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HYDROTHERMAL ALTERATION AND Pb/Zn MINERALISATION IN THE ALLANRIDGE FORMATION, VENTERSDORP SUPERGROUP, NEAR DOUGLAS, NORTHERN CAPE PROVINCE, SOUTH AFRICA.

by

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ABSTRACT

Hydrothermal galena and sphalerite mineralisation is present in amygdales and isolated linear breccia zones within andesite lavas of the Allanridge Formation, Ventersdorp Supergroup in the Northern Cape Province, South Africa.

The amygdale ores are believed to be a separate generation from the breccia zone ores and formed during burial metamorphism to greenschist facies, which was coupled with slight metasomatic action. Metal ions from the mafic Allanridge lavas were able to migrate on a small scale and precipitate as sulphides in the amygdales. A later hydrothermal event overprinted the pre-existing alteration with a potassic assemblage, and hydraulic fracturing created the mineralised breccia zones.

Fluid inclusion studies indicate the fluids are of sedimentary brine origin (18 wt. % equivalent NaCl). Homogenisation temperatures of fluid inclusions in late stage quartz veins (118°C) suggest higher temperatures during the main stage of ore deposition. δ^{34} S values correlate with the Kuruman and Griquatown Banded Iron Formations, which is therefore believed to be the fluid and sulphur source.

⁸⁷Rb/⁸⁶Sr analyses on amygdale chlorite and highly altered whole rock samples from Kalkdam yield an age of 2014 m.y, which is similar to those obtained for other Mississippi

Valley type (MVT) deposits and ore occurrences in the Transvaal dolomites of the Griqualand West basin, e.g. Bushy Park, Langrug and Balloch.

Pb isotope results for galena and sphalerite also show similarities with other Pb/Zn deposits in the Griqualand West basin, suggesting similar ages of formation. Samples from Katlani are very similar to those from Pering and Geelbekdam and derivation from the Ventersdorp mafic lavas is indicated. On the other hand, Kalkdam samples are more radiogenic, show younger model ages and are similar to the Bushy Park deposit and the other occurrences around the Griquatown Fault. The Makwassie Formation and the basement are believed to be the source of the more radiogenic lead in the breccia zones and the K source which gave rise to the potassic alteration of the flow tops at Kalkdam.

Basinal brines, squeezed out of the Asbestos Hills BIFs by continuing compaction and slight pressure from the west, were channelled into faults and fractures which cut deep into the basement. Heating of these brines at depth allowed them to leach metals and potassium from the basement and Makwassie Formation on their convection driven ascent. Faults and fractures provided pathways enabling migration of the metal bearing fluids.

Fluids flowing along faults and fractures which cross cut lavas at Kalkdam were tapped off into the porous flow tops. Wall rock alteration and hydraulic fracturing of the less permeable massive lava and possible mixing with cold surface waters resulted in ore deposition in the breccia zones.

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UITTREKSEL

Hidrotermale galeniet en sfalerietmineralisasie kom in amandels asook geïsoleerde liniêre breksiesones in andesitiese lawa van die Allanridge Formasie, Ventersdorp Supergroep in die Noord Kaap Provinsie, Suid Afrika voor.

Die erts in die amandels is moontlik van 'n ander ouderdom as dié van die breksiesones en het gedurende groenskis beladingsmetamorfose gevorm. Metasomatose het ook tot 'n mate 'n rol gespeel tydens die proses van ertsvorming. Metaalione van die Allanridge lawas het oor relatief kort afstande migreer en is as sulfiedes in die amandels gepresipiteer. 'n Jonger hidrotermale gebeurtenis het die bestaande verandering gesuperponeer met 'n kaliumryke paragenese terwyl hidroliese breking die gemineraliseerde breksiesones tot gevolg gehad het.

Vloeistofinsluitselstudies dui daarop dat die vloeistowwe van sedimentêre pekel oorsprong was (18 gewigs % ekwivalent NaCl). Homogeniseringstemperature van vloeistofinsluitsels in laatgevormde kwartsare (118°C) dui op hoër temperature gedurende die hoofstadium van ertsvorming. ³⁴S waardes korreleer met die van die Kuruman en Griekwastad Gebande Ysterformasies, wat moontlik die bron van die swawel was. Rb/Sr analises van chloriet in amandels en van baie veranderde lavamonsters van Kalkdam lewer 'n ouderdom van 2014 m.j. wat ooreenstem met ouderdomme van ander Mississippi Vallei tipe (MVT) afsettings en ertsvoorkomste in die Transvaal dolomiete van. Griekwaland-Wes soos bv. Bushy Park, Langrug en Balloch, verkry is.

Pb-isotoopstudies van galeniet en sfaleriet dui ook op ooreenkomste met ander Pb/Zn afsettings in die Griekwaland-Weskom, asook op soortgelyke ouderdomme van vorming. Monsters van Katlani is soortgelyk aan die van Pering en Geelbekdam en dui op 'n oorsprong vanaf mafiese Ventersdorplawas. Die monsters vanaf Kalkdam is egter meer radiogeen, toon jonger model-ouderdomme en is soortgelyk aan Bushy Park en ander voorkomste in die omgewing van die Griekwastadverskuiwing. Die Makwassie Formasie en die vloergesteentes word as moontlike bron van die meer radioaktiewe lood in die breksiesones beskou asook die K-bron wat die kaliumverandering van die vloeitoppe by Kalkdam veroorsaak het.

Vloerpekels wat uit die Asbesheuwel Gebande Ysterformasie gepers is deur volgehoue kompaksie en druk vanuit die weste, is in verskuiwings en nate diep in die vloer gekanaliseer. Verhitting van die vloeistowwe in diepte het loging van metale sowel as kalium vanuit die vloergesteentes en die Makwassie Formasie tydens opwaartse konveksie veroorsaak. Verskuiwings en naatstelsels het as vervoerkanale vir die migrasie van die metaaldraende vloeistowwe gedien. Vloeistowwe wat langs geskikte kanale beweeg het, het in die vloeitoppe van lawas by Kalkdam gekonsentreer. Wandgesteenteverandering en hidroliese breking van ondeurlatende massiewe lawa, asook moontlike vermenging met koue oppervlaktewater, het die afsetting van erts in die breksiesones tot gevolg gehad.

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1. INTRODUCTION

This study deals with lead/zinc mineralisation in the Allanridge Formation, which forms the top of the Ventersdorp Supergroup, a volcano-sedimentary sequence on the Kaapvaal Craton, Southern Africa. The mineralisation occurs within amygdaloidal flow tops, as well as along linear breccia zones on the farms Kalkdam and Katlani.

The Ventersdorp Supergroup has been affected by greenschist facies metamorphism which grades into propylitic alteration at the localities of mineralisation. Local overprinting of potassic alteration has accompanied the deposition of galena and sphalerite. The potassic alteration is interpreted to have resulted from interaction with hydrothermal fluids approximately 2000 m.y ago.

1.1 Locality

Two localities near the town of Douglas in the Northern Cape Province were investigated. The larger of the two occurrences is found on the property Kalkdam (28°53'S, 23°45'E) which is situated 16 km North of Douglas (Figs. 1.1 and 1.2). The smaller occurrence is found approximately 35 km WSW of Douglas on the farm Katlani (29°07'S, 23°33'E). Field mapping was restricted to Kalkdam, but samples from both Kalkdam and Katlani were used for geochemical, isotopic and fluid inclusion studies.

1.2 Physiography

The area shows little relief. The andesite lava flows outcrop as small topographic highs within an essentially peneplainal region with Kalahari sand cover. These "topographic highs" rise only about 50 meters above the peneplain, which is itself between 1100 to 1500 m above sea level (Van der Merwe, 1973).

1.3 Climate and Vegetation

The area around Douglas is semi-arid, receiving 125 - 250 mm of rainfall per annum, which falls mainly as thundershowers during the summer months (Wheatley *et al.*, 1986a). Summer temperatures can reach up to 41°C during the days but cool considerably at night. The winters are typically cold and hard frosts are frequent (Van der Merwe, 1973).

Vegetation is sparse in the region and has been described in detail by Acocks (1953). A variety of acacia species are present, of which the Soetdoring (Acacia karoo) is the most common. Other trees and shrubs present are wag-'n-bietjie (Ziziphus mucronata) and

karoobossies. Steekgras is present on calcrete substrate, whilst katstertjies, boesmangras and aloes are found in sand substrate and between volcanic boulders.



Figure 1.1: Locality map of study area. KD = Kalkdam, KL= Katlani.



Figure 1.2: Farm locations with respect to Douglas.

1.4 Previous work

Little work has been published on the Allanridge Formation in the Northern Cape Province. The earliest work done by Stow (1876) and Du Toit (1906) discussed the volcanic rocks of the Northern Cape. Greeff (1968) produced a detailed account of the linear structures in the Northern Cape. Detailed mapping projects of the regions around Douglas and Campbell were undertaken by Van der Merwe (1973) and Potgieter (1973). No research has been conducted on similar types of deposits found within the Ventersdorp volcanic rocks. In 1993, Alec Birch of Shell exploration conducted surface mapping, soil chemistry analyses, and induced polarisation surveys over the area (exploration grid system). The soil geochemistry profiles show a large Zn anomaly over much of the area (Fig. 1.3). The concentration of lead (Fig. 1.4) in the soil at Kalkdam is greater than normal values on this substrate, but less than that of the zinc. A soil chemistry profile for copper gave very low values, with very few locations giving concentrations greater than 48 ppm. This shows a similarity with the deposit at Bushy Park which lies approximately 50 km to the North West of Kalkdam (Wheatley *et al.*, 1986b). Although Shell Exploration have decided against the continuation of work at Kalkdam, it is possible that Kalkdam may provide a greater tonnage of ore than Bushy Park: the soil geochemistry analyses of Kalkdam give far greater metal values than Bushy Park and are continuous over a greater area.

An induced polarisation and resistivity survey was also carried out by Alec Birch at Kalkdam (Fig. 1.5). Two anomalies were identified showing low resistivity values and high chargeability values. These together are associated with high metal factor values. Both anomalies are located on the grid line 8600E: one at 10000N; and the other at 10300N (Fig. 1.5). Both sources of these high metal factor values have been interpreted to dip steeply toward the north. The larger of the anomalies at 10300N, centres over an area where the amygdales at the surface are significantly mineralised. This source is believed to strike obliquely to the survey line direction and also lies along the strike of a heavily mineralised breccia zone. The top of the source is between 40 and 80 m below the surface, and may represent a deeper mineralised amygdaloidal flow top or a continuation

of the breccia zone. The smaller source is sub-cropping and probably dips steeply to the north. Since the lavas dip only slightly to the north, it is unlikely that the mineralisation is contained within a buried amygdaloidal flow top. Comparison of the metal factor data with the Pb soil chemistry profile, indicates that the lead contours run in the same direction as the breccia zone toward the buried source of the 10300N anomaly.

There are a number of other lead/zinc deposits found in the Griqualand West sub-basin. These differ from Kalkdam and Katlani in that they are all hosted by carbonates of the Transvaal Supergroup. The Pb/Zn deposit at Pering is regarded as a typical Mississippi Valley Type deposit, (Altermann and Hälbich, 1991) whereas the others, most of which are situated along, and in the vicinity of the Griquatown fault zone (Altermann, 1997), tend to be of vein type, or have a breccia zone association (Duane *et al.*, 1991).

1.5 Geological Setting

The Ventersdorp Supergroup has been sub - divided into 3 main units, separated by major unconformities (Cheney *et al.*, 1990). Each unit reflects a changing tectonic regime. This began with extensional tectonics, resulting in the extrusion of the Klipriviersberg Group flood basalts. This group, however, is not present in the Griqualand West basin, being found mainly in the Witwatersrand basin. Graben formation in the basement during Platberg times resulted in erosion and deposition of clastic sediments by fluvial processes (Buck, 1980).

Bimodal volcanism (Makwassie and Rietgat Formations) followed and is possibly related to subduction processes (Burke *et al.*, 1985; Crow and Condie, 1988). The upper sequence consists of the Bothaville and Allanridge Formations: the lower Bothaville Formation is made up of localised arenaceous sediments, graywackes and conglomerate horizons (Grobler *et al.*, 1989).

Thermal subsidence (Clendenin *et al.*, 1988), and further extensional tectonism gave rise to the outpouring of widespread basaltic andesites of the uppermost Allanridge Formation. Allanridge lavas often rest unconformably on the Rietgat mafic lavas - the distinction between these two formations is difficult and has been addressed by Grobler *et al.* (1982). It is in these lavas that the lead and zinc mineralisation has been found.

The Allanridge lavas have been classed as andesites and basaltic andesites which plot as tholeiites (Crow and Condie, 1988; Bowen *et al.*, 1986). These lavas appear relatively fresh and are characteristically dark blue-grey to green coloured. Small green patches where alteration mineral aggregates have formed are typical of Allanridge lavas and the presence of these have been utilised by Grobler *et al.* (1982) to distinguish between Allanridge lavas and those of the Rietgat Formation. Individual lava flows are thin,

usually ranging from about 3-15 m in thickness. While flow tops and bottoms are usually amygdaloidal, the flow centres are massive.

Similar to all the volcanics in the Ventersdorp Supergroup, the Allanridge lavas have been subjected to greenschist facies non-deformative metamorphism (Tankard *et al.*, 1982), with alteration mineral assemblages of chlorite, epidote, actinolite, and minor calcite indicating lower greenschist facies (Cornell, 1978; Crow and Condie, 1988).

This metamorphism is interpreted to have been caused by burial to the depth of about 6 km contemporaneous with metasomatic alteration (Cornell, 1978). Although the Allanridge Formation is considered to be the most intensely altered of all the formations (Van der Westhuizen *et al.*, 1991), it is the least deformed and is thought to have been deposited after termination of deformation of the Witwatersrand Supergroup, and the Klipriviersberg and Platberg Groups of the Ventersdorp Supergroup (Roering, 1984; Winter, 1987).

The Ghaap Group which hosts the Pb-Zn deposits at Pering and Bushy Park (Wheatley *et al.*, 1986a; 1986b), overlies the Allanridge Formation. The stratigraphic column illustrated in Figure 1.6 shows the formations which host these deposits. The distance from the top of the Allanridge to these formations is not great, and the likelihood that the fluids which deposited the Pering and Bushy Park ores also deposited some ore as they flowed through the Allanridge lavas, will be addressed later.











Figure 1.5: Induced Polarisation map of Kalkdam.

Approx.		Characteristic	Member	Formation	Sub-	Group	Super-
Thick-		Lithologies	or Bcd		group		group
ness (m)	} {	6- -					
>2()()()		Schist		Groblers-		Olifants-	
				hoop	Volop	hock	
700		Lava with tuff and breccia		Hartley			
450		Quartzite with minor dolomite		Lucknow			
10-1500		Shale with lava and quartzite bands		Mapedi		unconformity	
250		Dolomite, chert, jasper and lava		Mooidraai	Voel-	Post-	Trans-
		Jasper, dolomite banded Fe and Mn		Hotazel	water	masburg	vaal
300-900		Basaltic andesites and pillow lavas		Ongeluk			
50-150		Diamictite and minor banded jasper		Makganyene		unconformity	
560		Jaspilite			Koegas	Ghaap	
200-300		Clastic textured Fe formation		Griquatown	Asbestos Hills		
150-750		Banded Fe formation		Kuruman			
50		Algal dolomite	Lime Acres	Gamohaan	Campbell- rand		
			Bushy Park	-	Bushy Park		
320		Dolomite		Kogelbeen			
40		Dark siliceous cherty dolomite	•	Klippan			
300		Stromatolitic dolomite		Papkuil			
40		Siliceous cherty dolomite		Klipfontein			
200			ļ	Heuwels			
200		Stromatonitic and algal dolomite		Fairlield	disconformity	-	
350		Ferruginous chert	Kamden	Reivilo			
		Stromatolitic dolomite and shale	Steek- dorings		Pering		
ļ		Quartzite and shale	Motiton				
120		Cryptalgal and clastic dolomite		Monteville			
120		Carbonaceous shale		Lokammona	Schmidts-		
7		Chert breccia	}	Boomplaas	drif		
103		Oolitic and shaley dolomite					
15		Andesitic lava	Water- loo	Vryburg			
115	0	Quartzite, grit, siltstone and shale				unconformity	
100		Andesitic lava	1	Allanridge			Venter-
60		Proto and ortho sandstone		Bothaville	1		sdorp
40	1.1.1	Vitric and lithic rhyolitic tuff		Makwassie		Platberg	1
-	++++	Schist and gneiss	1				Base-
L	+++		1	<u> </u>		1	ment

Figure 1.6: Stratigraphic column of Griqualand West sub-basin (Beukes and Smit, 1987; Visser et al.,

1975; Cornell et al., 1996; SACS, 1980).

The 1000 -1200 m.y Namaqua and 1750-1850 m.y Kheis metamorphic/orogenic provinces lie to the west of the study area. The Kheis metamorphic terrain occupies an area along the NW margin of the Kaapvaal craton. This province displays greenschist facies metamorphism (Cornell, 1978) and has been greatly thickened by both thrusting and recumbent folding (Stowe, 1986). It is composed predominantly of folded sequences of sandstones and shales, previously deposited in a deltaic to shallow marine environment. Thrusting in the region has exploited the less competent phyllite zones (Stowe, 1986).

1.6 Structure of region

The region has experienced very little tectonic activity: the Ventersdorp rocks dip only slightly to the west and north, except, near Campbell where a small anticline exists (Van Der Merwe, 1973). Lineament maps of the area around Douglas show many large scale linear structures which could represent faults, fractures or dykes (Fig. 1.7). Both Kalkdam and Katlani are situated on two of these major structures as highlighted in the figure. Van Der Merwe (1973) has also noted many faults and fractures over the region which strike predominantly in a NNW direction and have been brecciated and silicified. Fluids have therefore exploited these large structures, and may subsequently have been tapped off into smaller structures such as joints and the porous amygdaloidal flow tops at Kalkdam and Katlani where precipitation of metallic minerals occurred. Duane *et al.* (1991) note the lack of a suitable aquifer below the Allanridge volcanics and have suggested that the faults

and thrusts provided the majority of flow pathways. Figure 1.8 shows linear features around Kalkdam as depicted by aerial photographs. The breccia zones where the lead and zinc minerals are found are also recognisable on the aerial photographs.

Other structures possibly aiding the flow of fluids across the craton are those faults involved with graben formation which were active during Platberg times. Gravity faulting gave rise to structures over 200 km in width (Clendenin *et al.*, 1988). Further renewed rifting facilitated the eruption of the Allanridge lavas across the province (Clendenin *et al.*, 1988).

Figure 1.7 also shows the locations of other mineral occurrences (Cu, Pb, Zn) found within this region - in both Ventersdorp and Transvaal rocks. Many of these occurrences are situated on or very close to one of these large linear structures.

1.7 Present study

The mineralisation was originally discovered by Alec Birch of Shell exploration (S.A). The aims of this investigation are:

- To establish field relationships between the mineralised areas as well as the differences between the more and less altered outcrops in order to give information on the pathways and mechanisms of fluid migration and mineral deposition.
- 2. To establish the type and intensity of alteration affecting the andesitic lavas. The more altered areas having been subjected to more intense and pervasive fluid flow.
- 3. Conduct geochemical analyses on samples collected to compare chemistry of the highly altered and the less altered samples.
- Geochronological studies (Rb/Sr) will constrain the age of the mineralising event and possibly relate these mineral occurrences to other deposits in the Griqualand West subbasin.
- 5. Carry out Pb/Pb isotopic studies on galena and sphalerite from both Kalkdam and Katlani to try and establish a model age for the lead - i.e. the theoretical age at which the lead system became closed when galena crystallised. This will give an upper age limit for the ore deposit. Back projection from the common lead ratio will give

information for the age of the lead source and therefore will put constraints on the lead source itself.

- Establish the sulphide source by using stable isotope mass spectrometry techniques, and from the information obtained, calculate approximate temperatures of mineral precipitation.
- 7. To investigate the fluid composition by fluid inclusion methods the salinity of the fluid will define it's origin: basinal brine; volcanic; or circulating seawater from an oceanic volcanic setting. Geothermometry and barometry from fluid inclusions will give a minimum temperature of deposition.
- 8. Try to establish whether other similar occurrences are present that are related in time to this hydrothermal event, and if conditions of deposition are favourable, give rise to a whole new metalliferous province.






Figure 1.8: Aerial photograph interpretation of linear s

2. FIELD DESCRIPTIONS

2.1 Introduction

A succession of seven gently northward dipping (7-15°) lava flows (F1 - F7) with an average thickness of 12 m occurs at Kalkdam. These lavas have been subjected to significant fluid migration, which has resulted in severe metasomatic alteration. The intensity of the alteration is not uniform, but is directly related to the porosity and permeability of the lava flows. Flows are amygdaloidal at the base and top, and these areas have been more intensely altered - whilst the flow centres are generally massive and finely crystalline. Although some flow centres possess amygdales, these are generally well spaced and much larger (up to 8 cm in diameter) than at the flow tops and bottoms. As a result of this increased spacing, the permeability of these zones is much reduced and has rendered them less susceptible to fluid flow and alteration.

An entire spectrum from essentially unaltered massive lava to extremely altered amygdaloidal varieties is present in each flow. The lavas are either light or dark coloured, which is a reflection of the degree of alteration. Flow tops are usually much paler than the central and lower zones of the flows and are termed light amygdaloidal, compared with dark amygdaloidal lower zones and dark massive central zones. Figure 2.1 shows the geology of the Kalkdam area.

2.2 Light amygdaloidal lava

The light amygdaloidal zones are bleached to a pale blue-grey colour (Fig. 2.2). The amygdales are of uniform size (between 8-10 mm) and are well distributed throughout this zone.

The shape of the amygdales varies slightly, but are generally ellipsoid. Chlorite is more abundant in the amygdales of the lower flows (F1 to F3) compared with the upper flows (F4 to F7) where calcite and quartz dominate. In the middle flows, chlorite and quartz show varying stages of calcite replacement in the amygdales and pseudomorphs after primary mineral phenocrysts. Chlorite, the alteration product of primary ferromagnesian minerals (pyroxene and amphibole), is also present in the groundmass, where it is associated with the reaction by-product: quartz, (Deer *et al.*, 1992). This secondary quartz occurs as either small milky coloured patches or as secondary veinlets, which have formed when the alteration products have migrated away from the reaction sites (Evans, 1993).

Alteration within this more vesicular zone is not entirely uniform, and small regions of darker and less altered lava will be completely surrounded by the lighter variety. This indicates that the alteration has not been totally penetrative and is somewhat incomplete i.e. equilibrium has not been reached. A few of the very light amygdaloidal lavas have rare galena present in the amygdales. Sphalerite and smithsonite are intimately associated with amygdale and vein calcite throughout the lava succession.













Figure 2.2: Light amygdaloidal lava from Kalkdam with amygdales containing calcite and chlorite. Scale 1 cm = 0.5 cm.

2.3 Dark amygdaloidal lava

This lava type possesses a rough textured dark red-purple weathered surface which is easily distinguished from the light amygdaloidal lava (Fig. 2.3). Amygdales range in size from 2 to 8 cm in length and up to 5 cm in width. The larger amygdales dominate towards the top of the succession, whilst the spacing between individual amygdales increases proportionally with amygdale size. Quartz is the dominant amygdale filler of the largest amygdales. The groundmass is generally dark blue-grey and cryptocrystalline which makes identification of individual minerals difficult. Sphalerite, galena and chalcopyrite are sporadically present in the amygdales of the lavas. Usually, the sphalerite (± smithsonite) is associated with calcite, but in some samples, galena is also present. The galena is mostly found in association with quartz and chlorite, which replaces the calcite and sphalerite. This suggests the presence of two generations of galena at Kalkdam. In contrast to Kalkdam, sphalerite and lesser galena are present in most amygdales at Katlani, which are uniformly dark blue-grey and appear unaltered in hand specimen.

Sphalerite and chalcopyrite are also common within the matrix of the intermediate coloured areas, identified by their smithsonite and malachite haloes respectively. Galena is not observed in this association.



Figure 2.3: Dark amygdaloidal lava at Kalkdam showing calcite filled amygdales.

2.4 Massive dark lava

The massive lavas have a similar weathered surface to the dark amygdaloidal lava type. It appears relatively unaltered in hand specimen (Fig. 2.4), which suggests limited hydrothermal fluid interaction. This lava type is cryptocrystalline in texture, darker greyblue, and dark green when wet. Individual minerals are unrecognisable by the naked eye or with a X10 handlens. Another massive dark lava forms the top of the succession, but is more coarsely crystalline with crystals up to 2 mm in length. A recently weathered surface displays a felted texture where feldspar crystals stand out from the other constituent minerals. Veining is more dominant in this lava type than in the amygdaloidal type. This is probably because the fluid flow through this zone is negligible and quartz and chlorite produced in alteration reactions (reactions can occur by diffusion of ions between minerals rather than by direct interaction with a fluid phase: Rose and Burt, 1979) is moved away in tiny vein systems, and not incorporated into the main fluid phase. This coarser lava also outcrops at the peneplain level at the head of the valley (Fig. 2.1) and is likely to be a continuation of the top of the succession dipping toward the north by about 7°.

2.5 Breccia zones

Brecciated zones are found both discordantly and concordantly with the lava flows at Kalkdam. Only one brecciated zone can be described as a flow top breccia (between

Flows 5 and 6) whilst the other occurrences are attributed to hydrothermal action. Three discrete sub-vertical breccia "corridors", each about one metre in width, cross-cut the dark, coarsely crystalline massive lava on the southern hill. Two of these are approximately parallel and strike at 135°E and 140°E, whilst the 3rd cuts the other striking 015°E (Fig. 2.1).



Figure 2.4: Dark massive lava at Kalkdam displaying typical blue-grey colour and finely crystalline texture.

The fragments within the breccia consist mainly of finely crystalline massive lava, but coarse massive lava fragments are also present.

These breccias fulfil the criteria given by Jebrak (1997) for fluid assisted brecciation:

- 1. This type of brecciation typically occurs in rocks with low permeability. At Kalkdam these zones cross-cut the coarsely crystalline massive lava which is the least permeable of all the lava types at Kalkdam.
- Hydraulic brecciation results in mosaic textures with insignificant rotation of the fragments. Figure 2.5 shows a similar mosaic texture.
- Hydraulic brecciation preferentially exploits pre-existing planes of discontinuity. The breccia zones at Kalkdam are bounded by well defined straight edges, suggesting they formed where fluid exploited pre-existing joints.
- 4. At Kalkdam, the breccia fragments are predominantly angular, but some of the smaller fragments do display a slight rounding (Fig. 2.5). This is consistent with Jebrak's' (1997) criteria, and Sillitoe's' (1985) fragment rounding by hypogene exfoliation as a result of pressure fluctuations. Changing fault permeability or mineral deposition may result in an increase in the fluid pressure (Jebrak, 1997).
- The apparent simplicity of the infilling material is also typical of this kind of brecciation. The infilling material at Kalkdam is mainly quartz and chlorite with minor calcite.



Figure 2.5: Hydrothermal breccia zone at Kalkdam showing angular fragments of massive lava with limited size distribution.

The fragment size distribution is related to the fluid pressure: low pressure generates isometric particle distribution, whereas high pressure generates anisometric distribution. Kalkdam breccias generally display isometric distribution (majority are between 8 and 15 cm) suggesting a low to medium fluid pressure. Breccia zones were not observed at Katlani.

Unlike the ore occurrences in the amygdaloidal zones (at both Kalkdam and Katlani), where sphalerite dominates over galena, the reverse is true for the breccia zones. Galena is abundant in the breccia zones where it forms large aggregates of euhedral crystals which are approximately 5 mm in diameter. Individual sphalerite crystals are present within the quartz veining which suggests a late stage of crystallisation. These characteristics as well as the sub-vertical nature of the zones are similar to breccias observed at Pering (Southwood, 1986; Wheatley *et al.*, 1986a) and at Bushy Park (Wheatley *et al.*, 1986b).

Most of the highly altered light amygdaloidal flow tops display brecciation, but on a much smaller scale (fragments up to 5 mm in diameter) and without significant mineralisation. The fragments are uniform in size and display no rotation. Dilation of the veining is also insignificant.

The finely crystalline massive lava adjacent to the breccia zones, is locally affected by the fluid flow through the breccia zones, which introduced abundant pyrite to the areas affected. Discrete euhedral pyrite cubes approximately 1 mm in diameter are visible in hand specimen. The zones of pyritisation extends about 10 m on either side of the breccia zones.

Similar breccia zones are found elsewhere in the study area, which can be recognised on aerial photographs. These breccia zones are probably localised along pre-existing structural discontinuities.

2.6 Faults and jointing

Post hydrothermal jointing is much in evidence throughout the area. The dark amygdaloidal and dark massive lavas host these joint populations. The prominent joint directions are 050-060° and 100-120° and less importantly between 005-025° (Fig. 2.6).



Figure 2.6: Rose diagram of jointing orientations observed in massive and dark amygdaloidal Allanridge lavas at Kalkdam. Majority of joints strike between $050-070^{\circ}$ and $100-120^{\circ}$ (n = 85).

Correlation of the jointing at Kalkdam with fold and fault structures of the Kheis and Namaqua Provinces could help to constrain an absolute minimum age for the hydrothermal event. NE verging folding has been described by Stowe (1986) in the Langeberg-Boegoeberg Terranes at approximately 1750 m.y, and in the Gordonia subprovince between 1200 and 1000 m.y. It is possible that the jointing observed at Kalkdam is related to one of these deformation stages. Folding in the Gordonia sub-province is unlikely to have caused jointing so far onto the craton and therefore the most reasonable candidate is the deformation of the Kheis Province at around 1750 m.y (Stowe, 1986). Duane *et al.* (1991) have suggested that the mineralisation at Pering was deposited from fluids which were tectonically expelled by Kheis thrusting and overpressure. The joints (which have not been resealed by quartz and ore minerals deposited by migrating fluids) are unlikely to be related to this event. Further research is required at this stage before the theory of tectonically expelled brines is disregarded.

An intensely jointed area occurs at the interface of one flow top and the overlying flow bottom. The jointing in the flow top is very intense with spacing between joints as little as 3 mm. This is in response to a competence increase in the light amygdaloidal zone - i.e. the increased fluid flow through the flow top has resulted in silicification and hence has become more competent. The overlying less porous flow bottom has not experienced such intense silicification and therefore its competence remains lower -in this part, the jointing is much more widely spaced (greater than 5 cm apart) as the less altered rock can deform more plastically than the highly altered lava (Fig. 2.7).

2.7 Summary

- Chlorite replaces calcite in amygdales, altered phenocrysts and as a groundmass constituent with increasing depth. This probably relates to a facies changes in response to greater depth of burial.
- 2. Sphalerite is associated with calcite, whereas galena is associated with both chlorite and quartz, especially in the upper flows.
- 3. Breccia zones are localised along pre-existing structural discontinuities and have occurred as a result of hydraulic fracturing. These strike at 135° and 015°.
- 4. The mineralised amygdaloidal flow zones at Kalkdam and Katlani have greater proportions of sphalerite to galena. Galena dominates in the breccia zones at Kalkdam.
- 5. Post hydrothermal joints display different orientation from the breccia zones and strike at 050-060°, 100-120° and 005-025°.



Figure 2.7: Jointed zone at lava flow interface, displaying differing competence of highly silicified flow top and relatively non-silicified flow bottom, Allanridge Formation lavas at Kalkdam.

3. MINERALOGY AND ALTERATION

Optical mineral identification was supplemented with X-ray diffraction by powder goniometer and camera techniques at the University of the Free State. The major minerals identified were: plagioclase, chlorite; calcite; quartz; epidote-clinozoisite, actinolite with minor sericite; sphene; pyrite; galena and sphalerite.

3.1 Primary phases

Of all the primary mineral phases typical of andesitic lavas (plagioclase, clinopyroxene +/hypersthene and olivine), plagioclase and augite are the only phases which remains in samples from Kalkdam and Katlani. Pseudomorphs of other primary phases are preserved as chlorite and calcite. Plagioclase has become more sodic through the process of albitisation which has later altered to K-feldspar and sericite. Calcite and epidoteclinozoisite have formed from Ca released by the plagioclase.

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3.1.1 Pyroxene

Pyroxene is scarce in lava flows at Kalkdam, but was identified from microprobe analysis in the massive central zone of flow 5 (F5m). Pyroxenes have been totally replaced by dolomite and chlorite in all of the other flows except the massive caorsely crystalline lava at the head of the valley where alteration to actinolite has occurred. Pyroxene compositions were reduced to their end-members En-Fs-Wo and plotted on the pyroxene ternary system (Fig. 3.1). Pyroxene compositions here are similar to pyroxene analyses in the lower Klipriviersberg group (Winter, 1995), plotting in the augite compositional field as defined by Poldervaart and Hess (1951).



Figure 3.1: Ternary plot showing Wo-En-Fs end members for Kalkdam pyroxene microprobe analyses. Data for F5m (filled circle) and 1A (cross) plot in the augite field (after Poldervaart and Hess, 1951).

3.2 Secondary Phases.

3.2.1 Quartz

Quartz is present in all of the flow zones at Kalkdam, but is most abundant in the amygdales of the flow tops where it constitutes over 50% (values from XRD analyses) of the total mineral assemblage of the whole rock. Reduction in the number of amygdales in the lower and central portions of each flow results in a 30-40% decrease in the total quartz content. In comparison with the amygdaloidal flow tops, the central and lower flow zones possess a greater proportion of silica in the groundmass, where it exists as microcrystalline blebs, released as a result of the breakdown of primary ferromagnesian minerals to chlorite (Evans, 1993). In some instances, the silica released is carried away in solution and forms a veinlet. This is more pronounced in the coarsely crystalline massive flows that are not as permeable as the finely crystalline massive zones with respect to the retardation of ion movement by diffusion.

Many small veinlets are also observed in some of the highly amygdaloidal flow zones. These appear to be microbreccias, which are unlikely to be flow top breccias, but rather formed by the pressure of the fluid traversing the porous zone. The pressure may have been great enough to shatter, but not displace the rock fragments (Fig. 3.2). The ore minerals galena and sphalerite are found mainly in association with quartz filled amygdales (Figs. 3.3, - 3.5) of the lower flow tops and within the quartz veining of the breccia zones.

In the coarsely crystalline massive lava zone, the proportion of free quartz relative to the other minerals is greatly reduced (approximately 5%) This quartz, however, has not been removed from the rock, but is utilised in the formation of new minerals. Albite (NaAlSi₃O₈) is more silica saturated than its precursor anorthite [Ca(Al₂Si₂O₈)] and constitutes over 50% of the total mineral assemblage. The appearance of actinolite (Ca₂(Mg,Fe)₅(Si₈O₂₂)(OH)₂), with 8 moles of silica per formula unit, constituting approximately 20% of the total new mineral assemblage, also explains the reduction in free quartz.



Figure 3.2: Hydrothermal microbrecciation of flow top (Sample F5t). Magnification = X10, plane polarised light.



Fig 3.3: Quartz, galena and minor chalcopyrite infill amygdale in light amygdaloidal lava. Larger amygdale is 1cm in length.



Fig 3.4: Reflected light photomicrograph of galena (bright white with characteristic cdlevage pits) and quartz (mid grey) infilling amygdale of light amygdaloidal lava. Magnification = X50.



Fig 3.5: Light amygdaloidal lava with quartz, galena and chalcopyrite within amygdales. Amygdale is 1.3 cm in length.

3.2.2 Albite

Plagioclase has undergone a process of albitisation in all of the flow zones, and K⁺ substitution in the flow tops. Crystals in the flow tops appear essentially fresh to only slightly altered and may represent unstable relics which were unable to equilibrate with the fluid. The crystal habit is well preserved, as are the twinning features. The crystals become less pristine in the dark amygdaloidal flow bases and more altered still in the dark massive flow centres, where microcrystalline quartz and chlorite from the groundmass invade the crystal boundaries (Fig. 3.6). Alteration to sericite is also observed in some samples.

As mentioned previously, the dark, coarsely crystalline lava has plagioclase in proportions over 50% of the total mineral assemblage. This has arisen from the recrystallisation of secondary albite, which forms large euhedral crystals (Fig. 3.7). The size of these secondary crystals indicate that this process was slow, and probably under equilibrium conditions. XRD analyses show the plagioclase composition to be on the albite-oligoclase boundary at An_{10} and of the low temperature variety. It is common for anorthite to lose calcium when in contact with low temperature hydrothermal fluids and residually leave the more stable sodic variety (Deer *et al.*, 1992).

Plagioclase mineral chemistry was determined by microprobe. Although the majority of plagioclase crystals are of albite composition, it appears that potassic alteration has to a

small extent been in effect. Feldspar compositions were reduced to their end members An-Ab-Or and plotted in Figure 3.8. Those which have a strong potassic character are predominantly samples from within the light amygdaloidal flow tops.



Figure 3.6 Quartz and chlorite invade plagioclase crystals in dark massive lavas matrix, Kalkdam. Magnification = X10, plane polarised light.

Flow top feldspars are shown by open circles (Fig. 3.8) and constitute over 50% of the total feldspars plotting as potassic. The localisation of potassic feldspars in the flow tops suggests that they have arisen as a result of the hydrothermal event. Liou (1979) states that replacement of albite by K-feldspar strongly suggests substantial transport of K^+ and Fe^{2+} into the plagioclase phenocrysts. The most common K-feldspar encountered by Liou (1979) is the low temperature adularia (80 - 93% K component) which is probably the predominant potassium feldspar seen at Kalkdam.



Figure 3.7: Secondary albite with large crystal size is observed in the coarsely crystalline dark massive lavas at the head of the valley, Kalkdam. Magnification = X10, crossed polarised light.



Figure 3.8: Ternary composition plot for Kalkdam feldspars. Samples from flow tops (open circles) are affected by potassium substitution.

The K-feldspar distribution in the east Taiwan ophiolite (Liou, 1979), is similar to Kalkdam, with K-feldspar being more abundant in the zones of greater permeability. The less porous lava flow bases and centres at Kalkdam probably did not interact significantly with the fluid and the albitisation of calcic plagioclase arose from burial only.



Figure 3.9: Potassic alteration on plagioclase feldspars from Kalkdam lavas, where K⁺ substitutes for Na⁺.

The effects of potassic alteration are shown in Figure 3.9 where Na⁺ per formula unit is plotted against K^+ per formula unit. Many samples plot close to zero for both Na⁺ and K^+ . The majority of these samples are from the flow tops and possess a very high SiO₂ content.

3.2.3 Chlorite

Chlorite is the next most abundant secondary phase throughout the lava succession. It is present within amygdales (Fig. 3.10) and as pseudomorphs after primary ferromagnesian minerals (Fig. 3.11). An important groundmass constituent, chlorite forms microcrystalline blebs along with secondary quartz. In hand specimen and petrographically, it appears that chlorite is more abundant in the amygdaloidal flow tops than in the flow centres and bases. However, from XRD analyses, it is apparent that the proportion of chlorite in the flow tops is far less (approx. 10 %) than in the massive and dark amygdaloidal zones (15-20 %). XRD analyses indicate that two types of chlorite exist: a Cr-rich clinochlore and an Fe-rich clinochlore. Optically, it is difficult to distinguish between the two types.



Figure 3.10: Chlorite (centre) and quartz (fringe) infills amygdale in highly altered light amygdaloidal lava, Kalkdam. Magnification = X50, plane polarised light.



Figure 3.11: Chlorite pseudomorph after primary ferromagnesian minerals in sample F5b (Flow 5 bottom) from Kalkdam. Magnification = X50, plane polarised light.

Chlorite compositions were determined by microprobe and classified according to Hey (1954). Figure 3.12 shows the majority of chlorites plot between the ripidolite and pycnochlorite composition fields whilst a few plot randomly about this composition. The tight cluster correlate with the flow centre chlorites, whilst those scattered are samples from the flow interfaces F2/F3, F4/F5 and F5/F6. Figure 3.13 (reduced to Fe, Mg and Al components) also shows the majority of chlorites plotting in a tight cluster. These are the compositions of chlorites from the flow centres. The other compositions are significantly different, and reflect the compositions of chlorites formed in the zones of fluid movement (F2/F3, F4/F5. F5/F6).



Figure 3.12: Composition of Kalkdam chlorites. After Hey (1954).



Figure 3.13: Al-Mg-Fe ternary diagram. Chlorite compositions change with stratigraphic height.

The pattern of variation in chlorite composition with respect to flow zone and height in the succession define the major pathways of fluid flow throughout the succession. For example, chlorite compositions in flow top 6 (F6t) differ greatly from those in flow top 2 (F2t). Although both flow tops have been bleached by reaction with the fluid, the composition of F2t chlorites is still very close to those from the flow centres which have had little contact with the fluid. The chlorite compositions in the basal zone of flow 5 (F5b) differ from the other flow bases and approach the composition of the chlorites from F6t. This suggests that although fluid flow has occurred along all the lava flow interfaces, it appears to have been concentrated toward the top of the succession. F2t chlorites still possess a composition reflecting burial processes.

3.2.3.1 Temperatures of formation

The variation of Fe²⁺ and Mg²⁺ occupying the octahedral sites is a function of temperature (Cathlineau, 1988), but is strongly dependant on the geological environment and the solution composition. Sawai (1984) showed that the Fe²⁺ content decreases away from Pb-Zn veins, suggesting that with increasing temperature, the Fe²⁺ content increases (Laird, 1988; Zhong *et al.*, 1985). Shikazono and Kawahata (1987) have also shown the dependence of the Fe²⁺ content on the geological environment which result in different Fe²⁺/(Fe²⁺ + Mg²⁺) values. The values in propylitically altered rocks with Pb-Zn vein-type associations range from 0.25-0.45, whilst those from terrestrial and submarine geothermal

systems range from 0.25-0.74. $Fe^{2+}/(Fe^{2+} + Mg^{2+})$ values from Kalkdam range between 0.45-0.63. The highest values are found toward the top of the lava succession (F5t, F6t and F7t). The lowest values are found within the massive flow middles (F5m, F4m and F3m), as well as at the top of flow 2 (F2t) and correspond to propylitic alteration caused by burial. The intermediate values define flow interfaces where minor fluid migration has occurred (F3b, F5b).

Foster (1962) has shown that an increase in Al^{VI}, results in a corresponding decrease in Al^{IV}. A plot of Al^{IV} against Al^{VI}, (Fig. 3.14) also shows two types of chlorites present at Kalkdam. Type A clusters in the centre of the diagram at moderately uniform values whilst Type B marks a linear trend where octahedral Al increases proportionally with a decrease in tetrahedral Al.



Figure 3.14. Kalkdam chlorite compositional variations regarding Al^{VI} content and Al^{IV}. The tight cluster represent chlorite from flow centres. Samples from flow tops and toward the top of the lava succession plot along the line marked.

Cathelineau and Nieva (1985) have shown that an increase of AI^{3+} in the tetrahedral sites is also proportional to an increase in temperature. Chlorites from two different geothermal systems display a strict linear dependency of AI^{IV} content with temperature with a good regression coefficient R = 0.97 (Cathelineau, 1988). The relationship between AI^{IV} and temperature is given by the equation:

$$T (^{\circ}C) = -61.9229 + 321.9772(Al^{1V})$$
 (Temp 1)

Winter (1995) calculated an alternative equation on data from Cathelineau and Nieva (1985) and Cathelineau (1988) which utilises both Al^{3+} occupancy of tetrahedral sites as well as octahedral vacancy. This relationship is given by the equation:

$$T (^{\circ}C) = 160.77 + 89.35(Al^{IV}) - 167.92(Vac)$$
 (Temp 2)

Reconstructed structural formulae (on basis of 14 oxygens) of selected samples and corresponding temperatures are given in Table 3.2. Temperatures calculated by Temp 1 equation differ significantly from those calculated by the Temp 2 equation.

Although the temperatures from equation 1 fall outside the Cathelineau (1988) range 130°C to 310°C (where R = 0.97), they follow approximately the same trend as those calculated by equation 2 and highlight flow interfaces which have had significant fluid migration along them. These are F2/F3, F4/F5 and F5/F6 (Fig. 3.15). The effect of the

fluid movement increases toward the top of the succession. On the basis of temperature calculations, very little fluid movement has occurred between F3 and F4. This is in accordance with field observations where F3 appears to be the least altered in terms of colour index. A few chlorite samples (1A) show slightly higher formation temperatures, but no evidence of significant reaction with a fluid. These higher temperatures have been attributed to increased burial, which is confirmed by the composition (Kuniyoshi and Liou, 1976; Zen, 1974).



Figure 3.15: Calculated chlorite formation temperatures at various flow zones at Kalkdam. Higher temperatures between F2/F3, F4/F5 and F5/F6 suggest that the hydrothermal fluid exploited these zones.

Sample	# Si IV	# ALIV	T	# AI VI	# Ti	# Fe	# Mn	# Mg	# Ča	# Na	#K	O site	Vac	Temp 1	Temp 2
			site												
1A 3	2.874147	1.125853	4	1.182651	0	2.421206	0.060538	2.290143	0.005715	0.005715	0.018615	5.984582	0.045462	300.5762	253.7309
1A 7	2.850552	1.149448	4	1.162892	0	2.354088	0.057208	2.404271	0.007793	0.007793	0.010073	6.00412	0.02154	308.1732	259.8561
1A 33	2.860604	1.139396	4	1.120226	0	2.428685	0.057529	2.355076	0.003521	0.003521	0.080713	6.04927	0.038485	304.9365	256.1126
F2t 8	2.654296	1.345704	4	1.414094	0	2.114591	0.032263	2.37839	0.0012	0.0012	0.039099	5.980838	0.060662	371.363	270.8223
F2t 12	2.655126	1.344874	4	1.367759	0.002402	2.048405	0.036967	2.499528	0.002281	0.002281	0.045406	6.005029	0.047341	371.0958	272.985
F3bm 3	2.665319	1.334681	4	1.313857	0.003939	2.472292	0.03283	2.150576	0.005612	0.005612	0.046716	6.031434	0.030446	367.8139	274.9113
F3bm 7	2.668598	1.331402	4	1.302222	0.005504	2.499927	0.035424	2.137119	0.002241	0.002241	0.046627	6.031304	0.025308	366.758	275.4811
F3bm 11	2.661662	1.338338	4	1.324471	0	2.386186	0.038046	2.177911	0.006563	0.006563	0.126677	6.066416	0.073386	368.9914	268.0275
F3mb 12	2.756574	1.243426	4	1.467434	0.00683	2.275619	0.03173	2.069837	0.00973	0.00973	0.011005	5.881917	0.155379	338.4318	245.7789
F3mb 15	2.778581	1.221419	4	1.434224	0.002489	2.198882	0.033644	2.192735	0.003547	0.003547	0.038508	5.907574	0.140515	331.3463	246.3085
F3mb 19	2.750011	1.249989	4	1.470533	0.00486	2.094195	0.033754	2.264078	0.004616	0.004616	0.018795	5.895446	0.13744	340.5452	249.3776
F3t	2.778901	1.221099	4	1.37619	0.005604	2.040598	0.34265	2.388678	0.11407	0.037155	0.078771	5.974098	0.153234	331.2433	244.1443
F4bm 14	2.778901	1.221099	4	1.377619	0.005604	2.040599	0.034265	2.388678	0.011407	0.011407	0.037155	5.906734	0.158838	331.2433	243.2032
F4m 10	2.710428	1.289572	4	1.352156	0.005425	2.325063	0.034913	2.172302	0.009937	0.109888	0.01709	6.026772	0.110142	353.2899	257.4982
F4t	2.684898	1.1315102	4	1.27865	0.003207	2.411848	0.03881	2.244375	0.006854	0.047545	0.014961	6.046272	0.023089	361.5099	274.3973
F5b 1	2.531011	1.468989	4	1.374121	0.006487	2.671918	0.042926	1.901754	0.002311	0.002311	0.077355	6.079183	0.00928	411.058	290.4658
F5b 2	2.600466	1.399534	4	1.386974	0.001659	2.656096	0.04672	1.881509	0.003546	0.003546	0.049196	6.029246	0.028701	388.6952	280.999
F5m 2	2.859052	1.140948	4	1.062305	0	2.175121	0.058427	2.682278	0.002423	0.002423	0.107435	6.090413	0.021869	305.4364	259.0415
F5t 7	2.387651	1.612349	4	1.865703	0	2.51007	0.034781	1.457872	0.00307	0.00307	0	5.874565	0.131574	457.2166	282.7395
F6b	2.639807	1.360193	4	1.277696	0	2.52051	0.0318	2.161143	0.006704	0.74815	0.011924	6.084643	0.00885	376.0281	280.8171
F6m	2.698689	1.301411	4	1.271831	0.00401	2.875975	0.34327	2.202189	0.004571	0.04895	0.006803	6.028656	6.011668	357.1019	275.0919
F6t 8	2.663961	1.336039	4	1.475684	0.000854	2.629259	0.036545	1.753671	0.00365	0.00365	0.050633	5.953945	0.104841	368.2513	262.5401

Table 3.1: Structural formulae and calculated crystallisation temperatures for chlorite samples (groundmass, pseudomorph and amygdale) from each lava zone,

Kalkdam.

3.2.4 Calcite

Calcite is present throughout the whole succession, but its concentration varies in relation to its position. In the upper flows, calcite is the dominant phase infilling amygdales, and as pseudomorphs after primary ferromagnesian minerals (Fig. 3.16). Calcite diminishes down the succession, where it is progressively replaced by chlorite. The chlorite replaces the calcite by forming haloes around the edge of the amygdale or pseudomorph, then by growing inwards, exploiting weaknesses in the calcite crystal structure. Fragments become suspended within the chlorite and diminish in size with increasing replacement. With further replacement, a rim of microcrystalline quartz forms around the edge of the amygdale (Fig. 3.16). Well distributed, finely crystalline sphalerite is associated with the calcite, the effect of which is bronze/red staining of the calcite. Sphalerite only comes into contact with quartz and chlorite when the calcite is "engulfed" by the latter. Carbonatisation and sphalerite mineralisation therefore took place prior to the chlorite/quartz/galena event.

Although not very important, calcite is also present in small amounts in the groundmass of the upper flows, constituting about 5 % of the total mineral assemblage. However, adjacent to the hydrothermal breccia zones, the dark massive lava is enriched in calcite by approximately 10 %. Calcite is also present as a minor vein constituent in the breccia zones where it cross cuts earlier calcite/ sphalerite amygdales.

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148 811

984

07

1999
From the observed textural relationships, it can be deduced that there were two separate phases of calcite crystallisation. Calcite crystallisation occurred prior to the hydrothermal event and may have arisen from supergene or burial processes. Formation waters from the Transvaal Sequence above may have percolated down through the limestone sequence dissolving calcite and sphalerite, which later precipitated in the Allanridge lavas. Dolomitisation of the Transvaal Sequence probably occurred later during the hydrothermal event. The enrichment of calcite adjacent to the breccia zones indicates that calcite was either brought in with the fluid from an external source or pre-existing calcite was remobilised during the hydrothermal event.



Figure 3.16: Chlorite and quartz replace calcite in the dark amygdaloidal lava zone, Kalkdam. Magnification = X50, crossed polarised light.



Figure 3.17: Calcite pseudomorph after primary hornblende. Magnification = X50, plane polarised light.

3.2.5 Amphibole

Secondary amphibole is present only in flow zone 1A, where it occurs as stubby prismatic crystals of high relief and high second order birefringence colours. XRD analyses indicate it to be actinolite and constitutes approximately 20 % of the total mineral assemblage. Recalculated structural formulae were determined from microprobe analyses on the basis of 23 oxygens (anhydrous). Although anhydrous calculations differ slightly from hydrous, the amount is negligible and all analyses plot in the actinolite field (Fig. 3.18). The amphibole compositions differ from average actinolite (Deer *et al.*, 1992) found in actinolite schists and are similar to those formed after clinopyroxene (Schweitzer and Kröner, 1985).

The actinolite present in sample 1A has formed as a result of burial metamorphism, and is typical of low pressure metamorphic regions of the greenschist facies. Sample 1A outcrops at the greatest depth at Kalkdam and merely marks the onset of a new mineral in the assemblage (Winkler, 1979).



Figure 3.18: Plot of Mg/(Mg + Fe) against Si for Kalkdam amphibole analyses from sample 1A (coarse crystalline lava). After Winter (1995).

3.2.6 Sphene

Sphene is common throughout the lava succession, but is more abundant in the amygdaloidal lava flow tops. As a secondary mineral, it does not just replace another pre-

existing phase, but first forms its characteristic diamond shape around a few other plagioclase crystals. When infilling begins, it does not grow inwards from the faces, but more as random dots which eventually join together to form the whole crystal. Plate 2 in Kuniyoshi and Liou (1976) shows sphene morphology similar to that observed at Kalkdam. Sphene is a typical mineral of metamorphic burial sequences as the replacer of Ti-oxides because, as observed at Kalkdam, it appears to be intimately related to the albitisation of plagioclase (Kuniyoshi and Liou, 1976).

3.2.7 Other phases

A minor phase present is clinozoisite which is found within quartz veins in the hydrothermal breccia. This has probably crystallised in response to the increased availability of Ca^{2+} in this region. Pyrite has also become an important secondary constituent in the massive lavas adjacent to all of the breccia zones where it is abundant throughout the matrix as euhedral crystals up to 1mm in diameter. This occurrence is typical of pyrite that precipitated from a hydrothermal solution percolating through the wall rock adjacent to the breccia zones, the drop in pressure results in pyrite precipitation.

3.3 Texture.

The massive flow centres and dark amygdaloidal lava zones are more altered than the flow tops, and have lost much of their primary texture. Quartz and chlorite in the groundmass have almost completely obliterated the plagioclase and other ferromagnesian minerals, whereas in the flow tops, the plagioclase looks almost pristine where it has been left as unstable relics. Minor substitution of K^+ for Na⁺ has also occurred in some flow top samples.

3.4 Discussion

The presence of chlorite and actinolite is indicative of low grade metamorphism with temperatures ranging from 200°C to 400°C (Winkler, 1979). At temperatures below 500°C, hornblende ceases to be stable and alters to actinolite. The absence of lower grade species such as prehnite and pumpellyite, but the presence of calcite and actinolite at Kalkdam may suggest that the altering fluid was high in dissolved CO_2 (Winkler, 1979). Throughout the lava flow succession, it appears that the type of alteration taking place is chloritisation in the lower flows, and carbonatisation in the upper flows (Table 3.2). The presence of abundant albite and actinolite more dominantly in the lower flows, far from the highly altered and mineralised zones, suggests that their presence is related to burial depth rather than as a result of the hydrothermal event. The disappearance of calcite and the

appearance of chlorite marks a facies change in response to increased depth of burial. The mineralogical changes occurring throughout the lava succession are indeed typical of greenschist facies metamorphism of intermediate-mafic rocks as a result of burial (Winkler, 1979), and is also similar to metabasites in the Barrovian chlorite zone in Scotland, as first described by Wiseman (1934). Hyndman (1972) indicates that "greenschist facies rocks develop under conditions of "normal" geothermal gradient in a geosynclinal environment" as well as in regions where the geothermal gradient is high (Tomasson and Kristmansdottir, 1972). The same mineralogical changes occur at Reykjanes Peninsula, Iceland at a depth of 500 m and approximately 160°C (Tomasson and Kristmansdottir, 1972).

From mineralogical observations, it is deduced that the alteration caused by a hydrothermal event overprinted a previous, more widespread burial metamorphism which is known to have affected the whole of the Ventersdorp succession (Cornell, 1978; Bowen, M.P., 1984). The presence of two distinct kinds of chlorite substantiate this, with one kind occurring as a result of burial metamorphism, and the other in relation to the passage of hot fluids through the porous amygdaloidal flow tops. Two generations of calcite have also been observed. The texture of the central massive lava zones has been greatly obliterated in comparison with the flow tops. For this to occur, equilibrium conditions must have prevailed, which could not have happened with the rapid through flow of fluid and has been ascribed to burial processes.

Sample	Colour	Amygdales	Groundmass	Ferromagnesian	Plagioclase	New minerals
				minerals		
F7t	Pale grey/ white	Calcite only	Microcrystalline quartz blebs, with calcite core	Replaced by calcite.	Fairly fresh.	Much sphene.
F7m	Pale green white	Calcite and quartz.	As F7t	Not identified.		Sphene
F6t	Mid green/ white	Calcite only.	Microcrystalline quartz blebs. Vague veining	Not identified.	Faily altered.	Sphene, Actinolite.
F5t	Greyish white	Calcite.	Vienlets of calcite and quartz joining amygdales.	Mainly calcite and minor quartz.	Porphyrytic texture. Crystals fairly fresh.	None.
F41	Pale grey- green	Calcite with quartz rims.	Lack of chlorite. Abundant microcrystalline quartz recrystallising. Minor calcite	Altered to chlorite and calcite.	Fairly fresh	None
F4m	Dark green.	Mainly calcite with chlorite and quartz rims.	Chlorite rich with many vienlets of microcrystalline quartz	Altered to chlorite	Moderately altered.	Sphene
F4b	Dark grey-green	No amygdales present	Abundant quartz/chlorite aggregates taking over much of groundmass.	Altered to chlorite and quartz.	Very altered with crystal form diminishing	Pyrite.
F5b	Dark green with white speckles.	No amygdales present	Microcrystalline quartz blebs. Devitrified glassy matrix.	Altered to chlorite and quartz.	Almost pristine.	Sphene
F5m	Dark Grey	No amygdales present	Much micro- crystalline quartz and calcite	Not identified	Almost totally obliterated.	Ругіте
F31	Very pale white/ green	Filled with calcite	Predominantly calcite with minor chlorite and quartz.	Not identified	Very altered.	Sphene Galena
F3m	Pale greenish white	Filled with calcite	Mixture of chlorite and calcite with minor quartz.	Not identified	Very fresh.	Sphene
F3b	Dark grey green	Chlorite and quartz replacing calcite core.	Microcrystalline quartz/chlorite aggregates. Minor calcite	Altered to chlorite	in colour and showing vague twinning	Pyrite, sphene
F2t	Pale to mid green	Calcite suspended in chlorite	Microcrystalline quartz/chlorite aggregates with chlorite core. Some minor calcite also	Altered to chlorite	Fairly fresh with good crystal form	None
Flt	Pale grey green	Calcite and chlorite	Predominantly microcrystalline quartz and chlorite aggregates	None noticeable	Fairly pristine, showing twinning, but also with sericite	None

Table 3.2: Petrographic descriptions of successive lava flows.

3.5 ALTERATION

Helgeson (1979) states that "the association of sulphides with altered wall rocks is a manifestation of the chemical link between the alteration process and the precipitation of ore minerals in hydrothermal veins." This highlights the "interdependency of wall rock alteration and mineralisation" (Meyer and Hemley, 1967; Helgeson, 1979; Evans, 1993).

Reactions occurring between the silicate wall rock and an aqueous electrolyte solution are essentially acid - base exchange reactions in which the relatively acidic solution is neutralised by the basic wall rock (Rose and Burt, 1979). In cation exchange reactions, the more acidic cation enters the wall rock and the less acidic cation is released into the fluid.

The change in activity of different ions in the fluid will affect the solubilities of the metal complexes and may result in either dissolution or precipitation, e.g. in a hydration reaction, the rock consumes H^+ (most acidic cation) ions and releases the same mole equivalent of a metal cation e.g. K^+ ions, thus altering the H^+/K^+ ratio of the fluid. This in turn alters the pH of the fluid, which will affect the degree of dissociation of dissolved HCl. The activity of the hydrogen ion decreases, increasing the availability of Cl⁻ ions for complexing with metal ions. In other words, the solubility of the metals in the fluid is increased, and deposition of metallic minerals will be reduced or terminated.

The acidity of a particular cation is related to its relative field strength or charge/radius ratio. Common cations other than K⁺ that are involved in alteration reactions are Na⁺. Ca^{2+} , Mg^{2+} , Fe^{2+} and Al^{3+} , although due to the high field strength of Al^{3+} it is the least mobile of all the cations and for most alteration reactions the constancy of Al^{3+} can be assumed (Meyer and Hemley, 1967). Banded alteration zones around an ore body display progressively smaller amounts of cation extraction. This can be related to the decreasing activity gradient of H⁺ along a diffusion curve (Meyer and Hemley, 1967). In the outer zones, where the H^+/M^+ ratio is at a minimum, the most common minerals to crystallise are pyrite and calcite. This is indeed observed in the rocks adjacent to breccia zones at Kalkdam. Pyrite appears at a distance of approximately 6 m from the breccia zones, and is abundant within the matrix of the fine-grained dark massive lava. The intensity of the alteration is a function of the chemical potential between the rock and the fluid. The rate at which equilibrium is reached is dependant on the temperature, pressure and composition of the fluid phase. However, the chemistry of the fluid will change over the time in which it is reacting with the wall rock, and will result in a zoning pattern of different alteration types (Evans, 1993). The flow tops at Kalkdam have been subjected to potassic alteration by cation exchange: Na^+ in the feldspars has been substituted by K^+ . H^{*} has probably also been added to the wall rocks which helped to form the amygdale chlorite. It is probable that the early mineralising event deposited sphalerite and galena in the amygdaloidal flow tops, but loss of H⁺ by the secondary fluid would have liberated Cl⁻ ions to allow complexing and dissolution of the metal ores.

The reactions occurring result in the formation of an alteration halo around the deposit, which on identification is extremely useful in exploration (Evans, 1993). In modern deposits, the alteration halo tends to consist of intense argillic alteration closest to the ore which grades into argillic, propylitic and then unaltered rock away from the vein or breccia zone (Latvalahti, 1979). Boyle (1970) has mentioned that argillic and intense argillic alteration around an ore body is uncommon in rocks older than the Tertiary: instead propylitic alteration dominates. The disadvantage of this is that propylitic alteration is usually very widespread due to the large amount of water involved. In some places it grades into the greenschist facies of regional metamorphism (Boyle, 1970).

At Kalkdam, wall rock alteration is only significant at the amygdaloidal flow tops, and in the vicinity of the breccia zones. The rest of the volcanics display low grade greenschist facies assemblages similar to other Allanridge lavas across the depository (Tankard *et al.*, 1982, Crow and Condie, 1988; Bowen *et al.*, 1986). Cornell (1978) has attributed this to burial processes.

Although a greenschist facies mineral assemblage exists, there is a very large proportion of chlorite compared with other minerals. Since chloritisation involves the introduction of water \pm sulphur \pm arsenic and the removal of SiO₂, the alteration is better described as propylitic. Propylitic alteration involves large volumes of water infiltrating great volumes of rock. This alteration type is complex and is subdivided into 3 categories:

- Chloritisation in which chlorite is present with or without quartz. The chlorite may develop from alteration of primary mafic phases or with the introduction of Fe and Mg by the fluid phase.
- Albitisation new albite or K-feldspar may form as a result of Na or K-metasomatism.
 The other phases characteristic of potassic alteration may or may not be present.
- Carbonisation in the case of Mississippi valley type Pb/Zn deposits, this involves the low temperature alteration of limestone to dolomite.

Sodic varieties of plagioclase are more stable than the calcic varieties when in contact with hydrothermal solutions (Deer, *et al.*, 1992; Evans, 1993). Anorthite will become more sodic, not by exchange reactions, but by substitution which usually progresses as far as the composition of oligoclase (An₁₀). The Ca released may then be incorporated into newly forming calcic amphiboles e.g. actinolite or perhaps, if the CO_3^{2-} concentration is high enough, calcite (Winkler, 1979). XRD powder analyses of samples from Kalkdam indicate that the principle plagioclase type is on the albite-oligoclase boundary at An₁₀. Albite is also present in the lowermost flow where it has recrystallised to form larger crystals.

The replacement of calcite by chlorite down the lava succession describes a zoning pattern similar to greenschist facies rocks of burial origin (Yardley, 1989). The zones however,

are far smaller and have probably formed by reaction with warm fluids which increased the local geothermal gradient. The zonation pattern observed at Kalkdam also mimics that at the active geothermal field at Rekjanes Ridge in Iceland (Tomassen and Kristmansdottir, 1972).

The processes of pyritisation, carbonatisation and chloritisation of intermediate rocks generally involves the introduction of CO_2 , H_2O and S into the system (Boyle, 1970). Fe, Ca, Mg and Mn remain more or less constant whilst Na and K show variable behaviour.

Burial processes have not been entirely discounted, considering the great thickness of Transvaal sediments overlying the Ventersdorp at this time. The continuance of greenschist assemblages across the Province also indicate that burial must have occurred in conjunction with the fluid infiltration.

The texture in the darker finely crystalline flow zones has been greatly affected, with no primary mineral relicts present and much of the matrix made up of microcrystalline quartz and chlorite. This loss of texture is governed by the original grain size: the potential surface area prone to attack by fluids (along the grain boundaries) or diffusion currents is much greater for the finely crystalline rock, and the resulting alteration is more intense than in an equivalent coarsely crystalline lava. This process is much slower, but more pervasive as equilibrium is more likely to be attained.

In contrast, the alteration in the flow tops is typical wall rock alteration which is usually found in the vicinity of area of permeability - either primary: in the case of porous sediments and vesicular lavas or by secondary permeability caused by joints, faults, fractures and unconformities (Boyle, 1970; Rose and Burt, 1979). Compared with regional and contact metamorphism this is a fairly rapid process and therefore tends to be incomplete (Evans, 1993).

The duration that a fluid is in contact with the rock through which it is passing, will determine the intensity of the alteration. If there is a constant flux of a fluid with a continually changing composition, equilibrium will never be attained. The resulting alteration will also be constantly changing, resulting in zonation of different alteration assemblages. Where the fluid flux is greater, many primary minerals will be left as unstable relics (Evans, 1993). This is indeed observed in the flow tops at Kalkdam, where plagioclase has remained as unstable relics.

3.6 Summary

1. Potassic alteration overprints the pre-existing greenschist burial metamorphism and propylitic alteration event. The porous flow tops have been the most intensely affected.

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- 2. The interaction of the fluid with the wall rocks of the flow tops has altered the fluid chemistry which, combined with a reduction in pressure on reaching the breccia zones has resulted in the deposition of galena in these zones. The rocks adjacent to the breccia zones appear relatively unaltered apart from the pyritisation and carbonatisation reaction of the fluid with the flow tops has resulted in the chemical difference between the fluid and wall rocks adjacent to the breccia zones to become smaller and hence less intense alteration is observed.
- 3. Chlorite temperature variations indicate the zones where fluid flow has been greatest at the flow interfaces between F2/F3, F4/F5 and F5/F6. The temperatures also increase with height.

4. GEOCHEMISTRY

4.1 Introduction

Whole rock samples of the light amygdaloidal, dark amygdaloidal and dark massive lavas from Kalkdam were analysed by XRF techniques. In order to assess the extent of the fluid migration, Allanridge samples from various localities in the Northern Cape Province were collected for comparison with those from Kalkdam. Allanridge bore-core samples from several localities between Allanridge and Bothaville (Crozier, in prep) were used as protolith "type" samples to assess the relative enrichment and depletion of components resulting from the hydrothermal alteration. For data see Appendix B.

4.2 Discrimination diagrams

Allanridge lavas have previously been described in literature as tholeilitic basaltic-andesites (Bowen, M.P., 1984). The "type" Allanridge samples and the majority of Northern Cape samples plot in the expected basaltic-andesite field of the total alkali-silica variation diagram (Fig. 4.1). The majority of samples from Kalkdam plot within the expected ranges, but a few have become enriched in potassium (Fig. 4.2). Some Northern Cape

Allanridge samples have also gained potassium and plot beside the altered Kalkdam samples.



Figure 4.1: Total alkali-silica diagram for Kalkdam Allanridge (circles); Type Allanridge (squares) and Northern Cape Allanridge (triangles). Fields: B=basalt; BA=basaltic andesite; A=andesite; D=dacite; R=rhyolite; T=trachyte; TA=trachyandesite; BTA=basaltic trachyandesite and TB=trachybasalt. After Cox et al. 1979.

Although the Northern Cape Province Allanridge samples have chemically gained potassium and silica, they do not differ significantly in either hand specimen or thin section from the dark massive lavas of the Kalkdam flow centres: all are massive, finely crystalline, dark blue-green and appear relatively fresh.



Figure 4.2: Na₂O versus K₂O for Allanridge samples (after Middlemost, 1975). Symbols as in Fig. 4.1.



Figure 4.3: Ti/P vs Ti/Zr discrimination plot showing majority of Kalkdam samples within the Allanridge field. A few samples from the flow tops plot outside the Allanridge field (after T.B. Bowen, 1984).



Figure 4.4: P/Ti vs Zr/P discrimination plot (after T.B. Bowen, 1984).

Immobile element plots show similar trends (Figs. 4.3 and 4.4). T.B. Bowen (1984) devised discrimination diagrams using the immobile elements Ti, P and Zr. Again, the majority of samples lie within the Allanridge field, the few which plot outside are from Kalkdam and lie in the Dominion Group field and the Rietgat/Goedgenoeg Formation field. Three samples plot just inside the Klipriviersberg Group field. All of the Northern Cape Allanridge samples plot within the Allanridge field.

Deviation of the immobile elements from the protolith composition can mean either that in this situation these elements were mobile (Finlow-Bates and Stumpfl, 1981) or that mass gains or losses of mobile elements into and out of the parent rock resulted in a dilution or concentration effect (Gresens, 1967; Grant, 1986; MacLean and Krandiotis, 1987).

Figures 4.1 to 4.4 show that although most samples from Kalkdam are similar to Allanridge samples of widespread origin, a few samples are significantly altered.

The Jensen (1976) cation plot (Fig. 4.5), however, shows the Northern Cape Allanridge to differ significantly from the "type" Allanridge. "Type" Allanridge samples plot within the calc-alkaline basalt field and at the intersection between the tholeiitic andesite, calc-alkaline basalt and the high Fe-tholeiite fields. The Northern Cape Allanridge samples are more calc-alkaline in character, plotting between the calc-alkaline andesite and the high Mg-tholeiite fields. The majority of Kalkdam samples are also calc-alkaline in character, with compositions ranging from rhyolite to high Mg-tholeiite. This linear trend (Fig. 4.5), marks the continuous compositional change, as a result of alteration, from the light amygdaloidal lava, through the dark amygdaloidal lava to the dark massive lava. Samples adjacent to the breccia zones do not, however, follow this trend and plot in the tholeiitic andesite field.

4.3 Enrichment/depletion diagrams

Enrichment/depletion diagrams were constructed to establish how individual components differ in concentration between altered Kalkdam samples and the unaltered parent rock. The mean of each lava-type was normalised to mean "type" Allanridge. Figure 4.7 shows relative enrichment and depletion of major oxides in the light amygdaloidal (LA), dark

massive (DM) and dark amygdaloidal (DA) lavas at Kalkdam. Fine lines mark the range of each component in the "type" Allanridge. Varying element mobility results in a broad mobile component range, and a narrow immobile component range. Components of samples falling outside the "type" range hence show significant enrichment or depletion.



Figure 4.5: Jensen (1976) diagram for Kalkdam samples. Open circles=light amygdaloidal flow tops; open triangles=dark amygdaloidal lava; crosses=dark massive flow bases; open sqaures=samples in vicinity of breccia zones; Filled circles=Northern Cape Allanridge samples.

The light amygdaloidal-type is the most enriched in terms of SiO_2 . The dark amygdaloidal-type shows only moderate enrichment. This is explained by the presence of more quartz-filled amygdales in the light amygdaloidal-type. The dark massive-type does not differ significantly from the mean "type" Allanridge. Although alteration has occurred, it has been isochemical with no net enrichment or depletion of silica.



Figure 4.6: Major oxide enrichment/depletion diagram for Kalkdam lava types. Symbols: light amygdaloidal (triangles); dark amygdaloidal (diamonds) and dark massive (squares).

TiO₂ displays slight depletion in all three lava types, but remains within the "type" range. Although all three are depleted, the differences between each lava type are very small. Ti is essentially an immobile transition element, and the depletion displayed may have arisen by dilution. Finlow-Bates and Stumpfl (1981) have, however, pointed out that prolonged hydrothermal activity on a specific rock will eventually result in the mobilisation of the essentially immobile elements. The hydrothermal activity may continue to a point when the resulting altered rock becomes mono-minerallic (Rose and Burt, 1979). Al_2O_3 is also assumed to be constant during alteration reactions, however, the light and dark amygdaloidal-types show approximately equal relative enrichment. The occurrence of chlorite in amygdales, however, suggests that aluminium must have been somewhat mobile (Valsami *et al.*, 1994). Since the values fit within the range for the unaltered Allanridge, this enrichment is assumed to be negligible.

The transition metals, Mg and Fe are significantly depleted in the light amygdaloidal-type. Depletion of Fe_2O_3 is approximately equal to the most depleted "type" Allanridge, whilst the depletion in MgO lies outside the "type" Allanridge range. Neither MgO nor Fe_2O_3 are significantly depleted or enriched in the dark amygdaloidal and dark massive lavas. The only exceptions are those dark massive samples adjacent to the breccia zones, which show Fe enrichment, but depletion of Mg.

CaO and Na₂O are usually heavily depleted in hydrothermally altered lavas except where carbonatisation and albitisation have taken place (Meyer and Hemley, 1967). Both the light and dark amygdaloidal-types are greatly depleted in CaO compared with the dark massive lava, which possess free calcite in the matrix. It is probable that the fluid phase which penetrated this zone was limited, slow moving and only able to carry plagioclase released Ca²⁺ a short distance. In the light and dark amygdaloidal lavas, the majority of plagioclase crystals have retained their primary igneous texture, but losing Ca has resulted in albitisation. The light amygdaloidal-type is slightly less depleted in CaO than the dark

amygdaloidal type due to the presence of calcite in amygdales and veins systems. Na_2O is slightly depleted in all three lava-types, but lies within the range of the "type" Allanridge.

 K_2O shows the greatest enrichment of all the major oxides in the light amygdaloidal-type. Although K^+ is extremely mobile, the depletion in the dark amygdaloidal-type cannot account for the enrichment in the light amygdaloidal-type. For such a great enrichment factor, K^+ must have been introduced into the lavas from an external source. K^+ is an essential constituent of K-feldspar and biotite, both of which phases are present in the Makwassie quartz-feldspar porphyry. It is possible that the Makwassie is the source of K^+ since it is known to have experienced a major hydrothermal event at 2000 m.y (Duane *et al.*, 1991). The basement granites provide an additional or alternative source.

Phosphorous is slightly enriched in the light amygdaloidal-type, whilst the dark massivetype shows a depletion of the same order. The dark amygdaloidal-type is essentially similar to the "type" Allanridge. Rollinson (1993) indicates that during greenschist facies metamorphism of basaltic rocks, P is immobile. The differences observed at Kalkdam would suggest that in this locality, P is slightly mobile, or has experienced a concentration effect.

The enrichment and depletion trends shown by the dark massive and dark amygdaloidal lavas are typical of propylitic alteration of andesitic rocks. The light amygdaloidal lavas

differ by significant depletion in Fe, Mg and Ca with enrichment of Si and K. This is typical of potassic alteration of andesitic rocks (Liou, 1979).

4.3.1 Comparison with Northern Cape Allanridge

The Northern Cape Allanridge samples were also normalised with mean "type" Allanridge and plotted on enrichment/depletion diagrams, but showed very varied behaviour. Some samples were similar to Kalkdam samples, showing enrichment in K_2O and SiO_2 . These samples plotted beside altered Allanridge in Figures 4.2 to 4.5.

Plotting the localities of these samples on a map suggests that they are located along, or proximal to one or two linear structures (Fig. 4.7) which acted as pathways for fluid migration. Different samples from the same locality do show variation however, suggesting that this alteration was not pervasive and not in equilibrium. Rapidly flowing fluids along a fault or joint would give rise to this phenomena.

4.3.2 Trace elements.

Trace element data from Kalkdam lava types were normalised to the "type" Allanridge as described in the above section (Fig. 4.8). Although most of the trace elements show large

deviations from the norm, enrichment and depletion is still within the range of the "type" Allanridge. Those with large ranges are the mobile elements, and this scale of deviation is to be expected. Elements which fall outside the "type" range are Zn, Rb, Cu, Sr, Ni and Y. Of these, Sr is the most mobile and its depletion is due to its release and removal during the breakdown of plagioclase (Deer *et al.*, 1992). In the light amygdaloidal lava, both Cu and Ni are markedly depleted by release from clinopyroxene and its alteration product chlorite. Zn is greatly enriched in all lava zones at Kalkdam and has probably become concentrated in the fluid phase as a result of continual extraction from pyroxenes and amphiboles (Johnson, 1994) in sedimentary arenites and mafic lavas (lower portion of the Allanridge Formations as well as the Rietgat Formation) further down in the succession. Rb is also significantly enriched in the light amygdaloidal lava and behaves in a fashion similar to potassium: substituting in chlorite and K-feldspars.



Figure 4.7: Lat/long positions of Northern Cape Allanridge which differ in chemistry from "type" Allanridge.

Y is essentially an immobile element, but is depleted in all 3 lava types. This depletion may have arisen by a dilution effect where other mobile elements have been added to the original rock resulting in a gross mass gain (Grant, 1986; MacLean and Krandiotis, 1987; MacLean, 1990; MacLean and Barrett, 1993; Liaghat and MacLean, 1995; Tiwary and Deb, 1997).

4.4 Mass transfer calculations

Mass transfer calculations have been utilised by many workers; (Maxeiner, *et al.*, 1995; Mountain and Williams-Jones, 1996; Gutzmer and Beukes, 1997; and others). The use of these calculations allow the alteration process to be monitored in terms of mass gains and losses by depletion or enrichment of mobile elements (Shriver and MacLean, 1993). Studies of immobile elements allow one to quantitatively estimate the mass, volume and mineralogical changes occurring during hydrothermal alteration (MacLean and Barrett, 1993). This provides many parameters which, when shown on maps and diagrams can be of use in terms of exploration and drilling projects (MacLean and Barrett, 1993), i.e. observation of similar gains and losses in specific environments will help to identify potential mineralisation sites. If the original parent rock can be identified, then the degree of alteration can be quantified for different zones of an ore body or prospective ore bodies.



Figure 4.8: Trace element enrichment/depletion diagram for Kalkdam lava samples. ◆ LA Norm ■ DA Norm ▲ DM Norm

Mass transfer studies of metasomatically altered rocks were first initiated by Gresens (1967), where he looked at composition-volume relationships between an altered rock and its unaltered equivalent. The concentration of an immobile element in the altered rock is a function of the mass gain or loss of mobile components to the precursor. Gresens (ibid.) devised an equation, which has since been simplified by Grant (1986):

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

$$(4.1)$$

Where C_i^A = concentration of component (i) in altered rock (A).

 C_i^{o} = concentration of component (i) in original rock (O).

 M^{O} = mass of original rock (O).

 M^{A} = mass of altered rock (A).

 ΔC_i = change in concentration of component (i).

Grant (1986) further simplified Gresens' equation and devised the isocon diagram. In a plot of the least altered equivalent (identified from petrography, minimum loss of Na₂O, CaO, LOI and low $K_2O/(K_2O + Na_2O)$ values - Shriver and MacLean, 1993) against the altered rock for the different components, a best fit line through all the points marks a line of equal concentration. The components which lie along this line are the least mobile. These components have either had little mass transfer during the alteration process or, relative to one another, their concentrations have remained the same (Grant, 1986).

The selection of elements assumed to be immobile presents a problem due to the variations in element behaviour in response to different parameters of the altering fluid (Liaghat and MacLean, 1995). The occurrence of titanium, aluminium and zirconium-rich veins indicates that in some situations, these normally considered immobile elements have been found to be significantly mobile (Baumgartner and Olsen, 1995; Rubin *et al.*, 1993; Valsami *et al.*, 1994). The most accurate isocon will be that of a rock with only very slight alteration where the majority of elements have been immobile (Baumgartner and Olsen, 1995).

In order to quantify the immobility of the "immobile" elements (Al, Ti, Zr, Y and Nb), MacLean and Krandiotis (1987), plotted each against Zr which, in igneous processes, is a good index of differentiation due to its classic incompatibility with normal mantle phases (Wilson, 1989). The immobile element pair with the highest correlation coefficient is the most immobile pair. At Kalkdam, Al₂O₃-Zr has the highest correlation coefficient, closely followed by TiO_2 -Zr (Figs. 4.9 and 4.10). These components were used to define isocons for samples from Kalkdam. The immobile elements Y and Nb in this case displayed wide scatter when plotted against Zr indicating moderate mobility. Y and Nb are readily accepted into the structures of amphibole, sphene, and to a lesser extent pyroxene (Wilson, 1989; Rollinson, 1993). Since the alteration process at Kalkdam involves the breakdown of amphibole and pyroxene to calcite and chlorite as well as the formation of secondary sphene, it is to be expected that both Y and Nb have been moderately mobilised.

The isocon marks a line of constant concentration, where $\Delta C_i = 0$. By rearranging equation 4.1, $M^O/M^A = C_i^A/C_i^O$, i.e. the mass relationship is equal to the gradient of the isocon. A line parallel to the isocon which passes through the position of one of the mobile components will cross the C^O axis at the equivalent concentration of this component in the altered rock if no mass change had occurred. The percentage loss or gain of components can then be calculated. Once the loss or gain is quantified, a line from the origin passing through the mobile component will mark the percentage lost or gained.

Any other mobile component which falls on this line will have had a similar loss or gain to that of the calculated component. A sample from Pniel was taken to be the least altered based on criteria suggested by Shriver and MacLean (1993). This sample also showed the least deviation from the "type" Allanridge in enrichment/depletion diagrams. Figure 4.11 (a, b, and c) show isocon diagrams for least, moderately and intensely altered samples from Kalkdam. Mass change calculations for other samples are shown in Table 4.1.

Sample F4bm (Fig. 4.11a) displays an isocon (slope $(M^{O}/M^{A}) = 1.045$) which is the least altered of all the lava zones. CaO and to a lesser extent, Fe₂O₃ and MgO are the only components which have lost mass during the alteration process. This is equivalent to a 4.3% decrease in total mass as a result of alteration. The components which have been essentially immobile are MnO, P₂O₅, TiO₂ and Al₂O₃. Those which have lost mass (CaO, MgO, Fe₂O₃ and Na₂O) plot below the isocon whilst those which have gained mass (SiO₂ and K₂O) lie above the isocon. The percentage mass loss for CaO = 100(CB/AB)=29%.



Figure 4.9: Al₂O₃-Zr variation diagram for Kalkdam samples.



Figure 4.10: TiO₂-Zr variation diagram for Kalkdam samples.

The percentage mass loss for $Fe_2O_3 = 100(ED/AD)=15\%$. A line through the origin and Fe_2O_3 marks a depletion of a 15%. MgO also lies on this line and therefore has also had a mass loss of 15%. The percentage of mass gain for K₂O and SiO₂ is less than 10%. The loss of Na₂O is also less than 10%. Figure 4.11b gives an isocon with equation $C^A = 1.058(C^O)$, which corresponds to a total mass loss of 5.5%.

Different trends in mass changes are in response to different alteration processes. Mass reductions are usually as a result of chloritisation which releases silica. The flow tops display the greatest mass reductions and this highlights the zone of the most intense alteration. The flow tops have become silicified by open space filling of amygdales, but a net loss of mass still occurs. Chloritisation releases silica, sodium and calcium. In the flow centres, there has not been enough migration of components and so they have remained and become incorporated into other new minerals which are forming. In the flow tops however, the released components have been carried away to other zones by the mineralising fluid.

MacLean and Barrett (1993) have utilised an alternative method in which they calculate a reconstructed composition for the altered rock from the immobile elements. An immobile element monitor (factor = concentration in precursor/ concentration in altered) determines the mass change as a result of the alteration. Multiplication of the immobile monitor with the concentration of a mobile component in the altered rock gives the actual concentration, had there been no change in mass during the alteration process. Subtraction of the mobile component in the precursor (least altered sample) from the reconstructed composition gives the actual mass change resulting from the alteration. MacLean and Barrett (1993) use variation diagrams of mass changes to identify mineral deposits. Figure 4.12 compares the ΔFe_2O_3 with ΔMgO . A distinct pattern can be seen where ΔMgO and ΔFe_2O_3 display a linear relationship from light amygdaloidal flow tops to dark massive middle zones. A graph of ΔCo with ΔMgO also shows the same relationship.



Figure 4.11a: Isocon diagram for sample F4bm from Kalkdam.





Sample	Mass	Isocon	Components	Components	Immobile
	change		lost	gained	components
1A	10% gain	C ^A =	CaO=11%, Na ₂ O=18%	MgO=44%,	Al ₂ O ₃ ,TiO ₂ ,
		0.909C ^O		Fe ₂ O ₃ =15%	
				K ₂ O=15%, SiO ₂ =11%	MnO
F2t	19% loss	$C^{A}=1.23C^{O}$	CaO=76%, Fe ₂ O ₃ =57%	K ₂ O=100%,	Al ₂ O ₃ ,TiO ₂ ,
				Na ₂ O=10%	
			MgO=79%, SiO ₂ =5%		MnO
F3b	7% loss	$C^{A}=1.076C^{O}$	CaO=63%, Fe ₂ O ₃ =10%	$Na_2O = 10\%$,	Al ₂ O ₃ ,TiO ₂ ,
				$P_2O_5=10\%$	
			K ₂ O =60%, MgO=22%		MnO, SiO ₂
F3m	5.5% loss	C ^A =	CaO=83%, Fe ₂ O ₃ =4.9%	$Na_2O = 29\%$,	Al ₂ O ₃ ,TiO ₂ ,
		1.058C ^o		SiO ₂ =11%	
			MgO=11%, K ₂ O =40%		P ₂ O ₅ , MnO
F3t	20% loss	$C^{A} = 1.25 C^{O}$	CaO=80%, Fe ₂ O ₃ =68%	K ₂ O =80%	Al ₂ O ₃ ,TiO ₂ ,
			MgO=78%, Na ₂ O=10%		P ₂ O ₅ , MnO
			SiO ₂ =10%		
F4bm	4.3% loss	C ^A =	CaO=29%, Fe ₂ O ₃ =15%	K ₂ O =5%, SiO ₂ =5%	Al ₂ O ₃ ,TiO ₂ ,
		1.044C ^o			
			MgO=15%		P ₂ O ₅ , MnO
F4t	4% loss	C ^A =	CaO=71%, Fe ₂ O ₃ =61%	K ₂ O=77%,	Al ₂ O ₃ ,TiO ₂ ,
		1.042C ^o		SiO ₂ =12.5%	
			MgO=67%, Na ₂ O=58%		P ₂ O ₅ , MnO
F5m	3% gain	C ^A =	CaO=49%, Fe ₂ O ₃ =34%	K ₂ O=100%, SiO ₂ =12%	Al ₂ O ₃ ,TiO ₂ ,
		0.969C ⁰			
		2	MgO=27%, Na ₂ O=45%		P_2O_5 , MnO
F6t	20% loss	$C^{A} = 1.25 C^{O}$	CaO=90%, Fe ₂ O ₃ =73%	$K_2O = 230\%$	Al ₂ O ₃ , TiO ₂ ,
			MgO = 78%, SiO ₂ =9%	$Na_2O = 14\%$	P ₂ O ₅ , MnO

Table 4.1: Mass balance calculations for Kalkdam samples, based on Grant (1986) isocon method.
Dark amygdaloidal flow bases lie approximately mid-way between the two end members (Fig. 4.12). This linear relationship can be attributed to chlorite formation throughout the lava succession (as described in chapter 3). Increased porosity of the light and dark amygdaloidal flow zones has rendered the magnesium and iron more mobile and hence greater depletion occurs in the more amygdaloidal zones. Samples from within 10 m of two of the heavily mineralised breccia zones all plot in the lower right quadrant of the diagram. This marks a distinct removal from the trend (as marked by the arrows). This variation from the "greenschist facies burial metamorphism" may help to identify other mineralised zones within the Allanridge Formation that have formed during this event.



Figure 4.12: ΔFe₂O₃ vs ΔMgO for Kalkdam samples. Open circle = Light amygdaloidal; filled circle = samples in vicinity of breccia zones; open squares = dark massive lava; filled squares = dark amygdaloidal lava.

4.5 Summary

- Immobile element plots show the majority of Allanridge samples to plot in the Allanridge field as defined by T.B. Bowen (1984). A few samples from the flow tops at Kalkdam deviate by concentration or dilution effected by addition or removal of mobile elements.
- Flow tops show chemistry typical of potassic alteration with depletions in Fe, Mg, Ca, Na along with enrichment in K and Si. Flow centres display chemistry typical of propylitic alteration: Mg, Fe, Ca and Na remain unaffected as a result of albitisation and precipitation of free calcite.
- The flow tops have also lost metallic trace elements: Cu, Ni, whilst gaining substantial Zn. Rb shows significant enrichment, which is coupled with K-enrichment.
- 4. The lavas adjacent to the breccia zones have a unique chemistry, where a gain in Fe is coupled with a loss in Mg. This feature may help to identify other zones of mineralised breccia within Allanridge volcanics.

5. FLUID INCLUSION STUDIES

5.1 Introduction

Fluid inclusions were identified in quartz veins at both Kalkdam and Katlani, but are surprisingly scant in the samples examined. This suggests that these veins represent a late stage of the hydrothermal event. Quartz amygdales possessed no inclusions, probably having undergone a subsequent heating event which caused the pre-existing inclusions to migrate to the edge of the amygdales and grain boundaries. Inclusions are also likely to have been destroyed in this fashion in the vein quartz.

Only small localised areas with large concentrations of inclusions were found to be suitable for thermometric analysis. At least 4 populations were identified (Fig. 5.1):

- A: Large liquid + vapour (L +V) aqueous brine inclusions that tend to occur in clusters and range in size from 15μ to 80μ . It was decided to concentrate measurements on this population as it is the dominant population.
- B: Isolated aqueous brine inclusions with high viscosity.
- C: Irregular decrepitated inclusions that occur along grain boundaries.

D: Tiny inclusion trails crosscut the grain boundaries and are assumed to be of a later generation. These inclusions are too small to be useful in terms of thermometric measurements.

5.2 Thermometric analyses

Thermometric analyses were performed using Chaixmeca equipment at the University of the Orange Free State. The aqueous brine of population A must represent a fluid with at least 3 components, because at least two different ices can be observed to melt during freezing point depression investigations. The T_{fm} (final melting temperature) is -12.9°C \pm 0.1 (Fig. 5.2). Melting temperatures for the other ices were less accurately determined, with ice 2 melting at approximately -14.7°C and ice 3 between -15 and -17°C. The most relevant model system by which to explain these results is H₂0-NaCl-KCl-X. The inclusions of population A display eutectic melting temperatures around -22°C, which allows the system H₂O-NaCl-CaCl₂ (eutectic melting temperature of -52°C) to be disregarded. The presence of a second ice indicates a more complex system than H₂O-NaCl-MCl-XCl-X system has been assumed.

Using Brown and Lamb's equation (1989) for the system H_20 - NaCl - KCl in conjunction with Flincor (Version 1.4) software, the average salinity was calculated to be 17.907 wt % NaCl equivalent (Fig. 5.3).



Figure 5.1: Fluid inclusion map showing 4 populations, A, B ,C and D (as described in the text), in quartz veining of late hydrothermal stage, Kalkdam.

Homogenisation temperatures for inclusions of population A are 117°C \pm 0.25, (Fig. 5.4). The relevant isochore was determined using the Brown and Lamb (1989) density equations for the system H₂0 - NaCl - KCl, (Fig. 5.5). The fluid is slightly more dense than pure water with a density of 1.075.



Figure 5.2: Histogram of final melting temperatures (T_{fin}) for inclusions of population A, late stage vein



Figure 5.3: T-X plot for low salinity part of system H2O-NaCl, Fig. 7.10 (after Goldstein and Reynolds, 1994).



Figure 5.4: Histogram of homogenisation temperatures (T_h) for inclusions of population A, late stage quartz veins, Kalkdam. $H_20 - NaCI - KCI$



Figure 5.5: P-T diagram with density isochore for population A inclusions, late stage quartz, Kalkdam.

5.3 Discussion

The information obtained from the inclusions of population A shows a similarity to inclusions from many other Mississippi Valley type (MVT) lead/zinc deposits (Fig. 5.6). Roedder (1984) has observed, that although many MVT deposits occur in varying depositional environments and deposit a wide range of ore minerals, the fluid inclusion data remain remarkably uniform.

Mississippi Valley Type fluid inclusion homogenisation temperatures usually range between 100° and 150°C; salinities are often >20 wt % NaCl equivalent (not less than 15 wt % NaCl equivalent), with a low total pressure (but greater than the vapour pressure of the brines) so that no boiling has occurred. Although there is no evidence of boiling in the samples from Kalkdam (the liquid to vapour ratio remains constant within each population), these are late stage veins which formed after the fluid had cooled significantly. There is no evidence to suggest that boiling did not take place during the main hydrothermal stages, but the possibility cannot be ruled out. The brecciation process may indeed have been a direct result of boiling and vapour phase expansion (Nash *et al.*, 1995).

Other Mississippi Valley type deposits have fluid temperatures and salinities similar to those found at Kalkdam and Katlani (Fig. 5.6). This, however, relates to the primary fluid inclusions found in milky quartz which have formed during the main stages of the hydrothermal event. The fluid inclusions of population A are regarded to be primary in origin (angular morphology and clustering), and found in late stage veins: the quartz that hosts these inclusions is very transparent and the inclusions themselves are scarce. It can therefore be assumed, that crystallisation of this specific quartz occurred during the later stages of the hydrothermal activity and the mineralisation took place at higher temperatures. As mentioned in chapter 3, the higher formation temperatures of chlorite gangue confirm this.

Epithermal vein type mineralisation are usually formed from fluids at higher temperatures and lower salinities than those of MVT (Roedder, 1984). The Kalkdam and Katlani fluids are therefore intermediate between the MVT and epithermal deposits. The resulting temperatures and salinities at Kalkdam and Katlani could have arisen from a variety of different processes, since they do not fit entirely with the general characteristic of either the MVT or epithermal vein type processes. Kalkdam fluids are similar to MVT in density and salinity, but differ in temperature and cation abundance (Na and Ca are most abundant in MVT - Roedder, 1984). Temperatures are similar to epithermal deposits, but the salinity is greater - meteoric water (<5 wt% NaCl equivalent) is the major source in these deposits (Roedder, 1984). Atmospheric precipitation has been recorded (raindrop imprints) in Platberg (~ 2.7 Ga) sediments (Van der Westhuizen *et al.*, 1989), which suggests that meteoric water could have contributed to the fluid phase at Kalkdam. Mississippi Valley type deposits form by migration of brines up-dip onto the carbonate shelf from nearby sedimentary basins (Snyder, 1967). Leaching of Ca from the carbonates gives the fluid a high Ca content with minor K, Mg and B (Roedder, 1984). The fluid involved at Kalkdam may have a similar origin, but fractures in the underlying rocks and basement may have allowed deep penetration which heated the fluids and enabled them to leach potassium from the Makwassie Formation and/or the basement. This would account for the similar salinity and fluid density but differing cation concentrations and temperatures. Russell and Skauli (1991), have proposed a similar mechanism for the formation of the Irish lead-zinc and the English Pennine deposits, where brines circulating in convective cells at depth were able to maintain higher temperatures than those reached at the bottom of the sedimentary basin.



Figure 5.6: T_h (°C) versus T_{fm} (°C) showing comparison of Kalkdam with other Pb - Zn deposits.

It is also possible that Kalkdam and Katlani were formed in the same way as other, younger MVT deposits, but the greater temperatures observed were facilitated by a heightened geothermal gradient during the Proterozoic which lessened during the Phanerozoic when most MVT deposits were formed. This is however, purely speculative.

The deposit at Kalkdam is again similar to MVT deposits in terms of the type of mineralisation found: Pb usually dominants over Zn. The style of mineralisation however differs, with MVT deposits occurring as stratabound, solution collapse breccias, whereas Kalkdam breccias formed as a result of hydraulic fracturing in response to pressure fluctuations when the fluid encountered impermeable rocks.

Many of the Mississippi Valley type occurrences have been shown to involve the mixing of 2 discrete fluids of differing temperatures and salinities (Duane and de Wit, 1988; Leach, 1994). In the case of the Viburnum trend MVT deposits, fluid inclusions suggest the presence of a regional wide fluid which mixed with the Viburnum trend fluid and resulted in precipitation of the ores, not only in the main ore areas, but also sporadically throughout the region (Leach, 1994). For fluids to mix, they must be of approximately the same density (Lindblom, 1986).

When fluids having different densities come into contact with one another, the more dense fluid will flow beneath the less dense fluid and very little mixing will occur. With continued cooling, the densities of each fluid may approach equilibrium when mixing will proceed. Lindblom (1986) has suggested that for the sandstone hosted MVT deposits at Laisvall in Sweden, mixing occurred between a hot highly saline fluid and cooler, less saline ground water.

If Kalkdam is similar to other MVT deposits and has formed as a result of fluid mixing, the random inclusions of population B may represent another fluid Although detailed thermometric investigations were not carried out on this population, they were observed to freeze around -93°C and remelt (eutectic melting) at -56.5°C which suggests it to be CO_2 rich. At least four other ices were observed to melt prior to final melting, which suggests a more complex solution. These melting temperatures were not accurately determined. The high viscosity of population B suggests a highly saline aqueous brine, and may represent a fluid typical of MVT deposits (Roedder, 1984).

This highly saline brine may have mixed with regional groundwater of low salinity and temperature, which could have diluted the solution to the salinity recorded. Groundwater was probably present in the karst features of the overlying carbonates; joints and faults in the carbonates and Allanridge volcanics as well as in the porous flow tops of the Allanridge. Enrichment in CO_2 may have arisen from interaction with the carbonates.

If this mixing occurred, it may also be partly responsible for the precipitation of the ore minerals in the breccia zones, however further fluid inclusion studies are required to confirm or disregard this possibility.

5.3 Summary

- Four different populations of inclusions exist in late stage quartz veins at Kalkdam and Katlani. Thermometric analyses were only conducted in detail on population A, a L + V aqueous brine inclusion represented by the 4 component system NaCl-KCl-H₂O-X.
- Final melting temperatures are -12.9 ±0.1 °C relating to a salinity of 17.907 wt% NaCl equivalent (5 times the salinity of seawater).
- Homogenisation temperatures give a minimum trapping temperature of 119°C which relates to the later stages of the hydrothermal event. Main stage temperatures are believed to have been much higher ≈ ≤ 300°C.
- 4. Salinities are similar to those of fluids involved in Mississippi Valley Type mineralisation, but temperatures are similar to epigenetic vein deposits.
- 5. MVT brines which had access to the deep basement via faults and fractures, are probably responsible for the mineralisation observed in the breccia zones at Kalkdam.

6. ISOTOPE ANALYSES

6.1 Introduction

Rb/Sr, Pb/Pb and S isotope studies were conducted on secondary minerals and ore minerals found at the locations of Kalkdam and Katlani. Secondary chlorite, calcite and altered whole rocks were chosen for Rb/Sr analyses, whilst galena and sphalerite were used for lead and sulphur studies. These studies were carried out in order to constrain the timing of this hydrothermal event and to identify the metal and sulphur sources. The sulphur source may also give information of the fluid source.

6.2 Rubidium/Strontium

The Rb/Sr technique is considered to be a very useful tool in determining the time of crystallisation of magma bodies as well as timing metamorphic events. Radioactive ⁸⁷Rb decays to ⁸⁷Sr by emission of a β particle. Rb has one other isotope: stable ⁸⁶Rb. Sr has 4 naturally occurring isotopes, all of which are stable. The amount of Sr found in a mineral at any one time is a function of the initial value of Sr incorporated into the crystal at the time of its formation and the amount of ⁸⁷Sr which has accumulated through the decay of ⁸⁷Rb. The duration for which the system has been closed will affect the amount

of radiogenic Sr produced. Since the half life of ⁸⁷Rb is known to be 48.8 x 10^9 years, with a decay constant of 1.42 x 10^{-11} y⁻¹ (Steiger and Jäger, 1977), the age can be deduced, providing the initial ⁸⁷Sr/⁸⁶Sr ratio is known. If the concentrations of Rb, Sr and the ⁸⁷Sr/⁸⁶Sr ratio are measured from a suite of genetically related rocks, with a wide range of Rb and Sr values, plotting ⁸⁷Sr/⁸⁶Sr against ⁸⁷Rb/⁸⁶Sr, should give a straight line with the equation :

$$y = b + mx$$

where b is the point at which the line crosses the y-axis, representing the initial ⁸⁷Sr/⁸⁶Sr ratio, and the gradient of the line (mx) represents the age of the suite. This line is called an isochron and can only be applied to rocks of the same age and initial ⁸⁷Sr/⁸⁶Sr ratio (Faure, 1986).

On crystallisation, Rb^+ , which is chemically similar to K^+ , will substitute for K^+ in K-rich phases such as K-feldspar. Similarly, Sr^{2+} will substitute for Ca^{2+} in phases such as plagioclase. Both ⁸⁷Rb and ⁸⁶Rb will be incorporated into a mineral at the time of its formation along with a mixture of Sr isotopes. On closure of the system, the isotopic clock is activated. An open system becomes closed when the temperature drops to a level at which ionic diffusion throughout the crystal lattice and across grain boundaries becomes negligible (Faure, 1986). In the case of metamorphic rocks that have undergone heating only, whilst remaining a closed system, Rb/Sr dating is very useful in that the original age of the rock as well as the age of the metamorphism can be determined (Faure, 1986). Remobilisation of ions into new minerals due to temperature increases will cause a change in the ratios between different minerals although the ratio of the bulk rock will remain unaltered. Therefore, newly formed minerals which are rich in Rb will give a model age for the metamorphic event. On recooling, a new "initial" ratio value for the new secondary minerals will become effective and a new isotopic clock activated. Minerals with low Rb concentrations (e.g. calcite) will have ⁸⁷Sr/⁸⁶Sr values which have not changed from the bulk rock value. These can be taken as initial values for a model age to be calculated (Faure, 1986).

For rocks which have been subjected to metasomatic processes, components are both added and removed, which renders the system open. Both Rb and Sr are mobile elements and will be preferentially concentrated into a fluid phase (Winter, 1995). Providing fluid action throughout a rock is pervasive, significant ion exchange between rock and fluid will take place, and new minerals will possess a component of the fluid phase. Further cooling and a decrease in fluid migration will close the system, and a new "reset" isotopic clock will be activated. In this case, determination of the formation age of the rocks is no longer possible. As indicated in both chapters 3 and 4, the process of alteration at Kalkdam is open system metasomatism, therefore, the original age of the lavas cannot be determined as the bulk rock ratios will have been completely reset by the event.

6.2.1 Sample selection

Two of the most altered samples were chosen for analyses on amygdaloidal chlorite, amygdaloidal calcite, and crushed rock matrix (without amygdales). A whole rock sample of the least altered specimen was also analysed to determine if the host volcanics were the source of the Rb and Sr.

Sample preparation techniques and analytical procedures are described in appendix A.

6.2.2 Presentation of results

Chlorites and altered whole rock plots of 87 Rb/ 86 Sr vs 87 Sr/ 86 Sr (Fig. 6.1) give a good isochron of 2014.05 ± 38.02 m.y (using GEODATE v 2.2; Eglington and Harmer, 1991). This is the age at which the hydrothermal fluid flowed through the Allanridge volcanics and reset all the pre-existing isotopic decay systems, i.e. the age at which the system cooled and became closed. This marks a lower age limit for the hydrothermal event and is similar to that obtained by Duane *et al.* (1991) for Mississippi Valley type Pb/Zn deposits in the Transvaal dolomites; for metasomatism of the Ventersdorp lavas at T'Kuip (Cornell, 1978) and various other formations across the Kaapvaal craton (Allsopp, 1961; Crockett, 1971).



Figure 6.1: Isochron diagram showing relationship between ⁸⁷Rb/⁸⁶Sr vs. ⁸⁷Sr/⁸⁶Sr of altered whole rock and chlorite samples from Kalkdam.

Sample	Rb (ppm)	Sr (ppm)	⁸⁷ Rb/ ⁸⁶ Sr ⁸⁷ Sr/ ⁸⁶ Sr		Ro (2.014)
3 WRa	7.589380	48.7279	0.303875 0.720950		0.71226
3 WRb	7.532000	48.7000	0.301148	0.301148 0.700302	
F4t WRa	76.234375	68.9884	2.167117 0.773729		0.71175
F4t WRb	76.551450	68.9884	2.176128	0.773729	0.71149
6 WRa	18.494290	50.4684	0.715598	0.729862	0.70940
6 WRb	19.029870	53.6150	0.693105	0.729829	0.71000
7 WRa	113.096500	64.2918	3.462616	0.811774	0.71274
9 WRb	68.176670	56.3537	2.373528	0.7 7784 0	0.70996
F4t CHL	491.956500	10.3290	124.384524	4.215662	0.65832
F4t CHLb	486.383100	11.5486	105.992314	3.688022	0.65669
7 CHL	502.847300	13.3158	91.967172	3.261526	0.63131
7 CHLc	497.338400	13.3158	90.959643	3.261526	0.66012
9 CHIL	433.844800	8.8469	131.542425	4.557440	0.79539
9 CHLb	436.183100	8.5407	140.477181	4.915347	0.89777
9 CHLc	431.506500	8.8469	130.833448	4.557440	0.81567
F4t CAL	0.040170	32.5592	0.002399	0.705524	0.70545
9 CAL	0.040100	62.3042	0.001253	0.704295	0.70426
9 CALb	0.040100	47.9276	0.001629	0.701277	0.70123

Table 6.1 gives Rb and Sr concentrations and ratios for samples analysed from Kalkdam.

Table 6.1: Concentrations and ratios for Rb/Sr samples. Abbreviations: WR = whole rock, CHL = chlorite, CAL = calcite. Sample 3 is least altered, followed by 6 with medium alteration and then F4t, 7 and 9 which are all highly altered. $Ro_{(2.014)} = {}^{87}Sr/{}^{86}Sr$ at 2.014 Ga. Calculated using ${}^{87}Sr/{}^{86}Sr = ({}^{87}Sr/{}^{86}Sr)_i + ({}^{87}Rb/{}^{86}Sr)\lambda t$.

Individual mineral ratios can give some information on the source of the strontium. The chlorites with their high ⁸⁷Rb/⁸⁶Sr ratios, are very sensitive as geological chronometers, which increases as the parent/daughter ratio increases (Faure, 1986). This high sensitivity, however, renders the initial values meaningless as very slight changes in the age used (i.e. the slope of the isochron) can give rise to significant changes in the initial ratio obtained (i.e. crossing point on y-axis) (Faure, 1986). Sr substitutes very readily into the calcite structure due to the chemical similarity between Ca and Sr. Rb is chemically dissimilar in terms of ion size and charge and does not readily substitute into the structure. Values for both ⁸⁷Rb/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr in calcite are therefore very low and are of little value as geochronometers. The calcite ⁸⁷Sr/⁸⁶Sr ratio, however, has not changed significantly since formation, and may therefore represent the initial ⁸⁷Sr/⁸⁶Sr value of the fluid (Kessen *et al.*, 1981), and give information to the source of the radiogenic Sr.

6.2.3 Discussion

As discussed in the petrography section, textures observed indicate that the calcite in the amygdales, and as pseudomorphs are replaced by quartz and chlorite. The quartz and chlorite is associated with lead and minor zinc mineralization, whereas the calcite is intimately associated with sphalerite. The altered whole rock samples have also been extensively silicified concurrently with the chlorite formation. The calcite therefore, represent a previous alteration product prior to the hydrothermal event. Calcite

precipitation may have occurred only as a result of supergene processes - perhaps meteoric waters percolated downward through the dolomites of the Transvaal sequence to recrystallise in the amygdales of the lower Allanridge formation, or it may have formed by release of Ca from plagioclase in response to burial processes (Kuniyoshi and Liou, 1976). Comparing the Kalkdam calcite ⁸⁷Sr/⁸⁶Sr ratio (mean 0.70369) with ⁸⁷Sr/⁸⁶Sr ratios at 2014 m.y. for the Griqualand dolomites above (0.7092: Duane *et al.*, 1991) and the Ventersdorp mafic lavas (0.7043: Armstrong, 1987), the percolation of calcite rich fluids from the overlying Transvaal sequence can be discarded. The Vryburg Formation also yields values similar to the dolomites (Armstrong, 1987). It is therefore concluded that the calcite and associated sphalerite observed at Kalkdam arose from calcium mobilisation during burial and fluid activity prior to the main hydrothermal event. Use of the calcite ⁸⁷Sr/⁸⁶Sr as an initial ratio also results in an impossible model age for the hydrothermal chlorites.

The highly altered whole rock samples show a wide range of calculated initial ⁸⁷Sr/⁸⁶Sr ratios (mean 0.71148, range 0.70996 - 0.71274). This suggests that the alteration has not been completely pervasive with variable mixing of the two reservoirs. The "unaltered" whole rock sample does not differ significantly (0.71226) from the altered, but with only one useful initial ratio, it is subject to error. The mean value of the unaltered samples is similar to that of the calcite and may represent the initial ratio for the unaltered whole rock. This suggests that the Sr in the chlorites is derived from an external source.

The strontium source is likely to be significantly more radiogenic than the unaltered lavas. Mixing of the unradiogenic Allanridge strontium with radiogenic strontium will result in the intermediate value of the altered lavas. The overlying lavas and dolomites of the Griqualand West sequence are too unradiogenic to have contributed to the radiogenic content of the altered lavas. Many possible sources based on ⁸⁷Sr/⁸⁶Sr values at ca. 2.0 Ga exist (Duane *et al.*, 1991). Of these, only the Transvaal dolomites (0.716), the Vredefort and Johannesburg domes (0.7244) and the Zoetlief Formation (0.7366) will be diluted by the unradiogenic nature of the Allanridge lavas. It is unlikely that fluids migrating from as far as the Transvaal basin or Vredefort region could maintain their original isotopic signature, and it is assumed that the Makwassie/Zoetlief quartz-feldspar porphyry was the dominant contributor to the Sr/Sr isotopic signature of the fluid.

It is apparent that the hydrothermal fluid introduced much Rb into the host rocks and gave rise to Rb rich chlorites, which over time have developed high ⁸⁷Sr/⁸⁶Sr ratios. Although Rb is very mobile, and could have been leached from many possible sources, such large values indicate derivation from an enriched source. With increasing crystallisation of a magma, Rb will preferentially remain in the melt increasing the Rb/Sr ratio as Sr is incorporated into plagioclase (Faure, 1986). Of all the possible sources, the Makwassie quartz-feldspar porphyry will have the highest Rb/Sr ratio. The basement could also have contributed to the Rb content, especially since in the Griqualand West sub-basin, the Klipriviersberg Group is not present.

6.3 Natural lead analyses

Galena's from Kalkdam and Katlani as well as one sphalerite sample were chosen for Pb/Pb analysis. Since galena consists of lead and sulphide, with no U or Th, the lead present is "dead" lead. In other words, at the time of crystallization, this lead system became closed. The lead ratio observed today is the same as the ratio at the time of formation. By the lead - lead method, the date obtained is a theoretical age for the time at which the galena was formed. This is also the time at which the decay of U and Th to Pb terminated and the system died. This is termed the model age and will usually give the upper age limit for the deposit (Faure, 1986). If the amount of radiogenic lead is large in comparison to the non- radiogenic lead, it indicates that prior to crystallisation, these leads were evolving in an environment which had a large U/Pb or Th/Pb ratio. If, however, the non-radiogenic lead is more in abundance, the leads have evolved in a depleted environment in terms of U and Th. This can help constrain the source region of the leads.

Although the Kalkdam whole rock samples give a wide range of values, when plotted on the ²⁰⁶Pb/²⁰⁴Pb vs ²⁰⁷Pb/²⁰⁴Pb diagram (Fig. 6.2), the "unaltered" samples (3WR) mark a linear array. The altered samples (7WR) are more varied, but one sample plots close to the galena sample. The Katlani samples are noticeably less radiogenic, but due to the lack of galena samples from Kalkdam, at this stage, it cannot be established if the lead is derived from a single or multiple sources.



Figure 6.2: ²⁰⁷Pb/²⁰⁶Pb vs ²⁰⁶Pb/²⁰⁴Pb for Kalkdam and Katlani ore and whole rock samples.

Sample	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb	²⁰⁴ Pb/ ²⁰⁶ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb
30 Gal	14.15307	14.76109	1.043074	0.070654	2.406280
RK 7 WRb	13.93829	14.84785	1.058112	0.071516	2.407682
RK 7WR-b	14.12279	14.54128	1.029454	0.070908	2.371645
RK 3WR-b	13.59041	14.07529	1.036120	0.073647	2.349096
3 WRb	15.21695	14.47107	0.956130	0.066888	-
3 WR	16.25244	14.88136	0.915645	0.061493	2.161759
7 WR	15.39335	15.19602	0.986634	0.064897	2.307886
KL SPH	13.56403	14.55336	1.072777	0.073726	2.451960
KL Gal	13.67190	14.62260	1.070647	0.032153	2.448860
KL SPH-b	13.59459	14.52524	1.068840	0.073559	2.437920
KL1 Gal-b	13.45303	14.66628	1.069630	0.074330	-
KL1 Gal	13.43500	14.35055	1.068221	0.074460	2.429950

The Pb/ Pb results (using GEODATE v 2.2; Eglington and Harmer, 1991) for Kalkdam and Katlani are given in Table 6.2. below:

Table: 6.2. Lead isotope results for samples from Kalkdam and Katlani (RK=Kalkdam; KL=Katlani; WR=whole rock; Gal=galena; Sph=sphalerite).

The model ages (Table 6.3) for the ores and the whole rocks however, display Katiani to be significantly older than Kalkdam and may suggest derivation from a different source or sources.

Sample	Model age	Sample	Model age
3 WR	0.316 Ga	KL Sph	2.533 Ga
3 WRb	0.214 Ga	KL Sph-b	2.435 Ga
3 WR-b	1.174 Ga	KL Gal	2.547 Ga
7 WRb	2.622 Ga	KL1 Gal	2.266 Ga
7 WR-b	1.808 Ga	KL1 Gal-b	2.878 Ga
30 Gal	2.234 Ga		

Table 6.3: Pb model ages for Kalkdam and Katlani whole rock and ore minerals.Abbreviations as for Table 6.2.

6.3.1 Discussion

The model ages for the "unaltered" Kalkdam whole rock sample are extremely young possibly due to the removal of radiogenic lead. The range of model ages given for these whole rock samples is quite broad and probably indicates variable Pb removal and overprinting. This emphasises that the ore deposition, hydrothermal alteration and the fluid flow was not entirely pervasive in this region.

Samples from Kalkdam and Katlani were compared with ores from other Pb/Zn deposits in the Griqualand West sub-basin (Nicholaysen *et al.*, 1958; Duane *et al.*, 1991), and a simple pattern emerged. The outer locations (Pering, Katlani and Geelbekdam) display the least radiogenic values. Not only is the range of lead ratios from Pering very similar to the range at Katlani, but the least radiogenic value is also approximately the same. Alternately, the other samples around Griquatown cluster tightly together close to the Kalkdam galena and altered whole rock ratios (Fig. 6.3). A radiogenic contour map (²⁰⁶Pb/²⁰⁴Pb) of the Griqualand West sub-basin deposits (Fig. 6.4) shows much more radiogenic lead in the deposits around the Griquatown fault zone which suggests that these deposits have a more radiogenic source than the outer localities.

Although Pering hosts the least radiogenic lead, the range of leads does overlap slightly with the other Griquatown deposits, and may indicate that Pering contains a component of these leads. As mentioned by Southwood (1986), Pering is believed to have experienced a

secondary remobilisation event, where the possibility of external lead introduction has not been ruled out.



Figure 6.3: Location of other Griqualand West lead-zinc deposits. P = Pering; BP = Bushy Park; L = Langrug; KF = Kalkfontein; B = Balloch; G = Geelbekdam; KD = Kalkdam; KL = Katlani.



Figure 6.4: Radiogenic contour map of Griqualand West sub-basin (abbreviations as in Fig. 6.3).

As mentioned in chapter 2, the remobilised leads are represented by the breccia zones, whereas the stratabound mineralisation is assumed to represent the primary event. The one galena sample from Kalkdam (30 GAL) comes from a breccia zone and probably relates to this remobilisation event. Galena from amygdales at Kalkdam ought to relate to the first event and possess the unradiogenic characteristics of Katlani leads. Further analytical studies need to be carried out to confirm this.

Evidence suggesting that the Griqualand West sub-basin has experienced two hydrothermal events has been established not only by field and ore occurrences (Southwood, 1986; Altermann, 1997), but also by the lead isotope results. The remobilisation event is more evident around the Griquatown fault zone which obviously played an important role as a pathway of fluid migration (Altermann, 1997). The Pering deposit is also proximal to a large fault zone, which, like the Griquatown fault was probably exploited during the remobilisation event.

The difference in Pb isotope ratios between localities does suggest that along with the primary event lead, the second hydrothermal fluid contained a component of lead from a different source. Figure 6.5 shows the live lead arrays of various possible lead sources. Back projection of these arrays cross-cut the galena array and suggest that the Ventersdorp mafic lavas (Allanridge and Rietgat) provided the least radiogenic leads observed at Katlani and Pering. Since mafic rocks are usually associated with copper and zinc deposits (Hutchinson, 1973), this would account for the predominance of sphalerite over galena for the first event.

Back projection of the Zoetlief/Makwassie array cuts the Griqualand West array at the lower end of the Griquatown deposit range, and probably has contributed significantly to the second remobilisation event. It is a likely candidate since at the time of its crystallisation, the Makwassie quartz porphyry would have had high U/Pb and Th/Pb ratios due to the preferential concentration of U and Th into silicate melts compared to Pb (Wilson, 1989).



Figure 6.5: ²⁰⁷Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb of Griqualand West leads and possible Pb source arrays.

The Makwassie and Zoetlief Formations have been dated by U/Pb (zircon) and other methods at approximately 2700 Ma (Armstrong, *et al.*, 1991, and see other references in Van der Westhuizen *et al.*, 1991). Whole rock lead ratios, however, give it a reset age of 2000 my. At this time, the system was flushed by hydrothermal fluids which removed uranogenic and thorogenic lead but did not remove U and Th (F.J. Kruger: pers. comm., 1997). Thus the isotopic clock was reset at this time. Ordinary lead ratios today suggest that the decay of U and Th has been occurring since 2000 m.y. This stripping event coincides with the Rb/Sr date for the hydrothermal event.

The Makwassie array cuts the galena array at the lower end of the more radiogenic Griquatown samples. The source of the most radiogenic leads has not yet been established, but the basement granites may have contributed significantly to the radiogenic lead content of the ores.

6.4 Sulphur analyses

Four different species of sulphur exist in nature of which ³⁴S and ³²S are the most abundant. The relative abundance's of these are 95.02 % and 4.21 % respectively (Faure, 1986). The ratio of these two isotopes differ from one environment to another due to processes, operating now and in the past, which fractionate each isotope from one another. The ratios are standardised to the Canon Diablo meteorite (troilite, FeS) reference standard. This is expressed by:

$$\delta^{34}S \%_{00} = \left[\left(\frac{{}^{34}S}{^{32}S}_{\text{(sample)}} - \frac{{}^{34}S}{^{32}S}_{\text{(standard)}} \right] \frac{{}^{34}S}{^{32}S}_{\text{(standard)}} \right] \times 1000$$

The δ^{34} S values obtained for galenas and sphalerites from Kalkdam and Katlani show a very limited range between -3.4 and -6.1 ‰ (Fig. 6.6).

6.4.1 Discussion

The narrow δ^{34} S range for both Kalkdam and Katlani indicates a specific source region (Ohmoto, 1986) and corresponds with δ^{34} S values for volcanic H₂S (Fig. 6.6). Two possible volcanic sources are the Ongeluk Andesite or the Hartley Andesite Formation. The Ongeluk andesites of the Transvaal Supergroup are dated at 2222 m.y (Cornell *et al.*, 1996). This marks a time span of 208 m.y between active seafloor hydrothermal processes and deposition of ore minerals 100 km from the craton margin. Lewchuk and Symons (1995) found that most hydrothermal mineralising events have only a 4 m.y duration, which suggests that it is highly unlikely that the Ongeluk Andesite Formation was the sulphur or fluid source. The Hartley Andesite Formation, within the Olifantshoek Group, has been assigned a variety of ages by different workers (minimum age):

2070 ± 90 Ma (Crampton, 1974); 1929 ± 3 Ma (Cornell *et al.*, 1998) 1928 ± 4 Ma (Beukes and Smit, 1987) 1881 ± 57 Ma (Armstrong, 1987).

It is possible with this range, that the Hartley Andesite Formation may have contributed the sulphur to the sulphides found at Kalkdam and Katlani, however it is not conclusive and further refinement of its age is required.

Other possible alternatives for the sulphur source are the volcanics of the Ventersdorp Supergroup themselves:

- 1. the Makwassi quartz-feldspar porphyry;
- 2. the Rietgat andesitic lavas and
- 3. the host Allanridge andesite lavas.

It is difficult in this instance to distinguish between the mafic and felsic volcanics in terms of their S isotopic signatures. Present day felsic volcanics show a wide range of δ^{34} S values (Hoefs, 1980), whereas the S isotopic composition of mantle derived igneous rocks is similar to that of meteorites with a δ^{34} S value close to zero (Shima *et al.*, 1963). Other workers have since confirmed this e.g. Smitheringale and Jensen (1963); Schneider (1970); and Kanehiro *et al.*, (1973).

Differences in sulphur isotope signature between mafic and felsic volcanics can possibly arise by degassing of SO₂. SO₂ is enriched in 34 S compared with the H₂S in the melt, resulting in a depletion in δ^{34} S in the remaining melt (Sakai *et al.*, 1962). Release of SO₂ during extrusion will be far greater for the felsic lava than for the mafic as the eruptions are more explosive - this may render the felsic volcanics more severely depleted in $\delta^{34}S$ than the mafics. Outgassing is more intense for sub-aerially extruded volcanics than for those extruded in a sub-marine environments and can account for greater depletion of δ^{34} S. All three formations were extruded sub-aerially (Van der Westhuizen *et al.*, 1991). Sulphide minerals from granitic rocks show wide variations in their $\delta^{34}S$ values, which range from +9 to -11³. This indicates that the S isotopic composition has been altered during or since crystallisation (Faure, 1986). Crustal contamination of mafic magmas with rocks of sedimentary origin can upset the sulphur isotopic signatures. The Makwassie quartz-feldspar porphyry has been dated at 2708 \pm 5 m.y. (Armstrong et al., 1991) and is known to have assimilated crustal material by the presence of xenocrystic zircon (Rettmann: pers. comm., 1991). Alternately, M.P. Bowen (1984) has suggested that the Makwassie quartz porphyry is a crustal melt rather than a differentiate and therefore will have similar δ^{34} S values to the Rietgat and Allanridge lavas. On the other hand, Crow and Condie (1988) have suggested that the Makwassie Formation is related to the Rietgat-Goedgenoeg basaltic andesites by 25 - 45 % fractional crystallisation by removal of plagioclase and pyroxene with minor amounts of magnetite, zircon and apatite. It is therefore inconclusive to suggest any of the above volcanic formations as the single

sulphur source, indeed it is possible that all 3 formations could have contributed to the sulphur content of the ores.

Sedimentary rocks have an isotopic signature of their own which is derived from the biogenic reduction of sulphate to sulphide which causes fractionation of sulphur isotopes. In modern sediments, a wide range of δ^{34} S values are observed with relative proportions skewed in the favour of the lighter ³²S isotope (Cameron, 1982). This is a generally accepted process, but much controversy exists over the time at which bacterial reduction became important, and whether it plays a significant role at Kalkdam and Katlani.

The parameters required for reduction to take place are the availability of seawater sulphate and the presence of sulphate-reducing bacteria. Sulphate deposits exist, but are rare in Archaean sequences (Cameron and Hattori, 1987), which may be due to their low preservation potential (Ohmoto and Felder, 1987). Most workers agree that an isotopic transition took place at 2.3 Ga (Cameron, 1983), although evidence does suggest that in localised restricted basins (Canadian Shield especially), bacterial reduction was a major process from about 2.7 Ga (Thode and Goodwin, 1983; Cameron and Hattori, 1987). The narrow range and signature for Kalkdam and Katlani rules out a restricted basin source. Crustal contamination of the Makwassie would have had no effect on the δ^{34} S signature. The volcanic sulphur source observed at Kalkdam and Katlani is therefore still ambiguous.

In the case of South Africa, Hattori *et al.* (1983) showed that 2.5 Ga sulphates and sulphides from both organic and carbon-free environments did not differ significantly in δ^{34} S values i.e. no isotopic fractionation had occurred. The sedimentary sulphides existing at this time must therefore have formed without the aid of sulphate-reducing bacteria (Monster *et al.*, 1979). Other workers have confirmed these findings in studies on conglomerates of the Witwatersrand basin, South Africa and in sedimentary rocks to the south of the Sudbury basin (Pretorius, 1976). Cameron, (1982), observed an isotopic transition at 2.35 Ga from a consistently small positive δ^{34} S to a negative value in the sediments of the Malmani sub-group of the Transvaal Supergroup. δ^{34} S values range from $-14 \rightarrow +16\%$ with a mode at -3%. The overlying Penge Iron Formation has a mode of -5% and a much narrower range from $-8 \rightarrow -2\%$.

A limited number of samples from equivalent formations in the Griqualand West sub-basin (Campbellrand subgroup; Kuruman and Griquastad Iron Formations) have been analysed and show similar signatures (Strauss and Beukes, 1996).

6.4.1 Sulphur isotope geothermometry

Ohmoto and Rye (1979) have shown experimentally, that when two sulphur bearing compounds are in isotopic equilibrium, the isotopic fractionation factor is dependent on
the equilibrium constant which itself is a function of the temperature. An equilibrium relationship between galena and sphalerite as observed at Kalkdam is given as

$$Zn^{34}S + Pb^{32}S \iff Zn^{32}S + Pb^{34}S$$

The isotope fractionation factor (α) is related to the equilibrium constant (K) as follows:

$$\alpha_{(ZnS-PbS)} = \left[\left(\frac{{}^{34}S}{3^{2}S} \right)_{ZnS} / \left(\frac{{}^{34}S}{3^{2}S} \right)_{PbS} \right] = K$$

The difference (Δ) in the δ^{34} S values between the two compounds is related to α (Ohmoto and Rye, 1979). The isotopic equilibrium constants are a function of temperature, and for most reactions are approximately proportional to $1/T^2$ (K). Therefore, the temperature of equilibration between two compounds can be defined by measuring the difference in their δ^{34} S values.

Equilibrium isotopic fractionation factors most sensitive to temperature are those between sulphate-sulphide pairs. Preferential enrichment in the higher oxidation states of the heavier isotopes results in large equilibrium factors between oxidised and reduced species. However, these usually give fractionation factors which are lower than the observed equilibrium values and so are unsuitable to obtain the temperature of mineralisation. At Kalkdam and Katlani, no sulphate species are present for reasons previously discussed. Instead galena and sphalerite are the most common ore minerals. Of the sulphide pairs, these are the most useful as geothermometers as they have the greatest fractionation factor at equilibrium and thus give isotopic temperatures very close to the fluid inclusion homogenisation temperatures. This however, is only the case in environments where the pressure is low and where the formational temperatures are greater than 120°C. Equilibrium is very difficult to attain at temperatures below 120°C (Ohmoto, 1986).

Stable isotope geothermometry gives the true temperature of mineralisation, but to be reliable, requires several conditions to be satisfied:

- The fractionation factors are well calibrated and strongly temperature dependent. As mentioned above, the sphalerite-galena pair is the most useful of the sulphide pairs and display the steepest equilibrium fractionation factor slope versus temperature.
- 2. The species were in isotopic equilibrium at the time of deposition. Rollinson (1993) states that agreement of temperature estimates between three co-existing minerals is a good indication of equilibrium. Unfortunately, only two ore minerals from Kalkdam and Katlani were analysed. Although pyrite and chalcopyrite are present at both Katlani and Kalkdam, knowledge of their δ³⁴S values and hence temperature estimates will not necessarily give an indication of equilibrium. This pair of sulphides commonly show disequilibrium possibly as a result that they have not precipitated along with other simple sulphides (sphalerite and galena), or by the same mechanism as the simple

sulphides e.g. by mixing with oxygenated fluid or by reaction with sulphate (Ohmoto *et al.*, 1983). Other methods of determining equilibrium must be utilised e.g. petrographic textural evidence of equilibrium.

They have retained their isotopic composition since formation i.e. isotopic exchange between mineral phases or between fluid and mineral did not occur after formation of the minerals (Ohmoto and Rye, 1979).

Experimental data for simple sulphides residing together (H₂S, ZnS and PbS), suggest that chemical and isotopic equilibrium is easily achieved (Rollinson, 1993). Ohmoto and Rye (1979), have shown that under isotopic equilibrium at 150 °C, the difference (Δ) in δ^{34} S between the simple sulphides should be:

 $\Delta ZnS - H_2S = 0.3 \%$ $\Delta H_2S - PbS = 4.0 \%$ $\Delta ZnS - PbS = 3.7 \%$

These values increase with decreasing temperature. $\Delta_{ZnS-PbS}$ for Kalkdam range between 2.3 and 2.9 % and those for Katlani between 1.1 and 3.2 %. This indicates temperatures above 150°C for both deposits suggesting that equilibrium was probably attained.



Figure 6.6: Comparison of sulphide δ^{34} S values from Kalkdam and Katlani with other environments (after Rollinson, 1993).

Temperatures of formation of the sulphides and therefore of the mineralising fluid were calculated following the experimental relationship given by Ohmoto and Rye (1979). Temperature estimates for Kalkdam range from $228 \rightarrow 290$ °C, whilst values for Katlani showed higher temperatures and a greater range from $290 \rightarrow 540$ °C. The temperatures of formation were calculated using the following equation:

$$1000 \ln \alpha_{sph-gal} = \delta^{34}S_{sph} - \delta^{34}S_{gal} = 0.73(10^6/T^2)$$

Temperature is in Kelvin. It is likely that at these temperatures, equilibrium between the different species present was easily attained.

These temperatures are similar to those calculated for chlorite formation temperatures (chapter 3) and suggest that chlorite and the sulphides were precipitating together in the same temperature range.

6.5 Summary

- Rb/Sr techniques on hydrothermal minerals and altered whole rocks give a well constrained age at 2014.05 ± 38.02 m.y.
- 2. Both rubidium and strontium are derived from an external source.
- 3. Calcite crystals give Sr ratios similar to the Allanridge volcanics at 2000 m.y., suggesting formation by burial processes and not timeously related to the hydrothermal event.
- 4. Lead isotopes suggest 2 or 3 possible lead sources. Source 1: the least radiogenic member correlates with the mafic lavas of the Ventersdorp Supergroup. Sources 2 and 3 are only recorded at a few localities, centred around the Griquatown fault and

relate with the Makwassie quartz-feldspar porphyry and possibly the basement granites.

- Due to the lack of a suitable volcanic sulphur source, the Iron Formations of the Griqualand West sub-basin are believed to be the dominant sulphur source.
- Sulphur isotope thermometry give sulphide formation temperatures similar to chlorite formation temperature (chapter 3) around 300°C.

7. MODEL

Alteration and concomitant mineralisation on the farm Katlani corresponds with the first of two separate mineralisation stages observed on the farm Kalkdam, toward the NE of Katlani. The first mineralising stage, at both localities, was contemporaneous with greenschist facies metamorphism that resulted from rapid subsidence and burial beneath the Griqualand West Sequence.

The secondary mineral assemblages at both Kalkdam and Katlani delineate facies changes in response to increased depth of burial: calcite is increasingly replaced downwards by chlorite, and the presence of actinolite in the lowest flow marks another facies change. Two generations of calcite exist: the first generation, present in the groundmass, amygdales and as pseudomorphs after primary ferromagnesian minerals, is cut by veinlets of the later generation in the flow tops and breccia zones. The first generation is intimately associated with sphalerite, and has Sr-isotope ratios suggesting derivation from the Ventersdorp mafic lavas. The second generation calcite was not analysed for strontium.

Altermann (1997) has suggested that rapid tectonic subsidence during deposition of the Griquatown and Kuruman Banded Iron Formations (2550-2430 m.y.), resulted in the loss of much of their water. This early expulsion by compaction has provided slow moving

low temperature fluids with low salinities, which would have moved laterally out of the BIFs and onto the stable shelf. It is possible that these fluids penetrated into the upper regions of the Allanridge Formation and facilitated the limited movement of Zn and Pb, released during burial metamorphism and the breakdown of pyroxene, amphibole and feldspar from the mafic lavas (Johnson, 1994). Reaction with reduced sulphides in the fluid allowed deposition of the ores in the amygdales at Kalkdam and Katlani. Although ore minerals are preserved predominantly in the amygdales intermediate between the highly porous light amygdaloidal lava and the less porous dark amygdaloidal lava, it is likely that during the first mineralising event, the amygdales in the lightest amygdaloidal lavas also contained an abundance of sphalerite and galena. Dissolution of ore minerals in the most porous zones by the later hydrothermal fluid resulted in a redistribution of the ore minerals.

The second mineralising event experienced by the Allanridge Formation lavas at Kalkdam, created mineralised breccia zones with a predominance of galena, in association with abundant quartz and lesser calcite, over sphalerite. Chlorite and quartz also recrystallised in the highly porous amygdaloidal flow tops at this time, and probably replaced preexisting sphalerite and galena (dissolved and redistributed by the fluid) from the first mineralising event.

The proximity of other similar lead-zinc deposits in the Griqualand West basin as well as the Rb/Sr isotopic age obtained (2014 m.y), suggests the mineral occurrences at Kalkdam

and Katlani are related in space and time to Pering, Bushy Park and other sporadic occurrences in the region (Duane et al., 1991; Altermann, 1997). The similarity in the lead isotope ratios between Kalkdam, Katlani and the other deposits as well as the similarities in the model ages indicates similar lead sources. The oldest possible model age for Katlani galena is 2547 m.y. which is similar to model ages of the early ore observed at Pering (Duane et al. 1991). If the present day lead array for the Ventersdorp mafic lavas is projected back to the ratio that would have been observed at 2014 m.y (Fig. 6.5), it joins the Griqualand West galena array at the least radiogenic end-member. This corresponds with the older Katlani and Pering model ages, and indicates that the least radiogenic end-member is derived from the Ventersdorp mafic lavas. The younger model ages from Kalkdam correlate with those from Bushy Park. The more radiogenic endmember has, however, not been identified, but the Makwassie quartz-feldspar porphyry is known to have undergone a flushing event at the time of the Kalkdam mineralisation (Duane et al., 1991). A back projection line of the present day Zoetlief (Makwassie) Formation cross-cuts the Griqualand West galena array (Fig. 6.5) and is likely to have been a major contributor of lead and potassium. The basement may be the source of the most radiogenic leads observed at Kalkdam.

According to Altermann (1997), the base metal Pb-Zn deposits of Pering and Bushy Park are "typical Mississippi Valley type" (MVT) deposits. The similarities in structure, age and lead isotope ratios between Kalkdam, Katlani, Bushy Park and Pering suggest that, Kalkdam and Katlani can also be regarded as MVT deposits. In classic MVT environments, hot metaliferous basinal brines migrate out of a basin, in response to sedimentary overpressure, and deposit ore minerals on the stable passive margin (Mitchell and Garson, 1981). More recently, it has been observed that MVT mineralisations do not only form in extensional environments as previously thought, but also throughout all stages of basin evolution (Kesler, 1994). These stages are:

- 1. Early: compaction of sediments drives fluids out of the basin onto the surrounding carbonate platform (Jackson and Beales, 1967).
- Regional tilting, where uplift at one side of the basin creates a hydraulic head and fluids migrate by gravitational forces (Cathles and Smith, 1983; Garven, 1985; Bethke, 1986).
- 3. Hinterland recharge of the foreland basin; where deformation of an existing volcanic arc results in greater uplift (Garven and Freeze, 1984; Garven, 1985; Bethke, 1986).
- Late: basin deformation and regional thrusting squeeze deep basinal fluids ahead of the orogenic front (Rickard *et al.*, 1979; Oliver, 1986; Lindblom, 1986; Duane and de Wit, 1988).

From stage 1 to 4, the associated mineral deposits increase in size, number, and spatial distribution, which is related to the volume of water available and the intensity of the fluid

driving force. Kesler (1994), states that once a basinal brine has been expelled, it will deposit ore in the most favourable location available in its flow path, irrespective of lithology. However, as a control on MVT mineralisation, regional thrusting is more important than the presence of favourable host rocks.

Several workers have attempted to understand the mineralising processes which resulted in the MVT deposits at Pering and Bushy Park. Wheatley *et al.* (1986a), suggested basinal overpressure caused dewatering of metal-rich fluids from the underlying Lokammona shales of the Transvaal Supergroup, which became hypersaline and capable of causing chemical dissolution, hydraulic fracturing, resulting in ore deposition in the Reivilo Formation at Pering. In contrast, connate waters rich in lead and zinc expelled from dewatering basinal sediments exploited pre-existing joints and fractures, resulting in hydraulic fracturing and deposition of ore at Bushy Park (Wheatley *et al.*, 1986b). The hypothesis for the Pering formation is unsatisfactory to explain the ore occurrences at Kalkdam and Katlani, since it would be unlikely for fluids from the Lokammona shales to penetrate to the depth of the Allanridge Formation unless faulting provided suitable pathways for fluids to follow. The S-isotope signature of the ores at Kalkdam and Katlani are not compatible with those of the Lokammona Formation. The lead signatures from Pering do not correlate with the Lokammona Formation either, suggesting an alternative metal source. Duane *et al.* (1991) have suggested that regional thrusting during the Kheis orogeny was responsible for the Pb/Zn deposits at Pering and Bushy Park. The fluids, squeezed ahead of the orogenic front, leached lead and zinc from the Makwassie Formation before mixing with cold surface waters of the Red Beds. Deposition occurred in the carbonates in open space collapse breccia and karst features. They explained the deep vein nature of Bushy Park by its closer proximity to the orogenic front. Cornell *et al.* (1998), however, have redated the Hartley Andesite Formation at 1929 m.y., which relates to the final extension phase prior to the Kheis compression event.

The size of the Griqualand West deposits are small in comparison with deposits that are known to be associated with the final stages of geosynclinal closure (Kesler, 1994), which again suggests an alternative driving force for the fluids.

Martini *et al.* (1995) have suggested a more "classic" extensional environment where basinal brines were heated by circulation into pre-Chuniespoort rocks and leached metals from the rocks they permeated, and then rose as hydrothermal plumes to shallow depth where they deposited ores after mixing with waters of surficial origin.

This scenario fails to mention the pathways of fluid flow - the rocks beneath the Ghaap Group in the Griqualand West Sequence are not particularly permeable. Faults would be required to focus the flow of fluids into the underlying rocks (Clendenin *et al.*, 1994; Bjorlykke, 1993). Haggarty and Bottrell (1997), have suggested that fractures initiated by

strain relaxation after regional deformation can facilitate deep penetration by fluids downward into the basement where they are able to leach metals.

Altermann (1997) mentions the existence of a volcanic arc south of Prieska between 2588 and 2549 m.y. and evidence of deformation to the south of the Griquatown fault dating from 2430-2223 m.y. The deformation is contemporaneous with deposition of the Griquatown and Kuruman Banded Iron Formations, and may relate to deformation of this volcanic arc. Fluids available for migration were possible released as a result of this by method of hinterland recharge. If this is the mechanism of fluid migration that resulted in the ore occurrences in the breccia zones at Kalkdam the fluids were probably channelled into deep seated faults, which penetrated to the basement. Saline fluids which flowed into these deep faults would have become heated and able to leach metals from the basement and the Makwassie Formation further up the succession.

7.1 Summary

7.1.1 Stage 1

During deposition of the Asbestos Hills Iron Formations, uplift on the southern margin of the basin and dewatering by compaction allowed low salinity, cool waters to slowly migrate out of the basin onto the stable carbonate platform. This fluid leached metals from the Ventersdorp mafic volcanics, later depositing them in amygdales and further up the succession at Pering and Bushy Park. The timing of this small scale fluid migration event was coupled with the burial metamorphism which affected the whole of the Ventersdorp succession.

7.1.2 Stage 2

Later tectonic pressure from the west and continued compaction of the Asbestos Hills Iron Formations squeezed highly saline fluids into deep faults where they migrated downward and with heating were able to leach metals and potassium from the basement and the Makwassie Formation. Further heating caused these fluids to rise upwards - again through fracture systems toward the surface. On meeting the porous lava flows of the upper Allanridge Formation, tapping of fluids occurred resulting in micro-brecciation of the flow tops. Larger breccia zones formed as a result of hydraulic fracturing, which by pressure reduction, deposited galena and remobilised sphalerite. Further upward migration gave rise to breccia zones observed at Bushy Park and Pering, where mixing with cold surface waters (probably of Red Bed origin) resulted in the deposition of ores (Fig. 7.1).



Figure 7.1: Model for Pb/Zn mineralisation process in Griqualand West sub-basin (modified after Beukes, 1986).

7.2 Suggestions for further work

Further comparative studies between Kalkdam, Katlani, Pering, Bushy Park and other deposits in the Griquatown area are required:

- Lead isotope studies on the different galena generations will help to identify the possibility of two separate mineralising stages affecting the Griqualand West sub-basin. This would also constrain the lead source/sources further.
- 2. Sulphur isotope studies of the sulphides at Pering and Bushy Park need to be carried out and compared with Kalkdam and Katlani.
- 3. Further fluid inclusion studies at Kalkdam will hopefully shed light on fluid salinities and temperatures during the main stages of the mineralising event. Further investigation is also required on population A inclusions as well as the other inclusion populations in order to constrain the precipitation process i.e. is there evidence for fluid mixing.

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APPENDIX A

ANALYTICAL PROCEDURES

A.1 Sample collection and preparation

Rock samples were collected from successive lava flows at Kalkdam as well as from breccia zones for geochemical, geochronological, petrographical and mineralogical studies. Allanridge samples from other localities in the NW Province and bore-hole cores between Allanridge and Bothaville were also sampled for geochemical comparison.

Sample powders were prepared at the Department of Geology, University of the Orange Free State following the procedure given below:

- 1. Sampling in the field was conducted in a manner to reduce contamination weathered surfaces were kept to a minimum.
- 2. Samples were broken into fragments by a precleaned tungsten-carbide jaw crusher.
- 3. Fresh fragments only were milled to a powder using carbon-steel grinders.
- 4. All possible precautions were taken to prevent contamination of the samples.

A.2 XRF Analyses

Major oxide concentrations were analysed by XRF at the University of the Orange Free State, using a Philips PW-1404-spectrometer. Sample preparation was conducted according to the technique of Norrish and Hutton (1969), where approximately 0.28g of each powder sample was mixed with NaNO₃ and spectroflux 105 (Johnson and Mathey), melted at 980°C and made into fusion discs. Major elements analysed included: SiO₂; Al₂O₃; TiO₂; Fe₂O₃ (total iron); MnO; MgO; CaO; Na₂O; K₂O and P₂O₅.

Trace element concentrations were also analysed by XRF at the University of the Orange Free State on pressed powder pellets: approximately 10g of powder from each sample was mixed with 6 drops of binding movial agent and pressed under 2 tons/cm² into pellets with a boric acid base and shell. Trace elements analysed included: Sc, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb and Ba.

Volatile constituents H_2O^+ and CO_2 , were gravimetrically determined by sample weight loss after a silica crucible containing 2g of sample was ignited at 1000°C for 6 hours. The weight loss obtained was used to calculate the loss on ignition (LOI).

Results of major oxide and trace element XRF analyses for Kalkdam, NW Province Allanridge and bore core Allanridge samples are given in appendix B.

A.3 XRD Analyses

Powder X-ray diffraction analyses were carried out on selected samples using a Siemens D5000 diffractometer at the University of the Orange Free State. Minerals present included albite, quartz, chlorite, actinolite and clino-zoizite. Debye-Scherrer films were obtained for pure crystals of individual minerals following the technique of Hiemstra (1956).

A.4 Microprobe analyses

Polished thin sections were coated with carbon using a sputter coater S150B prior to being loaded into a Cameca Camebax electron microprobe at the University of the Orange Free State. Operating conditions were 15kV, 30 nA beam current with a beam diameter of 3 μ m. PAP intensity correction techniques were used in conjunction with mineral standards. Mineral species analysed were chlorite, plagioclase, actinolite and pyroxene.

A.5 Isotope analyses

Analyses for Rb, Sr, and Pb were conducted at the Bernard Price Institute at the University of the Witwatersrand. S isotope samples were prepared at the University of the Witwatersrand and analysed at the Council for Geoscience in Pretoria.

A.5.1 Rubidium-Strontium

Selection of samples for Rb/Sr isotope analyses was based on the degree of overall alteration of the rock and on the secondary minerals filling the amygdales. Three of the rock samples were highly altered whilst two were comparatively unaltered. Calcite and chlorites were removed from the amygdales using an etching tool. Parts of the whole rock matrix were chipped off with a hammer and then ground into a fine powder. The calcite and chlorite were purified by hand-picking using a binocular microscope.

A.5.1.1 Sample preparation

Approximately 0.1 gram of each sample was weighed into a teflon beaker which had first been cleaned with hot 6N HCl and then cooled. Rubidium and strontium spikes were then added to each sample. For whole rock samples, the proportions of Sr spike (82%) to sample was approximately 1:1, as well as 2 - 3 drops of Rb standard spike. For the chlorites, a spike: sample ratio of 2:3 for the Rb standard spike was used and 2 drops of Sr spike (99%).

Calcite samples were prepared with 1 drop of Rb standard spike and a ratio of 1:1 with Sr spike (82%). See Table A.1 for sample and spike weights.

After weighing, HF and a small amount of HNO₃ were added to the whole rock and chlorite samples. The nitric acid acts as an oxidising agent which prevents the formation of insoluble fluorides. The chlorite and whole rock solutions were then covered and left to dissolve on a hot plate at approximately 115°C. After they had fully dissolved (which may take up to 3 days), the lids were removed and the samples dried to a fluoride salt. The fluoride salt was then converted to a chloride salt by dissolving in 6N HCl and then dried. In the case of the calcite samples, dissolving in HCl converts it immediately into a chloride salt.

500 μ l of 2.15N HCl was then added to each sample and transferred to an Eppindorf tube. Each sample was centrifuged for approximately 10 minutes at 800 rpm.

After centrifugation, 500 µl of each sample from the Eppindorf tube was added to a separation column. The resin filled columns were first cleaned with 6N HCl and then conditioned with 2.15N HCl prior to each sample being added. Care was taken to ensure no sediment was included in the fraction. The remaining sample left in each Eppindorf tube was saved and used later for Rb analysis.

Strontium was collected by cation exchange chemistry where the separation column (including sample) was flushed with 2.15N HCl. The volume of acid required was dependent on the calibration of each column. The final collection of pure Sr was then dried under infra-red light to a small colourless film.

Date	Sample	Sample weight	Spike weight		
		(grams)	99% Rb spike	82% Sr spike	99% Sr spike
24/10/96	3 WRa	0.09982	0.04048	0.11907	-
	3 WRb	0.10013	0.03338	0.10032	-
	7 WRa	0.11209	0.05031	0.10784	-
	7 WRb	0.10031	0.03022	0.11408	-
	7 CHL	0.12119	0.01677	-	0.01507
	7 CAL	0.08662	0.01515	0.07976	-
30/10/96	F4t WRa	0.10103	0.04437	0.11382	-
	F4t WRb	0.10234	0.06152	0.11598	-
	6 WRa	0.09985	0.04300	0.10427	-
	6 WRb	0.10321	0.03259	0.10792	-
	9 WRa	0.12402	0.02980	0.11778	-
	9 WRb	0.11196	0.03144	0.10779	-
	F4t CAL	0.10046	0.02682	0.12123	-
	9 CAL	0.10614	0.02953	0.11010	-
	F4t CHL	0.12671	0.02991	-	0.01435
	9 CHL	0.10199	0.01374	-	0.01602
6/11/96	KL-SPH	0.04321	0.02674	-	0.00935
27/11/96	7 CHLb	0.0320	0.06121	-	0.03070
	9 CHLb	0.03013	0.07796	-	0.02554
	F4t CHLb	0.03073	0.07790	-	0.02024
	7 CHLc	0.03436	0.08857	-	0.01789
	9 CHLc	0.03474	0.07040	-	0.02359
	F4t CHLc	0.03248	0.06035	-	0.02863
12/12/96	9 CALb	0.09012	-	0.10052	-
	9 CALc	0.09012		0.09385	-
	F4t CALb	0.06951	-	0.08300	
	F4t CALc	0.07618	-	0.08823	-
	7 CALb	0.06795	-	0.04460	

Table A.1: Sample and spike weights for Rb/Sr analyses. WR=whole rock, CHL=chlorite; CAL=calcite;

SPH=sphalerite

A.5.2 Natural lead analyses

Samples were chosen for lead-lead analyses from the most altered whole rock, the least altered whole rock and galenas from both Kalkdam and Katlani. One sphalerite sample from Katlani was also included. The galena samples were easily removed from thin sections, whilst the sphalerite sample was removed from the whole rock using an electric etcher. Further purification was achieved by magnetic separation, liquid separation using bromoform and methyl iodide as well as hand-picking using a binocular microscope.

A.5.2.1 Sample preparation

For isotope work, the amount of lead required is approximately 5 μ g. The proportion of Pb to S in galena is very high and constitutes approximately 5/6 of the total weight.

mol % Pb = mol wt Pb/(mol wt Pb + mol wt S)
=
$$207.21/239.276$$

 $\approx 200/240 = 5/6.$

In order to ensure that only $5\mu g$ were taken, each sample was weighed, the weight of Pb calculated and a 6N HCl solution made, of which 1 ml contained approximately 5 μg Pb.

```
e.g. Sample KL1-GAL weighs 0.00061g
weight of lead in sample = 0.00061 x 5/6
\approx 0.0005g
\approx 500 µg.
```

This sample was dissolved in 100 ml 6N HCl and 1 ml (5 μ g) was extracted for analyses.
In the case of the whole rock powders, the total concentration of Pb is unknown, so approximately one gram of each whole rock powder was dissolved in 6N HCl and then dried.

Separation of the Pb fraction was done using calibrated separation columns and flushing with 3N HCl and HBr. The final separate containing the lead fraction was then dried under infra-red light.

A.5.3 Filament loading procedure

Samples were loaded using clean pyrex micro-pipettes with doubly or triply distilled reagents onto precleaned and outgassed filaments:

a) Rubidium samples were loaded directly from the samples remaining in the Eppindorf tubes onto the side filament of double configuration tantalum filaments and then dried.

b) Strontium samples were converted to a nitrate using 2% nitric acid and loaded onto single configuration tantalum filaments which had been pre-treated with 0.5 μ l phosphoric acid.

c) Lead samples were converted to a nitrate using 2% nitric acid and loaded onto single configuration rhenium filaments pre-treated with phosphoric acid and silica gel (Cameron *et al.*, 1969).

A.5.4 Mass Spectrometry

Isotopic compositions and concentrations of rubidium samples were obtained using a semi-automatic VG Micromass MM30 mass spectrometer with a Keithley Electrometer and PC286 based control software.

Strontium and natural lead samples were analysed on a fully automatic VG 354 thermal ionisation mass spectrometer with 5 faraday cups and run using a 486 PC and new Pyramid TIMS operating software.

A.5.4.1 Experimental uncertainties

Experimental uncertainties can be quantified by the use of a known standard. The accuracy of the measurements are gauged by the results of analyses on standards whose values have been agreed. Repeated measurement of samples and normalisation with the standards reduces the uncertainty of the values obtained. Blank measurements identify

background levels for the elements in question, which, depending on the concentration of the sample may or may not be negligible.

Sources of error can be analytical or preparatory:

- Weighing errors: A significant source of error may arise from the rapid evaporation of spike tracer solutions involved in isotope dilution analyses. This can be minimised by quick measurement of these solutions after samples have been weighed and securing with a lid immediately after weighing. These errors can be regarded as negligible when the accuracy of the scale (5 decimal places) is taken into account.
- Incomplete sample dissolution or isotopic homogenisation: this might be the cause of poor reproducibility for some of the samples. Samples which did not produce a transparent deposit after dissolution (separating columns) were repeated until a clean sample was produced.
- Sample heterogeneity: for some duplicates of the altered whole rock samples, results varied, in these cases the odd samples were discarded from the regression.
- 4. Mass spectrometry uncertainties: uncertainties can arise from mass fractionation which occurs during thermal ionisation of the sample from the filament. Lighter isotopes are more readily ionised than the heavy isotopes of the same element. As a result of this, a

fractionation correction factor must be applied. In the case of the lead analyses where there is a large difference in ionic weight between ²⁰⁴Pb and ²⁰⁸Pb, a correction factor is required. This is obtained by repeated analyses on the internationally accepted natural lead standard SRM 981 during the time for which the lead samples were being run. Frequent changes in temperature and pressure may affect the instrumental running conditions. It is therefore important to run the lead standard regularly to obtain a reliable correction factor:

> Precision factor (%) = 100 s/ xwhere s = standard deviation and x = mean.

The above formula was applied to data for the lead standard SRM 981. The following correction factors for each ratio were calculated:

²⁰⁶ Pb/ ²⁰⁴ Pb	1.00477
²⁰⁷ Pb/ ²⁰⁴ Pb	1.00534
²⁰⁸ Pb/ ²⁰⁴ Pb	1.00086

5. Incorrect spiking in isotope dilution analyses: usually the amount of an element in a particular mineral can be roughly estimated. The chlorite samples used are very rich in Rb compared with "normal" chlorites. As a result of this, the chlorite samples were

initially greatly underspiked. Large errors can be incurred if this is not identified: the volume of spike (known concentration) used is too small in comparison with the concentration and volume of sample. The first calculated values were therefore unreliable, and further samples were prepared.

A.5.5 Sulphur isotope analyses.

Galena and sphalerite from both Kalkdam and Katlani were chosen for isotopic work. Conversion to SO_2 gas was carried out by heating the samples with copper oxide over a furnace. Mixing of various gases was prevented by following a specific procedure. SO_2 gas was collected in a trap by freezing with liquid nitrogen. The collection tube was then sealed with a flame. Table A.2 gives the pressures and temperatures of CO_2 and SO_2 gas collected from each sample.

SO₂ gas samples were run through a MAT 250 mass spectrometer. Six different standards were used to calibrate the working gas which results in slightly different values for the individual standards. The standard used (Kabwe galena: $\delta^{34}S = -16.8$ per mil) did not agree with the values obtained during the run ($\delta^{34}S = -15.9$ per mil). The error was, however, constant and hence the isotope ratios obtained are also constant. Table A.3 gives $\delta^{34}S$ results for Kalkdam and Katlani samples.

Formation temperatures calculated from isotopic equilibrium fractionation following the equation given by Ohmoto and Rye (1979) are given in Table A.4.

Date	Sample Name	Pinitial	CC	D ₂	S	02
			T (°C)	Р	T (°C)	P
25/11/96	30 GAL a	-0.06	-74.2	4.64	-55	5.99
25/11/96	KABWE II STD	-0.07	-74.9	4.35	-41.7	8.95
26/11/96	30 GAL b	-0.08	-80.4	4.43	-58.5	8.4
26/11/96	KL GAL a	-0.07	-76	4.93	-49.5	9.4
26/11/96	KL GAL b	-0.07	-74.4	3.58	-51.4	9.08
26/11/96	KABWE II STD	-0.07	-75.1	4.4	-51.8	10.43
27/11/96	KL SPH a	-0.09	-74.8	4.91	-46.3	15.55
28/11/96	KABWE II STD	-0.13	-74.9	5.59	-47.2	7.48
28/11/96	RK SPH a	-0.13	-75	3.41	-32.7	27.46
28/11/96	RK SPH b	-0.17	-78.1	4.5	-34.1	24.9
28/11/96	KABWE II STD	-0.2	-76	3.46	-39.6	6.3
28/11/96	KL-1 GAL a	-0.22	-75.1	4.44	-42.9	10.93
29/11/96	KL-1 GAL b	-0.12	-75.5	6.96	-47.6	11.98

Table A.2: Temperatures and pressures recorded during SO₂ extraction for galena and sphalerite samples

from Kalkdam and Katlani.

	Sample	δ ³⁴ S
KALKDAM	30 GAL a	-6.3
1	30 GAL b	-6
	RK SPH a	-3.7
	RK SPH b	-3.4
KATLANI	KL GAL a	-4.8
	KL GAL b	-5.3
	KL-1 GAL a	-5.9
	KL-1 GAL b	-6
	KL SPH	-3.7

Table A.3: δ^{34} S values for Kalkdam and Katlani galena and sphalerite.

	1	KALK	DAM						
Sample	30 GAL	30 GAL	RK SPH	RK	KL GAL 2	KL GAL b	KL-1 GAL a	KL-1 GAL b	KL SPH
δ 34S	-6.3	-6	-3.7	-3.4	-4.8	-5.3	-5.9	-6	-3.7
$\Delta_{sph-gal}$ range	2.3-2.9	2.3-2.6			1.1	1.6	2.2	2.3	
T range (K)	501-563	530-563			814	675	576	563	
T range (°C)	228-290	257-290			541	402	303	290	

Table A.4: Calculated equilibrium temperatures of formation for galena and sphalerite from Kalkdam

and Katlani.

Sample	SiO2 Wt %	TiO ₂ Wt %	Al ₂ O ₃ Wt %	Fe_2O_3 (total)	MnO Wt %	MgO Wt %	CaO Wt %	Na ₂ O Wt %	K ₂ O Wt %	P ₂ O ₅ Wt %	H2O-	LOI	Total	Lava Type
Ft1	60.01	0.93	16.97	2.90	0.13	1.02	4.28	3.48	3.74	0.34	0.34	5.03	99.17	LA
9a	67.73	0.73	13.50	3.55	0.10	1.27	3.39	2.58	2.08	0.18	0.17	3.72	99.00	LA
14a	66.05	0.86	17.12	2.49	0.09	0.96	3.30	1.29	2.87	0.22	0.07	3.62	98.94	LA
F6t a	62.26	0.91	17.61	4.29	0.08	1.42	1.50	3.71	4.77	0.23	0.02	2.51	99.31	LA
DRK 50	73.88	0.92	13.76	1.49	0.03	0.38	0.25	4.19	3.19	0.15	0.01	0.62	98.87	LA
F4t a	53.31	0.58	11.43	2.98	0.06	1.09	1.98	0.9	2.01	0.12	21.88	2.6	98.94	LA
5	58.86	0.73	15.89	2.79	0.15	0.89	5.42	4.20	4.56	0.38	0.11	5.31	99.29	LA
F3t a	62.85	0.97	17.76	3.85	0.07	1.43	2.12	3.01	3.76	0.21	0.13	3.16	99.32	LA
26	51.78	0.73	14.84	11.05	0.24	2.37	6.15	4.27	0.38	0.47	0.07	6.68	99.03	Nr Breccia
6a	56.71	0.86	15.34	11.04	0.15	3.19	2.43	3.59	0.81	0.16	0.11	4.45	98.84	Nr Breccia
D	47.98	0.83	12.88	9.03	0.22	5.09	7.77	2.19	0.46	0.14	0.17	8.12	98.2	Nr Breccia
24	52.03	0.82	12.60	9.16	0.21	2.75	8.26	3.97	0.68	0.14	0.30	8.24	99.16	Nr Breccia
DRK 30	59.94	0.81	14.19	9.96	0.14	3.86	2.49	2.54	1.45	0.16	0.06	4.30	99.90	Nr Breccia
23a	54.51	0.84	15.14	12.36	0.19	3.65	3.07	4.06	0.24	0.17	0.14	4.92	99.29	Nr Breccia
17a	58.49	0.85	14.95	11.82	0.13	4.22	1.38	2.33	0.20	0.17	0.24	4.13	98.91	Nr Breccia

Table B.1. Major oxide data from Allandridge samples at Kalkdam, Northern Cape Province, South Africa. LA=light amygdaloidal; DA=dark amygdaloidal; DM=dark massive lava; Nr breccia= lava adjacent to breccia zones.

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H2O-	LOI	Total	Lava
	Wt %	Wt %	Wt %	(total)	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %				Type
18a	54.45	0.79	14.94	9.42	0.20	3.60	4.33	3.72	1.26	0.25	0.17	5.95	99.08	Nr
														Breccia
F3m	56.52	0.76	14.08	6.54	0.20	2.13	5.54	3.44	1.84	0.24	0.09	6.5	97.88	DA
1	55.85	0.80	12.87	10.50	0.23	6.04	6.53	1.81	1.50	0.13	0.17	2.84	99.27	DA
8	55.96	0.79	12.83	9.35	0.18	4.86	6.75	2.23	1.34	0.14	0.20	4.97	99.61	DA
DRK 26	62.38	0.91	16.71	6.55	0.12	1.83	0.87	3.61	3.62	0.18	0.35	2.38	99.51	DA
13	51.11	0.98	17.65	9.52	0.16	3.46	5.91	1.75	1.34	0.19	0.23	6.71	99.01	DA
A	53.68	0.86	12.85	10.13	0.22	6.06	5.42	2.44	0.46	0.14	0.24	6.8	99.3	DA
11	53.68	0.73	14.04	6.36	0.14	3.49	7.07	3.07	2.56	0.15	0.23	8.01	99.53	DA
21	55.42	0.78	13.88	8.34	0.15	4.72	5.19	2.77	1.74	0.15	0.14	6.67	99.95	DA
15	52.32	0.82	12.88	9.03	0.22	5.09	7.77	2.19	0.46	0.14	0.17	8.12	99.21	DA
F5m	62.41	0.74	13.90	6.07	0.15	3.19	4.19	3.44	2.90	0.15	0.06	3.07	100.27	DM
F4bm	55.84	0.81	14.14	8.31	0.12	4.10	5.87	2.48	1.51	0.15	0.05	7.03	100.41	DM
F3b a	58.67	0.76	14.93	9.49	0.15	3.74	3.19	2.9	0.52	0.31	0.06	4.47	99.19	DM
FLOW 3	61.69	0.80	14.56	9.58	0.13	3.79	1.36	3.09	0.64	0.18	0.02	3.45	99.29	DM
3a	56,99	0.75	13.82	10.72	0.19	3.38	4.62	2.14	0.19	0.17	0.11	5.96	99.04	DM
10a	61.23	0.75	13.13	9.08	0.12	3.49	2.01	4.27	0.79	0.15	0.25	4.1	99.37	DM
DRK 31	55.65	0.61	12.30	8.48	0.24	1.88	6.90	3.92	1.25	0.83	0.22	6.84	99.12	DM
27	47.73	0.69	13.54	10.63	0.32	2.47	9.72	3.79	0.90	0.93	0.21	9.28	100.20	DM

Table B.1. (cont.).

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Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H2O-	LOI	Total	Locality	
	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt%				
HTW 1	56.86	1.03	12.82	10.56	0.11	6.97	2.97	2.09	0.50	0.21	0.09	5.23	99.45	Voetpadsdrift 1	
HTW 2	63.96	0.75	13.02	5.47	0.08	3.32	3.99	4.26	1.58	0.17	0.09	3.18	99.87	Voetpadsdrift 2	
HTW 3	55.50	1.02	12.74	10.20	0.13	5.74	3.86	3.86	1.20	0.22	0.12	5.56	100.15	Schutsekama 1	
HTW 4	54.94	0.76	14.12	9.29	0.13	5.36	6.71	3.50	2.13	0.17	0.12	2.08	99.31	Schutsekama 2	
HTW 5	60.75	1.12	13.91	8.64	0.08	4.83	2.17	3.46	0.96	0.21	0.05	3.54	99.72	Schutsekama 3	
HTW 6	57.63	0.80	14.18	9.68	0.12	4.82	4.86	4.67	0.77	0.16	0.06	1.48	99.23	Ou Brug inc	
HTW 7	55.91	0.74	13.87	9.49	0.18	5.99	5.06	3.75	0.72	0.16	0.16	3.87	99.89	Orange River Bend 1	
HTW 8	54.88	0.75	14.25	9.72	0.12	5.53	6.35	3.56	1.89	0.16	0.08	2.16	99.44	Orange River Bend 2	
HTW 9	54.96	0.77	14.27	9.45	0.12	5.43	6.46	3.99	1.84	0.17	0.12	1.98	99.57	Kalkpunt	
HTW 10	56.63	0.66	11.31	9.41	0.10	7.00	4.19	0.24	2.75	0.11	0.06	7.32	99.78	Merwesrust 1	
HTW 11	54.28	0.81	14.47	9.79	0.12	4.53	7.42	3.60	1.36	0.18	0.12	2.71	99.37	Merwesrust beacon 1	
HTW 12	59.52	0.73	12.98	5.81	0.09	2.98	6.57	3.92	0.45	0.15	0.07	6.26	99.53	Merwesrust beacon 2	

Table B.2. Major oxide concentrations for Allanridge samples throughout Northern Cape Province.

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Sample	SiO ₂	TiO ₂ wt	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	H2O-	LOI	total	Locality
HTW 13	66.26	0.63	10.61	6.32	0.06	5.90	1.41	0.39	3.62	0.09	0.06	3.65	99.00	Maritzdam 1
HTW 14	55.61	0.81	14.60	10.03	0.11	4.60	8.62	2.68	1.35	0.17	0.03	0.75	99.37	Maritzdam 2
HTW 15	53.06	0.72	12.92	11.51	0.12	6.87	4.47	2.42	0.09	0.16	0.13	6.63	99.10	Maritzdam 3
HTW 16	72.07	0.82	14.57	1.16	0.01	0.26	1.18	5.12	4.01	0.18	0.06	0.62	100.07	Pampoenpan
HTW 17	58.55	0.84	14.78	6.64	0.11	3.54	5.66	2.92	3.26	0.18	0.09	2.81	99.38	Rooikop 1
HTW 18	54.75	0.83	14.70	9.99	0.14	4.77	7.71	3.46	1.49	0.17	0.10	1.08	99.21	Rooikop 2
HTW 19	58.68	1.07	13.30	9.31	0.11	4.93	3.34	2.57	0.95	0.23	0.15	5.14	99.77	Rooikop 3
HTW 20	56.64	0.77	14.12	9.67	0.16	6.19	4.09	3.63	0.76	0.16	0.12	2.96	99.27	Pniel 1
HTW 21	55.21	0.84	14.49	9.14	0.12	4.69	7.68	3.73	1.41	0.19	0.12	2.71	100.33	Pniel 2
HTW 22	55.89	0.78	14.40	9.49	0.12	4.98	5.92	3.50	1.63	0.17	0.13	2.37	99.37	Pniel beacon 1
HTW 23	58.72	0.77	13.82	6.68	0.09	3.47	5.36	4.10	0.51	0.16	0.08	5.53	99.29	Pniel beacon 2

Table B.2. (cont).

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H2O-	LOI	Total
	wt %	wt %	wt %	(total)	wt %	wt %	wt %	wt %	wt %	wt %			
DH1-1	56.83	0.76	12.99	8.11	0.08	3.21	4.95	2.48	2.54	0.15	0.14	4.34	96.58
DH1-2	52.00	0.94	15.77	9.13	0.13	4.28	6.58	3.61	0.23	0.17	0.31	5.18	98.33
DH1-3	55.58	0.78	13.17	8.55	0.12	4.54	6.69	3.98	0.64	0.15	0.56	2.57	97.33
DH1-4	53.41	0.80	13.57	9.98	0.14	4.94	6.21	3.64	0.95	0.15	0.34	2.98	97.11
DH1-5	56.94	0.87	13.44	9.89	0.12	4.27	6.71	3.47	1.45	0.16	0.14	2.68	100.14
DH1-6	55.87	0.76	13.12	9.95	0.12	4.15	6.69	3.33	1.96	0.16	0.12	2.23	98.46
DH1-7	55.01	0.72	13.77	9.09	0.12	5.33	4.80	3.79	1.20	0.15	0.32	2.61	96.91
DH1-8	58.17	0.73	13.03	7.68	0.11	4.77	4.56	4.51	0.67	0.15	0.34	2.26	96.98
DH1-9	53.67	0.73	15.89	8.91	0.09	3.78	6.25	4.17	0.19	0.16	0.18	3.29	97.31
DH1-10	60.13	0.75	13.43	6.61	0.08	4.31	4.21	4.79	1.11	0.16	0.15	2.35	98.08
DH1-11	56.92	0.72	13.56	7.89	0.13	4.82	5.93	4.65	0.42	0.15	0.20	2.11	97.50
DH1-12	58.29	0.76	13.58	8.41	0.09	3.66	6.24	3.60	1.76	0.13	0.24	2.59	99.35
DH1-13	56.97	0.66	12.67	7.85	0.10	3.87	6.36	3.03	1.65	0.14	0.23	4.10	97.63
DH1-14	54.36	0.89	12.72	9.98	0.14	4.66	6.88	3.34	1.64	0.20	0.13	2.67	97.61
DH1-15	51.21	1.01	13.22	10.43	0.13	3.32	. 7.95	3.31	0.84	0.20	0.34	5.15	97.11
DH1-16	52.68	0.99	12.98	10.66	0.12	3.40	6.38	2.91	2.48	0.21	0.24	4.12	97.17
DH1-17	53.92	1.03	13.05	10.82	0.13	2.93	6.76	3.41	1.16	0.23	0.17	3.80	97.41
DH1-18	54.50	0.95	13.19	10.56	0.13	3.62	6.66	3.44	1.45	0.21	0.15	3.03	97.89

Table B.3. Major oxide data for Allanridge bore core samples from Allanridge and Bothaville, (From Crozier, 1998).

Sample	SiO ₂	TiO ₂	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	H2O-	LOI	Total
DH1-10	53.83	0.06	12 70		0.15	4.00	WL 70	WL 70	WL 70	WL 70	0.17	2.01	07.42
		0.90	12.79	11.24	0.15	4.00	0.04	3.73	0.79	0.21	0.17	2.91	97.42
DH1-20	55.00	0.92	12.47	10.84	0.14	4.27	6.92	3.50	1.72	0.21	0.18	2.14	98.31
DH1-21	54.91	1.04	12.94	11.33	0.15	4.08	6.02	3.91	1.45	0.23	0.22	2.01	98.29
DH1-22	54.04	1.01	12.92	10.89	0.13	3.62	6.71	3.31	2.13	0.23	0.13	2.95	98.07
DH1-23	50.20	1.13	13.63	10.28	0.14	4.85	6.02	2.54	0.86	0.23	0.14	6.39	96.41
DH1-24	52.89	1.03	13.33	10.73	0.15	3.67	7.09	3.41	1.31	0.24	0.08	3.36	97.29
DH1-25	52.00	0.97	13.15	10.35	0.14	4.57	7.88	4.11	0.15	0.23	0.15	4.10	97.80
DH1-26	52.47	1.01	13.28	10.44	0.13	4.20	8.19	3.49	0.77	0.23	0.14	4.68	99.03
DH1-29	49.54	1.03	12.78	11.63	0.13	3.61	7.95	2.97	2.38	0.23	0.20	4.70	97.15
DH1-30	51.21	1.08	13.21	11.27	0.13	4.00	7.71	3.73	1.74	0.24	0.17	3.64	98.13
DH1-31	51.34	1.03	12.61	6.39	0.11	2.88	10.13	3.97	1.49	0.23	0.16	6.84	97.18
DH1-32	44.25	1.06	13.60	4.51	0.15	1.86	13.51	3.80	2.40	0.24	0.13	10.99	96.50
DH1-33	56.03	1.01	12.30	8.29	0.13	4.45	6.83	4.31	0.90	0.23	0.19	3.40	98.07
DH1-34	48.38	1.04	13.13	11.96	0.16	4.18	6.93	2.50	0.24	0.21	0.07	7.25	96.05
DH1-35	48.87	1.17	12.88	8.27	0.14	3.49	10.15	3.06	0.64	0.24	0.13	8.57	97.61
DH1-36	52.89	1.05	13.20	11.62	0.12	3.94	5.70	3.62	1.01	0.22	0.16	3.30	96.83
DH1-37	52.53	1.09	13.38	10.52	0.13	3.85	6.95	4.07	1.16	0.24	0.15	2.60	96.67
DH1-38	51.77	1.07	13.48	9.51	0.13	3.87	7.34	3.85	1.02	0.24	0.16	5.15	97.59
DH1-39	52.51	1.06	13.37	11.01	0.13	4.21	6.93	3.13	1.89	0.24	0.17	2.51	97.16

Table B.3. (cont.).

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Sample	Rb (ppm)	Ba (ppm)	Sr (ppm)	Zr (ppm)	Nb (ppm)	Ni (ppm)	Zn (ppm)	Cr (ppm)	Cu (ppm)	V (ppm)	Y (ppm)	Sc (ppm)	Co (ppm)	Lava Type
Flt	110.4	728.5	45.6	195.5	5.2	22	318.3	158	9	178.6	22.4	15.8	8.9	LA
9a	35.6	502.2	60.7	149.2	3.2	33.5	903.3	140.8	12.1	154.8	8.7	12.6	18.6	LA
14a	61.6	534.5	72.9	182.3	4.6	36.6	340	149.5	9	150.7	11	16.5	22	LA
F6t a	106.2	1072.4	51.9	184.5	5.1	54.4	3586.9	170.4	9.3	189.3	22.6	19.2	18.8	LA
DRK 50	40.3	611.5	39.4	121.6	1.8	16.8	210.9	397.2	3.2	143.1	3	9.4	2	LA
F4t a	45.4	646.6	66.9	157.9	4.6	36.9	964.7	139.8	8.7	119.5	9.5	14.3	24.2	LA
F3t a	112.1	612.1	46.6	204.1	6	34.8	1155.3	163.1	7.2	207.2	25.1	16.2	66.1	LA
5	87.7	1133.2	71.9	156.2	4.8	31.6	1062.3	119.4	9	121.1	13.1	15.5	9.5	LA
26	4.2	281.3	48.7	148.4	5.9	79.9	652.6	132	12.4	166.8	8.3	0	53.9	Nr Breccia
6a	8.1	292.1	53.2	174	6.2	104.9	168.7	181.3	11.3	201.8	12	22.1	66.6	Nr Breccia
D	13	222.1	73.2	113.8	6.9	92.1	239.9	346.2	302.6	216.6	10.1	34.9	49	Nr Breccia
24	10.8	242.7	69.2	112.7	10.6	96.6	158.7	349.9	438.6	209.7	8.6	30.5	48.3	Nr Breccia
DRK 30	32.8	428.1	51.6	167.5	5.6	94	342.8	160.2	29.7	200.6	13.5	17.7	61.9	Nr Breccia
23a	0	116.1	54	167.7	6.1	108.2	225.6	161.2	40.7	205.4	15.8	14.5	71.4	Nr Breccia
17a	0	78.4	44.4	172.2	6.4	119.2	1223.5	152.9	159.5	204.5	13.8	18.5	71.2	Nr Breccia
18a	17.5	364	64.6	167	6.3	81.6	114.6	146.1	42.3	181.1	12.7	18.2	48.4	Nr Breccia

Table B.4 Trace element data for Kalkdam samples. LA=light amygdaloidal lava; DA=dark amygdaloidal lava; DM=dark massive lava; Nr breccia=lava adjacent to breccia zones.

Sample	Rb	Ba	Sr	Zr	Nb	Ni	Zn	Cr	Cu	V	Y	Sc	Co	Lava
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	Туре
1	29.8	1305	237.5	108.4	6.2	91.9	114.7	269.1	63.2	216.8	14.4	23.1	56.1	DA
8	25.5	701.2	161	124.6	6.1	93.3	201.4	264.6	75.4	192.2	16.3	18.5	56.4	DA
13	29.7	255.4	70	195.2	7.8	92.1	180.4	174.7	63.8	220.1	16	20.4	56.9	DA
DRK 26	59.6	920.5	40.3	183.6	6.2	63.8	12470.4	177.8	32.1	166.2	14.7	11.6	41.5	DA
A	4.7	328.5	137.9	113.3	5.2	92.5	303.1	351.6	85.3	229.1	14.5	33.2	64.8	DA
F3m	49		56.2	165.3	5.8					156.8	16.8		29.8	DA
11	83.6	669.8	98.4	156.1	4.8	86.1	99.5	137.7	44.6	157	13	25.6	35.6	DA
21	36	867	147.4	158.6	8	89.9	152.3	148.6	46.2	162.1	14.9	16.5	50.3	DA
15	5.8	613	165.8	113.8	7.6	96	305.3	355.7	79	227.8	15.7	17	52.3	DA
F5m	46.6	1032.9	287.4	158.9	5.3	74	70.6	129	49.8	155	12.8	18.5	38.6	DM
F4bm	46.5	495.2	108.4	164.3	6.2	91.3	151.3	154.2	35.7	169.9	13.6	19.4	48.8	DM
F3b a	1.5	452.5	62.8	156.2	5.1	97.2	638.9	150.9	199	174.7	16.8	17.7	54.4	DM
Flow 3	7.3	694.5	53.5	160.4	4.7	88.3	312.8	162.8	171.6	186.6	10.7	18	51.5	DM
3a	1.7	108.3	53.9	155.3	6.7	101.4	142.8	132.4	20.8	168	13.3	17.5	60.6	DM
10a	19.5	232.8	54.6	152.9	64.4	83.4	289.2	134.8	28.2	180.5	12.4	17.2	51.5	DM

Table B.4. (cont.).

			r	1											
Sample	Rb	Ba	Sr	Zr	Nb	Ni	Zn	Cr	Cu	V	Y	Sc	Co	Locality	
	(ppin)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	_(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	······································	
HTW 1	7.5	69.08	140.4	174	7.7	117.9	123.8	45.3	214.7	215.9	19.8	19.9	67.8	Voetpadsdrift 1	
HTW 2	18.7	675.8	80.3	178.5	8.5	117.3	138.5	39.1	220.8	197	19.4	19.4	65.5	Voetpadsdrift 2	
HTW 3	35.6	641.1	315.6	136.3	7.1	138.5	81.3	278.8	61.5	176	17.9	20.2	53.6	Schutsekama 1	
HTW 4	44.9	773.9	346.8	139.2	7.9	136.4	79.6	266.5	64	168.4	19.6	19.9	50.8	Schutsekama 2	
HTW 5	34.8	748	344.8	137.7	7.3	134.8	74.4	280.5	64.7	170.4	18.4	20.4	52.9	Schutsekama 3	
HTW 6	12.5	283.4	81.4	192.7	8.4	77.8	60.3	93.7	171.7	225	22.2	19.2	49	Ou Brug inc	
HTW 7	14	356.4	190	135.2	7.2	152.8	99.4	412.9	75.2	203.1	17.4	24.3	57.2	Orange River Bend 1	
HTW 8	12	290.8	160.9	136.1	6.4	152.6	104	434.4	33.3	199.7	16.1	24.3	64.6	Orange River Bend 2	
HTW 9	26.2	197.1	48.6	172.2	6.7	111.5	55.2	92	13.4	230.8	17.8	18	63.7	Kalkpunt	
HTW 10	15.7	343.8	424.8	144.3	7.1	108.8	74.2	76.1	53.6	157	14.2	17.2	56.6	Merwesrust 1	
HTW 11	5.7	262.6	131	138	5.2	66.7	88.1	74.9	89.3	144.5	12.7	17.7	31.9	Merwesrust beacon 1	
HTW 12	27.2	412.7	104.5	141.7	4.7	74.5	56.6	87	109.7	147.2	11.2	22.9	35.4	Merwesrust beacon 2	
HTW 13	86.5	820.5	231.1	153.7	3.9	147.4	16.5	112.8	49.6	170.3	13.9	20.7	79.2	Maritzdam 1	
HTW 14	64.9	366.4	73.8	121.6	5.1	72.8	78.2	71.3	26.4	159	11.3	15.8	47.8	Maritzdam 2	
HTW 15	83.2	410.9	67.6	117	4.6	54.7	50.4	69.7	7.5	156	6.6	18	35.6	Maritzdam 3	
HTW 16	17.6	190.6	138.2	144.9	6.1	127.4	83.7	309.4	152	205.2	16.9	25.1	51.9	Pampoenpan	
HTW 17	33.3	886.3	420.6	128.7	6.5	104.9	71.3	115.7	56.8	193.2	17.5	22.9	51.9	Rooikop I	
HTW 18	1.5	92.9	84.5	126.8	5.7	105.7	116.3	124.5	259.4	203.5	16.7	26.1	69.7	Rooikop 2	
HTW 19	13.8	263.2	166.3	181.7	7.3	115.7	102	45.4	49.8	210.9	16.9	19.7	61.5	Rooikop 3	
HTW 20	58.5	797.8	310.1	144.2	7	84	53.7	134.1	95.6	188.5	17.3	22.4	36.1	Pniel I	
HTW 21	23.7	384.8	513.6	133	7.5	103.6	69.7	131.7	51.2	188.8	20.1	25.3	52.1	Pniel 2	
HTW 22	39.4	407.8	358.8	137.7	4.8	107.2	79.6	126.2	99.1	191.3	17.9	25.8	50.9	Pniel beacon 1	
HTW 23	37.6	375.2	336.9	140	8.5	103.8	81.8	139.5	86.4	185,8	20.1	22.6	51.4	Pniel beacon 2	
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Table B.5. Trace element concentrations for Northern Cape Province Allanridge samples.

Sample	Rb	Ва	Sr	Zr	Nb	Ni	Zn	Cr	Cu	V	Y	Sc	Со
	(ppm)	(ppm)	(ppm)	(ppin)	(ppm)								
DH1-1	59.5	517.3	339.2	134.1	5.5	79.5	68.2	176.1	135.6	165.7	15.9	18.1	29.7
DH1-2	8	88.7	604.5	142.1	6.6	92.9	76.3	135.4	7.8	212.5	20.4	23.6	38.2
DH1-3	15.4	203.4	404.9	135	6.1	90.6	68.9	166.6	125.3	203.9	20.1	28.7	34.3
DH1-4	21.3	277	176.6	144.2	5.8	104.3	76.7	147.4	108.3	182.7	18.7	10.8	47.1
DH1-5	38.5	345.8	299.7	146.9	6.6	94.6	90.2	118.6	89.1	169.9	21.1	21.4	44.5
DH1-6	60.3	401.4	343.7	139.8	7	92.5	84.6	123.3	86.2	167.3	20.3	16.4	42.9
DH1-7	28.7	363.8	161.3	160.3	4.7	129.6	82.1	198.6	46.5	160.8	17.3	18.6	42.9
DH1-8	17.3	258.7	218.7	155.6	3	114.6	68.5	194.5	112.6	151.6	15.3	17.5	31.3
DH1-9	5.8	91.2	867.7	133.2	4.2	108.3	73.4	177.8	29.7	203.6	17.1	21.4	33
DH1-10	25.6	369	171.9	163	3.2	110.4	62.2	195.8	23.1	128.8	12.6	16.9	28.8
DHI-II	11.1	127.6	411.2	148.6	4.1	107	67.5	192.9	52.9	177.6	17.4	18,1	33
DH1-12	45.1	637	270.8	154.6	4.5	114.5	70	193.2	56.3	149.2	16.9	20	37.8
DH1-13	41	672.1	348.1	139.6	4.4	116.6	68.9	194.7	57.2	145.8	15.9	18.6	29.3
DH1-14	46.6	503.8	294.1	164.1	7.6	121.5	84.3	262.1	94.3	180.7	22	18.1	44.5
DH1-15	23.9	316.5	487.1	175.3	8	99.8	87.4	85.2	79.6	171.8	25.2	10	46.6
DH1-16	68.4	935.1	302.9	188.9	10.4	99.8	97	73.9	107.1	164.9	25.6	14.4	47
DH1-17	30	444.3	579.9	198.1	9.8	100.5	90.3	30.3	140.9	178.5	27.7	13.6	46.9
DH1-18	36.9	379.3	399.2	183.3	9.5	109.6	98.5	33.6	94	177.7	25.3	16.7	47.4
DH1-19	18.1	378.5	368.5	177	8.3	135	91.7	74	103	175.5	23.5	19.2	54.6
DH1-20	39.7	510.8	418.2	169.4	7.6	144.5	97	86.8	87.1	175.1	23.3	19.2	51

Table B.6. Trace element data for Allanridge bore core from Allanridge and Bothaville (from Crozier, 1998).

Sample	Rb	Ba	Sr	Zr	Nb	Ni	Zn	Cr	Cu	V	Y	Sc	Со
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
DH1-21	33.1	493.1	449.6	190.7	9.9	124.7	94	45.9	66.3	183.8	24.9	23.4	50.8
DH1-22	49.7	957.1	422.3	188.1	10.6	123.7	100.3	33.5	106.4	173	12.5	16.9	48.7
DH1-23	19.7	885.1	367.5	195.9	8.2	131.8	120.9	32.4	19.7	196.9	26.7	20.3	48.9
DH1-24	28.1	579.6	423.7	184.9	8.4	125.6	82.1	30.4	102.1	178	24.5	16.9	48
DH1-25	4.5	49.2	506.9	176	7.8	161.9	89.2	148.5	43	162.6	25.3	15	45
DH1-26	31.9	492.3	453.5	183	9	177.1	100.4	191.2	93.1	161.2	27.3	16.9	44.8
DH1-29	52.9	1209.7	613.7	173.7	9.7	164	111.7	62.5	108.8	167.2	26.5	18.3	51.9
DH1-30	37.9	1090.5	635.2	177.5	9.8	150.8	103.5	53.9	113.5	185.2	26.8	16.1	52.7
DH1-31	29.8	469.1	478	176.2	8.1	146.5	76	68.4	45.2	160.9	24.7	25.3	29.2
DH1-32	41.6	696	248.3	189.9	7.1	52.3	50.6	64.2	13	128.8	27.4	21.1	15.7
DH1-33	17	419.6	332.2	172.8	6.9	163.9	84.4	69	36.2	166.9	23.1	18.6	41.2
DH1-34	6.7	147	330.4	176.1	8.3	175.3	127.1	62.1	122.5	198.7	26.1	21.4	59.5
DH1-35	12.5	373.2	375	181	7.6	150	89.9	74.2	111.5	168.2	26.7	22.8	35.8
DH1-36	16.9	446.6	314.9	176.2	8.1	186.2	120.7	80.2	54.4	201.5	23	19.2	55.9
DH1-37	22.6	693.9	721.2	177.6	8.8	162.1	92,5	53.2	111.5	178.5	26.5	16.1	48.3
DH1-38	18.8	419.4	538	177.8	8.1	167.1	97.7	56.8	81.9	184.4	25.4	18.3	46.2
DH1-39	33.5	870.5	559.2	181.7	9.9	164.8	105.6	56.6	116.6	177.5	27.4	20.9	49.6

Table B.6. (cont.).

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