Boscia albitrunca* (Shepherds tree)
- Shrubs: *Catophractes alexandii*
- Suffrutices: *Leucas pechelli*, *Hermania damarana*, *Pseudogaltonia clavata*
- Grass: *Enneapogon cenchroides*

Third association: characterising areas where the shales of the Buschmannsklippe Formation are capped by thin calcretes or outcrop:-

- Shrubs: *Catophractes alexandii*, *Grewia flava*
- Suffrutices: *Leucasphaera bainesii*, *Hermania damarana*, *Pseudogaltonia clavata*, *Pegolettia pinnatiloba*
- Grass: *Fingerhuthia africana*

Fourth association: characterising fossil drainage lines and pans floored by calcrete:-

- Trees: *Acacia giraffae*, *Acacia karoo* (Sweet thorn), *Acacia hebeclada* (Candle acacia), *Zizyphus mucronata* (Buffalo thorn)

The differences in the vegetation cover over different thicknesses of calcrete are believed to be related to availability of additional water below the thicker accumulations. Here analyses of the leaves and twigs of deeply rooted shrubs and trees are considered more likely to detect bedrock mineralisation than analyses of surface soils.

The application of biogeochemistry to mineral exploration in calcrete terrains is discussed further in the section dealing with gold mineralisation at Mararoa Reef.

<sup>7</sup>Common names of trees from Coates Palgrave (1977)

<sup>8</sup>Suffrutices: Sub-shrubs; they produce a woody growth which only lasts for a few years

## 5. GOLD MINERALISATION IN CALCRETE TERRAINS

### 5.1. CASE STUDIES

#### 5.1.1. Mararoa Reef Au, Norseman, Western Australia (B 1 Ca 1)

(Smith and Keele, 1984)

Mararoa Reef is one of the important gold mines of the eastern Goldfields Province of the Yilgarn Block. Mararoa Reef is located at the southern end of a major Archæan greenstone belt that includes the gold mining centres of Kalgoorlie and Coolgardie. The location and general geology are illustrated in Fig 34.

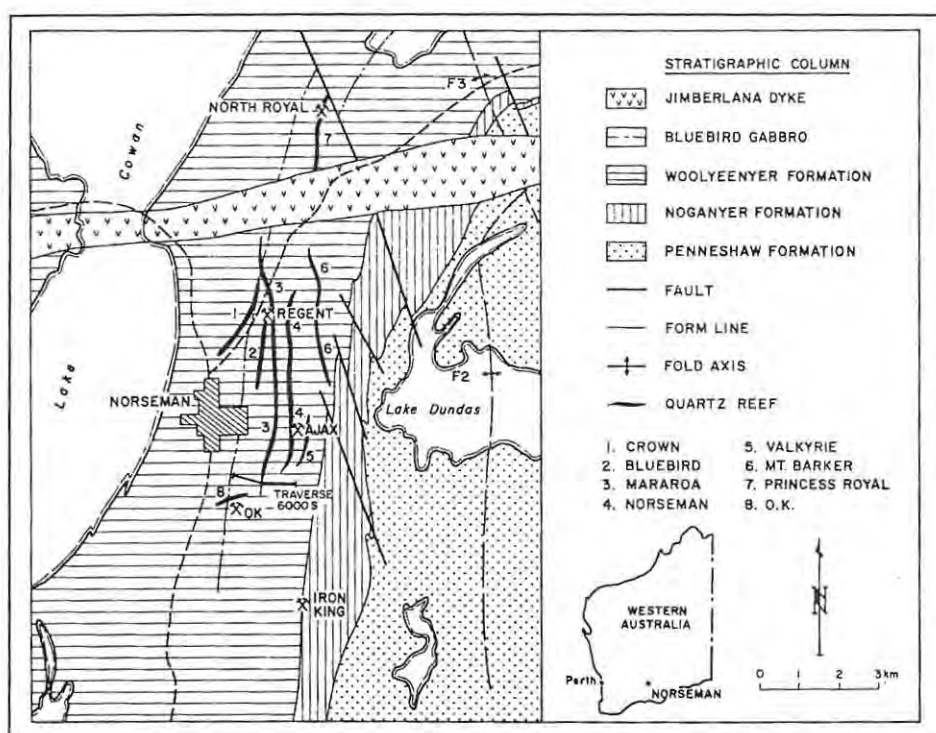


Fig 34: Locality plan and geological map of the Norseman goldfield (from Smith and Keele, 1984)

The lithologies in the area of the gold mineralisation are comprised mainly of westerly dipping ( $55^\circ$ ) pillow lavas, basaltic flows and gabbroic to pyroxenitic sills and dykes. Gold mineralisation occurs in N-S striking quartz reefs as infillings along reverse faults, dipping  $20-50^\circ$  east and is preferentially concentrated along dilational, flat lying sections of the faults. The actual quartz reef, which may be up to 2m wide, is laminated and contains thin bands of chlorite, sericite, tremolite, plagioclase and minor amounts of pyrite, pyrrhotite, galena, sphalerite, arsenopyrite, chalcopyrite and tellurides which are erratically associated with gold mineralisation.

The rocks in the area have been deeply weathered, but much of the ferricrete horizon so formed has been eroded away and the profile is therefore partially truncated. Overlying soils are mostly residual with a strong æolian and alluvial component derived from the nearby Lake Cowan salina. The upper horizon of the soil profile is 0.5 to 2m



thick and contains between 5 and 30% carbonate as calcite and dolomite in powdery and nodular forms and thus represents early stages of calcrete formation (Stage 2 of Netterberg, 1971). The Fe content, which has important implications to be discussed below, is less than 5% and the pH is buffered between 8.0 and 9.5 by the action of carbonate/bicarbonate.

Studies by Mazzucchelli (1965, in Smith and Keele, 1984) have shown the importance of As as a pathfinder element to gold mineralisation in the Norseman area. Fig 35 shows the distribution of As in the surficial cover above Mararoa Reef; it will be noted that As values in the 0-1m sample of the drill holes are generally low (15-25ppm), but soil samples taken from 10-15cm had even lower As values of 2-5ppm. Mazzucchelli (1965, in Smith and Keele, 1984) showed that a carbonate rich soil from Norseman sampled at a depth of 15-30cm and having a bulk analysis of 33ppm As had 150-400ppm As in separated iron oxide grains, while carbonate grains contained only 10-25ppm As. The low As contents of the 0-1m drill samples in Smith and Keele's (1984) study are therefore thought to reflect the low Fe contents (<5%). In addition, the alkaline pH of 8.0-9.5 would inhibit any non-specific adsorption of arsenate by either clay minerals or Fe- and Al-oxides. To overcome this problem Smith and Keele (1984) transformed the As data through a regression analysis (significant As:Fe correlation at  $P < 0.01$ ) to reduce the variation in As values caused by differences in the Fe content. Sample values were then replotted as a percentage ratio of the actual As value to the expected As value for the particular Fe content of the sample. This operation had the effect of extending the three As anomalous zones visible at or below 5m (in the 3rd section of Fig 35) up into the Fe deficient 0-1m layer (see the 2nd section of Fig 35). The fact that this operation was successful is indicative of the residual nature of the soil profile and that the added alluvial and aeolian components in the surface horizon are diluents only.

Smith and Keele (1984) also briefly note that the highest values for Pb occur in the top carbonate rich horizon which is probably due to the formation of insoluble hydroxy-Pb-carbonates.

Biogeochemistry also plays a role at Norseman: Smith and Keele (1984) examined the dispersion of Au and As in *Melaleuca pauperiflora* F. Muell., a tree which has a preference for the calcareous soils. Anomalous values of gold in ash are 100-150ppb with a peak value of 230ppb and a background for the traverse (Fig 36) of 60ppb. Interestingly there is poor correlation of the plant Au values with the soil values which may be due to plants taking up water from soil horizons lower than the shallow drill holes penetrated or perhaps the plants are taking up Au, and accumulating it, from soils which have total gold levels of less than 10ppb (the detection limit for the study). As values in plants at Norseman were erratic and not correlated to Au.

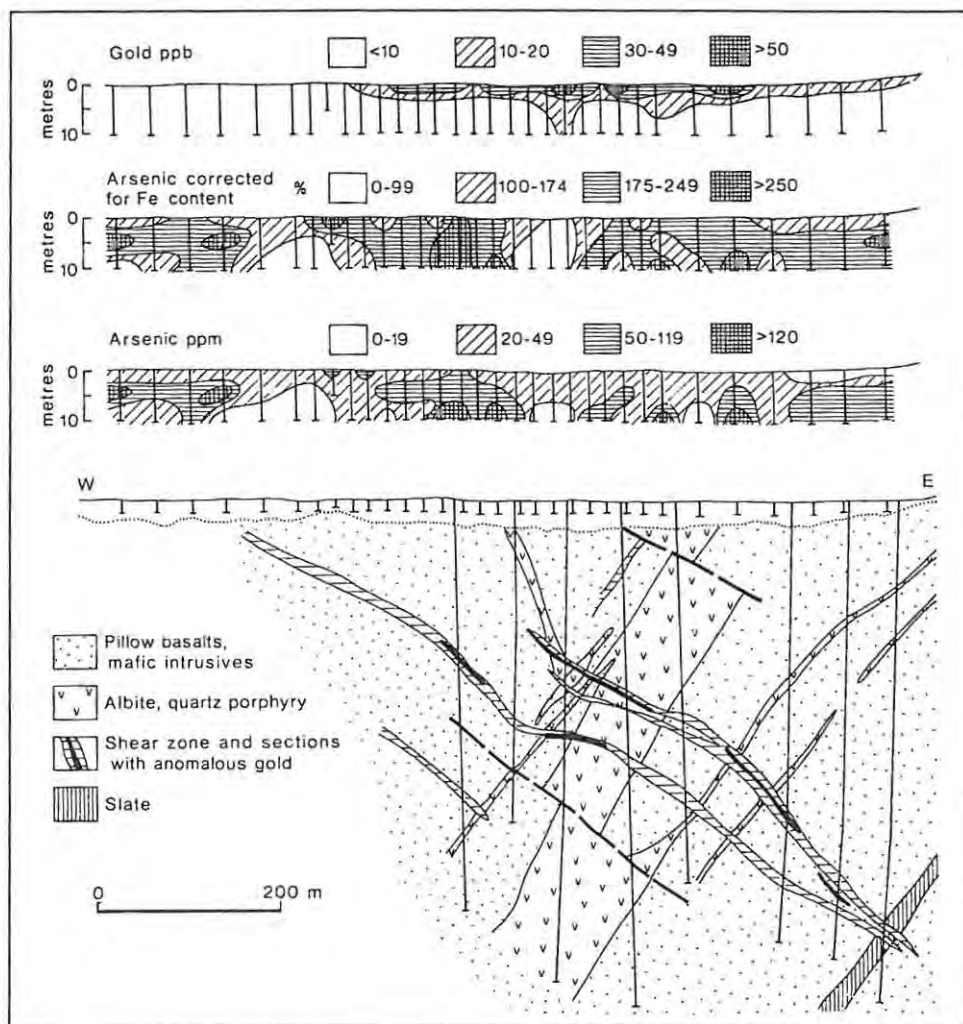


Fig 35: Distributions of Au, As and corrected As in surficial horizons of the regolith overlying Au mineralization at Mararoa Reef. Corrected As values are actual values as percentages of expected value based on the Fe content, derived from an As-Fe regression (from Butt, 1992 after Smith and Keele, 1984).

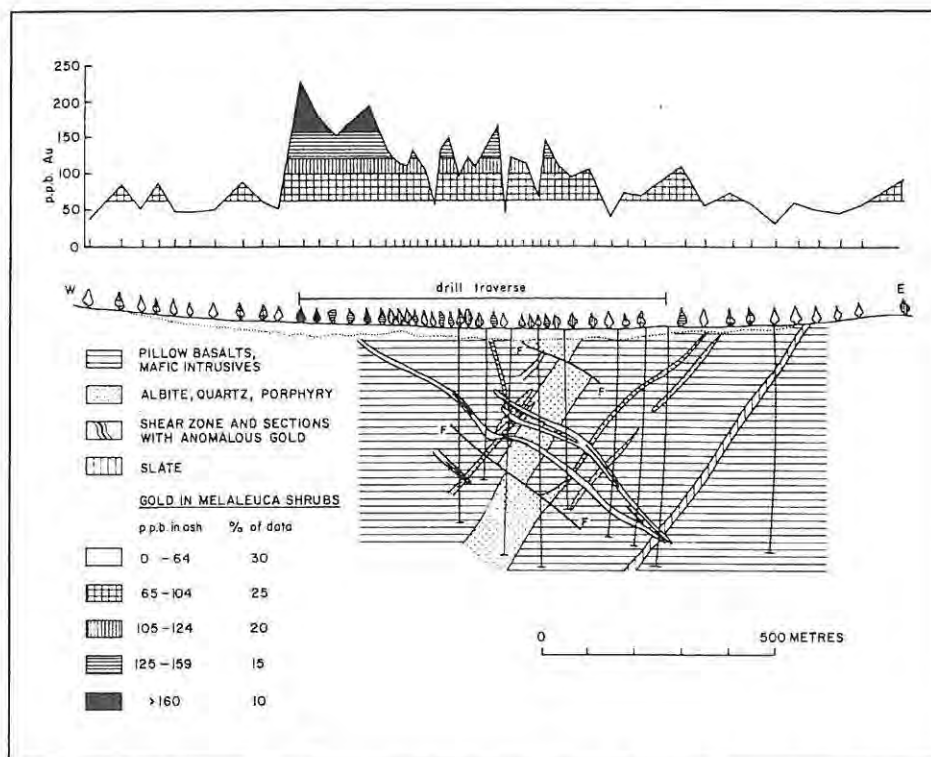


Fig 36: Gold in *Melaleuca pauperiflora* F. Muell. at Mararoa Reef. Note strong anomaly where extension of Mararoa Reef reaches surface (from Smith and Keele, 1984)

### 5.1.2. Eldorado Valley Au, Nevada (\* 3 Ca 3)

(Ypma, 1991)

The area of interest in the Eldorado Valley is situated about 75km SE of Las Vegas in Nevada, USA. Bedrock in the area consists of Precambrian gneisses, schists, diorites and gabbros, intruded by granites of Laramide age (Late Cretaceous-Early Tertiary) and acid porphyries. Porphyries and associated volcanics are host to the epithermal gold mineralisation at nearby Nelson (4 - 12 g/t).

Massive calcrete occurs in the Eldorado Valley floor and also on the alluvial fans coming off the Eldorado Mountains. The calcrete is a mixture of near surface (2 - 4m depth) pedogenic calcrete overlying a massive substratum of valley calcrete which may reach 60m depth. Typically, a profile looks as follows:-

- 0-2m surface rubble, aeolian sands
- 1-3m poorly sorted detrital material with calcareous cement
- 2-5m calcrete hardpan with laminar horizons
- 3-20m massive, carbonate cemented fan material, to massive carbonate
- 8-40m poorly cemented and poorly sorted fan material
- 15-60m altered basement rocks

A drilling and pitting exploration programme in the area produced grades of 0.03 to 7.23 g/t Au in calcrete. The West-We-Go claim was identified as having a resource of 16Mt down to 20m depth, grading 0.35 g/t Au. The whole alluvial fan surrounding the West-We-Go claim is estimated to contain some 60t of gold.

Ypma (1991) proposed a model of calcrete acting as a temporary reservoir for Witwatersrand gold; the gold being trapped within basin edge calcretes and being liberated upon dissolution of the calcrete during the higher erosion rates of a regressive phase.

### 5.1.3. Western Australia

Concentrations of gold in calcrete are also reported by Ypma (1991) from the Lake Way area of Western Australia, an area which is discussed further under the section on uranium in calcrete. Pedogenic calcrete developed immediately over greenstones revealed a four-fold increase of gold in calcrete (20ppb Au) over greenstone (5ppb Au). Similar enrichments and concentrations of gold in groundwater and pedogenic calcrete overlying greenstone are reported from the Cosmo Newberry area.

### 5.1.4. Callion Au Deposit, Western Australia (A 1 Ca, Si 0,1)

Callion is located 100km NNW of Kalgoorlie and gold occurs in quartz filled shear zones within a sequence of metamorphosed basalts, interflow sediments and acid tuffs within the Archaean Wiluna-Norseman greenstone belt (Glasson et al., 1988). The area is deeply weathered (40-60m) with the formation of a coarse pisolitic laterite profile of 1 - 3m thick underlain by a hardcap of mottled silicified kaolinite with ferruginous nodules and fragments. Glasson et al. (1988) report the delineation of a gold deposit within the pisolitic laterite itself; reserves were estimated at 71 000t at 2g/t over an average thickness of 3m. A pedogenic calcrete is frequently developed within the pisolitic laterite and contains numerous laterite fragments suggesting replacement of the laterite. Trenches were excavated and sampled in 5m horizontal channel sections. The highest gold value was 16ppm Au for a sample in calcrete (Fig 37); the gold occurring in association with the pisoliths and in the carbonate matrix (Lintern et al., 1992). It must be said that this section happened to be the one passing over the inferred surface projection of the quartz vein, but for our purposes it is sufficient to recognise that the calcrete was able to reflect the underlying mineralisation.

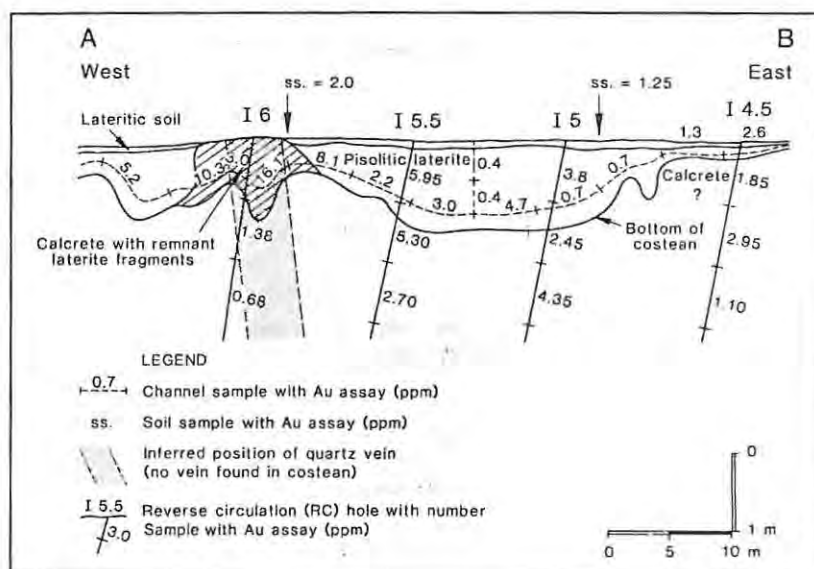


Fig 37: Section through a trench at Callion showing the gold grades in horizontal channel samples. Highest grade in calcrete (from Glasson et al., 1988).

#### 5.1.5. Bounty Au Deposit, Western Australia (B 1 Ca 1,2)

The Bounty gold deposit is located 200km SW of Kalgoorlie. Gold mineralisation occurs in shears within cherts and banded iron formation bounded by a mafic intrusion and a komatiitic flow sequence.

Investigations by Lintern (1989, in Lintern et al., 1992) showed that the Au distribution in the soils is closely related to that of pedogenic carbonate (Fig 38) such that successful sampling in this region requires inclusion of the calcareous horizon. Lintern et al. (1992) go so far as to say that exclusion of this pedogenic carbonate from the sampling medium may result in a failure to find any anomaly.

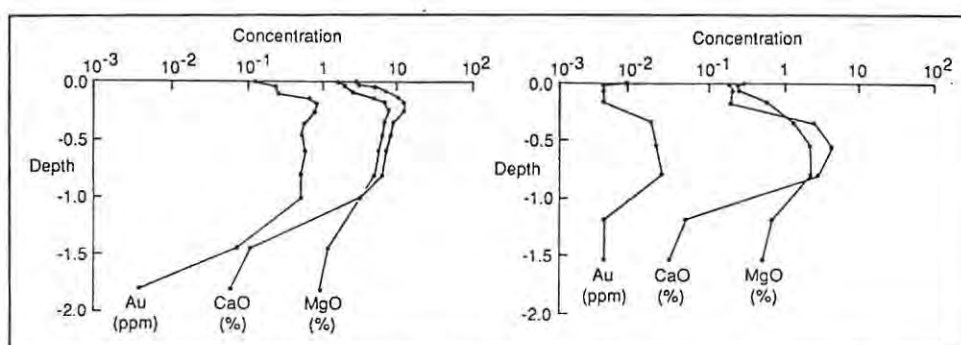


Fig 38: The association of Au with Ca and Mg in pedogenic carbonates at the Bounty gold deposit (from Lintern et al., 1992 after Lintern 1989).

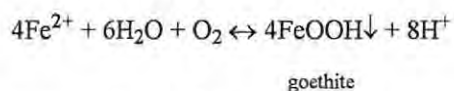
#### 5.1.6. Gold Dispersion in Soils

Initial thinking on the concentration of gold in calcretes of the Eldorado Valley lead to a model of incorporation of detrital gold in an upward accreting soil/calcrete profile. Despite the relative immobility of gold it is recognised that gold does move in solution in the weathering profile (Smith, 1987; Webster and Mann, 1984; Wilson, 1984).



Evidence for gold mobility in the weathered zone lies in textural features such as sponge gold, filigree gold, paint gold and thin lamellae of gold associated with concretionary growth of Fe-oxides and in the high fineness relative to primary gold.

In the Au/H<sub>2</sub>O system at 25°C in the absence of other complexing agents gold is only present in the normal Eh-pH conditions of soil as Au<sup>0</sup> metal. If complexing agents such as Cl<sup>-</sup> are introduced into the system it is possible for gold to be dissolved under conditions of low pH and high Eh (Fig 39). The introduction of Fe<sup>2+</sup> into a soil profile (by the weathering of basement rocks or from organic complexes for instance) will rapidly lower the pH as Fe<sup>2+</sup> is oxidised to Fe<sup>3+</sup> :-



Mann (1984) has recorded groundwater pH values as low as 2.8 and Cl<sup>-</sup> concentrations of 0.1M and showed that gold was dissolved in the solution.

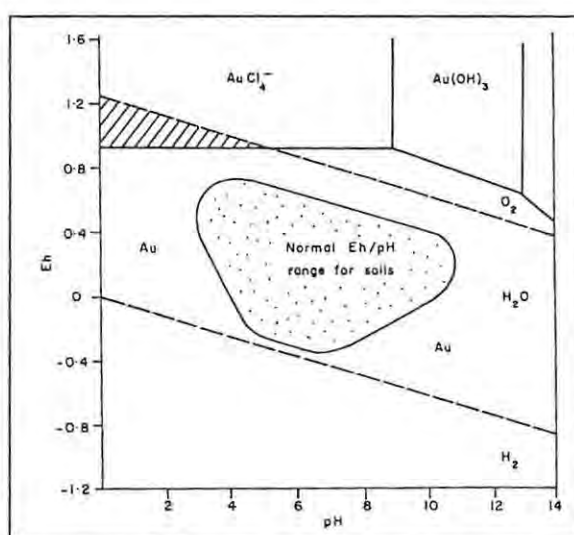
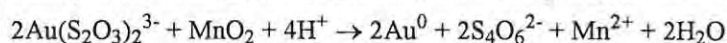


Fig 39: Eh / pH diagram for the system Au-H<sub>2</sub>O-Cl<sup>-</sup> at 25°C. Au<sup>3+</sup> = 10<sup>-2</sup>M and Cl<sup>-</sup> = 2M (from Smith, 1987)

Gold is often enriched in humus layers or in Fe-oxide and Mn-oxide concretions, usually at, or near, the water table (present day or ancient) where there is a major oxidation reduction boundary. Indeed, this phenomenon is of importance to the Edna May gold mine near Westonia (Western Australia) where narrow, tabular, high grade zones are developed at the water table (Webster and Mann, 1984).

Thiosulphate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) can also complex with gold as Au(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub><sup>3-</sup> and its formation is favoured in reducing conditions below the water table and also by slightly alkaline conditions. Thiosulphate is considered to be the migrating complex for secondary gold at the Upper Ridges Mine, Papua New Guinea. Oxidation of the thiosulphate complex by MnO<sub>2</sub> is one of the factors responsible for the re-precipitation of the secondary gold:-



The point being that gold can and does migrate in the secondary environment where it could be chemically and physically trapped by iron oxides in calcrete.

## 6. DIAMOND EXPLORATION IN CALCRETE TERRAINS

### 6.1. INTRODUCTION

The discussion which follows revolves around exploration for primary occurrences of diamond i.e. in kimberlites and olivine lamproites.

Economic concentrations of diamond are only known from kimberlites and from olivine lamproites, both of which are ultrabasic rocks containing high concentrations of trace elements normally associated with alkalic rocks. Olivine lamproite, in particular, is ultra-potassic. Despite having a varied trace element content it is the technique of heavy mineral sampling that is most commonly, and most successfully, used in diamond exploration. The main use of geochemical sampling in diamond exploration is as a complementary technique to other methods, but may be used as a stand-alone method when prospecting for olivine lamproites in which the typical pathfinder minerals are rare or absent (see Table 12). The heavy mineral suite used in prospecting consists of ilmenite, pyrope garnet, chromite, chrome-diopside and, of course, diamond itself. The discovery of these indicator minerals does not, of itself, constitute a kimberlite find since these minerals are available from sources other than kimberlite and lamproite. The chemistry of the heavy minerals provides further clues as to where they came from and, if from a kimberlitic source, also gives some idea of the diamond potential of that kimberlite. Some typical ranges of chemical characteristics of the principal kimberlite pathfinder minerals are shown in Table 12.

Table 12

Chemical characteristics of the principal kimberlite pathfinder minerals (from Gregory and Janse, 1992)

	Garnet	Chromian diopside	Ilmenite	Chromite
SiO <sub>2</sub> %	40-42	52-55	Nil	Nil
TiO <sub>2</sub> %	< 0.5	< 0.5	50-60	< 1.0
Al <sub>2</sub> O <sub>3</sub> %	12-17	1-3	Nil	3-9
Cr <sub>2</sub> O <sub>3</sub> %	<i>G9</i> 2-4 <i>G10</i> > 4	1-3	0.5-3	60-65
FeO <sup>a</sup> %	7-11	2-6	25-30	18-22
MgO %	18-20	18-22	10-15	10-15
CaO %	<i>G9</i> 3-8 <i>G10</i> 1-4	16-20	Nil	Nil
Na <sub>2</sub> O %	<i>G9</i> Nil	1-2	Nil	Nil
Kim	Common to abundant	Common	Common to abundant	Common to abundant
OL	Rare	Rare	Very rare	Abundant

Kim = occurrence in kimberlite.  
 OL = occurrence in olivine lamproite.  
<sup>a</sup> Total Fe as FeO.  
*G9, G10*: types of pyrope garnet (Dawson and Stephens, 1975).

Much of the information regarding prediction of the economic potential of a kimberlite pipe through mineral chemistry is the result of in-house exploration company research and is largely unpublished, but Gregory and Janse (1992) give some guides as to what constitutes a "high-interest" mineral composition:-

- The Cr-rich, Ca-poor pyrope garnets are particularly important. These garnets contain >4 wt% Cr<sub>2</sub>O<sub>3</sub> and <3 wt% CaO and are generally referred to as the "G10" group of Dawson and Stephens (1975). Such compositions indicate that the kimberlite originated in the diamond stability field and may therefore contain diamonds. However, generally less than 5% of pyropes are G10 garnets.
- Ilmenites with >10 wt% MgO (picroilmenites) and >1 wt% Cr<sub>2</sub>O<sub>3</sub> and in which the Cr content increases with increasing Mg content are accepted as positive indicators of diamondiferous kimberlites.
- Chromites with >62 wt% Cr<sub>2</sub>O<sub>3</sub>, 10-15 wt% MgO, <10 wt% Al<sub>2</sub>O<sub>3</sub> and <1 wt% TiO<sub>2</sub> are accepted as positive indicators of diamondiferous kimberlites.

The bulk geochemistry of kimberlite, although not a major tool, has been used during prospecting by analysing for Ni and Cr (which reflect the ultrabasic character) and Nb (reflecting the alkalic character).

- Nickel in kimberlites occurs primarily in olivine (Gregory, 1969 in Gregory and Janse, 1992) and is released at an early stage during weathering. The depletion of Ni in soil and saprolite in deeply weathered areas is due to the downward leaching of Ni by percolating waters. Below the water table, Ni concentrations are only slightly lower than that in fresh kimberlite. Interpretation of Ni data must, therefore, take note of the position of the sample with respect to the water table.
- Niobium in kimberlites is concentrated mostly in perovskite and ilmenite and possibly in priderite in olivine lamproites. Removal of Nb from the soil during chemical weathering is probably due to the decomposition of perovskite and removal of Nb as alkali niobates, soluble organo-metallic compounds or colloidal hydrolyzates (Gregory and Janse, 1992).
- Chromium in kimberlites is concentrated in chromite, magnetite, ilmenite and, to a lesser extent, substituting for Fe<sup>3+</sup> in ferromagnesian minerals.

Gregory and Janse (1992) report that distinctive and unequivocal anomalies occur in the upper saprolite of all the areas they studied and, if practical, this is the best horizon to sample in deeply weathered terrain. In areas of lesser chemical weathering, or where erosion has truncated a profile (NW Australia) anomalies may occur in near surface samples, but are generally confined to the area immediately overlying the kimberlitic rocks. In Australia some mechanical dispersion has been noted around the hillocks formed by leucite lamproites.

## 6.2. HEAVY MINERAL INDICATORS AND CALCRETE

Each kimberlite has a characteristic heavy mineral signature, meaning that the presence and abundance of a particular suite of heavy minerals is different for each kimberlite. The heavy minerals of interest to the prospector are, in most cases, in the macrocryst<sup>9</sup> fraction since a typical heavy mineral survey retrieves the 0.425 or 0.5mm to 2mm fraction and the primary matrix heavy minerals rarely exceed 0.1mm in size (Kilham, 1985). These macrocrysts generally constitute between 1 and 2% by mass of kimberlite.

The mineralogy of volatile-rich, mantle derived rocks, such as kimberlite, makes them susceptible to alteration when they reach the Earth's surface. This is due mainly to late-stage deuteric processes involving carbonates (calcite) and hydrates (serpentinisation of olivine). In particular the carbonate content of kimberlites renders them susceptible to calcretisation. Kilham (1985), for instance, reports that kimberlite pipes at Duiwelskop (near Jan Kempdorp) and Sanddrift (Prieska) are preferentially calcretised with respect to the surrounding country rocks. In the case of Duiwelskop calcretisation has formed positive topographic features.

As mentioned above, heavy mineral sampling forms an important part of the kimberlite prospectors armoury, but calcrete has the effect of reducing and/or masking heavy mineral anomalies. This masking/reducing effect manifests itself in at least four ways (Kilham, 1985) discussed further in the text below this listing:-

1. Calcrete forms a physical boundary through which heavy minerals cannot "migrate" to surface and also entraps those grains that are already near surface.
2. Calcrete formation destroys, either wholly or in part, some of the indicator grains.
3. Dissolution of indicator minerals reduces the size of the grains below the size of the smallest fraction normally sampled.
4. Alteration of the surface features of heavy minerals such that they are no longer recognizable during a routine heavy mineral survey.

Studies by Kilham (1985) indicate that there appears to be an inverse relationship between the abundance of heavy minerals and the amount of  $\text{CaCO}_3$  accumulation, cementation and replacement. The content of the heavy minerals in a vertical profile therefore decreases in proportion to the maturity of the calcrete cover. Table 13 below illustrates the depletion in heavy mineral content with increasing degree of calcretisation at the Duiwelskop kimberlites:-

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<sup>9</sup> *Macrocryst* is a non-genetic term for the large (0.5-10mm) rounded to anhedral crystals (usually olivine) set in a finer matrix. Cognate macrocrysts are *phenocrysts* while those derived from mantle harzburgites, lherzolites or the discrete nodule suite are *xenocrysts*.

Table 13

Average number of grains (and % depletion) per sample in various horizons over the Duiwelskop kimberlite (data from Kilham, 1985)

Calcrete Development	Garnet No. of Grains	Garnet % Depletion	Chromite No. of Grains	Chromite % Depletion
Hardpan Calcrete	90	75	78	30
Calcified, weathered kimberlite	210	41	88	21
Weathered kimberlite	356	0	112	0

It can be seen from the table above that chromite is relatively more stable than garnet in the calcretising environment. Further data from other centres in South Africa (in Kilham, 1985) indicate that the relative stability of heavy minerals in calcretes (in terms of the relative abundance of mineral grains present) is:-

Chromite & Ilmenite > Garnet > Chrome Diopside

most stable

least stable

The instability of chrome diopside in the calcretising environment may be a function of the good cleavage of diopside and its consequent breakage to finer sizes more rapidly than, say, chromite. Garvie (1981) obtained similar results at Jwaneng in Botswana. He found that ilmenite and, to a lesser extent, garnet are relatively stable in the calcretising and weathering environment, whereas chrome diopside shows a progressive decrease in abundance upwards and is eventually eliminated at the top of the profile.

In an attempt to determine the relationship between mineral breakdown and calcretisation Kilham (1985) conducted experimental dissolution experiments under laboratory conditions for periods of up to 126 days, during which time heavy mineral grains were immersed in waters of differing pH values. No connection was found between the formation of secondary etch features and pH, immersion time or temperature (up to 70°C). Results did, however, indicate an order of increasing susceptibility to alteration:-

Garnet > Ilmenite > Chromite > Chrome Diopside

least susceptible to alteration

most susceptible to alteration

There is some contradiction of results between the order of susceptibility to alteration in the etching experiments and the preservation of the heavy minerals in calcrete profiles, but there is agreement that chrome diopside has the lowest survival potential.



### 6.3. GEOCHEMICAL SIGNATURE OF KIMBERLITE IN CALCRETE

Kilham (1985) analysed calcretes developed over four South African kimberlites for the trace elements Nb, Zr, Y, Sr, Rb, Sc, Ba, Cr, V, Ti and Fe (as  $\text{Fe}_2\text{O}_3$ ). As a point of reference samples through calcrete-shale and calcrete-dolomite profiles were also analysed.

Concentrations of all the elements were observed to decrease upwards through the calcrete profiles although it is most marked for the elements Nb, Zr, Y, Sc, Cr, Ni,  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  in three of his four localities (Sanddrift, Venetia, Samaria). An interesting feature of the Samaria profile is an increase in the Zr, Sc, Cr, V,  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  concentrations in the upper parts of the profile where calcrete is mixed with aeolian sand. This is taken as evidence for contamination of the calcrete by heavy minerals concentrated in the sands (by deflation processes?). The most mobile elements Ba, Sr and Rb display variable distribution patterns. The decrease in concentration of Nb, V, Cr is probably a function of the upward decrease in the abundance of heavy minerals such as garnet, ilmenite and chromite in calcrete. Although element depletion takes place in the majority of Kilham's (1985) profiles the concentration of the elements remains above the "blank" values of the reference profiles in the topmost samples. Again, the maturity and thickness of the calcrete profile plays an important part in element depletions. The Duiwelskop kimberlite has up to 10m of hardpan calcrete developed above the kimberlite and contains lower element concentrations by a factor of 2 to 4 than the Sanddrift, Samaria and Venetia sections.

The results of Kilham's study indicate that Nb, Cr and V may be the most useful pathfinder elements, at least in areas of shale or dolomite host rock. Niobium concentrations in calcrete at the surface vary between 7 and 12ppm with a mean of 9ppm which is an enrichment of 3 times compared to calcretes overlying shales and dolomite (Table 14 and 15 ). Chromium and vanadium show a sympathetic variation in concentration through Kilham's profiles. Chromium shows enrichments of 2.5 to 5.5 times in calcrete overlying kimberlite compared to calcrete overlying shale and dolomite while vanadium is enriched 1.8 to 2.5 times. Although not selected by Kilham as one of his favoured pathfinder elements (due to its mobility in the oxidising environment) Ni does show enrichments of 2 to 8 times in calcrete over kimberlite compared to calcrete over shale and dolomite.

Table 14

Average trace element abundances in kimberlites (ppm) and their host phases (data compiled from Mitchell, 1986 and Kilham, 1985)

Li	29	phlogopite, apatite	Sb	-	
Be	1.6		Te	-	
B	36	serpentines after olivine	I	-	
F	2774	apatite?	Cs	2.2	
P	3880		Ba	1100	phlogopite, titanates, carbonates
S	1687	sulphides	La	150	perovskite, apatite
Cl	202	mica?	Ce	200	perovskite, apatite
Sc	14	garnet, magnetite, perovskite	Pr	22	
Ti	11800	perovskite	Nd	85	perovskite, apatite
V	100	chromite, ilmenite, diopside, garnet	Sm	13	perovskite, apatite
Cr	893	chromite, diopside, garnet, ilmenite	Eu	3	perovskite, apatite
Mn	1160		Gd	8	perovskite, apatite
Co	65	garnet	Tb	1	perovskite, apatite
Ni	965	olivine, sulphides, diopside, ilmenite	Dy	-	
Cu	93	sulphides, garnet	Ho	0.55	
Zn	69		Er	1.45	
Ga	5.7	garnet	Tm	0.23	
Ge	0.5		Yb	1.2	perovskite, apatite
As	-		Lu	0.16	perovskite, apatite
Se	0.15	sulphides	Hf	5.6	perovskite, ilmenite
Br	-		Ta	11	perovskite, ilmenite
Rb	73	phlogopite	W	-	
Sr	851	apatite, perovskite, calcite, diopside	Re	0.069	
Y	22	apatite, perovskite	Os	1.34	
Zr	184	perovskite, ilmenite, zircon, baddelyite	Ir	0.003	
Nb	141	perovskite, ilmenite	Pt	0.19	
Mo	1.7		Au	0.012	
Ru	0.065		Hg	0.008	
Rh	0.0071		Tl	0.219	
Pd	0.0081		Pb	15.3	sulphides, mica, garnet
Ag	0.134		Bi	0.024	
Cd	0.073		Th	17	perovskite, apatite
In	-		U	3.1	perovskite, apatite, zircon, baddelyite
Sn	5.4				

Table 15

Trace element concentrations of elements potentially useful for geochemical exploration for kimberlites in calcrete terrains.

	Calcretised Kimberlite <sup>1</sup> (S. A.)	Enrichment <sup>1</sup> (S. A.)	Calcretised Shale <sup>1</sup> (S. A.)	Calcretised Dolomite <sup>1</sup> (S. A.)	Non-Calc Shale <sup>2</sup> (World)	Non-Calc Carbonates <sup>2</sup> (World)	Non-Calc Kimberlite <sup>3</sup> (World)
Nb	7-12	3	3	3-4	11	0.3	141
Cr	1043-3716	2.5-5.5	435-476	609-728	90	11	893
V	361-495	2	158-189	173-273	130	20	100
Ni	39-165	2-8	19-21	19-22	68	20	965

Calcretised samples are from the upper surface of the calcretised profile. Enrichment refers to the ratio of the element in calcretised kimberlite to calcretised shale or dolomite (after the work of Kilham, 1985).

1. Data from Kilham (1985).

2. Data from Dutro et al. (1989)

3. Data from Mitchell (1986)

## 7. URANIUM MINERALISATION IN CALCRETE TERRAINS

### 7.1. INTRODUCTION

With the oil crisis and the rising importance of nuclear energy as an alternative the 1970'S saw a boom in exploration for uranium. In 1972 the calcrete hosted deposit at Yeelirrie, Western Australia, was discovered. Yeelirrie and others like it (Lake Austin, Hinkler Well-Centipede, Lake Maitland, Lake Way) have an intimate association with non-pedogenic calcretes. The success of Yeelirrie and the Western Australian deposits highlighted the importance of surface phenomena in uranium mineralisation and because of their association with calcrete the phrase "calcrete-type uranium" was much bandied about in the literature, sometimes with incorrect usage. Although unanimity has not been reached, it would seem that deposits usually termed uraniferous calcretes, dolocretes or gypcretes cannot, *sensu stricto*, be described as such, since in numerous cases the  $\text{CaCO}_3$  content is less than 5 or 10% (Toens and Hambleton-Jones, 1984). Surficial uranium deposits need not be associated with calcrete; for example the lacustrine fluviatile deposits at Henkries and Kanikwa, South Africa are associated with diatomaceous earth and carbonaceous sediments (Ralston et al., 1986)(see also Table 16). Toens and Hambleton-Jones (1984) proposed a classification system for surficial uranium deposits in which the "-crete" terminology has been discontinued (except for the case of their Pedogenic class of deposits)(Fig 40). Under this scheme Yeelirrie, which has an undisputed calcrete host, is classified as a fluviatile, valley-fill type. Langer Heinrich, which Carlisle (1978) describes as being a calcrete hosted deposit, is also classified by Hambleton-Jones et al. (1986) as a fluviatile, valley-fill type, but with nary a mention of calcrete. Other writers, such as Butt and Carlisle do not share the view of Toens and Hambleton-Jones and maintain usage of "calcrete" as a descriptor for their models. This difference of opinion between workers of Australian experience and those of southern African experience makes relating the two a difficult task.

Since this dissertation is concerned with mineral deposits in calcrete the classification of Toens and Hambleton-Jones (1984) will not be adhered to since it does not emphasize the influence of calcrete in uranium mineral deposits. The classification system is merely mentioned here to make the reader aware that surficial uranium deposits (which constitute 10-15% of global uranium resources (Toens, 1984)) are not all calcrete (*sensu stricto*) hosted.

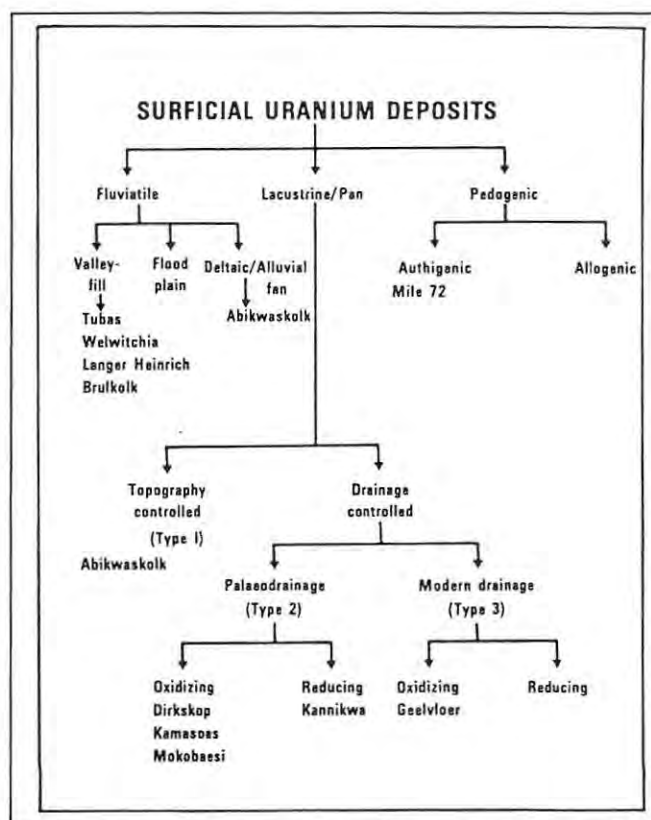


Fig 40: Classification of surficial uranium occurrences with southern African examples (from Hambleton-Jones et al., 1986 after Toens and Hambleton Jones, 1980).

Table 16

Main petrographic host rock features of some mineralised surficial uranium deposits (after Pagel, 1984)

Yeelirrie (Australia)	Valley fill calcrete characterised by an intense dolomitisation and development of sepiolite.
Lake Austin (Australia)	Calcrete (calcite and dolomite) with chalcedony in silicified zones overlying red-brown clays and/or weathered bedrock. A cover of sand or alluvium is locally present. Mineralisation in sandy clays, carbonate-rich with a kaolinite/smectite matrix.
Lake Way (Australia)	Mainly in carbonated reworked fluvial-clastics, also in valley fill calcrete and in the younger chemical delta carbonates.
Lake Raeside (Australia)	Red or brown calcareous clays and clayey grits.
Lake Maitland (Australia)	Essentially a discontinuous calcrete, rich in dolomite but mineralisation also occurs in sand, pale and sandy clays and brown silts.
Hinkler Well (Australia)	An elongate valley calcrete consisting of calcite and chalcedony with dolomite, gypsum and sepiolite. In chemical delta, dolomite and sepiolite are more important and aragonite is present.
Tubas (Namibia)	Fluviatile sediments constituted of poorly consolidated sand, sometimes gritty to pebbly bedded sand and gravel, presence of gypcrete capping.
Langer Heinrich (Namibia)	Conglomerates, gravel, grit, and clay sediments deposited under flash-flood conditions in deep palaeochannels.
Brulkolk (South Africa)	Gypsiferous red sand and gravel with calcareous nodules or clay-rich alluvium with grit bands or beds and clay with calcareous nodules
Abikwaskolk (South Africa)	Gypsiferous sand, silt and shales.
Mudugh (Somalia)	Calcrete, marls, clays and bentonite.
Kannikwa (South Africa)	Organic-rich diatomaceous earth between an upper calcified alluvial gravel and aeolian sand overlying gravel, sand and clay lenses.
NE Washington E Idaho (USA)	Organic-rich uranium host sediments (plant debris, peat) lacustrine shelly marls, clayey sand, air-fall ash, glacial? clay, coarse sand and gravel.
Lost Creek (USA)	Subhorizontal tabular bodies of schroëckingerite $[\text{NaCa}_3(\text{UO}_2)(\text{CO}_3)_3(\text{SO}_4)\text{F}\cdot 10\text{H}_2\text{O}]$ in Eocene sandstone and siltstone and Quaternary sand and gravel

## 7.2. URANIUM IN CALCRETES

Up to now the discussion has revolved around the problems of detecting anomalies through (mostly) pedogenic calcretes. The situation for uranium is somewhat different in that virtually all economic concentrations of uranium in calcrete are in non-pedogenic calcretes where the Ca, Mg,  $\text{CO}_3$ , U and V have been added by lateral transport rather than by vertical redistribution. Indeed, the presence of pedogenic calcrete may dilute the uranium ore. These



non-pedogenic host rocks draw upon a large terrain of weathering rock or regolith and occur along the axes and damming-up points of groundwater drainages. To become ore bodies they must have a source terrain which is large in comparison to their own size or be anomalously rich. The components must remain soluble until they reach areas of groundwater convergence where carnotite<sup>10</sup>, the only uranium-ore mineral in these deposits, will precipitate. As a result of the above factors these deposits develop in areas of predictable morphology and distribution related to the source terrain, ground-water flow and configuration of the bedrock (Carlisle, 1983).

### 7.2.1. A Classification of Calcretes

With uranium-bearing calcretes specifically in mind Carlisle (1983) proposed a genetic classification of calcretes (Fig 41).

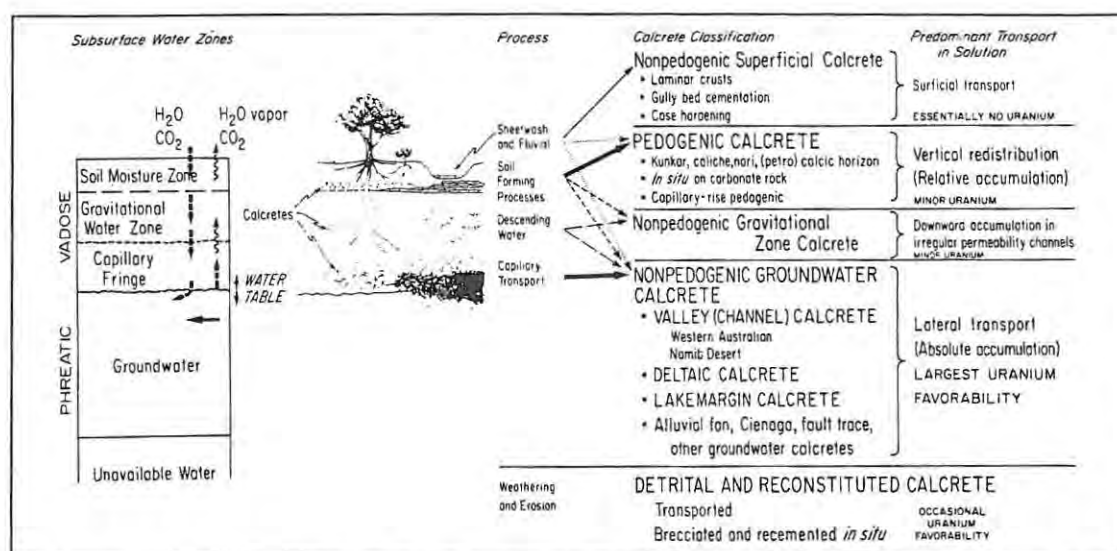


Fig 41: A genetic classification of calcretes and their uranium favourability. A given calcrete may result from multiple processes as suggested by the arrows (from Carlisle, 1983).

The variety of greatest interest are the non-pedogenic groundwater calcretes and, in particular, those labelled valley (channel), deltaic and lake margin calcrete. These form mainly in the capillary fringe directly above moving subsurface-water and, in some cases, slightly below the water table. Due to water table fluctuations and because flowing groundwater brings a continuous supply of chemical constituents these groundwater calcretes can be much thicker than a single pedogenic calcrete. In their simplest form groundwater calcretes are diagnostically free of any profile or sequence of nodular, laminar or plugged horizons as found in the pedogenic calcretes. Rather, their textures and structures tend to preserve the textures and structures of the host materials (Carlisle, 1983).

<sup>10</sup> Carnotite  $K_2(UO_2)_2V_2O_8 \cdot 3H_2O$

### *Valley Deposits*

(Butt et al., 1984)

These occur in calcretes and associated underlying sediments in the central channels of major drainages, and in the platforms and chemical deltas where the drainages enter playas/pans. The Yeelirrie, Langer Heinrich, Hinkler Well-Centipede, Lake Way and Lake Raeside deposits are of this type. They are typically tens of metres thick, kilometres wide and tens of kilometres long and concentrated in the axial portions of broad, very low relief (generally less than 1:1000), alluviated valleys. The calcretes frequently form positive relief features in the valleys, being raised and mounded to 3m or more. The model of formation of these calcretes as proposed by Mann and Horwitz (1979) involves precipitation of calcite below the water table (phreatic zone) and subsequent vertical displacement which results in the mounds of calcrete and a temporally inverted stratigraphy as suggested by carbon-14 dating. Uranium enrichments are not specifically associated with the calcretes, but transgress into all the units present, with the greatest concentration in the vicinity of the water table. Since the calcretes are the principal aquifers, they are the most frequent hosts to the mineralisation. The permeability of the calcretes arises as a result of shrinkage cracks and karstic features. Mineralisation occurs almost entirely as carnotite, commonly as late stage precipitate in cavities in which it may be associated with coatings of calcite, dolomite, silica, and/or sepiolite. Coatings of silica, 0.1-0.25mm thick at Lake Way, are important for the preservation of the carnotite crystals (Arakel et al., 1989). The calcretes form preferentially where converging drainages, flattening of gradients or subsurface constrictions bring the water table closer to the evaporative surface. In Western Australia the valley calcretes are still forming today with precipitation of calcite having started somewhere in the region of >36,500 to 25,000 BP (Mann and Horwitz, 1979 and Bowler, 1976 in Carlisle, 1983).

### *Playa Deposits*

(Butt et al., 1984)

These occur in near surface evaporitic and alluvial sediments of playas e.g. Lakes Maitland and Austin in Western Australia. Typically calcretes form the major supplying aquifer to the playa and may form a sub-surface hydrological link between some playas. The supplying calcrete drainage may itself show uranium enrichment. Mineralisation in the playa generally occurs near the water table, in near surface clays and muds, but at Lake Maitland uranium mineralisation occurs in thin calcretes at 2-4m in the playa itself. Again carnotite is the uranium mineral, usually disseminated in the mud.

## *Terrace Deposits*

(Butt et al., 1984)

These occur in calcrete terraces in dissected valleys west of the Meckering Line<sup>11</sup> in the Gascoyne Province of Western Australia. Terraces at 2-10 and 30-35m above the Gascoyne River-bed contain 3 to 5m of silcrete and silicified calcrete capping up to 8m of massive calcrete. Minor concentrations of uranium (50ppm) are present in the silica cap-rocks and locally, grades of up to 1000ppm are hosted by the calcretes. Although widespread in the area they are too small to be of economic significance.

### 7.2.2. Precipitation of Carbonate and Carnotite

(Carlisle, 1983)

Throughout the valley calcrete region, calcrete, with or without carnotite is only one component in a succession of authigenic near surface deposits:-

- Silica hardpan (e.g. Wiluna Hardpan) on the flanks of the catchment area where soils are acid and well drained and devoid of calcrete.
- Calcrete in the trunk palaeo-drainages with minor chalcedonic quartz, celestite ( $\text{SrSO}_4$ ) and gypsum becoming increasingly dolomitic down drainage.
- Dolomitic and gypsiferous silts on lake margins.
- Salines within the playa muds.

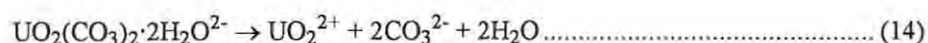
The total salinity, pH and concentration of Ca, Mg, Na, K, U, V,  $\text{SO}_4$  and Cl increase down drainage and deposition of calcrete, therefore, is a result of:-

1. Loss of  $\text{CO}_2$  and consequent rise in pH and  $\text{CO}_3^{2-}/\text{HCO}_3^-$
2. Evaporative concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  towards the axis of the drainage and towards the local base-level of the playa as the water table moves closer to surface.
3. Common-ion precipitation where Ca/Mg carbonate bearing waters encounter Ca/Mg sulphate or chloride brines in the playas.

Mechanisms 1 and 2 are vital to carnotite precipitation as well as calcrete formation because they allow calcrete / dolocrete to precipitate with ever diminishing activity of  $\text{CO}_3^{2-}$ , the combined result of which is to remove major proportions of  $\text{CO}_3^{2-}$  from solution. In carbonated groundwater uranium is transported as extremely soluble uranyl dicarbonate and tricarbonate complex ions subject to the following reactions:-

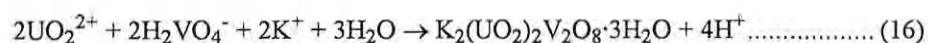
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<sup>11</sup> The Meckering Line is the upstream limit of erosion of the seaward flowing drainages of the Yilgarn Block. The Line runs parallel to the west coast about 70-140km inland except in the Gascoyne Province where it moves up to 600km inland. West of the Line the drainage is seaward while to the east it is mainly endoreic.



To precipitate carnotite it is therefore necessary to first decomplex these di- and bi-carbonates to make the uranyl ion available for combination with a vanadate ion.

Carnotite is precipitated according to:-



So, in a solution containing *only* the above components, removal of  $\text{CO}_2$  drives reactions 14 and 15 to the right, makes  $\text{VO}_2^{2+}$  available and decreases the solubility of carnotite, leading to precipitation. However, if  $\text{CaCO}_3$  is present, some amount of  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , or  $\text{H}_2\text{CO}_3$  is always present in solution and available to form uranyl carbonate complexes. The destabilisation of the uranyl carbonate complexes in this situation ( $\text{CaCO}_3$  present) can be achieved by lowering the activity of  $\text{CO}_3^{2-}$  which can, in turn, be achieved by evaporative or common-ion precipitation of carbonate, ergo the calcrete/carnotite association.

In addition to the mechanisms for carnotite precipitation described above Mann and Deutscher (1978) recognise the effect of redox changes. Redox control is important for vanadium in carnotite since it is transported as  $\text{V}^{4+}$ , but needs to be in the  $\text{V}^{5+}$  state for carnotite precipitation. The model involves transport of  $\text{V}^{4+}$  and  $\text{U}^{6+}$  in groundwaters that have an Eh not high enough to oxidise  $\text{V}^{4+}$  to  $\text{V}^{5+}$  and cause carnotite precipitation, nor is it low enough to reduce  $\text{U}^{6+}$  to  $\text{U}^{5+}$  and render it immobile. Upwelling of these groundwaters occurs at a constriction in the basement topography below a drainage line or where lacustrine clays block the passage of the groundwater (Fig 42). The resultant rise in Eh with the upwelling causes precipitation of carnotite.

The source of uranium in the calcrete-uranium deposits is no problem since there is an adequate granitic terrain to supply the uranium which is released from weathering and kaolinisation of the granite (<2 to 25ppm U). Potassium for carnotite could be supplied from the same source. Vanadium, on the other hand, is more problematic and possible sources for the Western Australian examples include greenstones and mafic rocks, vanadium rich clays (1-10ppm V) and ferricrete (Mann and Deutscher, 1978) and possibly mafic minerals within the granitoids (Butt et al., 1984).

Contemporaneous precipitation of calcrete and carnotite may not in itself yield ore, but ore grades may result from the dissolution and reconcentration of carnotite; indications of which are given by the epigenetic textures at Yeelirrie and by groundwater and uranium series analysis (Mann and Deutscher, 1978). The latter feature has proved useful in exploration for these deposits.

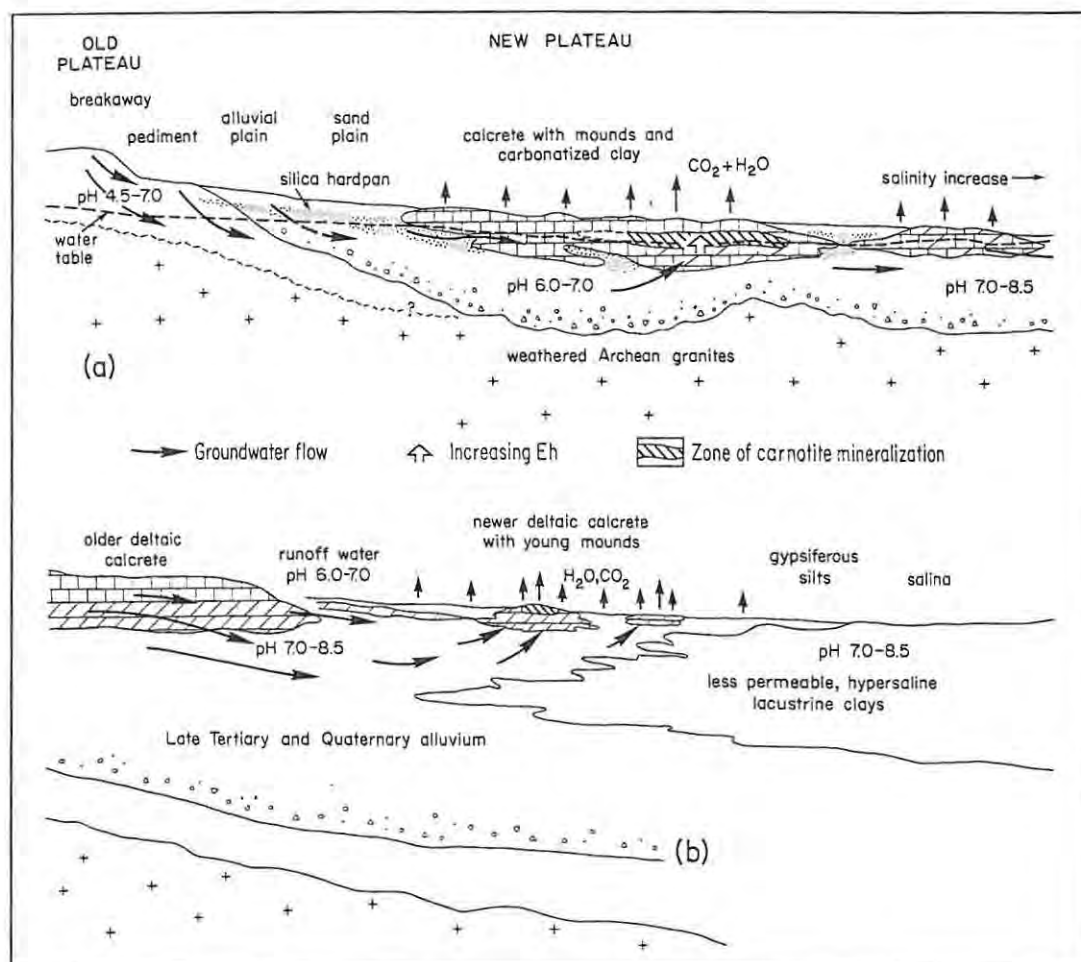


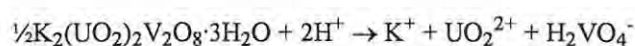
Fig 42: Schematic models for non-pedogenic, uranium-bearing calcrete. Top: Valley calcrete with bedrock constriction brings groundwater closer to evaporative surface; applies to all valley calcrete orebodies in Western Australia and Namibia. Bottom: Barrier formed by lacustrine clays forces groundwater to rise to surface. (from Carlisle, 1983)

### 7.2.3. Exploration for Calcrete-Type Uranium

In the early years of calcrete-uranium exploration, airborne and ground radiometric methods used in conjunction with regional hydrogeochemical surveys were the standard approach. As the more obvious outcropping carnotite mineralisations were discovered, reconnaissance radiometric prospecting has been replaced by hydrogeochemical surveys and follow up drilling in areas selected by, for example, Landsat image palaeodrainage interpretation. Use of the CSI (Carnotite Solubility Index, Middleton, 1984) in hydrogeochemical exploration is discussed below.

#### 7.2.3.1. Solubility Indices in Hydrogeochemical Exploration

Mann and Deutscher (1978) proposed the *Solubility Index* (SI) which reflects the saturation status of groundwater with respect to carnotite. Carnotite dissociates according to the reaction:-





and the SI is therefore defined as:-

$$SI = \log \frac{[K^+][UO_2^{2+}][H_2VO_4^-]}{[H^+]^2 K_{s.p.}}$$

where  $K_{s.p.}$  = solubility product of carnotite =  $10^{-6.85}$

and  $[UO_2^{2+}]$  is calculated from the uranium di- and tri-carbonate concentrations (see Mann and Deutscher, 1978).

Theoretically, negative values of SI indicate that the water is undersaturated with respect to carnotite and implies that carnotite, if in contact with the groundwater, should dissolve. Positive values of SI indicate an oversaturation w.r.t. carnotite and suggests carnotite precipitation.

Middleton (1984) submits a modified solubility index which he calls the *Carnotite Solubility Index* (CSI); being more useful for field use:-

$$CSI = \log \frac{[K^+][U][V]}{1.13 \times 10^4 [HCO_3^-]^2}$$

where uranium and vanadium concentrations are in ppb or  $\mu\text{g/l}$  and potassium and bicarbonate concentrations are in ppm or  $\text{mg/l}$ . In this case empirical evidence suggests that CSI's greater than -3 are prospective.

#### 7.2.3.2. Other Techniques

Landsat interpretation, radiometric surveys and hydrogeochemical surveys have been mentioned above as techniques applicable to the search for calcrete uranium deposits. Other techniques used are:-

- Beta/Gamma Analysis: Analyses for U, Th, K and can measure the degree of disequilibrium within the uranium decay chain, a feature which is important for the younger deposits where uranium disequilibrium may lead to no or subdued radiometric signature.  $10\text{ppm U} \pm 7\text{ppm}$  can be measured with an accuracy comparable to XRF or chemical analysis.
- Low-Energy Gamma Ray Spectrometry: Direct determination of both U and Th - not affected by disequilibrium. Easily applied in field and also used in down-hole logging.
- Radon Detection Methods: Problematic in Namibia where hardpan gypsum is impermeable to radon. Although it has been successfully used in Namibia this technique was unsatisfactory at Yeelirrie.
- Resistivity Surveys: Successfully used in Namibia to delineate palaeochannels and estimate depth of palaeochannel.
- Seismic Surveys: Useful for outlining the geometry of palaeochannels. Problematic in that some hard calcreted layers may have seismic velocities similar to or higher than those of basement rocks, thereby giving a false interpretation of the depth of the channel floor.
- Drilling and Pitting: Take care when percussion drilling or sampling - uranium mineralisation usually occurs in the fines which are easily lost in dry, windy desert conditions.

### 7.2.3.3. *Favourability Criteria for Economic Calcrete Uranium Deposits*

(Carlisle, 1978 and Mann and Deutsher, 1978)

1. Adequate source terrain, deeply weathered: Yilgarn granites contain <2 to 25ppm U. Damara metamorphics and post-Damara granitics are similar, but locally much richer. Vanadium from schists, granites, greenstones and derived sediments.
2. Anomalous groundwater uranium and vanadium contents: Present day groundwaters updrainage from calcrete contain 10-60ppb U; 1-12ppb V; 10-35mg/l K. It is also worth noting that at neutral pH's carnotite dissolves incongruently (i.e. dissolution does not yield stoichiometric proportions of the component ions) producing higher vanadium concentrations than might be expected. The implication is that in an area of anomalous V concentration some of the V could be the result of dissolution of carnotite itself.
3. Large catchment area: Yeelirrie 3000km<sup>2</sup>; Hinkler Well 850km<sup>2</sup>; Langer Heinrich - many hundreds of km<sup>2</sup>. Present flow or storage may be large, 4500m<sup>3</sup>/day at Yeelirrie slot.
4. Low drainage gradients: Yeelirrie 0.06° to 0.01° in calcrete, 0.2° above calcrete. Namib platform 0.7° to 0.4°.
5. Very limited runoff: No permanent streams, sporadic summer storms and little sedimentation.
6. Non-pedogenic calcrete: Indicative of subsurface flow into a trunk aquifer where carbonate precipitates.
7. Absence of pedogenic carbonate or other uranium fixing processes in catchment area: True in valley calcrete region of Western Australia (where siliceous hardpans develop instead of calcrete). True of Khomas Hochland, but not true for Namib Platform where gypcrete is developed downdrainage of calcrete.
8. Evaporative concentration of U, V and K downdrainage: Ten-fold increase on Hinkler Well. At Yeelirrie TDS increases from <750ppm near breakaways to 20,000ppm at orebody. U and V also increased by incongruent dissolution of carnotite.
9. Constricted, shallowing, or upwelling groundwater flow within the valley calcrete area due to bedrock topography or impermeable sediment:
  - Rising Eh: oxygenated near-surface water converts V<sup>4+</sup> to V<sup>5+</sup>.
  - Loss of CO<sub>2</sub>: into soil air above capillary fringe or warm upper soil moisture zone.
  - Abundant carbonate deposition: in capillary fringe and soil moisture zone which may overlap.
  - Accelerated evaporation: further concentrating ions.
  - Contemporaneous-penecontemporaneous precipitation of carnotite.
10. Reconcentration of Carnotite: Dissolution of early carnotite and reprecipitation as epigenetic fillings and replacements in smaller area.
11. Stabilisation of carnotite: By overgrowth of silica at Yeelirrie; by desiccation at Langer Heinrich.
12. Moderate to low relief and tectonic stability: Little sedimentation to prevent deep burial. No topographic rejuvenation and consequent leaching of carnotite.

## 7.2.4. Uraniferous, Non-Pedogenic Calcretes in Western Australia

### 7.2.4.1. *Distribution*

Numerous occurrences of surficial uranium mineralisation have been located in calcrete drainage channels in granitoid terrains of Western Australia and parts of South Australia and the Northern Territory. Nearly all calcretes in these terrains show traces of mineralisation, but not all are economic. The distribution of these deposits is controlled by the following features (Carlisle, 1983; Butt et al., 1984):-

1. The valley calcrete region of Western Australia coincides with: (1) a uniquely arid climate and corresponding soil moisture regime; (2) the distribution of soil containing abundant authigenic silica (the Wiluna Hardpan) and (3) Mulga, a characteristic plant assemblage. This association arises from the following situation: Rain from sporadic summer storms falls on hot, dry surfaces. Much evaporates directly and a large part infiltrates rapidly into the fractured, permeable mottled or pallid zone of weathered bedrock. Very little remains in the soil moisture zone that could be subject to evapotranspiration and CO<sub>2</sub> loss. As a result there is little opportunity for accumulation of pedogenic carbonate. Silica, released from the lateritic bedrock profile is continually at the point of saturation and precipitates as water evaporates in deeper soil. What little carbonate might form is dissolved away in the next storm but silica is not. In the acid, well drained soils of the upper valley flanks the pH and salinity is low, but rising gradually with evaporation as the water table moves closer to surface in the valley axis until the point of carbonate saturation is reached. Similarly there is little tendency for carnotite to precipitate in the acid, well drained soils of the valley flanks. South of the valley calcrete region the climate and soil moisture regime is different. Large fractions of the rainfall occur during the winter when evaporation rates and temperatures are low by comparison but high enough to cause a buildup of salts within the soil and carbonate is precipitated as pedogenic calcrete. There is no opportunity for lateral transport simply because the climate and soil moisture regime do not allow it. Carnotite may precipitate in these pedogenic environments, but without the lateral transport and concentration it remains sparsely disseminated.
2. Calcrete uranium occurrences are restricted to areas where granitoids are the predominant rocks in the catchment, suggesting a close genetic link with granitic terrain.
3. In the west and north-west, active erosion by major rivers and their tributaries has tended to destroy the calcretes and other sedimentary hosts to mineralisation. Thus no deposits are found west of the upstream limit of erosion (the Meckering Line) bar a few small terraces on the Gascoyne River

## 7.2.5. Uraniferous Non-Pedogenic Calcretes in Southern Africa

Due to the difference of interpretation of Australian and South African workers there is frequently differing opinion as to the importance of calcrete in the southern African surficial uranium deposits. Langer Heinrich for

instance is described as a calcrete uranium occurrence by Carlisle (1978), but the word calcrete is never used by Hambleton-Jones et al. (1986) and Hambleton-Jones (1984a and b) in their description.

#### 7.2.5.1. Distribution

The distribution of surficial uranium occurrences in southern Africa is illustrated in Fig 43. The two main areas are centred around Walvis Bay in Namibia and Pofadder in South Africa. In terms of world surficial uranium RAR+EAR South Africa contributes an insignificant 0.2% while Namibia contributes 27% (Hambleton-Jones et al., 1986). Detail of the two areas is shown in Figures 44 and 45.

While it is true that not all southern African occurrences have a calcrete association there are some which most definitely do e.g. Langer Heinrich (valley fill type), Abikwaskolk (deltaic type), Spitskoppe (valley fill). The geomorphological evolution of Southern Africa since the initial separation of Gondwanaland has played an important role in the later development of the surficial uranium occurrences. Uplift along the escarpment during the mid-Tertiary resulted in renewed incision and erosion, initiating the post-African erosion surface. Valleys up to hundreds of metres in depth (200m at Langer Heinrich) were filled and choked with poorly sorted angular material with little chemical weathering and no organic remains. This is the environment of deposition for the likes of the fluvial Langer Heinrich deposits (Hambleton-Jones et al., 1986).

Unconformably overlying the basement sequences of the Namibian occurrences are rocks of the Karoo Sequence

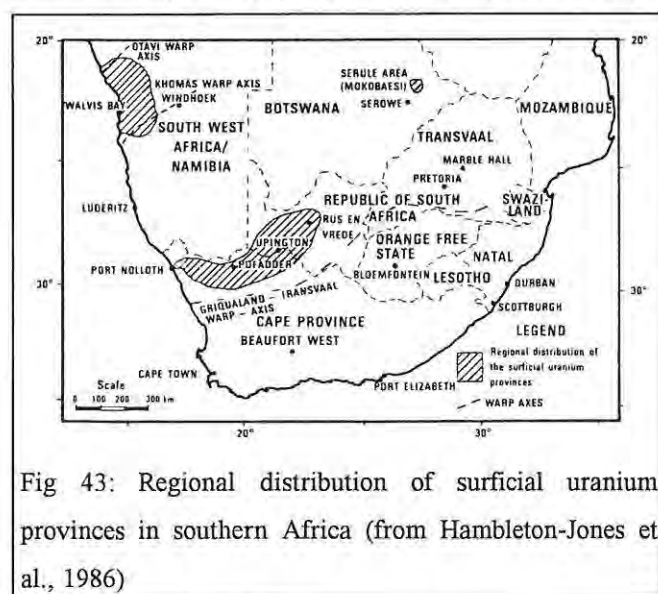


Fig 43: Regional distribution of surficial uranium provinces in southern Africa (from Hambleton-Jones et al., 1986)

and the Namib Group. It is within sediments of the Namib group, filling valleys, that the most economically significant uranium occurs. Mineralisation occurs mainly in the form of authigenic carnotite that has been precipitated from groundwater. Carnotite occurs interstitially within the sediment along grain boundaries and in cavities associated with calcite, dolomite and gypsum. Commonly it is found in those parts of the sediment that have maximum porosity and are thus the best aquifers. Distribution of carnotite is not entirely restricted to the Namib Group, but in places occurs in the weathered portions of the underlying

basement. Numerous granite intrusions (e.g. the Bloedkoppie Granite; up to 20ppm U) are thought to be the source of the uranium.

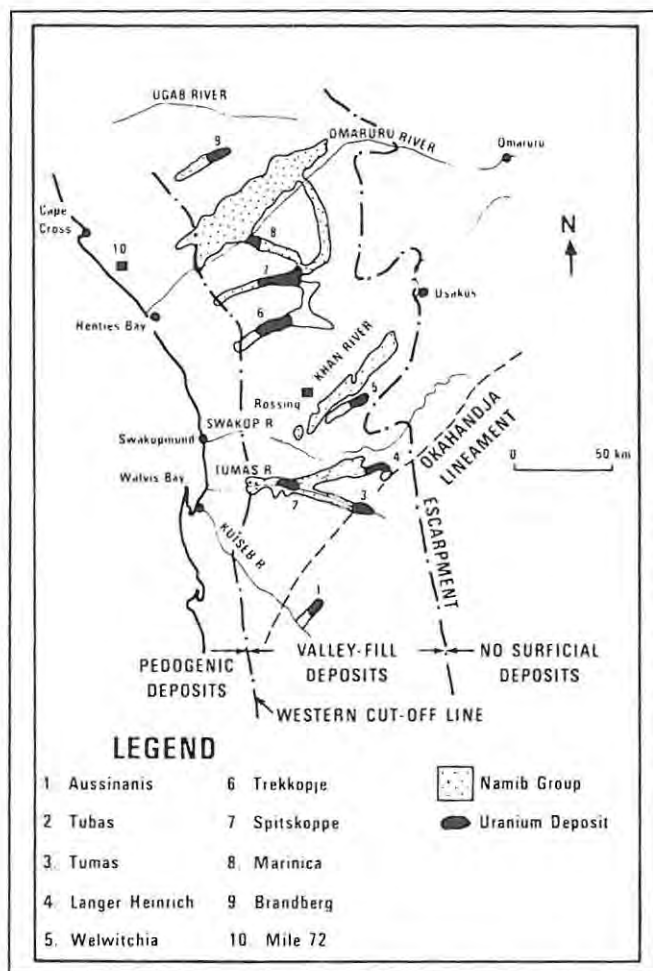


Fig 44: Distribution of the Namib Group and associated uranium deposits in Namibia ( from Hambleton-Jones et al., 1986)

The South African occurrences are somewhat different from their Namibian counterparts. The southern margin of the Namaqua Province may be taken as the watershed along the Late Tertiary Griqualand-Transvaal warp axis. Streams flowing northwards from this watershed traverse granitic rocks and shears with U concentrations of up to 100ppm. Tertiary to Recent surficial sediments in this region are of fluvial and aeolian origin, filling palaeodrainage channels e.g. the Koa, Sout, Hartbees, Arribeas, Caboop and Kanna. The valley fill material was deposited under much lower gradients and the thicknesses are, consequently, of the order of a few metres only. Due to warping along the Griqualand-Transvaal axis, gradients have been reduced to zero or even reversed causing ponding and the formation of pans e.g. Abikwaskolk (with calcrete uranium).



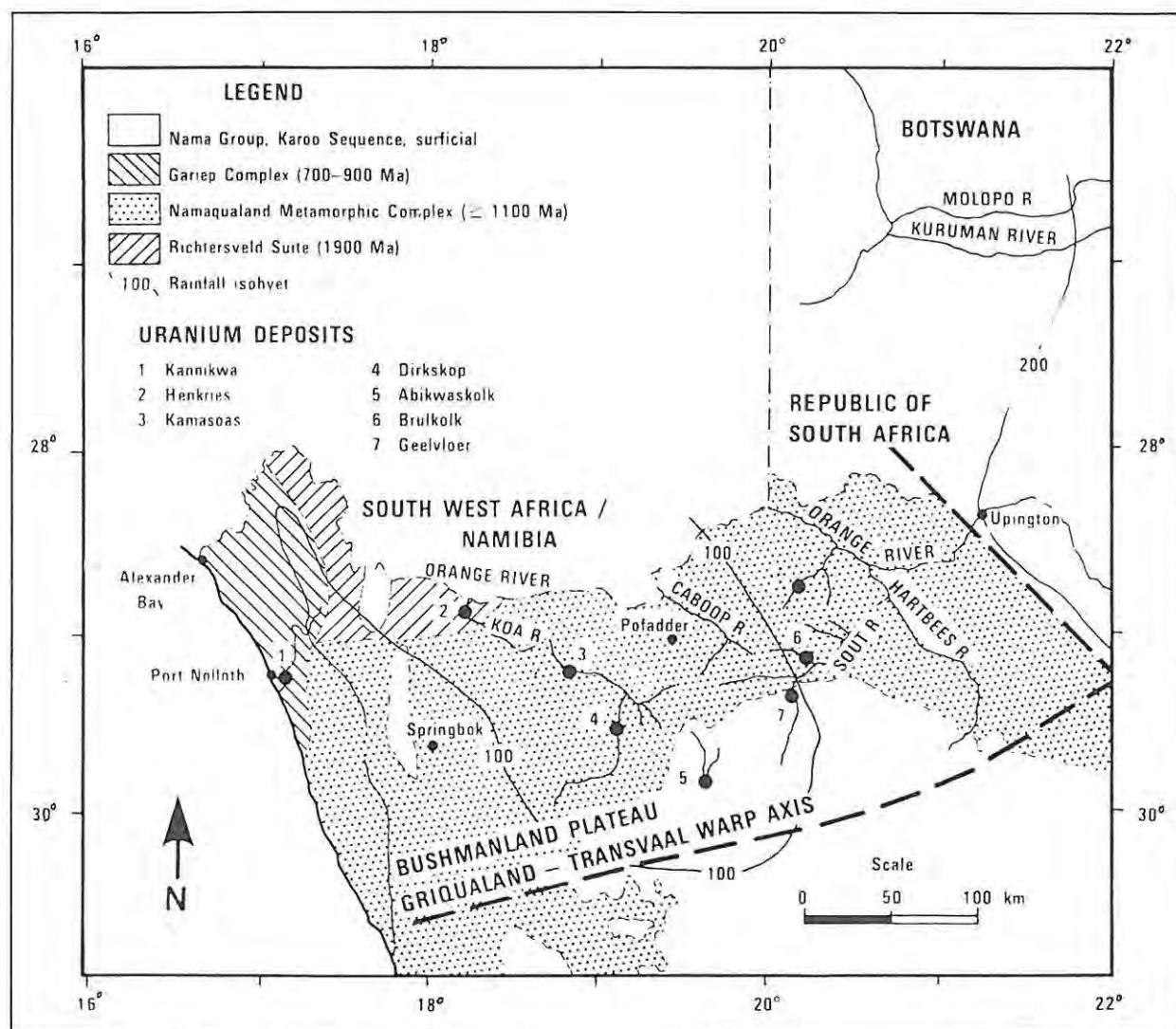


Fig 45: Distribution of major surficial uranium occurrences in the Pofadder area of South Africa (from Hambleton-Jones et al., 1986).

## 8. DISCUSSION AND CONCLUSION

The problem with calcrete formation is that it tends to replace, dissolve or leach ore minerals and metals from the soil profile. The resultant decrease in anomaly contrast is, most commonly, a function of the dilution of the metal concentrations by either an absolute or a relative addition of calcium carbonate to the soil profile. Successful geochemical sampling in calcrete terrains requires, first and foremost, an understanding of the processes operating during calcrete formation and therefore of the different genetic varieties of calcrete. In situations where the calcrete is pedogenic sampling of the upper surface of the calcrete is frequently preferable to sampling the overlying soil horizon (if any). It has been shown that the upper surface of pedogenic calcretes are able to reflect the underlying mineralisation (Jacomynspan, Putsberg. True, there is a progressive decrease in metal concentrations upwards through a calcretised profile, but there is usually enough anomalous metal in the top of the calcrete to make it a preferred sampling medium in comparison to the overlying soils which are frequently diluted by an aeolian component. In the case of the Bounty gold deposit the sampling of calcrete was vital to the success of the exploration program since gold is actually concentrated in calcrete at this locality. In some instances calcrete may host considerable quantities of gold; enough to be considered a protore (Eldorado Valley). In a pedogenic-calcrete terrain the best situation that one could hope for is one where *in situ* replacement of weathered bedrock has taken place by a relative increase in calcium carbonate i.e. the carbonate component is not externally derived (exogenous after Wheatley, 1975). Pedogenic calcretes are, as a sampling medium, far easier to interpret than non-pedogenic calcretes. Anomalies are far more likely to be preserved in the former, and if preserved are more likely to be related to nearby mineralisation rather than some distant source. Indeed, the recognition of anomalies through non-pedogenic calcretes may be near impossible. Many calcretes show evidence of having been exposed to alternating periods of weathering and calcification (Netterberg, 1980); such calcretes can be expected to be more depleted in metals than single phase calcretes. So, again, an understanding of calcrete genesis is important.

Outlined below are some further pointers to exploration in calcrete terrains:-

- *What Size Fraction To Sample:* The problem of which size fraction to sample in calcrete terrains has many facets and there is no one single answer. The ability of calcrete formation to fragment and liberate laterite or gossan to the surface is important at the Surprise gold mine, Western Australia where laterite with anomalous As values was fragmented as a result of carbonate accumulation and coarse fragments (+840 $\mu$ m) were dispersed over the surface. The resultant mechanically dispersed anomaly was wider than that of the fine fraction (-80mesh; -180 $\mu$ m) in the soils. At the Putsberg Cu prospect, on the other hand Garnett et al. (1982) advise screening the calcrete sample and analysing the fine fraction since it was in this fraction that they encountered the highest metal values. Progressively larger calcrete fractions (chips, nodules, boulders) showed progressively lower metal contents; a feature of the increasing maturity and carbonate content of the calcrete. This raises the issue of the explorationist being aware of the calcrete types and how they progress through "youthful" to "senile" forms. With greater degrees of replacement, leaching or carbonate accumulation there

may not be a fine fraction to analyse and the relatively resistant gossan or Fe-oxide fragments may then be a target.

Calcrete coatings on pebbles and cobbles have been used to detect anomalous values of copper from hydromorphic transport and to distinguish such anomalies from detrital anomalies in the same area (Rocky Range).

Some metals (Zn, Ni, Cu, Co, As) show an affinity for adsorption onto iron and manganese oxides. Calcareous soils sampled at Mararoa Reef had low As values (33ppm), but the hand separated iron-oxides had concentrations of As in the 150 - 400ppm range. The best response at Kantienpan was also achieved by hand-picking the +2mm gossan fragments from calcrete (Garnett, 1983). At Callion the highest gold values in a trench were associated with pisoliths in calcrete. Arsenic in calcrete overlying the Plat Reef was not associated with Fe-oxides, but may have been incorporated in the weillite structure after the reaction of arsenious acid with calcrete.

- *Metal Mobility:* The issue of relative metal mobilities in the calcrete environment is fraught with contradiction. Careful examination of the order of relative depletions of metals due to calcrete formation at Areachap (section 4.2.3.) and Putsberg (section 4.2.4.) reveals that they are not as different as might first seem. The only element that shows big differences between the two localities is copper. At Areachap copper is least depleted (due to its ready precipitation as a carbonate) while at Putsberg copper is strongly depleted and the top of the calcrete yields Cu concentrations only 4 - 11% of that in hand picked rock chips from the base of the calcrete. One element that does appear reliably immobile is Cd, and its use for pinpointing mineralisation at the follow-up stage is recommended by Garnett et al. (1982).

Whatever the inter-element mobility relationships are there is no doubt that calcrete, with its high pH environment, acts to restrict dispersion by causing precipitation of metals normally carried in acid solutions.

- *Sample Spacing:* Although calcrete is a widespread feature in drier parts of the world such crusts are by no means regularly developed even on the meso scale (metres to tens of metres). A sampling procedure that works well in one calcreted area may, therefore, be ineffectual in another area. At Putsberg large variations in metal values occur over distances as short as one metre. This, coupled with the fact that dispersion trains in calcretes are very short indeed means that the sampling interval will need to be small. At Jacomynspan Cu and Ni values drop to background levels within 30m and at Putsberg, Cu showed the longest dispersion train in the 75 - 180 $\mu$ m fraction of stream sediments, but that was only 200m long. Vermaak's (1984) recommendation is therefore a 50m sample spacing for the calcreted areas of the northern Cape.
- *Analytical Method:* Although it is true that the top of the calcrete frequently displays a higher (but more restricted) anomaly to background ratio than the overlying soil as analysed by some "total" technique (hot acid digestion + AA or XRF) much more information can be gained by conducting partial analyses. At Putsberg the total analysis of the residue (clays, sand, Fe-oxides) after an ammonium acetate-acetic acid leach (method of Gatehouse et al., 1977 in Garnett et al., 1982) yielded higher anomaly/background and greater lateral dispersion than a straight total analysis. Of course, the success of this method depends on finding where the ore-metals are hosted. Atomic absorption analysis of the leach liquor rather than the residue might reveal that the metals are concentrated in the carbonate fraction itself or loosely bound on the clay fraction as at Bou-Grine.

- *pH Contrast*: In situations where there is a pH contrast between the alkaline calcrete and acid water from underlying sulphides metals may precipitate at the boundary between the two. If follow up work is being carried out by drilling to bedrock it may prove necessary to drill only as far as the pH interface (Kadina).

Although there is doubt as to the origin of the calcium carbonate cementing the basal conglomerate in the Pima mining district (local geologists use the term "caliche", but Huff (1970) begs to differ) it can be used as a reliable sampling medium. Acid groundwaters (from oxidation of sulphides) deposit their copper upon encountering the alkaline carbonate environment of the cemented basal conglomerate and anomalous copper has been recorded from drill holes 2.4km away from any known mineralisation.

- *Biogeochemistry* has been useful for detecting anomalous copper (Botswana/Namibia - Katanga extensions) and gold (Mararoa Reef) in calcrete terrains. In the case of Botswana/Namibia such anomalies have been detected through 30m of calcrete.
- *Kimberlites*: In kimberlite exploration calcrete acts to dissolve the heavy indicator minerals and also to physically trap them from dispersion. This dissolution reduces the size of the grains, hence reducing the number of grains reporting to the normally sampled size fraction (0.425 or 0.5mm to 2mm). This problem could be alleviated to some extent by sampling finer fractions - not always a practical solution since optical identification of kimberlitic indicators becomes more difficult as size decreases.

Calcrete coatings on grains may also serve to mask them from optical identification or reduce the SG such that they no longer report to the heavy fraction. Boiling in acid prior to optical sorting helps with the former problem, but it would be too costly to boil large samples prior to heavy mineral separation.

Generally chromite and ilmenite are likely to have the best survival potential and chrome diopside the least. The presence of chrome diopside on a calcreted terrain would therefore suggest proximity to source (assuming that the kimberlite contains chrome diopside in the first place).

A whole field of expertise surrounding the interpretation of surface textures on kimberlitic indicators has arisen out of a need to gain some idea of the proximity of the primary source. Calcretisation alters the surface textures of the indicator minerals and their interpretation is thus complicated (see Kilham, 1985 for further details).

Kimberlites have been known to form both positive and negative topographic features, but the preferential calcretisation of kimberlite compared to other less carbonate rich host rocks may result in positive topographic features (see examples in Kilham, 1985).

Nb, Cr and V appear to be the most useful elements in geochemical kimberlite exploration in calcrete terrains.

- *Uranium*: The non-pedogenic calcrete/uranium association arises as a result of calcrete formation and carnotite precipitation being supported by the same processes (see section 7.2.2) although it must be stressed that the two do not always occur together. The presence of pedogenic calcrete in this case is an undesirable feature because it serves to dilute the anomalies. The gypcrete-carnotite association is just as common to Namibia as the calcrete-carnotite association is to Western Australia. Valley-fill calcretes, in which calcrete-uranium most commonly occurs, are found in a very specific soil moisture regime (Aridic regime, Carlisle, 1978) and the factors of source terrane and topography are predictable (see section 7.2). The use of hydrogeochemistry and the concept of the Carnotite Solubility Index has been used successfully in groundwater sampling for uranium mineralisation.

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