

Chapter 1

Introduction

1.1. Purpose of the investigation

The principal purpose of this study is to characterise the primary and secondary geochemical halo's related to volcanic-hosted massive sulphide (VHMS) deposits in the highly deformed and metamorphosed rocks in the eastern part of the Namaqua Province. For this purpose two unexploited (largely), but well explored, VHMS deposits were selected namely the Areachap and Kantienpan deposits. Lithogeochemical characterization of the primary haloes is based on borehole samples of the footwall, ore zone and hanging wall successions, whereas the secondary dispersion haloes are studied in samples of the calcrete and sand cover.

The principal research questions could be phrased as follows:

- a) Could primary geochemical halo's that formed at the time of sulphide mineralization be identified in these rocks that suffered various phases of deformation and metamorphism?
- b) Are secondary dispersion halo's evident in wind deposited sand cover and the underlying calcrete regolith that formed in a semi arid environment?

The objective with this investigation is to show which geochemical methods could be used in future exploration programmes. The proposed lithogeochemical methods would be demonstrated utilizing a set of lithogeochemical samples collected in the region.

1. 2. Locality of the study area

The area investigated in this study is located in the Northern Cape Province of the Republic of South Africa (Fig. 1.1). Within this area, the study focussed on the selected localities mentioned above.

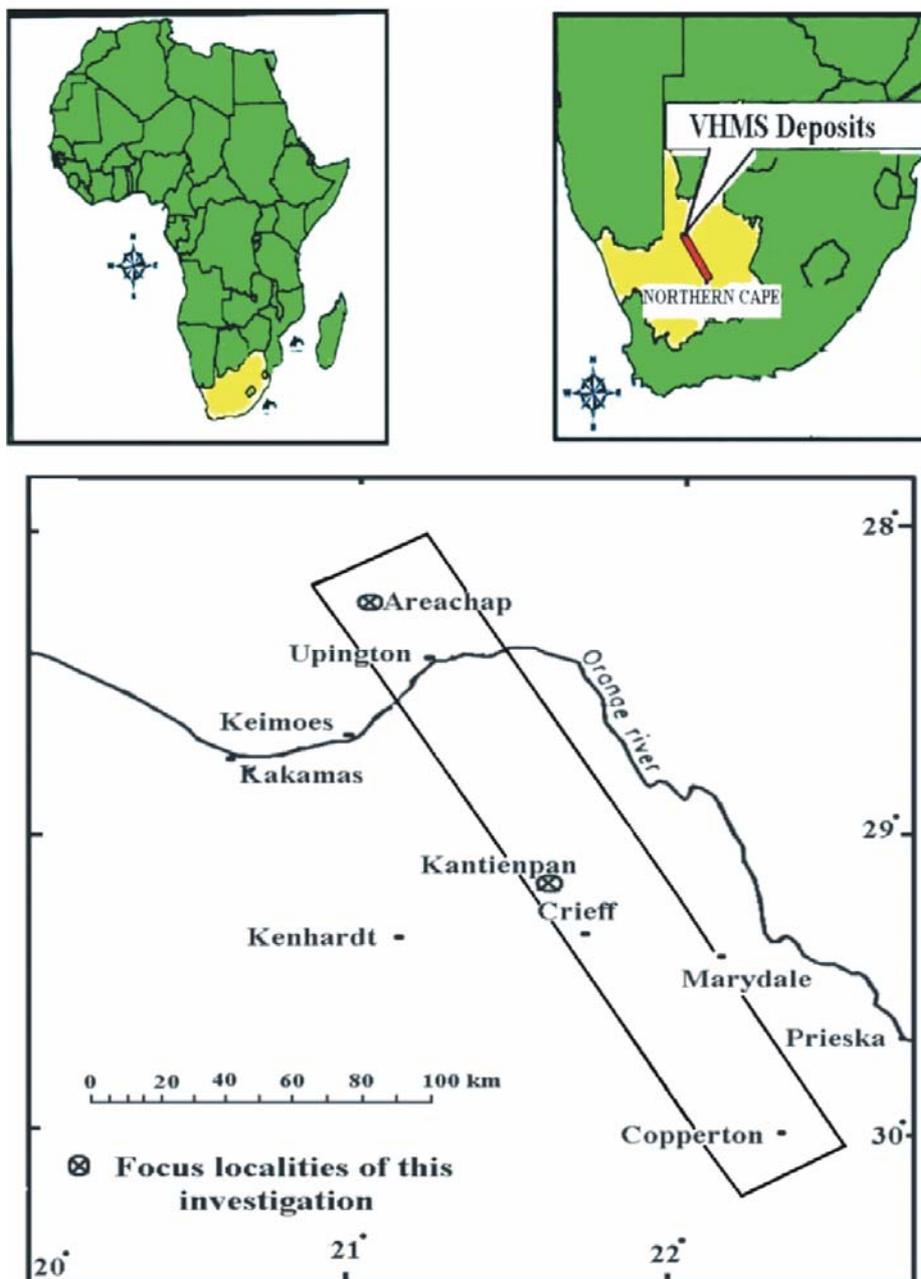


Figure 1.1: Location map

The defunct Areachap Cu-Zn mine is situated on the farm Areachap 426, 22 km northwest of Upington, in the Gordonia district. The area is flat, with an average height of 915 to 922 meter above sea level. The study area is readily accessible by gravel or sandy roads. A 12 km gravel road links the Areachap with Upington-Namibia national road.

The Kantienpan Cu-Zn deposit is situated on the farms Kantienpan 119 and Gemsbok Bult 120, about 85 km southeast of Upington in the Kenhardt district. The area is flat, with an

average height of 1060 meters above sea level. The study area is readily accessible by secondary sandy roads.

1.3. The method of investigation

The method of investigation is divided into four sections. The first of these entails a comprehensive literature review of the geology of the Upington Terranes, eastern Namaqua Province where previously recognized VHMS deposits occurring in an area affected by deformation and high grade of metamorphism, weathering and erosion in a dry, semi arid climate could be studied to determine the effectiveness of modern geochemical exploration methods. The second section encompasses a literature review of the formation of the VHMS deposit focussing on the alteration features that characterise the sulphide mineralization event. Thirdly the lithogeochemical dispersion of the primary hydrothermal alteration is studied in rocks that have suffered various phases of deformation and metamorphism. This is done by considering both whole rock and mineral chemistry. Lastly, the secondary dispersion of geochemical halo's in the more recent soil and sand cover would be identified to determine the most appropriate geochemical exploration methodology for the discovery of similar deposits in areas affected by similar climatic condition.

In addition, a private company, Kumba Resources Limited, has kindly provided a set of rock sample results from this area to demonstrate the applicability of lithogeochemical exploration factors that could lead to the detection of sulphide mineralization.

1.4. Acknowledgements

I would like to thank my supervisor, Prof H.F.J. Theart, for his support and effective guidance in this thesis. I am grateful to Prof S.A. de Waal for the financial support from the Centre for the Research of Magmatic Ore Deposits, University of Pretoria. Thanks are also due to Kumba Resources Limited for access to the borehole samples and field visits with Mr. D. Rossouw and for permission to use their regional lithogeochemical data base.

I am grateful to several people who helped during the course of this work. Mr. P.C. De Jager is thanked for his support and advice during the sand preparation and analysis. M

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I am extremely thankful to my wife, Jina, who left her relatives, friends and work to spend four years with me in South Africa. Without her support, patience, understanding and prayers during the long hours of working, this thesis would not have been possible.

Chapter 2

Geology of the Upington Terrane, Eastern Namaqua Province

2.1. Introduction

The Areachap Group in the eastern part of the Namaqua Province contains a number of volcanic hosted massive sulphide (VHMS) deposits such as the Copperton, Kantienpan, and Areachap ore bodies (Rossouw, 2003; Cornell et al., 1990a; Theart, 1985). In this chapter the crustal evolution of the eastern part of the Namaqua Metamorphic Province will be discussed to explain the metamorphism and deformation, which affected these deposits. This will be followed by a discussion of the regional geological succession and local geology of each of the areas mentioned above, focussing on the geological sequences near the ore body.

As this investigation also considers the secondary environment it is important to also discuss the evolution of the present erosion surface. For this, the different geomorphic events that affected the African earth's surface since the Mesozoic times till the present are considered. The calcretization process is particularly important because of its influence on the secondary dispersion of the ore forming elements.

2.2. Tectonic setting and regional geological succession

The Kibaran Supercrustal Sequence (1600 to 1300Ma) was deposited on the Eburnian basement (2000 Ma) in the western Namaqua Terrane (Thomas et al., 1994a). The lithology of this sequence may indicate that there was an oceanic basin between the Kaapvaal and the older parts of the Namaqua Province at approximately 1600 Ma (Theart, 1985) (Fig. 2.1). The oceanic basin was affected by calc-alkaline and tholeiite volcanism until 1285 ± 14 Ma (Cornell et al., 1990a) in the area now preserved in the east-central Namaqua-Natal Province. These extrusive rocks and associated sediments were preserved in the Areachap Group of the eastern part of the Namaqua Province and in the Mfongosi Group of Natal Province (Thomas et al., 1994a). During the period of volcanism, volcanogenic massive sulphide deposits formed on the sea floor due to reactions between the hydrothermal fluids and seawater (Cornell et al., 1990a). This was followed by plate convergence, thrusting, ductile transcurrent shearing, thickening of the crustal sequence, and intensive deformation from 1200 Ma to 1000 Ma due to a northwest-southeast-directed stress regime (Thomas et al., 1994a). The Koras and Sinclair Groups consisting of calc-alkaline volcanic and sedimentary rocks, were formed during the late syn-collision event at ~ 1150 Ma (Jacobs et al., 1993). The collision of cratons and the related events led to high-grade metamorphism and widespread melting and generation of voluminous granitoid batholiths magma (I-type granites) between 1200 to 1000Ma (Geringer et al., 1994).

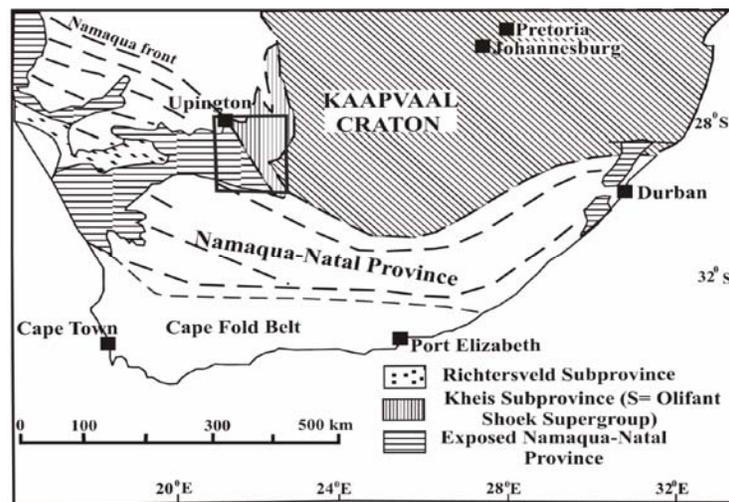


Figure 2.1: The location of Namaqua-Natal Province (After Moen, 1999) and the study area.

The study area considered here falls within the Gordonia Sub Province of the Namaqua Province (Fig. 2.2). Supercrustal rocks in this Sub Province belong to the Areachap Group comprising the Jannelsepan, Bokspuits and Copperton Formations (Barton et al., 1983; Cornell et al., 1990a; Rossouw, 2003). Middleton (1976) and later Geriner et al. (1994) suggested that the Copperton, Bokspuits and Jannelsepan Formations are time equivalents formed from separate volcanic centres.

Middleton (1976), Gorton (1981), Theart (1985) and Cornell et al. (1990a) suggested the volcanic precursors of the rocks related to deposits within the Copperton Formation. The major and trace elements geochemistry (Theart et al., 1989), and the zircon crystal form (Pupin, 1980) were interpreted as evidence for an igneous origin of the Smouspan Gneiss Member (Table 2.1), which forms the footwall to the Copperton VHMS deposit. It is suggested that this formed as dacitic lava (Theart, 1985; Cornell et al., 1992). The Copperton deposit itself is hosted within the Prieska Copper Mines Member (Theart, 1985) and this is overlain by the Volgelstruisbult Member (Theart, 1985; Theart et al., 1989; Cornell et al., 1992) (Table 2.1). The lithological succession of the Copperton Formation is summarized in Table 2.1.

Table 2.1: Regional succession of Copperton Formation

Member or Group	Lithological description [Reference]	Formation or sub-province
Volgelstruisbult Member	Interbanded amphibolites pelitic Gneiss, Hbl-and Bio-Gneiss and diopside-bearing calc-silicate ^[3]	Copperton Formation
Prieska Copper Mines Member	Peraluminous gneiss and schist including Metalliferous zone (massive sulphide) ^[2]	
Smouspan Member	Hornblende-biotite gneiss ^[1]	
Magazine Member	Interbanded calc-silicate quartzites and amphibolite ^[1]	
Doonerspan Leucogneiss Member	Leucocratic hornblende and biotite gneisses ^[4]	
Marydale Group	Amphibolites and quartzitic rocks ^[1]	Kheis sub-province

[1]: Geringer et al., 1994, [2]: Middleton, 1976; Theart et al., 1989; Cornell et al., 1990b

[3]: Humphreys et al., 1988a, [4]: Humphreys et al., 1988b

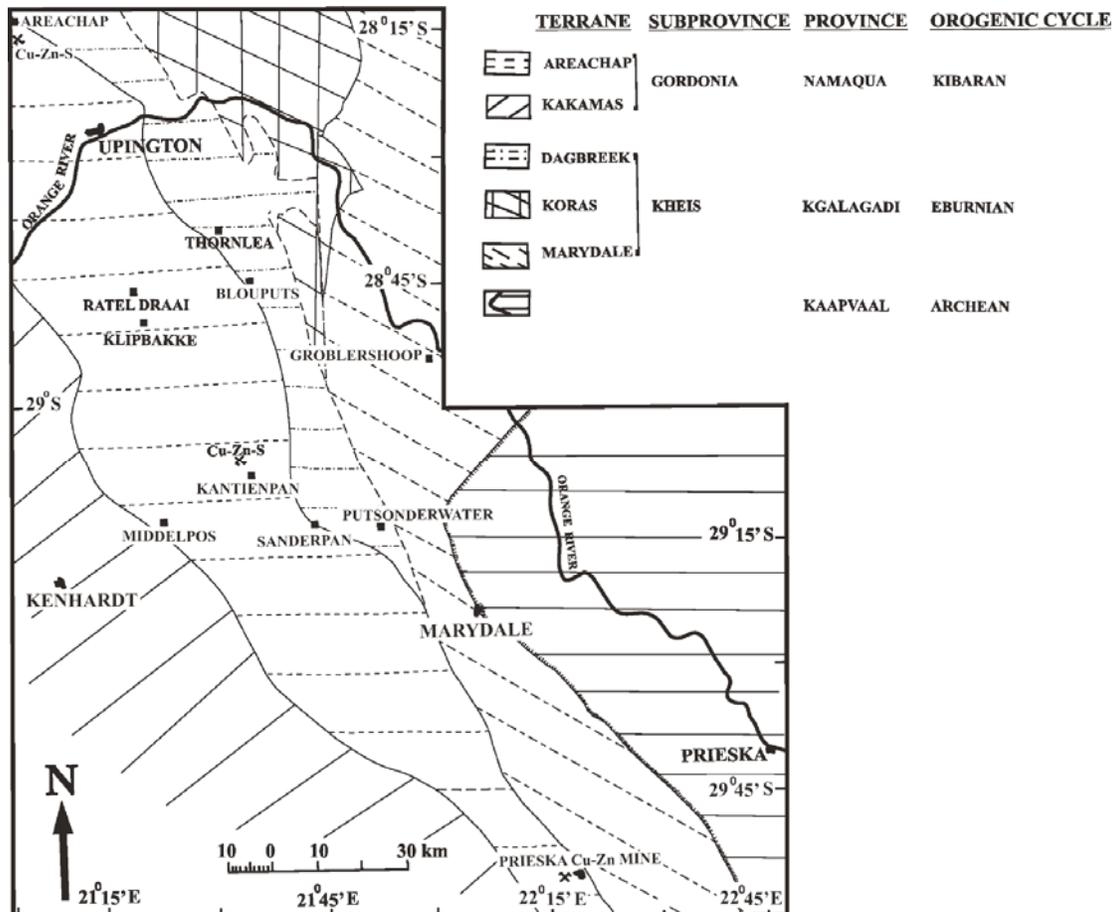


Figure 2.2: Geological map of the Areachap Group in the eastern part of Namaqua Sub-province.

The Jannelsepan Formation hosting the VHMS deposits at Areachap (Theart, 1985; Voet and King, 1986; Theart et al., 1989; Cornell et al., 1990a; Rossouw, 2003) comprise four members. These are the Swartkop, Quarry, Donkerkoekspruit and Skietbaan Members and a summary of the respective lithologies is given in Table 2.2.

Table 2.2: Regional succession of Jannelsepan Formation in Upington area

Member or Group	Lithological description [Reference]	Formation or sub-province
Swartkop Member	Porphyroblastic diopside bearing amphibolite with intercalated calc-silicate ^[2]	Jannelsepan Formation
Quarry Member	Banded biotite gneiss ^[1]	
Donkerkoekspruit Member	Hornblende-biotite gneiss, biotite-hornblende gneiss and massive amphibolite ^[1] including metalliferous zone	
Skietbaan Member	Quartzo-feldspathic gneiss ^[1]	
Micaceous schist (including quartz-feldspar gneiss, quartzites, amphibolite, and quartzitic conglomerate)		Sprigg Formation

[1]: Geringer, et al., 1994, [2]: Ludick, 1987

Geringer (1994) suggested that the Bokspuits Formation and Jannelsepan Formation are time equivalents. Rossouw (2003) described the Kantienpan deposit in the Bokspuits Formation, in the Van Wykspan area (see Table 2.3) as a VHMS deposit.

Table 2.3: Regional succession of Bokspuits Formation in Van Wykspan area

Lithological description [Reference]	Formation or sub-province
Diopside amphibolite ^[1]	Bokspuits Formation
Hornblende gneiss, massive amphibolite ^[1] and including metalliferous zone	
Quartzo-feldspathic gneiss ^[1]	

[1]: Geringer et al., 1994

2.3. Regional metamorphism and tectonism

The rocks belonging to the Areachap Group were affected by a complex deformation and metamorphic history closely related to the accretion of tectonic terranes within the Namaqua metamorphic complex and the subsequent accretion of these terranes with the Kaapvaal Craton (Hartnady et al., 1985; Moor et al., 1990; Thomas et al., 1994a).

Cornell et al. (1992) proposed an empirical pressure-temperature-time (P-T-t) path explaining the metamorphic evolution of the Areachap Group rocks at the Prieska Cu-Zn mine. This evolution will be summarized and amended to relate to the entire Areachap Terrane. They proposed an original age of the rock succession of 1285 Ma, which most probably represent an early metamorphic age with the age of the succession closer to 1599 Ma (Theart, 1985; Theart et al., 1989; Schade et al., 1989).

Rocks of the Areachap Group were affected by the early collision events (Cornell et al., 1992) that lead to a rapid increase in pressure during thrust dominated, deep level deformation resulting in the early phase of isoclinal to shear folding (F1 and F2) and mineral parageneses reflecting upper amphibolite to granulite grade (M₁) metamorphic conditions (Theart, 1985; Humphreys et al., 1988a) at a pressure of approximately 7Kbar and a temperature of approximately 525 to 600°C (Cornell et al., 1992). This event is most probably related to accretionary processes affecting the Areachap and Kakamas

Terranes as similar deformation and metamorphism are displayed by their supercrustal successions.

Thermal relaxation (Cornell et al., 1992) caused by the wide spread intrusion of granitic melts now seen as well foliated gneisses resulted in the pervasive high temperature (500°C) high pressure (7 Kbar) mineral parageneses largely replacing earlier metamorphic assemblages (Theart, 1985; Theart et al., 1989) giving rise to the predominant high grade M₂ metamorphic minerals assemblages reflecting upper amphibolite grade conditions. It is believed that these conditions also existed in the Kakamas Terrane. Uplift and erosion (Cornell et al., 1992) lead to a gradual decrease in pressure (5.5 Kbar) at almost the same temperature (500°C). Even through no discretely different mineral parageneses could be related to this time there is a marked difference in the style of deformation. Whereas the earlier isoclinal folds had predominantly sub horizontal axial cleavage foliation planes, deformation now resulted in a series of phases of folding where the axial planes are sub vertical and the folds themselves formed through a process of buckle folding (F3 and F4) (Theart, 1985). This deformation probably took place at higher tectonic levels during the assembly of the various terrains forming the Kibaran Namaqua Province. The folding, especially the later phase is directly related to the formation of shear zones responsible for the juxtaposition of the different terranes.

Cornell et al. (1992) referred to the next event as a thermal excursion, as its impact is seen in the development of grain boundary textures (M₃) indicative of an influx of fluids at a high temperature (800°C) and slightly lower pressure (4 Kbar), resulting in the replacement of M₁ cordierite along grain boundaries by sillimanite phlogopite and almandine. This event is characterized by the replacement of hypersthene by anthophyllite and gedrite, and the invasion of feldspar grains by myrmekitic intergrowths of quartz and albite (Theart et al., 1989). Cornell et al. (1992) ascribed this to a contact metamorphic effect caused by the intrusion of the Plat Sambok Anorthosite Suite in the vicinity of the Prieska Cu-Zn mine. However as these features are also evident throughout the Areachap Group, the events influence must be assumed to have affected

all the supracrustal rocks from the Prieska Cu-Zn mine in the south to the Areachap mine in the north (Theart, 1985). This is far more pervasive than contact metamorphism related to a localized intrusion and it is suggested here that this thermal excursion resulted from the wide spread intrusion of the late tectonic Vaalputs or Keimoes Suite. These often show intrusions a metasomatic contact metamorphic halo' surrounding them. Rocks within these contact metamorphic halo's were described as kinzigites by (Stowe, 1983; Moen, 1988). The intrusions of these granites at 1100 Ma may be regarded as a stitching event after the accretion of the Kakamus and Areachap Terranes, as the intrusions cut across tectonic boundaries.

Following the intrusion of these large batholiths, the steady state geotherm is re-established (Cornell et al., 1992) and conditions returned to a temperature of approximately 500°C and a pressure of less than 4 Kbar. The Areachap Terrane now becomes the leading edge during the northward convergence of the Namaqua-Natal Province and the Kaapvaal Craton (Van Zyl, 1981; Stowe, 1983). This accretionary event also incorporated the Eburnian Dagbreek and Koras Terranes, and the Archean Marydale Terrane of the Kheis Subprovince (Thomas et al., 1994a), situated between rocks belonging to the Namaqua Province and the Kaapvaal Craton. Shear zones within the Namaqua Province recorded north ward shortening in excess of 400 km (Stowe, 1983) and reflects retrogressive metamorphism (M₄) caused by ascending hydrothermal fluids (Theart et al., 1989). Cornell et al. (1992) suggested that this final accretionary event took place some 965 Ma ago and that the region reached surface at 550 Ma.

2.4. Regional data set

Kumba Resources Limited sampled rock outcrops in a long traverses and large area. In total 59481 records are in Kumba's data file, but most of these records include zero values. In total 2016 rock samples of this data set, which does not have zero value, were used in this investigation.

The following elements were analyzed in the Kumba data set:

- 1) Major oxides: FeO, Fe₂O₃, MnO, TiO₂, CaO, K₂O, P₂O₅, SiO₂, Al₂O₃, MgO, and Na₂O;
- 2) Trace elements: Cl, S, Cu, Zn, Ni, Pb, As, Ba, Cd, Rb, and Sr; and
- 3) LOI and Total values were calculated.

Multivariate analyses were only used on these elements, although the following trace elements were analyzed in this research:

Co, Cr, F, Sc, V, As, Ga, Mo, Nb, Ni, Rb, Sr, Th, U, W, Y, Zr, Ba, La, and Ce.

For confidentiality reasons and to protect the company's interests, none of the sample coordinates, or maps indicating the locality of anomalous samples could be included here. The relevant information was however reported to Kumba Resources Limited and to Prof H F J Theart.

2.5. Local geology

2.5.1 Lithological succession at Areachap mine

The lithological variations near the ore zone at the defunct Areachap mine were examined by Voet and King (1986) and Theart (1985). In the current investigation, two boreholes were selected, sampled and the results were logged (boreholes AP5 and AP2, Appendix A). Samples were taken at sampling intervals of 2 to 5m in the ore zone and 10 to 15m away from the ore zone. Borehole AP5 was selected for studying rock successions southwest of the ore body and for constructing the cross-section of the area as this borehole intersects hangingwall, ore zone and footwall, thus providing a complete section (Fig. 2.3). The geological units near the massive sulphide deposit are also shown in the geological map of the Areachap deposit (Fig. 2.4). The major lithological rock types of the Jannelsepan Formation at the Areachap mine as identified by Voet and King (1986) are described in the following paragraphs. Voet and King (1986) are of the opinion that the succession display repetition due to isoclinal folding.

Banded biotite-garnet gneiss (AR3)

The unit is composed of quartz, highly saussuritized plagioclase, microcline, biotite, garnet, cordierite, sillimanite and secondary minerals i.e., green biotite and chlorite, and greenish pinitite (Theart, 1985). The rocks have a foliation defined by quartz and biotite under the microscope. Voet and King (1986) named this unit banded and foliated biotite-gneiss to biotite-garnet gneiss (chloritized in part). On the geological map (Fig. 2.4) the unit is referred to as AR3.

Quartzo-feldspathic gneiss (AR4)

Unit AR4 represented by quartzo-feldspathic gneiss may have originated either a rhyolite or arkose layer, but this was not investigated here.

Banded hornblende-biotite gneiss (AR5)

The banding in this unit is caused by green hornblende alternating with plagioclase in amphibolite, and biotite layers alternating with plagioclase and quartz domains in biotite-rich gneisses. The mineralogy of amphibolites includes green hornblende, plagioclase (labradorite), and accessory sphene (Theart, 1985). The biotite-rich layers consist of quartz, plagioclase, biotite, hornblende, apatite and epidote. The mineralogy of the leucocratic zones comprise plagioclase, quartz and biotite accompanied by secondary minerals i.e., fine mica, chlorite and epidote (Theart,

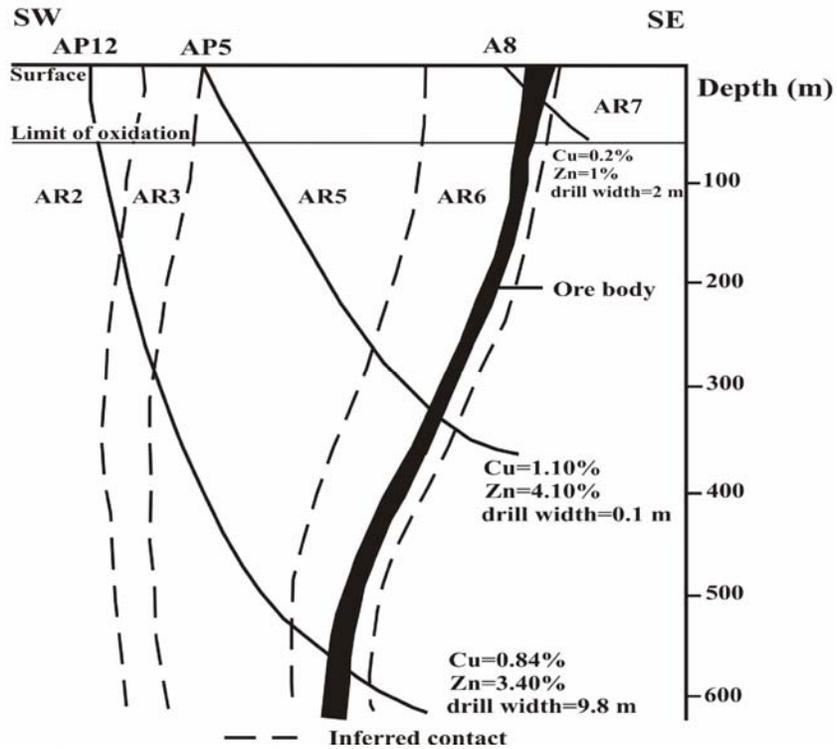


Figure 2.3: A cross-section of lithology at Areachap mine including the borehole AP5.

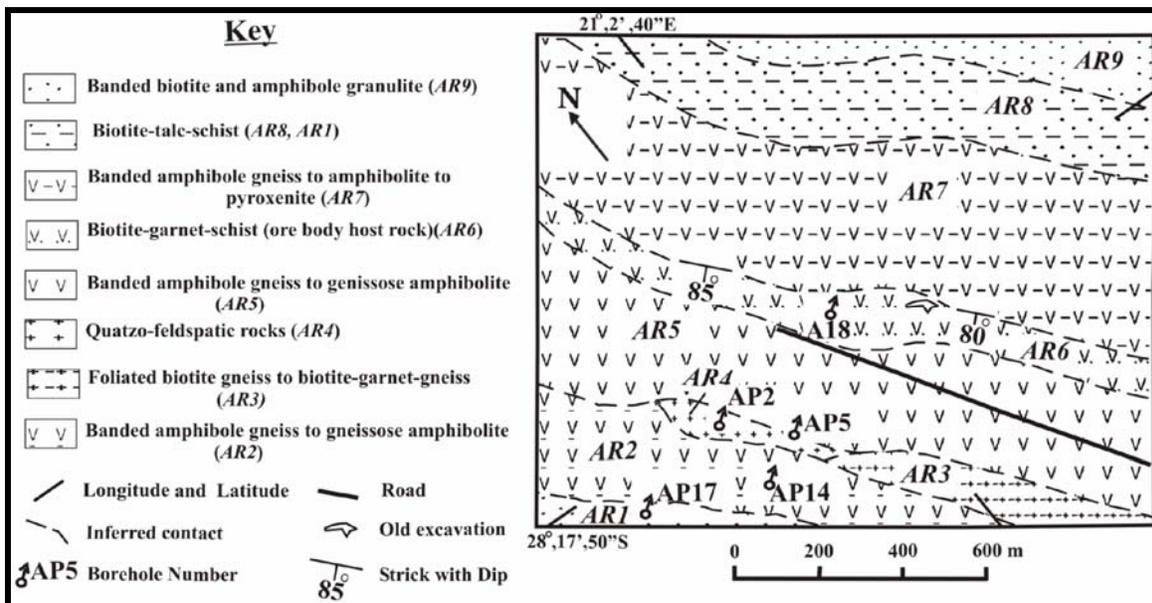


Figure 2.4: Geological map of the Areachap area (after Voet and King, 1986).

1985). Voet and King (1986) use the term grey green-banded amphibole gneiss for this unit which is referred to as AR5 on the map.

Banded amphibole gneiss to amphibolite (AR2)

Units AR2 and AR5 indicated on the map of Voet and King (1986) were regarded as equivalent by Theart (1985) and these rocks may be seen as a correlate of the dacitic Smouspan Gneiss Member of the Copperton Formation. The Smouspan Gneiss Member represents the original footwall of the Prieska Cu-Zn mine (Theart, 1985).

Garnet-biotite-cordierite gneiss (AR6)

This peraluminous unit forms the host rock of the massive sulphide deposit. The biotite is highly altered to chlorite. Cordierite rich rocks are more abundant on the southwestern side of the deposit compared to the northeastern side of the ore body (Theart, 1985).

The ore zone is characterised by two lensoid bodies (Voet and King, 1986). The massive sulphide layers include the sulphides pyrrhotite, pyrite, minor sphalerite, chalcopyrite and galena. Voet and King (1986) coined the name banded and foliated (amphibolitic) biotite-garnet schist (chloritized in part), AR6, for this unit.

A second unit of banded hornblende-biotite gneiss (AR7)

This unit occurs adjacent to the garnet-cordierite-biotite gneiss on the northeastern side of the massive sulphide deposit (Theart, 1985). This unit when compared with the banded hornblende-biotite-gneiss on the southwestern side of the ore differs in that it is richer in garnet and amphibolite layers (Theart, 1985). The garnetiferous-biotite schist layers have a pelitic composition, with minerals quartz, biotite, plagioclase, garnet, sillimanite and pyrite. The mineralogy of the amphibolite layers includes hornblende, plagioclase, biotite, quartz, and sphene. Voet and King (1986) used the term AR7 or banded amphibolite gneiss for this unit.

Banded pelitic gneiss (AR8 and AR1)

This unit is the only biotite-bearing gneiss in the area that does not have hornblende. The banded pelitic gneiss is similar to the host rocks of the sulphide ore body. Disseminated pyrite grains occur within some of the biotite schist bands of the unit (Theart, 1985). The mineralogy consists of quartz, plagioclase, biotite, fibrolitic

sillimanite, garnet, cummingtonite, and pyrite. Voet and King (1986) use the term garnet-biotite-talc schist, AR8 and AR1, for this unit.

Laminated biotite-gneiss (AR9)

The unit occurs on the north-eastern side of the ore body. The mineralogy includes andesine, quartz, biotite and hornblende with no K-feldspar present (Theart, 1985). Voet and King (1986) refer to this unit as a banded biotite and amphibole granulite, AR9.

2.5.2. Metamorphism in Areachap Mine

The mineral assemblages of the Areachap rocks i.e. feldspar, garnet, cordierite and sillimanite in AR6 unit and quartz-potassium feldspar-biotite-garnet or quartz-potassium feldspar-biotite-cordierite in AR3 unit are indicative of high-grade metamorphism (Theart, 1985). The rocks were then subjected to late-stage deformation as evidenced by the presence of a mylonitic fabric that is developed parallel to the lithological layering, and the large number of fractures present in the rocks. These fractures cause the rocks to be permeable resulting in aqueous fluids extensively altering the early mineral phases to muscovite, chlorite and epidote. These fluids were responsible for retrograde metamorphism, and partly destroyed the earlier metamorphic assemblages. These factors are related to M₄ conditions (Theart et al., 1989). Indicator minerals for this retrograde metamorphism could pinite after cordierite (in AR6), muscovite along late foliation planes (in AR5 and AR7 units) and chlorite after biotite (in AR5 and AR7 units) (Theart, 1985). The same sequences of tectono-metamorphic events have affected the Prieska Cu-Zn mine (Copperton Formation), Areachap mine (Jannelsepan Formation) and Kantienpan mine (Boksputs Formation) (Theart, 1985; Rossouw, 2003) of the Areachap Group (Wilson et al., 1998).

2.5.3. The sulphide minerals in the defunct Areachap mine

The sulphide minerals described in the assumed footwall of this deposit include chalcopyrite, pyrite, and sphalerite. The ore zones comprise pyrite, sphalerite,

pyrrhotite, chalcopyrite, barite, anhydrite, and trace amounts of galena. Magnetite, pyrite and sphalerite are present in the assumed hanging wall successions at this deposit.

2.5.4. Lithological succession of the Kantienpan deposit

The geology of the ore zone at Kantienpan mine was described by Rossouw (2003). The geological map (Fig. 2.5) provided in Rossouw (2003) shows the local geology of the massive sulphide deposit. In the current investigation two boreholes were selected for sampling. Samples were taken at sampling intervals of 2 to 5m in the ore zone and 5 to 10m, away from the ore zone. The cross-section as drawn from borehole KN11 (Fig 2.6) was selected because this borehole intersects the hanging wall, ore zone and footwall. The major rock types of the Kantienpan deposit are described in the following paragraphs.

Biotite-gneiss (Structural hanging wall)

This unit consists of quartz, plagioclase, microcline, biotite, magnetite, and trace amount of hornblende and zircon suggesting that it's granitic in composition. The rock has interstitial magnetite and ilmenite, green hornblende and zircon. Rossouw (2003) described this unit as an orthogneiss.

Hornblende-biotite-gneiss (Structural footwall)

The principal minerals of this gneiss are quartz with minor amounts of plagioclase, biotite and minor to trace amounts of pyroxene, hornblende, and garnet. Magnetite is the main opaque mineral, with pyrite, pyrrhotite and very small amounts of chalcopyrite also present. This unit contains amphibolite layers, which are interpreted to represent the metamorphic equivalent of earlier dykes or sills (Rossouw, 2003).

Rossouw (2003) is of the opinion that this rock also represents an orthogneiss derived from a granite parent. But an alternative interpretation is that it was derived from a dacite layer (H.F.J. Theart, 2004, pers. Comm.).

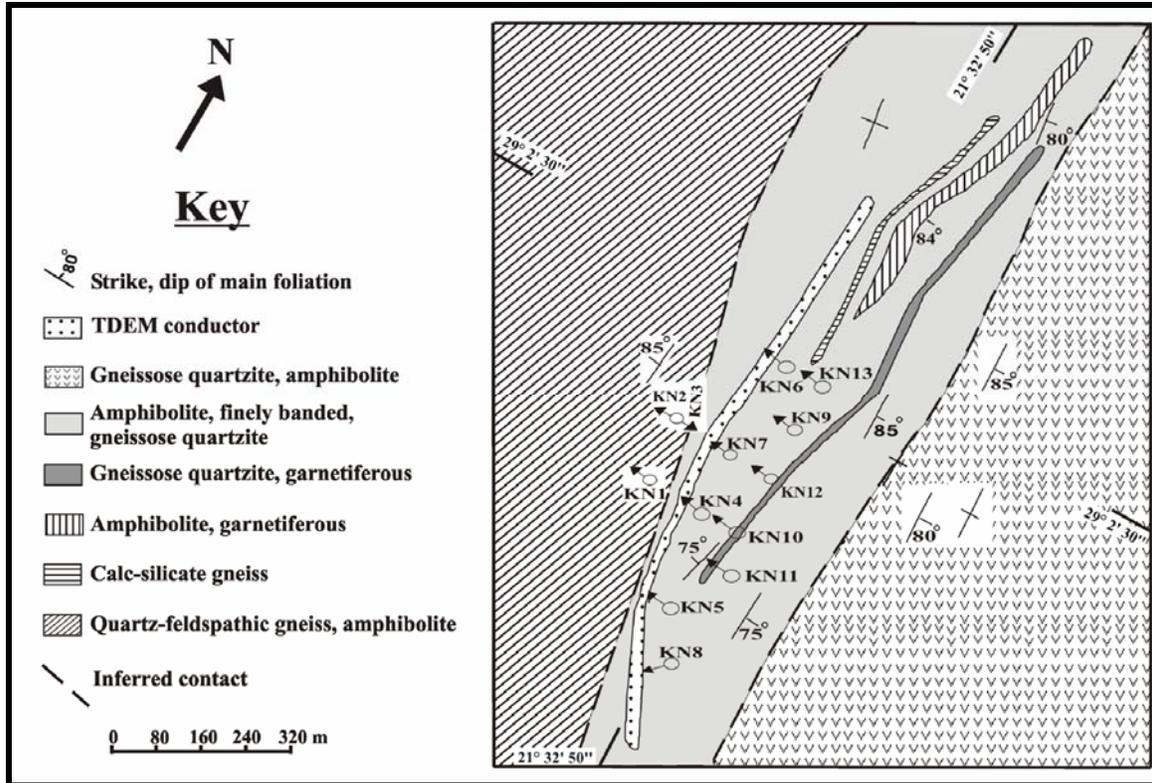


Figure 2.5: Geology map of the Kantienpan area (after Rossouw, 2003) (TDEM: Time domain electromagnetic conductor).

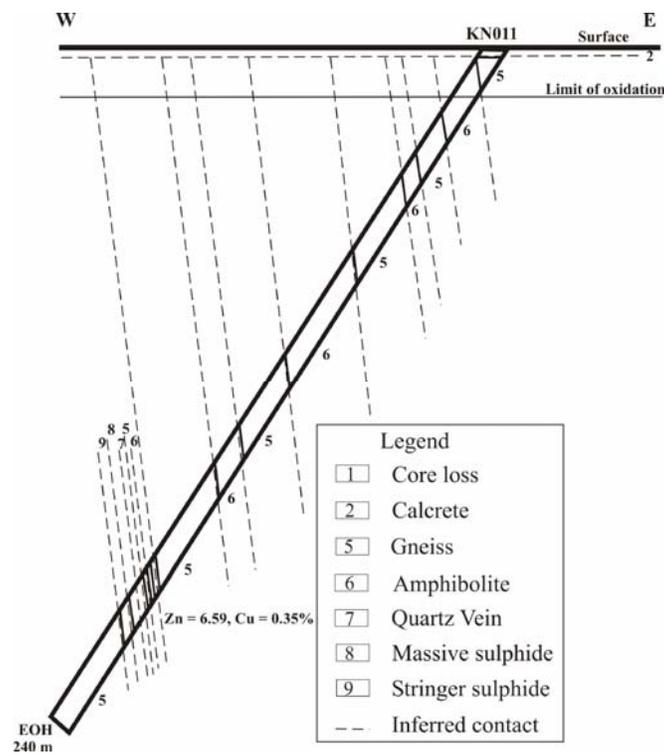


Figure 2.6: Cross-section of borehole KN11 (after Rossouw, 2003).

Mineralized zone

The ore zone is dominated by pyrrhotite and sphalerite with minor amounts of chalcopyrite, pyrite and trace amounts of galena (Rossouw, 2003). The sulphide minerals occur as either patches of massive sulphides or disseminations in the host rock.

The sulphide minerals described in the assumed footwall of this deposit include pyrrhotite, chalcopyrite, and pyrite. Magnetite, pyrite and sphalerite are present in the assumed hanging wall successions at this deposit.

2.6. Geomorphological evolution

Rocks belonging to the Areachap Group suffered repeated weathering and erosional events, since the first post metamorphic exposure to surface about 850 Ma ago (Cornell et al., 1992) prior to the Pan African sedimentation. In Table 2.4 a summary of geomorphological events is presented.

The earliest well-constrained geomorphological events coincided with the disintegration of Gondwanaland. This super-continent initially divided into east Gondwanaland and west Gondwanaland (Partridge et al., 1987; Moore, 1999). Although an earlier stage of separation dated at about 1150-1100 Ma were proposed by Partridge et al. (1987) this may coincide with the accretion of the Namaqua-Natal Province and the Kaapvaal Craton. More important is the second stage of Gondwana disintegration dated between 600-560 Ma (Cahen et al., 1984) as this follows on the first post metamorphic exposure of the Areachap Group discussed above. During this period the large parts of Africa were affected by convection generated orogenesis resulting in the formation of mobile belts during the Pan African episode (Cahen et al., 1984; Partridge et al., 1987). This was followed by denudation due to glaciation during the Dwyka times (300 Ma). Then a thick sedimentary cover belonging to the Karoo Sediment Group covered the entire region.

Table 2.4: Summary of geomorphological events

Era	Epoch	Age	Description
Cenozoic	Middle Pleistocene		Ice age and cover the whole area by eolian sand ^{1,2}
	Pliocene		Aridification ¹
	Miocene		Uplift and Post-African II erosion cycle ¹
			Deformation of the post-African I surface by further uplift ³
	Oligocene		Epirogenic uplift (Post-African I erosion cycle) ⁴
	Eocene		Kaolinization and laterite duricrusts ¹
	Palocene		Calcretization in the Kalahari Group ⁵
Mesozoic	Cretaceous	~ 86-78 Ma	Second peak of sedimentation (basal Kalahari Group) ^{3,6}
		~ 131-115 Ma	First peak of sedimentation ³
			African erosion cycle
	Jurassic	~ 200-120 Ma	Separation of Africa from south America by a volcanic cycle (opening of the Atlantic basin and creating a Great Escarpment ⁷
The precipitation of Karoo sediments			
Paleozoic	Carboniferous	~ 300-289 Ma	Denudation due to glaciation during the Dwyka times ¹
Neoproterozoic		~ 600-560 Ma	Secondary stage of Gondwana disintegration ¹
Mesoproterozoic		~ 850 Ma	Post metamorphic exposure of the Areachap Group to surface ⁸
		~1150-1100 Ma	Disintegration of Gondwanaland into east and west Gondwana ^{1,6}
		~ 1200-1050 Ma	Final stitching event of the different terranes belonging to the Namaqua-Natal Province ⁹
		~ 1600 Ma	VHMS deposits of Areachap Group in newly formed ocean floor ⁹
Palaeoproterozoic		~ 2000 Ma	Eburnian Basement currently to the west of the Areachap Terrane ⁹
Archaen		~ 3600 Ma	Kaapvaal Craton currently to the northeast of the Areachap Terrane ¹⁰

1. Partridge et al., 1987 3. Dingle et al., 1983 5. Netterberg, 1970 7. Summerfield, 1985 9. Thomas et al., 1994a
 2. Malherba, 1984 4. Cogley, 1985 6. Moore, 1999 8. Cornell et al., 1992 10. de Wit et al., 1992

The African surface was formed when Africa was separated from South America by a volcanic cycle giving rise to the seafloor basalts separating the two continents from each other. This event resulted in the opening of the Atlantic basin from 200Ma to 120Ma, and created a Great Escarpment (Summerfield, 1985). The African erosion cycle proceeded at different levels above and below the Great Escarpment. There were two peaks of

sedimentation, the early-Cretaceous peak in Valanginian to Barremian times (131-115Ma) and a late-Cretaceous peak in Coniacian/Santonian times (86-78Ma) (Dingle et al., 1983).

The most important succession of the basal Kalahari Group sediments accumulated during the late Cretaceous, and directly overlies the African surface (Moore, 1999). Netterberg (1970) presumed a post-upper Cretaceous age or “pre-Pliocene” for calcretization in the Kalahari group, which indicates a semi-arid environment. The calcrete layer works as geochemical barrier and reduced the mobility of mobile elements. It is therefore an important part of this research because it affects the lateral extend of geochemical dispersion haloes. The advanced planation, deep weathering and kaolinization of the underlying rocks, and massive laterite duricrusts formed at end-Cretaceous to Eocene times (Partridge et al., 1987). The kaolinization is an indicator of a humid condition. The erosion removed an enormous thickness of material in different parts of the continent. The accumulation of the Kalahari sediments was continued during the Eocene and Oligocene. As this area is situated on the edge of the Kalahari Basin it could be assumed that erosion here was not that severe during this period.

Another epirogenic uplift of the subcontinent deformed the African surface, during a major episode of landscape evolution in Miocene times (Cogley, 1985). This event was confined to the northern and north-western Cape or the Griqualand-Transvaal axis. This was the beginning for the Post-African I erosion cycle, and major deposition in the Kalahari basin. In this relatively short time of erosion, there was no advanced weathering and kaolinization and the processes were limited to the development of duricrusts on the Post-African I surface (Partridge et al., 1987).

Further uplift in the Pliocene resulted in deformation of the Post-African I surface (Dingle et al., 1983). This movement had greater amplitude in some areas, confined to the same axes as in the Miocene. The Post-African II cycle began at the end-Tertiary uplift and warping of the subcontinent. Aridification and major climate deterioration were the most important changes (Van Niekerk et al., 1999), which began during the late Pliocene

(Partridge et al., 1987). These changes occurred together with major changes in the extent of the earth's ice caps.

The “ice age” began at the start of the middle Pleistocene, which was an important event of the Pleistocene period (Partridge et al., 1987). The sea level decreased due to increasing global ice volume, and then later rose due to warmer conditions. The changing conditions drove fluvial, colluvial, and aeolian processes, which results in sediment accumulation in the continental basins (Partridge et al., 1987).

Changes during the late Tertiary probably contributed most to the present landscape of southern Africa. This includes the two phases of uplifting during the Miocene and Pliocene accompanied by a period of weathering, aridification and deposition of the last member of Kalahari Group, i.e., sand dunes. The windblown sand covered the whole area during a very arid period (Malherbe, 1984). Fossil dunes formed during this period are still preserved in the study area and the area has undergone very little subsequent change due to the semi arid to desert climate conditions.

2.7. Calcrete environments

2.7.1. Definition of calcrete

Calcrete, also known as caliche, croutes, calcaires, nari and kunkar, is a predominantly calcium carbonate component that is accumulated near the surface. It is formed either through pedogenic (soil forming processes) or groundwater processes or a combination of both (Khadkikar et al., 1998; Ringrose et al., 1999; Jimenez-Espinosa et al., 2003). The source of the carbonate may be aeolian dust, rainwater, plants, sheet wash or weathering of calcareous parent material and shells (Vermaak, 1984; Dhir et al., 2004). Calcrete may form in arid (50-100 mm mean annual rainfall) to subhumid (500-700 mm mean annual rainfall) conditions (Khadkikar et al., 2000; Jimenez-Espinosa et al., 2003) and the existence of calcrete in an area is evidence for dry periods, where evaporation exceeds precipitation. Calcareous sediments with a prominence of SiO₂ (quartz) are known as calcareous sands or sandstones depending on the degree of diagenesis (Ringrose et al., 1999).

2.7.2. Calcrete classification

Khadkikar et al. (1997) classified calcretes into three groups based on the processes of formation. These are pedogenic calcrete (soil-forming), groundwater calcrete (groundwater processes) and calcrete conglomerate (reworking of both groups).

The groundwater or non-pedogenic calcrete is formed by carbonate-bearing groundwater circulating through sediments during dry seasons (Vermaak, 1984; Ringrose et al., 1999). During these dry periods, groundwater with dissolved carbonates rises through the host sediments by capillary action. As the groundwater reaches to the surface, evaporation will cause precipitation of carbonate close to or on surface resulting in the formation of calcrete (Fig. 2.8) (Vermaak, 1984; Ringrose et al., 1999). Alternatively, Ringrose et al. (1999) suggested that carbonate is precipitated in the capillary fringe of a fluctuating water table (Fig. 2.7).

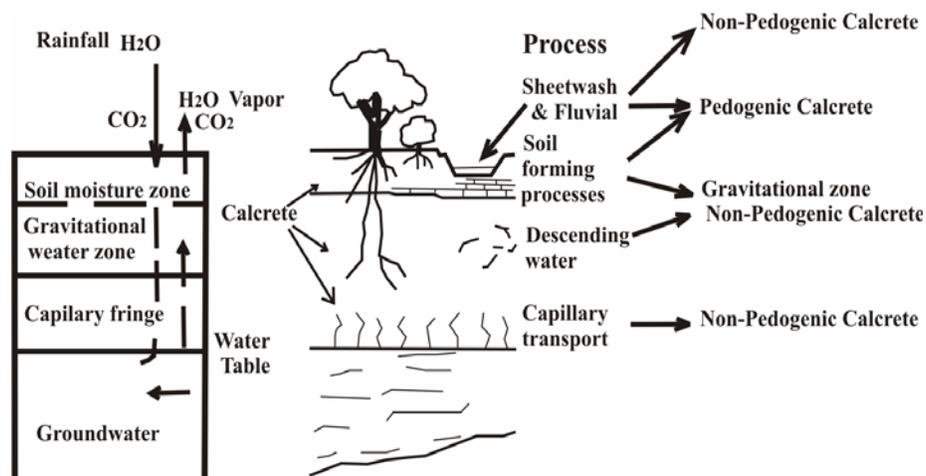


Figure 2.7: The genetic calcrete classification (after Carlisle, 1980).

Pedogenic calcrete develops in more arid areas where rainfall only moisturizes the soil and creates a soil moisture zone during wet seasons. The dissolved carbonates move through the soil moisture zone and are precipitated on the surface by evaporation during dry seasons (Fig. 2.7) (Vermaak, 1984; Ringrose et al., 1999). This type of calcrete is a residual product of weathering and soil forming processes (Vermaak, 1984). Khadkikar et al. (1998) subdivided pedogenic calcretes into two groups, the vertisols calcrete and red-soil-calcrete (Table 2.5). Vertisols calcrete is

formed in sub-humid conditions and is characterised by the presence of montmorillonite and illite (Khadkikar et al., 2000). Red-soil calcrete is formed in semi-arid conditions and is characterised by the presence of oxidised iron together with montmorillonite and illite (Khadkikar et al., 2000). Pedogenic calcretes are normally recognized by their laminar, highly indurated upper zones and a decrease in carbonate concentration with depth.

Calcrete conglomerates are formed by the reworking of both pedogenic as well as groundwater calcretes.

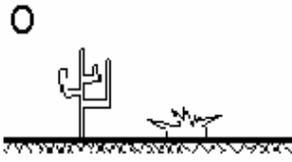
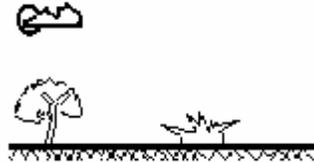
Calcrete may also form due to the interaction of plant root growth, water and the erosion-sedimentation processes (Jimenez-Espinosa et al., 2003). This type of calcrete is known as biogenic or β -calcretes and does not form layers. When water is available, high soil moisture may favour rapid plant colonisation. The plant would absorb the carbonate bearing groundwater via its roots (Jimenez-Espinosa et al., 2003). As the plant uses up the water, the carbonate is left behind to accumulate forming round micritic calcite particles. Khadkikar et al. (1998) introduced rhizogenic calcretes, which are calcretes formed by physiochemical processes in the root zone. The plant root uptakes the water causing the remaining soil water to be super saturated in Ca^{2+} ions (Khadkikar et al., 1998). These calcretes occur as sinuous cylindrical tubes (5-10 cm tubes), thus are referred to as calcrete tubes and are associated with both pedogenic and groundwater calcretes (Khadkikar et al., 1998).

2.7.3. Mineralogy of calcretes

Calcretes are mostly composed of calcite, quartz and feldspar (Vermaak, 1984), with the silica content affecting the hardness of calcretes, i.e. the higher the silica content, the harder the calcrete. Aragonite and calcium carbonate-hydrate minerals may be present in the early stages of calcrete formation. Dolomite (dolocrete) may also occur together with calcite (Vermaak, 1984). Khadkikar et al. (1998); Khadkikar et al. (2000) reported on the presence of clay minerals and trace amount of gypsum and barite in some calcretes. In drier climates (50-100 mm average annual rainfall, Table 2.5), sepiolite and palygorskite are usually formed (Jimenez-Espinosa et al., 2003).

The absence of sepiolite-palygorskite and the presence of smectite and hematite associated with low Mg calcite are characteristics of calcretes formed in semi-arid climates (100-500 mm average annual rainfall, Table 2.5) (Jimenez-Espinosa et al., 2003). The formation of pedogenic hematite requires enough moisture to enable chemical weathering of primary minerals and low activity of water that would propel dehydration processes like in the tropical environments (Khadkikar et al., 2000; Jimenez-Espinosa et al., 2003).

Table 2.5: Classification of calcrete based on the weather conditions (after Khadkikar et al., 2000)

Groundwater calcretes	Pedogenic calcretes	Pedogenic calcretes
ARID (50-100 mm)	SEMI-ARID (100-500 mm)	SUB-HUMID (500-700 mm)
		
Mineralogy of calcrete Calcium carbonate, sepiolite and palygorskite. Hydromorphic features are absent.	Mineralogy of calcrete Calcium carbonate, oxidised iron, montmorillonite and illite. Hydromorphic features may be present (Red-soil-calcrete)	Mineralogy of calcrete Calcium carbonate, montmorillonite and illite. Hydromorphic and vertic features are present (Vertisols calcretes)

2.7.4. Mechanism of carbonate accumulation

The calcium carbonate solubility is mainly controlled by pH (acidity of a solution) and the pH of the system is itself directly controlled by the CO₂-pressure. In general for calcium carbonate to precipitate, a pH of 8.4 or more is required. Evaporation, CO₂-loss, changes in temperature, pressure, grain size and mixing of solutions may also affect the pH of the solution leading to carbonate accumulation if favourable pH conditions are met.

During rainfall, acidic water percolates into the soil, and it carries with it dissolved CO₂ from river water as well as the aeolian dust. In the event that there is an ore body close to surface, the carbonate-bearing water will react with the ore body resulting in mobile elements in the ore body being dissolved. Later, evaporation processes take place and result in the solution rising to the surface by capillary action. H₂O and CO₂ are lost and this increases the pH of the solution. The pH may reach favourable

conditions for the precipitation of calcium carbonate resulting in deposition of calcite together with dolomite, quartz, iron oxides and other dissolved elements on surface.

Large parts of the dryer central parts of North-West and Northern Cape Provinces of South Africa are covered by well developed calcrete layers concealing the underlying geology. These calcrete layers may be correlated with the Mokalanen Formation of the Kalahari Group described by Malherbe (1984).

The dispersion of ore-related elements in the calcrete environments, as a geochemical barrier, is an interesting process to look into in this current research.

2.7.5. Calcrete of the study area

The calcrete layers at the base of the Kalahari Group formed during a dry period that existed during the later part of the Tertiary Period (Thomas, 1981), more specifically during the late Miocene Epoch (23.8-5.3 Ma) (Ward et al.,1983). Different formations of the Kalahari Group were studied by Malherbe (1984) (Table 2.6). The Mokalanen Formation, which is the calcrete unit of the Kalahari Group, comprises of three units and two varieties of calcrete layers, namely nodular and hardpan calcretes. The hardpan calcrete is hard and impermeable and forms when the nodular calcrete is cemented by calcrete or silcrete. It provides evidence of the semi-arid environmental conditions during the formation of the Mokalanen Formation. The hardpan calcrete is an extremely weathering-resistant rock.

The calcrete layer developed near surface throughout the study area from Areachap in the North to Copperton in the South, is correlated with Malherbe's (1984) Mokalanen Formation.

Vermaak (1984) suggested a pedogenic process for the formation of the calcrete at Areachap, Copperton and Jacomynspan areas. A non-pedogenic, groundwater, processes was suggested by Nash and McLaren (2003) for the Kalahari valley calcrete in the capillary fringe zone of the groundwater table. Based on the semi-arid

Table 2.6: Different Formations of the Kalahari Group. Data summarised from Malherbe (1984)

Name of the Formation	Lithologies in the Formation
Gordonia Formation	Sand dune deposits and Fe-rich minerals such as magnetite, haematite and Ilmenite
Goeboe Goeboe Formation	Sand sediment
Lonely Formation	Clayey diatomaceous limestone
Mokalanen Formation	- Harden calcrete -Nodular calcrete -Sharpstone calc-conglomerate
Eden Formation	Sandstones and conglomerate
Budin Formation	Red clay
Wessels Formation	Gravel

environmental conditions proposed by Malherbe (1984) during the formation of the Mokalanen Formation, and the classification of calcrete by Khadkikar et al. (2000) and Table 2.5, a pedogenic origin may be accepted for these calcretes.

Chapter 3

Literature review of VHMS deposits and related Lithogeochemical alteration

3.1. Introduction

The objective of this chapter is to discuss hydrothermal alteration that could be associated with volcanic hosted massive sulphide (VHMS) deposits, that may be used related to the classification of VHMS deposits, their tectonic setting, and the related hydrothermal fluid models will be discussed. This will be followed by discussions on the mineral zonation in the ore zone and footwall, and the alteration products and the effect of subsequent metamorphism. Finally some geochemical alteration indexes will be introduced.

3.2. Classification and geological setting of VHMS deposits

Massive sulphide deposits consist of 60% or more sulphide minerals (Sangster and Scott, 1976). Two main groups were suggested for these deposits based on the host rock lithology. The first group is composed of sedimentary-exhalative (SEDEX) or shale-hosted stratiform massive sulphides (Lydon, 1998a; Goodfellow et al., 1993; Lott, 1999; Sangster, 2002; Canet et al., 2004) e.g. Sullivan, Broken Hill, Mt. Isa and Rammelsberg. The volcanic-hosted massive sulphide (VHMS) deposit forms the second group (Lydon, 1998a; Sanchez-Espana, et al., 2000; Ulrich et al., 2002; Ruiz et al., 2002; Tornos, 2006; Aftabi et al., in proof). The origin of the immediate host rocks of VHMS deposits are

thought to be either derived directly from volcanic activity such as lava or pyroclastic rocks, or have no direct volcanic affiliation e.g. shales or greywackes (Lydon, 1998a).

Sillitoe (1973) suggested that VHMS deposits dominated by Cu are related to spreading centre tectonic setting, whereas the Pb, Zn, Ag and Ba enriched deposits formed in island arc or continental margin environments. Hutchinson (1973) classified these deposits into the Zn-Cu-type which is associated with fully differentiated magmatic suites of tholeiitic and calc-alkaline affinities, predominately of Archean age. This may also be referred to as the primitive of Noranda type deposits (Lydon, 1998a). The second group of deposits are characterized by high Pb, Zn and Cu contents and are associated with intermediate to felsic calc-alkaline volcanic rocks of predominantly Phanerozoic age (Hutchinson, 1973). This group may collectively be referred to as the Kuroko type deposits (Lydon, 1998a). The third and last group are Cu deposits related to ophiolite of tholeiitic suites of Phanerozoic age (Hutchinson, 1973) also referred to as Cyprus type deposits (Lydon, 1998a).

Lydon (1998a) classified the VHMS deposits based on major ore metals instead of geological characteristics, into Cu-Zn and Zn-Pb-Cu types.

The location of massive sulphide lenses seem to be strongly related to structural controls of the ocean floor e.g. synvolcanic faults with vertical displacements (Knuckey, 1975). Hodgson and Lydon (1977) documented that most of VHMS deposits are related to the fracture systems produced by subvolcanic intrusions or resurgent calderas. This relationship shows that particular hydrologic, topographic and geothermal features of the ocean floor are required to form VHMS deposits (Lydon, 1998a).

It is important to note that the hydrothermal solutions responsible for the sulphide mineralization escapes onto the ocean floor at temperature of 300-400°C (Lydon 1998a). To prevent such solutions from boiling below surface, basin depths in excess of 2500 m are required (Ohmoto and Skinner, 1983).

3.3. Classification of metamorphosed massive sulphide deposits of the Namaqua Province

The first massive and disseminated massive sulphide deposits exploited in Namaqualand are located within the Okiep copper district. These copper deposits are related to a late tectonic cross cutting group of mafic to intermediate intrusions collectively known as noritoids (Conradie and Schoch 1986; Lombaard and Schreuder, 1987). Theart (1985) suggested that the metamorphosed stratiform massive sulphide deposits of the Namaqua Province be divided into the SEDEX Aggeneys Group (Ryan et al., 1986; Thomas et al., 1994b) and the VHMS Copperton Group of deposits. This subdivision is based on lithological, compositional and isotopic characteristics. The VHMS deposits are confined to the Areachap Terran of the Namaqua Province and forms the focus of this investigation. The largest known deposit in this terran is the Prieska Cu-Zn deposit (47 mt @ 1.7% Cu and 3.8% Zn) located near the deserted mining town Copperton. This deposit was exploited during the 1970's and 1980's. Early workers in this region classified the Prieska Cu-Zn deposit and other small deposits in its immediate vicinity as VHMS deposits (Middleton, 1976; Gorton, 1981). Wagener and Van Schalkwyk (1986) opposed and suggested that it was a SEDEX deposit. Following further research (Theart, 1985; Theart et al., 1989; Schade et al., 1989) the VHMS nature of the ore body was established by the recognition of a metamorphosed and deformed equivalent of a chloritic footwall alteration zone and a sulphate-carbonate cap above the massive sulphide mineralization. The Areachap deposit (8.9 mt @ 0.4% Cu and 2.24% Zn) mined in the 1900's and further explored in the 1960's and 1970's was also classified as a VHMS deposit (Theart, 1985; Voet and King, 1986). Geringer et al. (1987) investigated small deposits in the Bokspuits area and classified these as VHMS deposits of the Besshi type. Rossouw (2003) discussed the financial viability of the latest discovery in this region on the farm Kantienpan (5 mt @ 0.49% Cu and 4.09% Zn). He provides a geological description of the deposit and classifies it as a VHMS deposit.

3.4. Hydrothermal Models for Formation of VHMS deposits

There are three different models for the genesis of hydrothermal fluids and the source of energy for fluid circulation that are related to VHMS deposit formation. These are the *convection cell model*, the *stratal aquifer model* and the *magmatic hydrothermal model* (Lydon, 1998b). Two of these, the convection cell and the stratal aquifer models, are more common, but the third magmatic hydrothermal model, has little scientific support (Sangster, 1972; Solomon, 1976). These models are discussed below.

3.4.1. Convection cell model

Francheteau et al. (1979) suggested the presence of operating hydrothermal convection cells in VHMS deposit formation based on the presence of hydrothermal vents at mid-ocean ridges. There are different sources of heat for the formation of these vents such as cooling rhyolite domes or plugs (e.g., Ohmoto and Rye, 1974), sub-volcanic sills (e.g., Campbell et al., 1981), felsic plutons (e.g., Cathles, 1983), and spreading ridge magma chambers (e.g., Spooner, 1977; Lowell and Rona, 1985). The heat released from the roof of a vigorously convecting magma chamber would cause the circulation of subsurface waters in the overlying strata. When the strongly acidic fluids rise (~3.5 pH), they leach out the ore components of rocks along their flow path. The hydrothermal convection cell would remain active as long as the source of the heat is sustained. The principal source of water in these systems is the overlying ocean. Brauhart et al. (2000) and Scherdt et al. (2005) presents heat and fluid flow modelling results, developed for a relatively undeformed and unmetamorphosed VHMS deposits, indicating temperature gradients of 300⁰C to 400⁰C in the convection cells with flow velocities of approximately 1.8 m/s, that could have operated for up to 200, 000 yr.

3.4.2. Stratal aquifer model

This model assumes that the source of ore fluids is from the pore waters of a permeable rock capped by an impermeable rock. During sedimentation and diagenesis, the lithostatic pressure on the cap-rock increases and compacts the permeable rocks below resulting in an increase in the geothermal gradient and pore-

fluid pressure. When the lithostatic pressure and pore-fluid pressure are greater than the strength of the cap-rock, hydraulic or mechanical fracturing in the cap-rock occurs (e.g., Sibson et al., 1975). Due to the high pore water pressure, the water would escape via the fractures developed as a result of the mechanical fracturing described above. In this model, very large quantities of fluids move upward to the surface in a short time with minimal energy. The model is best applicable to the formation of SEDEX massive sulphide deposits (e.g., Walker et al., 1977; Badham, 1981; Lydon, 1983; Sawkins, 1984; Lydon, 1986).

3.4.2. Magmatic hydrothermal model

In this model it is assumed that the ore fluids responsible for VHMS deposits are derived from the volatiles of magmas. Bryndzia et al. (1983) considered the source of ore fluids in Kourouko type deposits to be magmatic to explain the elevated salinities (up to 1.9 times greater than sea water) in fluid inclusions. This could be supported by the concept that VHMS deposits are products of a calc-alkaline magma (Solomon, 1979).

3.5. Mineral zonation within hydrothermal alteration pipes and ore zones

3.5.1. Mineral variation in the ore zone

Some of the evidences for VHMS deposits being precipitated by hydrothermal fluids include occurrence of massive sulphide lenses on the seafloor, sedimentary structures, the conformable contact between massive sulphide lenses and the hanging wall, and hydrothermal alteration pipes in the footwall (Lydon, 1998b). The high temperature fluids escape to the sea floor through structurally induced fracture systems. Within this fracture system reaction between the hydrothermal fluid and the rocks becomes more intense closer to the rock-ocean interface. Fluids escape through discrete chimney systems (Lydon, 1998a) or percolate through unconsolidated sediments at the sea floor (Lydon, 1998a). The reaction between the fluid and the surrounding wall rocks of the fracture system results in the formation of a footwall alteration zone containing disseminated sulphide mineralization below the massive sulphide lens that

can develop at the seafloor or within the sediments (Lydon, 1998a). The degree of alteration diminishes from the fracture system outwards into the wall rocks, and this depends on the permeability of the wall rocks and their composition (Lydon, 1998a). Sulphide mineralization varies from more Cu-rich, chalcopyrite dominated, to Zn and Pb-rich (sphalerite and galena dominated) disseminated fracture-controlled mineralization (Lydon, 1998b).

When the hydrothermal fluid mixes with seawater, the temperature of the hydrothermal fluids decrease rapidly leading to precipitation of anhydrite forming the walls of chimneys that develop. The physicochemical conditions inside the chimney are characterised by high temperature, acidic and reducing conditions, whereas alkaline, oxidising and low temperature conditions exist in the ocean water. The differences between the conditions inside and outside of the chimney lead to the formation of a variety of chemical phases that precipitate, and give rise to the mineral zonation observed within the chimney wall. The mineral zonation reflects the wide range of the physicochemical gradient between the mineralizing fluids and the seawater. This give rise to chalcopyrite (inside of the wall); pyrite, sphalerite and galena (toward the outside); anhydrite with minor sulphides, amorphous silica, and barite forms the exterior zone (Speiss et al., 1980; Haymon and Kastner, 1981; Oudin, 1981; Haymon, 1983; Oudin, 1983; Goldfarb et al., 1983; Tivey and Delaney, 1986). More further, the composition of the sulphide minerals depend on the temperature of the system. In high temperature systems, pyrrhotite forms first followed by chalcopyrite and sphalerite as the temperature decreases. At lower temperatures, galena or galena mixed with barite would precipitate. Pyrite could form in a wide range of temperatures and it accompanies all the other sulphide minerals mentioned above.

As the chimney grows, it becomes mechanically unstable and collapses. This could cause other chimneys to be formed due to rise in hydrothermal fluids via other permeable pathways. Eventually this process leads to formation of an impermeable mound, which causes an increase in the temperature and circulation of fluids inside

the mound. The circulation of the fluids may cause the replacement of previous sulphides by higher temperature minerals. Renewed episodes of fracturing (hydraulic or otherwise), on top of hydrothermal eruption create new channel ways for growing new chimneys and the mound (Lydon, 1998b).

One of the most important characteristics of VHMS deposits is the decrease in the Cu:Zn ratio upwards and outwards from the core of the massive sulphide lens. Computer modelling (Reed, 1983; Janecky and Seyfried, 1984; Bowers et al., 1985) shows that progressive local cooling of the solutions causes the Cu-dominant to Zn-dominant zonation (e.g., cf. Large, 1977).

The silica in hydrothermal fluids will precipitate to form quartz if the solution cools without any dilution (Janecky and Seyfried, 1984). When the temperature of seawater increases, if there is enough barium in the seawater, it would react with seawater sulphate and this would result in barite precipitation (e.g., Kowalik et al., 1981; Watanabe and Sakai, 1983). This occurs when a black smoker change (very fine-grained pyrrhotite with minor sphalerite and pyrite) to a white smoker (silica, barite and pyrite).

To prevent oxidation and of erosion the sulphide minerals, it would be necessary to insulate them from oxidising and erosive conditions by covering them with impermeable sediments or igneous rocks. The formation of iron oxide and manganese oxide might indicate oxidising conditions. These oxides could possibly precipitate in submarine brine pools (e.g., Pottorf and Barnes, 1983) or oxidation of a buoyant hydrothermal plume in a distal deposit (Kalogeropoulos and Scott, 1983; Large, 1977). A hydrothermal discharge system might produce these oxides contemporaneous with the sulphide mineralization or later, as well.

3.5.2. Wall rock alteration

Chlorite and sericite are the two major alteration products that form due the reaction between the hydrothermal fluid and the wall rocks. The nature of the alteration assemblage does however also depend on the composition of the original wall rocks.

In most cases the primary calcium and sodium rich silicate minerals such as pyroxenes and feldspars are the first to be destroyed during alteration resulting in a depletion of Ca and Na which is removed from the system in the escaping hydrothermal fluid (Lydon, 1998b). The remaining rock becomes enriched in Al, Mg, and Fe, and in some cases K, since the conditions are favourable for formation of chlorite (Miyashiro, 1994). Silica released in the solution precipitates as soon as the temperature of the fluid decreases and this may commence in the zone immediately below the massive sulphide zone, and also trends to seal the conduit during the waning stages of the ore forming process. Other minerals that may also be formed within the alteration zone below the massive sulphide zone include tourmaline if the hydrothermal fluid was enriched in B (Jiang, 2000; Kawakami, 2001) and apatite or monazite if the fluid was enriched phosphates (Large et al., 1996).

If biotite is present as a primary mineral, the hydrothermal fluid will alter it to chlorite by removing potassium from the biotite i.e.



Mg could also be added to the system from seawater-basalt interaction (e.g., Hajash, 1975; Mottl and Holland, 1978; Seyfried and Bischoff, 1979). The fluids may also introduce iron derived from the seawater-basalt interaction (Lydon and Galley, 1986; Richards and Boyle, 1986).

The abundance of Al in the altered rocks results in them displaying a peraluminous character, which means that in these rocks the percentage of Al_2O_3 is higher than the sum of Na_2O , CaO , and K_2O (Humphreys, 1993).

Utilizing the isocon method of Grant (1986) it could be demonstrated that the footwall alteration zone of the Prieska Cu-Zn deposit became enriched in Al, Mg, Fe, Mn, K, Ti, V, Sc, Ni, Ba, Cu and Zn, whereas elements such as Si, Ca, Na and Sr were removed from the precursor rock during the alteration process (Theart et al., 1989).

3.5.3. Metamorphism of VHMS deposits and their alteration zones

High grade metamorphosed VHMS deposits include the deposits of the Manitouwadge Camp in the Superior Province, Canada (the Geco, Nama Creek, Willray and Willecho deposits) which were metamorphosed to upper amphibolite grade (Cameron and Hattori, 1987; Pan and Fleet, 1995) and deposits of the Fennoscandian Shield, such as those in the Vihanti district of the Pyrite Belt and in the Aijala-Oryarvi region in Finland (Gaal, 1990; Tornos, 2006) and the deposits in the Skellfte district in Sweden (Sundblad, 1991).

The chlorite-rich rocks of the alteration zone are deformed to subparallelism with the massive sulphide layers and metamorphosed to cordierite-anthophyllite and cordierite-sericite assemblages.

Metamorphism of the massive sulphide rocks generally results in total recrystallization with a dramatic increase in grain size, the formation of granoblastic textures with foam texture triple grain junctions in monomineralic situations (Vokes, 1969; Theart, 1985). Theart et al. (1989) recognized textures of “Durchbewegung” in the ores of the Prieska Cu-Zn and Areachap deposits and suggested that the associated deformation was responsible for destruction of, and chemical, and isotopic variation that might have existed earlier across the ore body.

3.6. Quantification of chemical changes in altered rocks

3.6.1. The isocon method

The quantification of changes in the rock volume and elemental concentrations during hydrothermal alteration is an important component of lithogeochemical investigations of alteration zones. It is relatively easy to do the gain and loss calculations, when the altered rocks are distinguished as the least-altered equivalents or source rocks especially in relatively undeformed and unmetamorphosed rocks. Gresens (1967) presented equations for these calculations based on chemical analyses and specific

gravities of altered and unaltered rocks. Grant (1986) suggested a graphical solution to those equations, known as the isocon method. This contributes greatly to a more quantified approach in the study of these phenomena.

The Gresens's equations are based on mass rather than volume (Gresens, 1967). The mass of element after alteration (M_i^A) is defined by the original mass (M_i^O) plus any change in the mass (ΔM_i) of that element during the alteration (Grant, 1986):

$$M_i^A = M_i^O + \Delta M_i$$

Dividing throughout by M^O to get concentration units and multiplying by M^O/M^A to obtain the original concentration, one may derive the following equation:

$$M_i^A / M^A = M^O / M^A (M_i^O / M^O + \Delta M_i / M^O) \quad (1)$$

M_i^A / M^A may be substituted for C_i^A and M_i^O / M^O for C_i^O , with C being an abbreviation for concentration and the equation (1) becomes:

$$C_i^A = M^O / M^A (C_i^O + \Delta C_i) \quad (2)$$

For an immobile element $\Delta C_i = 0$, and:

$$C_i^A = M^O / M^A \cdot C_i^O$$

This is a linear equation that passes through the origin with the slope of this line (M^O/M^A), equal to $(C_i^A / C_i^O)_{\text{immobile element}}$. Therefore the final equation for an element in general is defined as:

$$C_i^A = (C_i^A / C_i^O)_{\text{Isocon line}} [C_i^O + \Delta C_i] \quad (3)$$

This is the general equation for the isocon line. If constant mass is assumed, then $C_{\text{immobile element}}^A$ will be equal to C^O for an immobile element. If constant volume is assumed, then:

$$C_{\text{immobile element}}^A = (\rho^O/\rho^A) C^O$$

Recognition of the mobile and immobile elements is an important aspect of this method. If we know which elements would behave immobile during the alteration process, the isocon line will pass through the origin and the concentration of these immobile elements, when comparing the original and altered rocks. The gain and loss of the mobile elements may then be calculated and any volume change can easily be deduced.

Jenner (1996) defined the high field strength elements (HFSE) and REE as immobile elements. Those elements with low ionic potential, i.e. a ratio of ionic radius to ionic charge less than 0.2, are generally referred to as HFSE and these together with the REE are regarded as immobile (Jenner, 1996; Jiang, 2000). Trace elements such as Sc, Y, Th, U, Pb, Zr, Hf, Nb, Ta, and Ti belong to the HFSE group. Ti, Zr, Hf, Nb, Ta, and Y are generally immobile during alteration and metamorphism (Jenner, 1996; Piercey et al., 2001). The low field strength elements have a high ionic potential (> 0.2) and are generally regarded as mobile elements (e.g. Cs, Rb, K, Ba, Sr) under these conditions.

The isocon diagrams between least altered biotite-gneiss, Co, and altered biotite-gneiss, Ca, in Areachap are given in Figure 3.1 to demonstrate the concept of the isocon line, gain and loss. The isocon line passes through the origin and immobile elements and oxides i.e., TiO₂, Al₂O₃, Zr, U, Th, Nb, Y, La, and Sc. Those elements, which plot in the upper part of isocon line, represent gain and those elements that plot below the isocon line represent loss. The delta value for each element is calculated based on the following formulae:

$$(\Delta \text{ value})_i = C_i^A - C_i^O \cdot (\text{Slope value of the isocon line}), \quad i: \text{the element of interest} \quad (4)$$

If the calculated delta value [(Δ value)_i] of an element is positive it means that the concentration of that element in the altered rock is greater than in the least altered

rock (a gain). Where the calculated delta value for an element is negative it means that the concentration of the element in the altered rock is less than that of the least altered rock (a loss). The delta value can be converted to percentage based on the following formula:

$$\text{Percentage of gain or loss} = [(\Delta \text{ value})_i / C^O_i] \cdot 100 \quad (5)$$

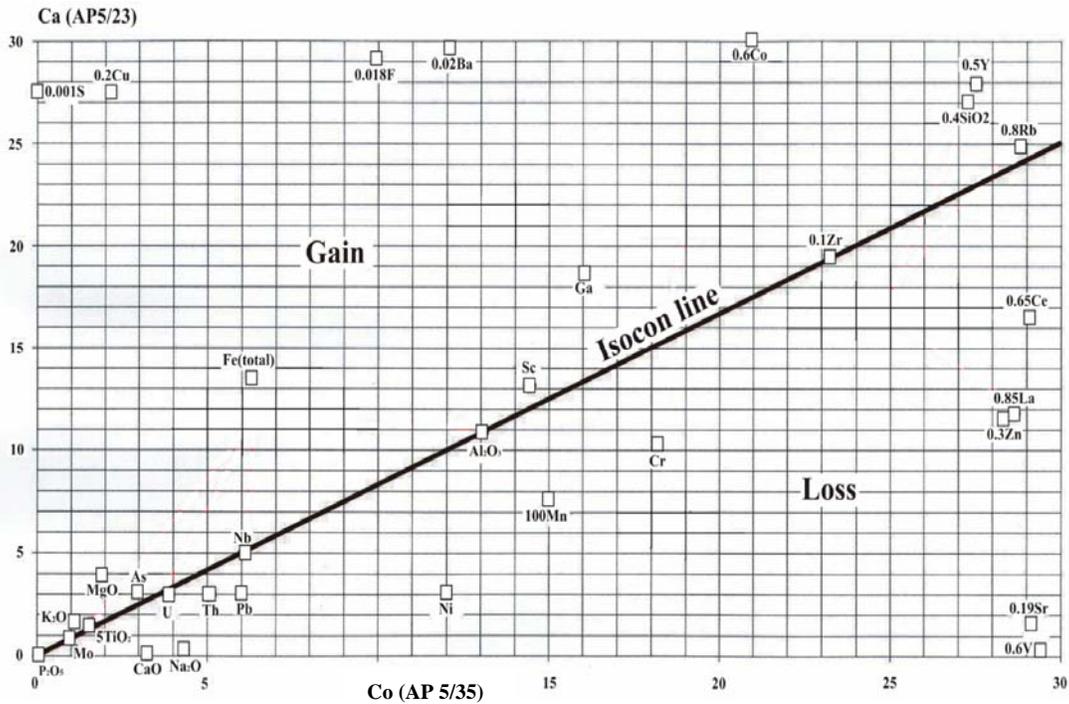


Figure 3.1: An isocon diagram for sample AP5/35 (least altered biotite-gneiss) and AP5/23 (altered biotite-gneiss) from drill hole AP5 in the Areachap area.

3.6.2. The alteration index and the Chlorite-Carbonate-Pyrite index

Ishikawa et al. (1976) defined the alteration index (AI) to measure the intensity of sericite and chlorite alteration in the footwall of VHMS deposits of the Kuroko type in Japan. The AI is defined as:

$$AI = 100 (K_2O + MgO) / (K_2O + MgO + Na_2O + CaO)$$

Large et al. (2001) used this index for calculating the intensity of sericitization and chloritization of plagioclase. Later Large et al. (2001) defined the Chlorite-Carbonate-Pyrite Index (CCPI) based on the following formula:

$$\text{CCPI} = 100 (\text{MgO} + \text{FeO}_{\text{total}}) / (\text{MgO} + \text{FeO}_{\text{total}} + \text{Na}_2\text{O} + \text{K}_2\text{O})$$

An increase in the AI and CCPI generally indicates a gain of MgO, FeO, and K₂O and a depletion of Na₂O and CaO. The box plot, an AI versus CCPI (Large et al., 2001) diagram, is a better way to demonstrate these variations. Other features that affect the CCPI ratio include Mg-Fe carbonate alteration, mineralization of pyrite and or hematite enrichments. These features are commonly present in the alteration zones of some of VHMS deposits.

The box plot is a useful method to separate hydrothermal alteration from diagenetic alteration (Large et al., 2001) (Fig. 3.2 and 3.3). If a diagonal line is drawn between epidote and K-feldspar, those samples plot above this line are hydrothermally altered and those samples that plot below the line reflect diagenetic alteration (Large et al., 2001).

In general, five fields can be demonstrated on the box plot (Fig. 3.2 and 3.3). Three of these trends are associated with hydrothermal alteration (after Large et al., 2001) (Fig. 3.2).

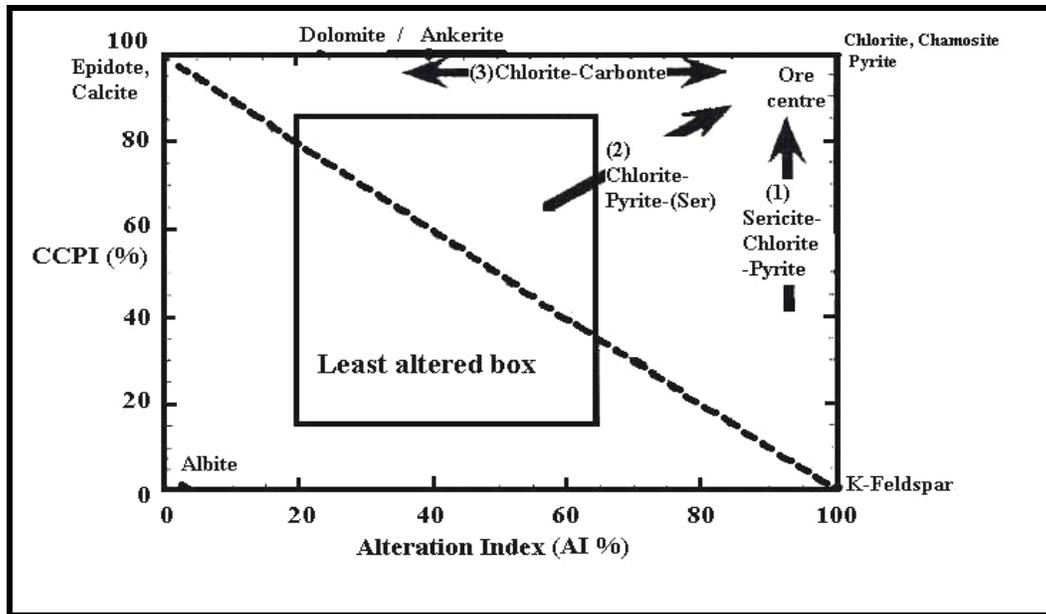


Figure 3.2: Field for hydrothermal alteration described in the text (modified after Large et al., 2001)

The fields that could be identified in the box plot are:

Field 1: Least altered rocks fall within a box bounded by an AI= 20 to 65% and a CCPI= 15 to 85%,

Field 2: Sericite-chlorite alteration in the footwall alteration close to the ore lenses, has AI>90% and CCPI>65%. This corresponds with trend 1 in Figure 3.2,

Field 3: Chlorite-pyrite (sericite) alteration typical of the footwall alteration system of the VHMS deposit corresponds with trend 2 in Figure 3.2,

Field 4: Chlorite-carbonate alteration typically developed in the ore zone and footwall alteration zone of massive sulphide. This corresponds with trend 3 in Figure 3.2.

The trend that could be related to diagenetic alteration (Large et al., 2001) is shown in Figure 3.3:

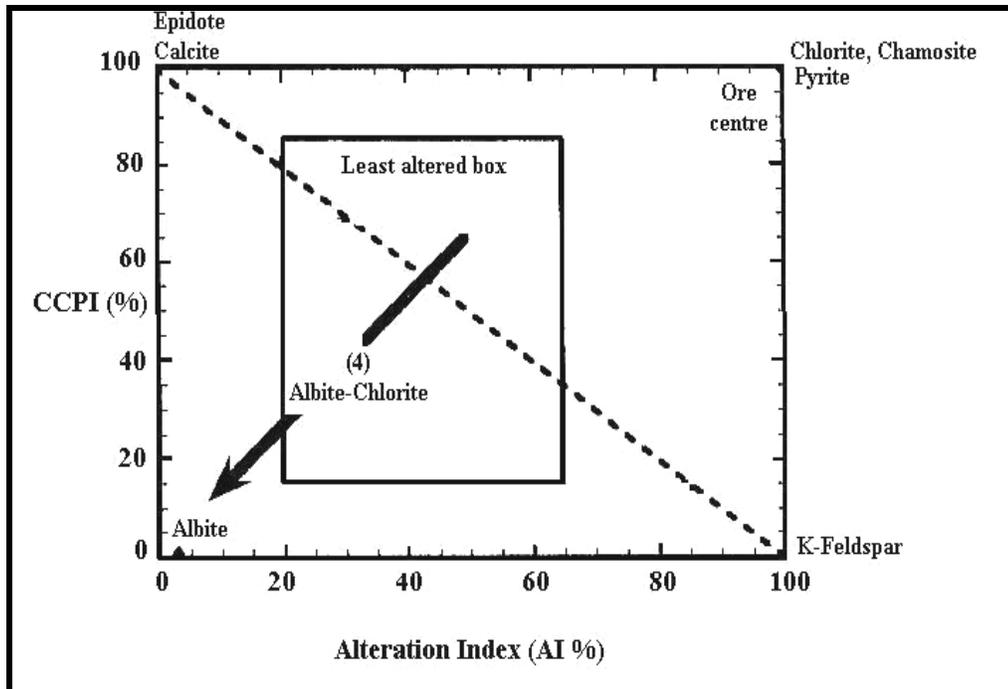


Figure 3.3: Field for diagenetic alteration described in the text (after Large et al., 2001)

Field 5: Albite-chlorite alteration (trend 4) is typical of seawater interaction at low temperatures (e.g., spilites and keratophyics; Hughes, 1972; Seyfried and Bischoff, 1979) (where albite \pm calcite \pm K-feldspar assemblages are absent in the mineralization) that has an AI < 57%, and occur below the epidote- K-feldspar join.

Albite, calcite, epidote, dolomite, ankerite, chlorite, chamosite and K-feldspar are located at the boundaries of the box plot (Large et al., 2001) (Fig. 3.2).

3.6.3. The mineralogical variation index (Pearce Element Ratio (PER) analysis)

This method was developed to avoid the effects of closure and/ or pre-existing lithological variations or background lithochemical trends in geochemical modelling during advanced geochemical investigations. In applied lithochemical methods, the major elements monitor mass balance and are used to identify relative or absolute variations in elements (Whitbread and Moore, 2004).

Variation in major element concentrations may be used as an index of mineralogical change, which is caused by alteration (Whitbread and Moore, 2004). The mineral changes are useful tools in exploration because the variations are process related. The PER analysis is based on mineral changes and uses the major element variations. This method presents a way to identify the hydrothermally altered rocks surrounding ore deposits. The weight percentage data is converted to molecular proportion in the PER diagrams. For this purpose the molar ratios, which is the molecular proportion of an element or a linear combination of elements divided by the molecular proportion of an immobile or conserved element, are used to plot the PER diagrams.

The PER diagram of an epigenetic Zn-Pb-Ag deposit (Elura ore deposit, 45 Mt @ 8.5% Zn, 5.3% Pb and 69 ppm Ag) is illustrated in Figure 3.4. The ore deposit is hosted within Devonian siltstone-sandstone turbidites of the Cobar Basin in central-west New South Wales, Australia (Whitbread and Moore, 2004). In this case, molar K/Ti versus Al/Ti diagram shows that the altered rock with the development of muscovite (boarder 1 and 2) are separated from the background rock, which has an illite \pm albite precursor (boarder 3 and 4).

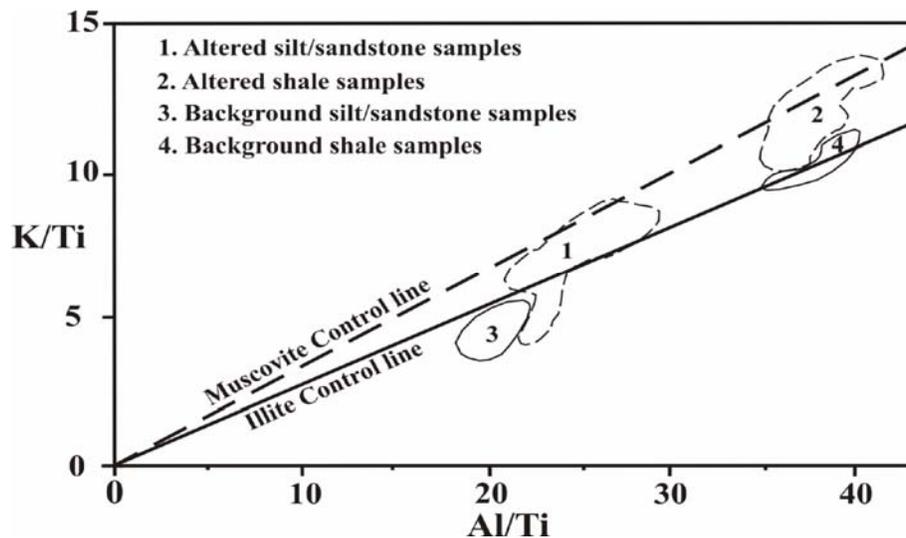


Figure 3.4: K/Ti versus Al/Ti PER diagram of Elura Zn-Pb-Ag deposit (adopted from Whitbread and Moore, 2004).