

**A MINERALOGICAL AND GEOCHEMICAL STUDY OF ALTERATION
ASSOCIATED WITH THE VENTERSDORP CONTACT REEF
IN THE WITWATERSRAND BASIN, SOUTH AFRICA**

Baojin Zhao

**A thesis submitted to the Faculty of Science, University of the Witwatersrand,
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Philosophy.**

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DECLARATION

I declare that this thesis is my own, unaided work. It is being submitted for the Degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not submitted before for any degree or examination in any other University.



(Signature of candidate)

17

Day of

November1998

ABSTRACT

The Ventersdorp Contact Reef (VCR) is a major gold-bearing reef in the Witwatersrand Basin. It occurs between the overlying Klipriviersberg Group lavas and the underlying Central Rand Group sediments, and was strongly altered by hydrothermal fluids circulating in the Witwatersrand Basin. A detailed study of the mineralogy, geochemistry of rocks and minerals, physicochemical conditions, stable isotopes and ages of hydrothermal alteration zones associated with the VCR were carried out at Western Deep Levels South Mine, South Africa.

Alteration zones were identified within and around the VCR, as well as in and around dykes, faults and pseudotachylite. The authigenic mineral assemblage comprises chlorite-muscovite-albite-quartz-carbonate-sulphide-epidote-sphene-rutile-talc-gold. Four alteration sequences were identified: (1) sulphide-gold; (2) albite-calcite; (3) chlorite-muscovite-gold; and (4) quartz-calcite veins. Bulk rock geochemistry suggests a relatively closed system during hydrothermal alteration, in which depletions of certain elements from one alteration zone were matched by enrichments in adjacent alteration zones, and vice versa. Chemical variations of the minerals in different alteration zones and rock types suggest a fluid-dominated system, in which the host rocks buffered the fluid and the authigenic mineral compositions. Hydrothermal fluids were H_2O -NaCl solutions with moderate to high salinities (8 to 23 wt% eNaCl) and neutral pH. Chlorite and muscovite temperatures were determined to be from 290 to 350 °C, implying pressures of 2,2 to 3,2 kbar, and a lithostatic geothermal gradient of 39 °C/km during peak hydrothermal alteration. Transportation of remobilised gold occurred as a bisulphide complex with subsequent precipitation possibly by electrochemical absorption on pyrite.

Sulphur, oxygen and hydrogen isotopes for the VCR suggest a metamorphic origin for the hydrothermal fluids and a dominantly magmatic source for detrital pyrite and possibly gold. K-Ar dates of separated micaceous material define an older age range of 1931 to 2054 Ma and younger age range of 1890 to 1965 Ma. These are suggested to be related to the Vredefort Cataclysm/Bushveld Complex and Eburnian orogeny, respectively. Three metamorphic and hydrothermal alteration stages are indicated: (1) burial metamorphism (2500-2300 Ma); (2) peak hydrothermal alteration (2054-2020 Ma) and (3) retrogression during the Eburnian Orogeny (1890-1965 Ma).

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ABBREVIATIONS

Ab - albite.	MC - MultiColour alteration (zone) in lava.
AGNQ - Apple Green Quartzite.	MORB - Mid-Ocean Ridge Basalt.
BMT - Burial Metamorphism.	Ms - muscovite.
Ca - circa.	MZ - Middle Zone.
Cc - calcite.	OZ - Outer Zone.
CGS - Centre de Géochimie de la Surface.	PHA - Peak Hydrothermal Alteration.
Ch (CH) - chlorite.	Po - pyrrhotite.
CL - Cathodoluminescence microscopy	Py - pyrite.
Cpy - chalcopyrite.	Qz (q) - quartz.
CRG - Central Rand Group.	Rt - rutile.
DG - Dark Green alteration (zone) in lava.	SACS - South Africa Committee for Stratigraphy.
DGG - Dark Grey alteration (zone) in quartzite.	SEM - Scanning Electron Microscopy.
DKGM - Deelkraal Gold Mine.	Sf - sulphides.
DZ - self-metamorphosed Dyke Zone.	Sp - sphene.
EBO - Eburnian Orogeny.	Sph - sphalerite.
EM - Electron Microprobe.	TEM - Transmission Electron Microscopy.
eNaCl - equivalent NaCl.	T _{fm} - temperature of final melting.
Ep - epidote.	T _h - temperature of homogenization.
F - fault.	VCF - Venterspost Conglomerate Formation.
Ga - galena.	VCM - Ventersdorp Contact Metamorphism.
GG - Greenish Grey alteration (zone) in quartzite.	VCR - Ventersdorp Contact Reef.
HAGS - Hydrothermally Altered Granitoids.	WDLSM - Western Deep Levels South Mine.
HGMS - High-gradient Magnetic Separation.	WG - Whitish Grey alteration (zone) in lava.
IML - Institut für Mineralogie & Lagerstättenlehre, RWTH, Aachen.	WRG - West Rand Group.
IZ - Inner Zone.	Wits Basin - Witwatersrand Basin.
LDG - Light Dark Grey alteration (zone) in quartzite.	wf% - weight percent.
LIL - Large Ion Lithophile Element.	WWL - West Wits Line.
LZ - Lava alteration Zone.	XRD - X-ray Diffraction.
	XRF - X-ray Fluorescence.

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PROJECT-RELATED PUBLICATIONS

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1 INTRODUCTION

1.1 Overview

The VCR, first exploited for gold in 1888 (Chunnett, 1994), has in recent years become one of the major gold-producing conglomerate reefs in the Witwatersrand Basin (Viljoen and Reimold, 1994). It is characterized by spectacularly well developed gold orebodies, preserved and buried by the overlying Klipriviersberg Group lavas, and by generally high albeit variable, gold concentrations. In addition, the VCR is pervasively altered, perhaps more so than any other conglomerate horizon in the Witwatersrand Basin.

Up to the present, there are two contrasting thoughts regarding the variable concentrations of gold in the VCR. As reviewed by Viljoen and Reimold (1994), the variability of gold concentrations within the VCR may either result from sedimentological, structural, or palaeogeomorphological factors, or alternatively, it may be related to a localized, but extensive secondary overprint of hydrothermal alteration. The sedimentology, structure and palaeogeomorphology of the VCR have been well documented (e.g., Krapez, 1985; McWha, 1988, 1994). However the hydrothermal alteration of the VCR has received little attention in the literature. Thus, study of the characteristics and genesis of the hydrothermal alteration in the VCR is an important topic and the results are very relevant to both gold exploration and mining practice.

1.2 Research area

A large number of gold mines currently exploit the VCR as the primary gold producer in the WWL, Klerksdorp (KD) and West Rand (WR) goldfields. In addition, the Anglovaal's Sun

project areas north of Welkom goldfield also contain VCR-related gold mineralization. Driefontein Consolidated, Deelkraal (now merged with the Elandsrand), Elandsrand, and Western Deep Levels South (WDLSM) Mines are the major gold mines exploiting the VCR in the WWL. The WDLSM was chosen for this study as an example of a typical operational mine exploiting the VCR (Fig. 1-1).

Fig. 1-2 shows the localities of underground samples from stopes and boreholes at the Western Deep Levels South Mine. With respect to the stope samples, they cover all longwalls (9, 53, 61 and 65) and different levels from 76 to 87 level in the research area. They are marked in A, B,...Y, representing sample clusters. The underground boreholes cover most of the mining area from 49 to 53 longwalls and lower elevations from -2600 to -3000 m below datum.

1.3 Study objectives

This thesis consists of a study of the mineralogy, geochemistry, physicochemical conditions, stable isotopes, and radiogenic dating of alteration associated with the VCR. The goals of this study are (i) to compile previous data relevant to the VCR, (ii) to characterize the mineralogical and geochemical features of hydrothermal alteration within and around the VCR, (iii) to estimate the physicochemical conditions of the alteration, (iv) to reconstruct the processes and timing of the alteration, and (v) to attempt to relate alteration to gold mineralization.

Table 1-1 summarizes the nature and extent of sampling in the present study, and the work undertaken on the sample collection. A total of 192 samples were selected from the collected underground and borehole samples at WDLSM. About 100 double polished sections, 28 polished slabs, and 10 polished handspecimens were made for reflected, and transmitted light

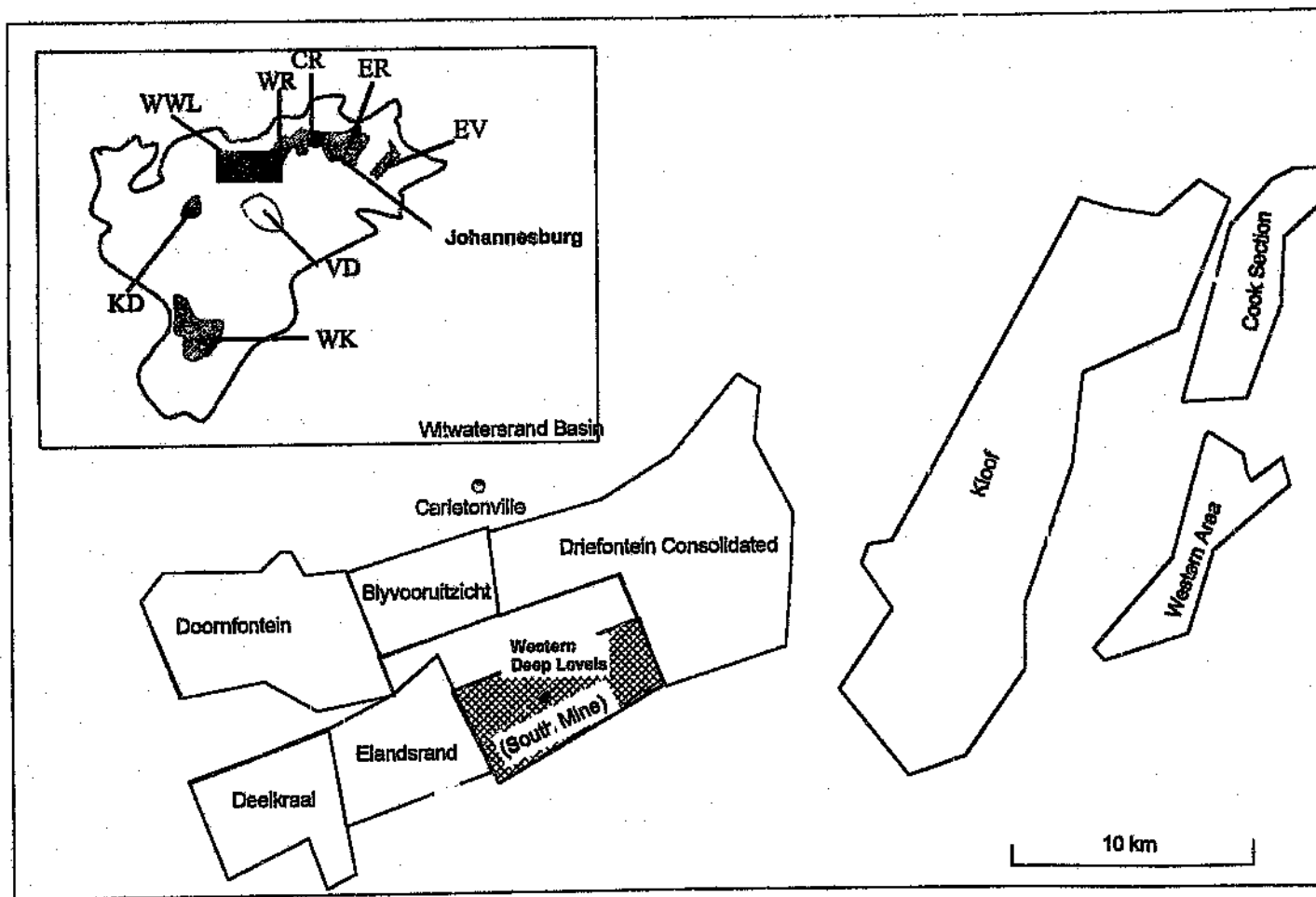


Fig. 1-1 Locality plan showing Western Deep Levels South Mine (hatched) within the West Wits Line, WWL - West Wits Line, WR - West Rand goldfield, CR - Central Rand goldfield, ER - East Rand goldfield, EV - Evander goldfield, KD - Klerksdorp goldfield, WK - Welkom goldfield, VD - Vredefort Dome.

microscope observation, and fluid inclusion study. Analyses of muscovite (22) and bulk rock powders (80) by XRD have been carried out for determining polytypes of muscovite and bulk rock mineral compositions. A total of 116 bulk rock samples and 26 rock-forming mineral and 55 sulphide samples have been analyzed for the chemical compositions. Stable isotope analyses include sulphur (28), hydrogen (10), oxygen (27), and carbon (3) isotope measurements. K-Ar (34) isotopic determinations were also carried out.

1.4 Research methodology

The study comprised an initial period of field work with subsequent laboratory analyses (Fig. 1-3). The initial field work consisted of underground mapping, sampling and borehole logging for five months. In the laboratory, X-ray Diffraction (XRD) analysis was used to determine mineral compositions of whole rocks, mineral separates as well as polytypes of muscovite. Scanning Electron Microscopy (SEM) was used to analyze the morphology, structure and genesis of minerals. Single mineral textures and generations were determined by Transmission Electron Microscopy (TEM). Chemical compositions of minerals were analyzed by Electron Microprobe (EM). Cathodoluminescence Microscopy (CL) was used to determine the genesis of quartz and calcite. X-ray Fluorescence (XRF) was utilized to analyze the chemical compositions of whole rocks. Temperatures, pressures and salinities of hydrothermal fluids were estimated by microthermometry of fluid inclusions in quartz, as well as from the chlorite and muscovite geothermometers. Stable isotopes of oxygen, hydrogen, sulphur and carbon for minerals and whole rocks were analyzed using concentrated isotopic extraction lines and gas-source mass spectrometers, respectively. In addition, radiogenic isotope determination of K-Ar on mineral separates from the alteration zone was also measured.

Table 1-1 Record of the work done in this study.

	Rocks				Rock-forming minerals						Sulphides							Totals
	Lava	VCR	Quartzites	Shales	Qz	Ch	Ms	Ab	Cs	Sd	Py	Po	Cp	Ga	Sph	Asp	Pen	
Hand specimen	34	43	105	10														192
Double polished sections	24	23	51	2														100
Polished slabs	4	4	20	-														28
Polished hand specimen	9			1														10
Ms polytype (XRD)							22											22
XRD analyses	10	15	20	5	30													80
Rock chemistry	21	25	65	5														116
Mineral chemistry						10	8	5	2	1	8	14	12	6	8	1	6	81
Fluid inclusion					10													10
S											10	10	2	3	3			28
II							10											10
O	5	3	6				10		3									27
C									3									3
K-Ar	11	7	16															34

Qz-quartz, Ch-chlorite, Ms-muscovite, Ab-albite, Cs-calcite, Sd-siderite, Py-pyrite, Po-pyrrhotite, Cp-chalcopyrite, Ga-galena, sph-sphalerite, Asp-arsenopyrite, Pen-pentlandite. Numbers include samples analyzed for the various processes listed here.

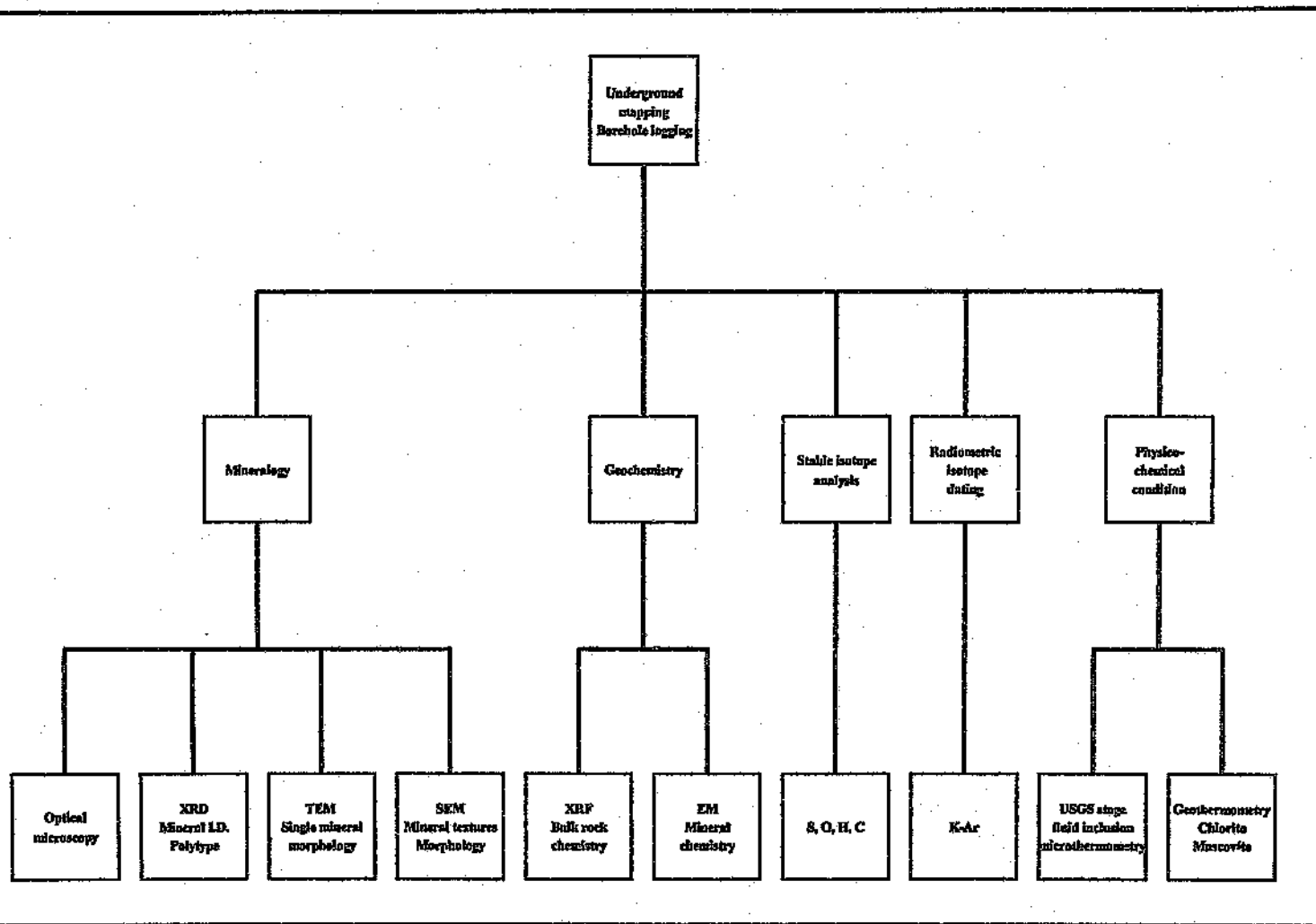


Fig. 1-3 A flow chart showing the methods used in different parts of this study. I.D. - identification.

1.5 Outline

This thesis consists of ten chapters. Chapter 1 provides a brief introduction of the project, including a short review of the history, and status of research on the VCR in the Witwatersrand Basin. It also defines the research area; the aims, objectives and statement of the major work undertaken; the methodologies and provides an outline of the thesis. In Chapters 2 and 3 the geological background of the Witwatersrand Basin and geology of the VCR are summarized, respectively. In Chapter 4, following a general description of alteration features observed in the VCR, the mineralogy of the alteration is studied in detail. Geochemistry of bulk rocks and of single minerals (rock-forming minerals and sulphides) is documented in Chapters 5 and 6, respectively. Chapter 7 presents an evaluation of the physicochemical conditions of alteration in the VCR, mainly utilizing chlorite and muscovite geothermometers and fluid inclusion microthermometry. S, O, H and C isotope geochemistry of whole rocks and single minerals is presented in Chapter 8. Radiogenic ages of post-depositional VCR alteration events are constrained by the K-Ar method on mineral separates in Chapter 9. Finally, summary and conclusions of the data documented in the different chapters are presented in Chapter 10.

2 GEOLOGICAL BACKGROUND

2.1 Introduction

Gold was first discovered in the Witwatersrand Basin in 1886, by George Harrison in a thin pebble conglomerate on the farm Langlaagte (Antrobus, 1986). Subsequently, tens of gold-bearing conglomerate horizons were found in the Basin. The Witwatersrand Basin has since produced around 45000 tons of gold, which has made the Basin the world's greatest goldfield.

The Witwatersrand Basin is underlain by porphyritic and andesitic volcanics and quartzites of the Dominion Group, and overlain by volcanics and sediments of the Ventersdorp, and Transvaal Supergroups. The basin is ellipsoidal in shape and extends from the north of Johannesburg to south of Welkom, and from the east of Evander to west of Klerksdorp (Fig. 2-1). The Witwatersrand Basin contains seven major goldfields, namely the Central Rand, East Rand, West Rand, Evander, West Wits Line, Klerksdorp and Welkom goldfields (Fig. 2-1).

2.2 Stratigraphy

The Witwatersrand System (Witwatersrand Supergroup) is closely related to the underlying Dominion Reef System (Dominion Group) and the overlying Ventersdorp System (Ventersdorp Supergroup). The three systems comprise the Witwatersrand Triad (Hamilton & Cooke, 1960). The rocks of the Triad lie unconformably on granite, gneiss and schist of the Swaziland System, which is early Precambrian in age, and largely concealed beneath a cover of rocks of the Transvaal System and Karoo System (SACS, 1980). The Venterspost Conglomerate Formation overlies the

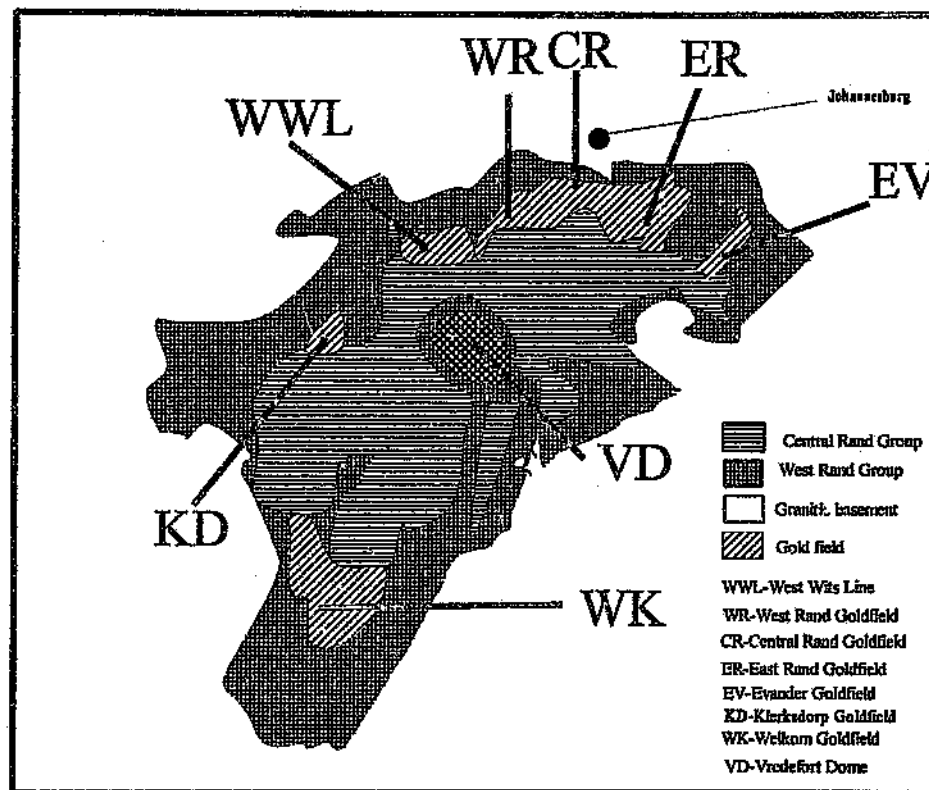


Fig. 2-1 Simplified stratigraphy of the Witwatersrand Basin showing the suboutcrop distribution of the West Rand and Central Rand Groups (modified after Pretorius, 1986).

Table 2-1 Stratigraphic column of the West Wits Line (summarized from SACS, 1980, 1996)

STRATIGRAPHY					AGE
TRANSVAAL SUPERGROUP (6 km)	Pretoria Group		Dolomite		2357 ¹ -2224 Ma ²
	Chemisspoort Group		Carbonaceous shale, quartzite, conglomerate		
	Black Reef Quartzite Fm		Quartzite, conglomerate, shale		
	Welkberg Group		Quartzite, arkoses, shale, basalt		
VENTERSDORP SUPERGROUP (±2 km)	Platberg Group	Rietgat Fm	Porphyritic lava, sediments		2714 Ma ³
		Makwassie Fm	Quartz porphyries		
		Kameeldoorns Fm	Volcanic clasts		
	Klipriviersberg Group	Edenville	Lavas and clasts		
		Orkney	Non-amygdaloidal aphanitic lava		
		Alberton	Porphyritic lava		
		Westmaria	Andesitic tuff, lava		
VENTERSPOST CONGLOMERATE Fm; Ventersdorp Contact Reef (VCR)					±2714 Ma ³
WITWATERSRAND SUPERGROUP (7 km)	CENTRAL RAND GROUP	TURFFONTEIN SUBGROUP	Mondoor Fm	Quartzite and conglomerate (Doelkraal Reef, Ub's Reef, Elusand Reef)	2894-2714 Ma ⁴
			Elsburg Fm	Quartzite	
			Gold Estates Fm	Quartzite and conglomerate (Kloof Reef, Libanon Reef)	
			Robinson Fm	Quartzite, shale, conglomerate (Kleinfontein Reef)	
		JOHANNESBURG SUBGROUP	Booyens Fm	Quartzite, argillaceous quartzite, shale,	
			Krugersdorp Fm	Quartzite, Conglomerate (Bird Reef)	
			Luiperdsvlei Fm	Quartzite and conglomerate (Cobble Reef, Doornfontein Reef, Basal Grit, Large Pebble Marker, Khaki Pebble Reef)	
			Randfontein Fm	Quartzite, conglomerate (Livingstone Reef, Johnstone Reef)	
			Main Fm	Quartzite, conglomerate (Main Reef Leader, Green Bar, Carbon Leader)	
			Blyvooruitzicht Fm	Quartzite, conglomerate (North Leader)	
	WEST RAND GROUP	JEPPESTOWN SUBGROUP	Rodepoort Fm	Shale, shaly quartzite	3970-2914 Ma ⁴
			Crown Fm	Amygdaloidal lava	
			Florida Quartzite Fm	Quartzite, small pebble conglomerate	
		GOVERNMENT SUBGROUP	Witpoortjie Fm	Green-black, green silty shale, siltstones, argillaceous, gritty quartzite	
			Coronation Shale Fm	Black magnetic shale	
			Promise Quartzite Fm	Sericitic, argillaceous quartzite, ferruginous, magnetic shale, conglomerate (Promise Reef)	
		HOSPITAL HILL SUBGROUP	Bruxton Fm	Green orthoquartzite, Shale	
			Parktown Shale Fm	Shale quartzite	
Dominion Group (2,3 km): Porphyritic and andesitic volcanics and quartzite					3086-3074 Ma ⁴
Archaean granitic basement					>3086 Ma ⁴

Witwatersrand Supergroup and underlies the Ventersdorp Supergroup. Table 2-1 shows the stratigraphic column which is mainly compiled from the South African Committee for Stratigraphy (SACS) (1980, 1996); Engelbrecht et al. (1986); Robb and Meyer (1995); Armstrong et al. (1991); Walraven (1997); and Jahn et al. (1990).

2.2.1 Dominion Group

The Dominion Group underlies the Witwatersrand Supergroup and outcrops in the Ottosdal, Klerksdorp and Vredefort Dome areas in Western Gauteng (SACS, 1980) and it is separated from the basement by palaeosols. The depositional age of this group is between 3086 and 3074 Ma (Robb and Meyer, 1995). The group consists of porphyritic and andesitic lavas and quartzite with a total thickness of 2,3 km (SACS, 1980). Economically, the Dominion Group conglomerate reefs are the oldest sedimentary gold-uranium horizons within the Witwatersrand Triad.

2.2.2 Witwatersrand Supergroup

The Witwatersrand Supergroup was named by Penning in 1888, and consists of the West Rand and Central Rand Groups (SACS, 1980). The Witwatersrand Supergroup is an approximately 7000 m thick terrigenous sequence comprising mainly arenaceous and argillaceous, as well as minor rudaceous sediments, which were deposited in a fluvio-deltaic environment in the centre of the Kaapvaal Craton (Robb and Meyer, 1995).

2.2.2.1 *West Rand Group (WRG)*

The WRG at the base occupies a roughly ovoid area with a northeast-extending axis and formed between 3074 and 2970 Ma (Robb and Meyer, 1995). This Group is composed of the Hospital Hill, Governmant, and Jeppeshtown Subgroups (SACS, 1980). Rock types comprise shales and

sandstones in roughly equal portions. The Crown Lava occurs towards the top of the sequence. The West Rand Group hosts three conglomerate reef horizons, confined to the Government Subgroup (SACS, 1980, 1996), none of which is pervasively mineralized.

2.2.2.2 *Central Rand Group (CRG)*

The CRG is preserved in a smaller area than the underlying WRG. This Group covers an area of 290 km along a northeast-trending axis by 150 km wide along the northwest of the basin, but much of it is overlain by younger rocks. The CRG consists of the Johannesburg Subgroup at the base, overlain by the Turffontein Subgroup (SACS, 1986). This sequence consists predominantly of coarse-grained subgraywacke with minor conglomerate, quartz arenite, shale, silt and lava. A maximum cumulative thickness of approximately 2880 m is preserved near Vredefort. Sediments of the CRG represent a series of fan-delta complexes. Most of the economic reef horizons in the Witwatersrand Basin are present in the CRG (Table 2-1). The depositional age of this group is 2914 to 2714 Ma (Robb and Meyer, 1995).

2.2.3 *Venterspost Conglomerate Formation (VCF)*

The VCF comprises the VCR conglomerates, and quartzites. In addition, the sedimentary sequence is often inter-digitated with lavas of the Westonia Formation of the Klipriviersberg Group, such as at Kloof Gold Mine and Driefontein Gold Mines. The conglomerates of the VCR are usually dark in colour and siliceous, chloritic and micaceous in composition. This formation unconformably overlies the Witwatersrand Supergroup.

2.2.4 *Ventersdorp Supergroup*

The Ventersdorp Supergroup is preserved within a large area, which generally conformably

overlies the VCF (SACS, 1980). The thickness of this group is greater than 1500 m in the Central Rand and 3350 to 4260 m in the Vredefort Dome (SACS, 1980). The generally accepted age of the Klipriviersberg Group is 2714 Ma, based on the precise U-Pb zircon dating of the lava (Armstrong et al., 1991).

The Ventersdorp Supergroup comprises the Klipriviersberg and Platberg Groups. The Klipriviersberg Group is composed of six formations: (i) the Westonaria Formation of dark green "talcoose tuffs" at the base, (ii) the Alberton Porphyry Formation of porphyritic lavas, (iii) the Orkney Formation of ash flows, (iv) the Loraine Formation of lavas, and (v) the Edenville Formation of amygdaloidal lava at the top (Winter, 1977, SACS, 1980). The overlying Platberg Group consists of three formations: (i) the Kameeldoon Formation representing reworked Klipriviersberg lavas, (ii) the Makwassie Porphyry Formation of quartz porphyritic lavas and (iii) the Rietgat Formation which is made up of alternating lavas and sediments (SACS, 1980).

2.2.5 Transvaal Supergroup

The Transvaal Supergroup is deposited in an large basin which covered much of the Kaapvaal Craton. This sequence consists of the Wolkberg Group, Black Reef Quartzite Formation, Chuniespoort, and Pretoria Groups, which are defined from the stratigraphy of the Eastern Transvaal (SACS, 1980). The rock units consist of andesitic-basaltic volcanics and clastic, quartzitic, dolomitic sediments in a long-lived large sedimentary basin. The thickness of this supergroup is about 6 km (SACS, 1980). The depositional age of this Supergroup is between 2224 Ma and 2557 Ma as shown by bulk rock Rb-Sr dating of Hekpoort andesite of the Pretoria Group (Van Niekerk & Burger, 1964) and the dolomite of the Chuniespoort Group (Jahn et al., 1990), respectively.

2.3 Overview of the tectonic history of the post-Witwatersrand Basin

The Witwatersrand Basin is a large hinterland basin of Archaean age developed on already consolidated continental crust south of the Limpopo plate margin (Coward et al., 1995). The Basin has experienced a complicated tectono-sedimentary history, indicated by various studies (McCarthy et al., 1986; Charlesworth & McCarthy, 1990; Myers et al., 1990, 1992; Stanistreet & McCarthy, 1991; Robb et al., 1991, 1997). A number of periods of deformation have affected post-Witwatersrand strata.

(1) Syn-Witwatersrand compression and block faulting are characterized by syndepositional tectonic folding and faulting (Robb et al., 1997), proved by occurrences of prominent northwesterly striking folds across the northern margin of the basin (McCarthy et al., 1986), major oblique-slip faults along the northern, western and southwestern margins of the basin and fault-related stratigraphic thinning of some Witwatersrand strata (Robb et al., 1997). Vermaak and co-workers (Vermaak & Roering, 1991; Vermaak & Sparrow, 1993; Vermaak & Chunnnett, 1994) studied the tectono-sedimentary processes of the VCR within the West Wits Line, explaining that the tectonic uplift and tilting during Witwatersrand time controlled the deposition of the Ventersdorp Contact Reef by providing a source for the VCR within the West Wits Line.

(2) Mid-Ventersdorp extension and graben development were characterized by outpouring of the Klipriviersberg lavas at 2714 Ma (Armstrong et al., 1991), changing from the previous compressional regime during the syn-Witwatersrand compression and faulting stage. This change may coincide with the onset of collision between the Kaapvaal and Zimbabwe cratons, resulting in the formation of number of major grabens to the west of and within the Witwatersrand Basin (Burke et al., 1985; Stanistreet and McCarthy, 1991). Half-grabens are also developed at this

stage by the inversion of pre-existing reverse (or thrust) faults to normal faults (Clendenin et al., 1988; Myers et al., 1992). Subsequent lava extrusion and extensional tectonics covered and preserved the VCR in graben and half-graben structures (Vermaak & Chunnnett, 1994).

(3) Deposition of the Transvaal Sequence between 2550 and 2200 Ma resulted in the development of extensive sedimentary cover which blanketed much of the Witwatersrand Basin. The Transvaal Sequence is characterized by large-scale open folding, a penetrative cleavage and faulting formed during a deformational event that is obviously post-Transvaal in age. Analysis of these structures has shown that their orientations vary radially with respect to the tectonic evolution of the prominent Vredefort dome feature (McCarthy et al., 1986). The Vredefort dome is associated with pseudotachylite, shatter cones and very high pressure silica minerals (e.g. coesite) which suggest that it may represent the scar of an ancient meteorite impact site that is about 2025 Ma old (Reimold, 1995). Locally reactivation of the Bank Fault during the post-Transvaal resulted in at least 200 m of normal displacement within the West Wits Line (Vermaak & Roering, 1991; Vermaarkt & Sparrow, 1993).

(4) Kibaran-aged deformation. Detailed structural studies of Friese et al. (1995) from the Free State goldfield, in conjunction with partial Ar-Ar resetting ages of various fault lithologies and tectonites have indicated localised tectono-magmatic activities at ca 1450-1315 Ma and ca 1280-1000 Ma. These are coincident with the Kibaran orogenic process of Thomas et al. (1994) within the Namaqua-Natal Mobile Belt. The process is characterized by northwest-directed thrusting into the core of the Kaapvaal Craton and Witwatersrand Basin and Pilanesburg magmatic activity along terrane boundary structures within the craton. However, the effects of the Kibaran Orogeny on mineralisation in the Witwatersrand Basin are unlikely to be significant (Robb et al., 1997).

2.4 Post-VCR Magmatic Events

The Ventersdorp lavas consist of the Klipriviersberg basalts and Makwassie quartz porphyritic lava, which were dated at 2714 and 2709 Ma by the U-Pb zircon method, respectively (Armstrong et al., 1991).

The Bushveld Complex, located on the north margin of the Witwatersrand Basin, comprises three major differentiated igneous suites. The complex is ultramafic to felsic in composition. The Rustenberg Layered Suite is ultramafic to mafic in composition and dated at 2095 Ma by Rb-Sr whole rock analysis (Hamilton, 1977) and 2061 Ma by U-Pb zircon dating (Walraven 1997). The Rashoop Granophyre Suite consists of predominantly homogeneous granophyre and granophyritic granite. A U-Pb zircon age of this suite is 2090 Ma (Faurie, 1977). The Lebowa Granite Suite comprises several granite bodies, and its U-Pb zircon age is 2054 Ma (Walraven 1997). The Rooikop Granite Porphyry related to the Rooiberg Group was recently dated at 2060 Ma by Walraven (1997), which probably represents the early phase of the Bushveld suites.

The Pilanesberg plutonism is characterized by local dyke intrusions, which occur abundantly in the Witwatersrand Basin and comprise carbonate, porphyritic diabase, Pilanesberg dolerite, syenite, quartz keratophyre and diorite (Pretorius, 1974a). The dykes are considered to be contemporaneous with the Pilanesberg activity at between 1250 and 1350 Ma (Pretorius, 1974a).

2.5 Metamorphic-hydrothermal Events

2.5.1 Features and physicochemical conditions of post-VCR metamorphism

The Witwatersrand Basin has undergone basin-wide metamorphism, as suggested by Phillips et al. (1987, 1989) and Phillips and Law (1994). Mineral assemblages of pyrophyllite-chloritoid-

muscovite-chlorite-quartz-tourmaline-rutile-pyrite occur in all the gold mines in the Witwatersrand Basin (Phillips et al., 1987). These were used to constrain the metamorphic conditions at 350 ± 50 °C (Phillips et al. 1987; Wallmach and Meyer (1990); Phillips and Law, 1994) and up to 3 kb (Phillips et al., 1987; Phillips and Law, 1994). However, metamorphic temperatures of up to 700 °C have been determined in the low-pressure granulite facies of the Vredefort Dome (Phillips, 1987; Stevens et al. 1997). The metamorphism was accompanied by widespread deformation, large fluxes of aqueous fluid, and considerable element mobility (Phillips, 1987, Phillips et al., 1989; Phillips and Law, 1994). Frimmel (1994) suggested that gold remobilization was dependent on the sulfur fugacity prevailing in a particular horizon, which, in turn, was determined by the amount of pyrite and other sulphides present in that horizon. Furthermore, with the sulfur being controlled by stratigraphy, low fluid:rock ratios in a pyrite-rich horizon were most conducive for the mobilization of the gold. Thus, long-range gold mobilization in the the Witwatersrand Basin can be expected to be the exception rather than the rule.

2.5.2 Timing of metamorphism and hydrothermal alteration

As discussed by Robb et al. (1991, 1997), metamorphism can be traced to as early as ca 3086 Ma. Three younger metamorphic ages have been detected in the Witwatersrand Basin at ca 2,5 Ga, 2,3 Ga and 2,0 Ga. The Kaapvaal Craton was subjected to a major thermal perturbation at 2050 Ma, which accompanied the emplacement of the Bushveld Complex and related igneous rocks (Robb et al., 1997). Similar ages have been reported at 1950 Ma on shales (whole rock K-Ar) by Layer et al. (1988), and at 1900 to 2050 Ma on clay separates of the VCR (K-Ar) by Zhao et al. (1995) and at 2006 Ma on pseudotachylite in the VCR (^{40}Ar - ^{39}Ar) by Trieloff et al. (1994). Pyrite and authigenic rutile were formed at ca 2,5 Ga in a fluid-circulation event that appears to be

related to the onset of Transvaal Sequence deposition. Circulation of hydrocarbon-bearing fluids and precipitation of bitumens by radiolytic polymerisation followed at ca 2,3 Ga (Robb et al, 1997). Based on studies of geochemistry and geothermometry, and summaries of previous publications on metamorphism and fluid conditions in the Witwatersrand Basin, Frimmel (1994, 1997) categorized the metamorphism and fluid evolution in the Witwatersrand Basin into five events: (1) thrust controlled pre-Transvaal alteration; (2) early Transvaal alteration; (3) basin wide burial metamorphism; (4) high grade thermal metamorphism in the collar of the Vredefort Dome; and (5) hydrothermal alteration related to the Vredefort impact event in the middle of the Witwatersrand Basin. The detailed review of the five stage events is presented in Chapter 7.

2.5.3 Contribution of metamorphic fluids to gold mineralization

There are widespread evidences of post-depositional fluids and fluid migration in the Witwatersrand Basin. However, the scale of fluid movements and its significance to gold mineralization remain to be an active topic of debate. Some workers (e.g. Phillips et al., 1987; Phillips & Myers, 1989; Phillips & Law, 1994, 1997; Barnicoat et al., 1997) suggested that the gold in the Witwatersrand Basin is of a hydrothermal origin, i.e. the dissolved gold was mainly introduced by hydrothermal fluids after the sediment deposition. Currently, Stevens et al. (1997) reviewed the metamorphism in the Witwatersrand Basin, with emphasis on metamorphic rocks exposed in the Vredefort Dome. The authors proposed that metamorphic-derived fluids had potential to mobilize tremendous amount of gold from the central portions of the depository towards the margins, i.e. the Witwatersrand goldfields. On contrary, others (e.g. Robb & Meyer, 1987, 1995; Frimmel 1994, 1997) evoked the modified placer model, i.e. gold is placer in origin and was only locally remobilized after the burial of sediments.

3 GEOLOGICAL CHARACTERISTICS OF THE WEST WITS LINE, AND AT WESTERN DEEP LEVELS SOUTH MINE

3.1 Introduction

The first mining of the VCR was carried out at the Zuurbult Mine in the West Wits Line (WWL) as early as 1888. Currently the VCR contributes 60% of the total gold extracted from the WWL (Chunnett, 1994) and contributes about 18% of the annual gold production of South Africa (Viljoen and Reimond, 1994). The VCR occurs at the contact between the Witwatersrand beds, and the basic lavas of the Klipriviersberg Group. This chapter reviews the geological characteristics of the VCR in the WWL and describes the mine geology at Western Deep Levels South Mine (WDLSM).

3.2 Review of the VCR Geology in the West Wits Line

3.2.1 Geological structures

Major geological structures in the WWL are the Rand and Bank anticlines, and the Bank fault. These features were developed contemporaneously with the VCR and subsequently modified by later structures such as the West Rand, Tear and Master Bedding faults (Engelbrecht et al., 1986) (Fig. 3-1, Table 3-1).

The Bank anticline strikes NNE, and affects the entire Witwatersrand Supergroup up to the VCR in the WWL. This deformation, however, predates the VCR and is possibly related to the Sotho Orogeny of Winter (1987). The Rand Anticline, however, has a ENE striking axis for the most

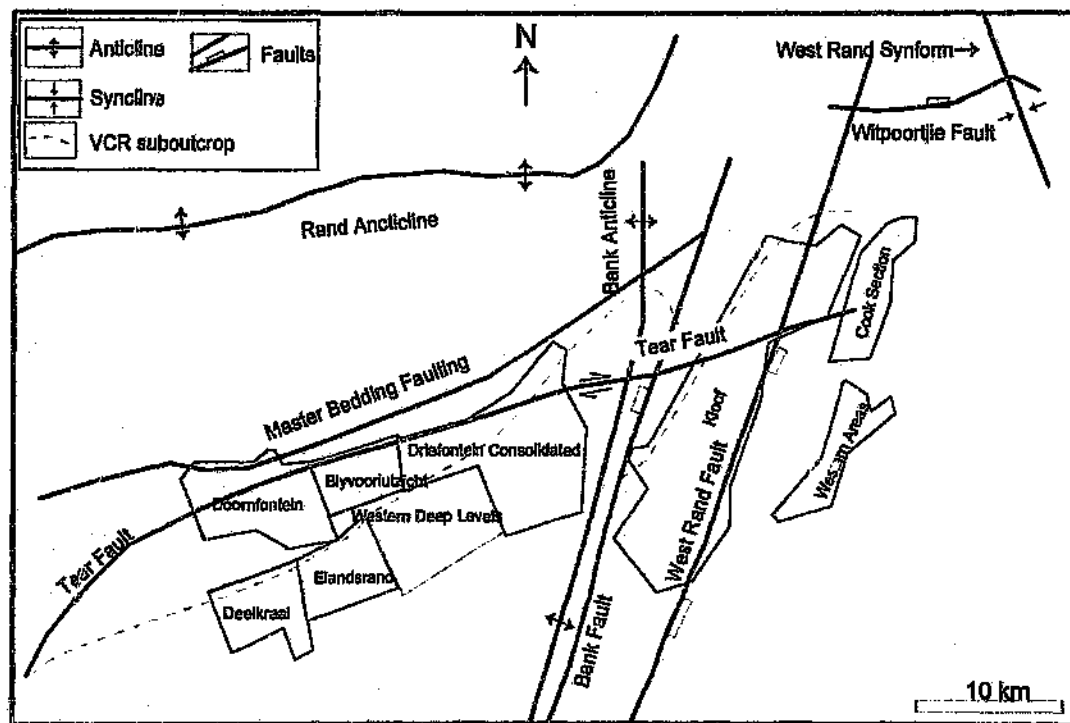


Fig. 3-1 Generalized structural map of the WWL and the adjacent West Rand Goldfield, Witwatersrand Basin (modified after Engelbrecht et al., 1986), showing the major tectonic features.

Table 3-1 Summary of geological characteristics of the VCR in the WWL

Structures		Pre-VCR Bank anticline, post-VCR (pre-Black Reef) anticline; Master Bedding Fault, Tear Fault, and Bank Fault.	Engelbrecht et al., 1986
VCR facies	Unit III	Conglomerate, >95% white quartz pebbles	Germs&Schweitzer, 1994; Reddy&Germs, 1994; Hall, (1994)
	Unit II	Four polymictic conglomerate cycles with Inter-Reef Lavas	
	Unit I	Three cycles of channel lag conglomerate	
VCR type	WDL type	Residual pediment deposits with palaeorelief and about <4° underlying unconformity, e.g., WDL SM, Deelkraal Gold Mine	McCarthy, 1994 (WDL-Western Deep Levels, SD-South Deep, WKGF-Welkom goldfield)
	SD type	Narrow zones of mineralized conglomerate adjacent to active faults about >10-15° underlying unconformity, e.g., SD Mine, to the north of Loraine at the WKGF	
Hanging wall and footwall		Hangingwall: major Alberton Fm with minor Westonia Fm in places. Footwall: Johannesburg and Turffontein Subgroups	VCR Working Group, 1994
Minerals	Major	Chlorite, muscovite, quartz, sulphides (po, py, apy, cpy, ga, and sph)	Smits, 1994 Henckel&Schweitzer, 1994 Zhao et al., 1994
	Minor	Albite, calcite, siderite, epidote, sphene, pyrophyllite, talc, titanite, pentlandite, zircon, chromite	
	Trace	Bismuthinite, tetrahedrite, stibnite, molybdenite, anatase, silver, monazite, xenotime, apatite, c. baltite, brannerite, gold	

po--pyrrhotite, py--pyrite, apy--arsenopyrite, cpy--chalcopyrite, ga--galena, sph-sphalerite.

part, but sharply deflected from ENE to NNE when it reaches the Bank Anticline. Deformation of the Rand Anticline was active from post-VCR to pre-Black Reef times, which resulted in a monocline of the VCR and the Ventersdorp Supergroup (Engelbrecht et al., 1986).

The Bank Fault has a NNE strike, whereas the Tear and Master Bedding faults are sub-parallel to the VCR strike. The Bank Fault is the major discontinuity separating the WWL and the West Rand Goldfield (Engelbrecht et al., 1986), and has been studied by Vermaak and coworkers (Vermaak and Roering, 1991; Vermaakt and Sparrow, 1993; Vermaak and Chunnett, 1994). According to the authors, the Bank Anticline was initiated as a thrust fault accompanying the Bank Fold as a result of E-W compression during Turffontein Subgroup times, and resulted in erosion of 1000 to 1500 m of the Witwatersrand Supergroup strata prior to and during VCR times. The tectonic activity of the Bank Fault was inverted from thrusting to normal movement during VCR times, during which times the VCR was channelized and reworked along the down-thrown side of the Bank Fault. Following this, the Klipriviersberg Group lavas were erupted and deposited during a period of the extension. Normal faulting continued until post VCR times and has a recognizable displacement of at least 200 m. These predominant normal fault structures in the WWL are believed to be related to gravity collapse of pre-existing structures (Engelbrecht et al., 1986).

The Master Bedding Fault (MBF) is intersected by mining activity at West Driefontein Gold Mine, and is characterized by crushing and mylonization of quartzite, shale and igneous materials (Engelbrecht et al., 1986). It exceeds 40 km along strike and has 4 km of downthrow to the south. MBF formed in post-VCR times by a southward directed gravity-glide. High concentrations of methane and hydrogen are also intersected in this fault. The Tear Fault has a right-lateral

movement, and runs along the north boundary of the WWL.

The block models of Myers et al. (1990a, 1992) and McCarthy (1994) suggested that the WWL is surrounded by tilted blocks of the Vreysrus Dome in the north and Westerdam Dome in the west. These blocks controlled the tectono-sedimentary development of the VCR. The channel directions of the VCR are mainly from ENE to WSW in the WWL, and NW-SE in the West Rand Goldfield (VCR Working Group, 1994).

3.2.2 VCR facies and reef types

De Kock (1940) first proposed that the VCR rests unconformably on the underlying Witwatersrand Supergroup and that its sedimentary facies are a function of degradational process. This was confirmed by Thomas (1979) and Els (1989), who worked at the Vaal Reef and Stilfontein Gold Mines, respectively. On the contrary, aggradational processes in the VCR have been suggested by Minter (1970); Chapman and Briggs (1989); and Mullins (1993) based on their work in the WWL and West Rand Gold Mines. More recently, Winter (1994) proposed a conceptual stratigraphic model for the VCR. This author suggested that the VCR was deposited in a beach environment and represents an unconformity-bounded depositional sequence, which becomes progressively more conformable with the underlying Witwatersrand sediments in a basinward direction.

A model consisting of three sedimentary facies for the VCR was proposed by Hall (1994) who classified the VCR into the Upper Unit, Inter Unit and Lower Unit, based on his work at Kloof Gold Mine. Germs and Schweitzer (1994) discussed the characteristics of the three sedimentary units in the VCR in detail and further subdivided the units into eight cycles to explain the regional

morphostratigraphy of the VCR (Table 3-1).

Unit I includes three cycles: cycle 1 is mainly composed of pebble lags of white vein-quartz pebbles and green quartzite; cycle 2 comprises black quartzite pebbles; and cycle 3 consists of grey quartzite pebbles. Five cycles mark Unit II: cycle 1 is composed of polymictic conglomerates of white and black vein-quartz pebbles; cycle 2 is formed predominantly by white vein quartz with minor black vein quartz, chert, quartzite and shale clasts; cycle 3 consists of green quartzite, tuff, mafic volcanic flows and shale; cycle 4 is characterized by polymictic conglomerates; and cycle 5 comprises white vein-quartz pebbles with a white-green matrix and more grey-green quartzite. Unit III is composed of conglomerates with more than 95% white vein-quartz pebbles, grey-black quartzite and tuffaceous deposits. These characteristics are summarized in Table 3-1.

McCarthy (1994) recognized two distinct types of VCR: the Western Deep Levels (WDL) type and South Deep (SD) type (Table 3-1). The WDL type characterized by pronounced palaeorelief at its base; extensive, residual pediment deposits; small angular unconformities ($<4^\circ$) in the footwall; and gravel sheets. This type mainly occurs west of the West Rand Fault in the WWL and is also present in the northwestern margin of the Klerksdorp goldfield. The SD type reef, by contrast, is characterized by narrow zones of conglomerates adjacent to active faults, greater angular unconformity (10 to 15°) with the footwall, and rapid facies changes. This type occurs in the South Deep Gold Mine and in the north of the Lorraine Gold Mine.

Ore bodies of the VCR consist of two types: the terrace facies and the slope (or riser) facies which were described at WDL SM by McWha (1994) and Henning et al. (1994). These are described in Section 3.3 in more detail.

3.2.3 Hanging wall and footwall of the VCR

The VCR working Group (1994) presented hanging wall and footwall plans of the VCR. The direct hanging wall of the VCR generally consists of the Alberton Formation in the west, i.e. Western Deep Levels, Elandsrand and Deelkraal gold mines, but the Westonia Formation occurs as the VCR hanging wall in the east i.e. at Kloof and Driefontein Mines. The footwall of the VCR consists of the Johannesburg Subgroup in the core of Bank Anticline and the Turffontein Subgroup on its flanks.

3.2.4 Mineralogy of the VCR

Based on the studies of Smits (1994) at Kloof Gold Mine, of Henckel and Schweitzer at Elandsrand, and of Zhao et al. (1994) at WDLMS, the mineralogy of the VCR can be documented in terms of major (>5%); minor (1-5%) and trace (<1%) components (Table 3-1). The major minerals in the VCR are quartz, chlorite, muscovite, and the major sulphides (pyrrhotite, pyrite, chalcopyrite, galena, sphalerite, arsenopyrite); minor minerals include albite, calcite, siderite, epidote, sphene, pyrophyllite, talc, titanite, pentlandite, zircon and chromite; and trace minerals are bismuthinite, tetrahedrite, stibnite, molybdenite, anatase, silver, monazite, apatite, and gold. This is discussed in more detail in Chapter 4.

3.3 Geology of the VCR at Western Deep Levels South Mine

3.3.1 Introduction

WDLMS is served by two shafts: the Main and Service Shaft. The mine produces 13 tons of gold per year from the VCR between 75 level (2000 m below the shaft collar) and 99 level (2735 m below the shaft collar). Currently 4 longwalls, namely 49, 53, 61, and 65, are mined down to

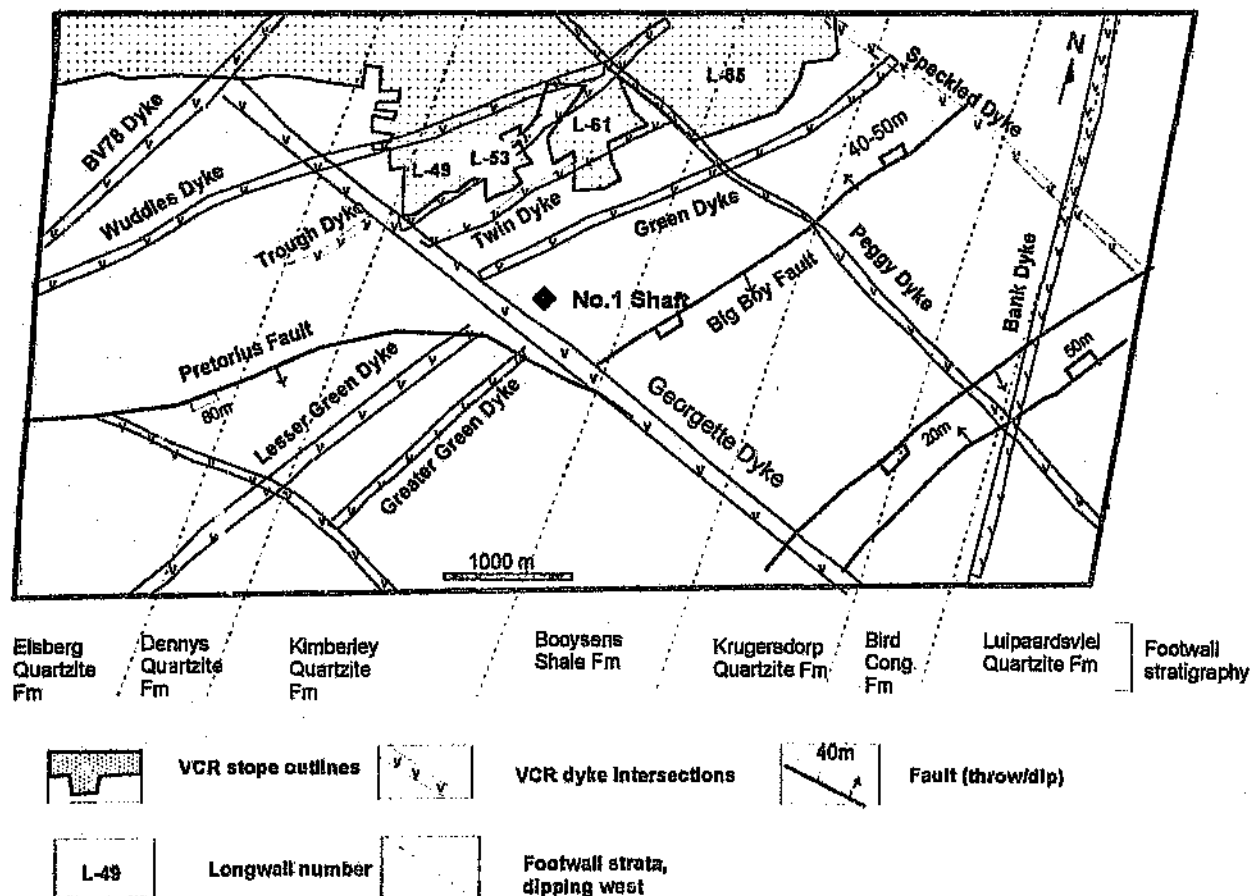


Fig. 3-2 Underground structure: plan of the VCR at WDSM (after McWha, 1994), showing major faults and dykes. The Footwall stratigraphy of the Central Rand Group is projected onto the plane, which is part of the west limb of the Bank Anticline (after Henning et al., 1994).

87 level (Fig. 3-2). Surface lithologies in the mine consist mainly of shales of the Timeball Hill Formation, Pretoria Group and minor sediments (quartzites, shales, and conglomerates) of the Black Reef Formation (Transvaal Supergroup).

Major structures observed at the surface include the Bank dyke which occurs to the east of the mine boundary. The geology exposed underground is described in more detail below.

3.3.2 Geological structures observed in the mine

Structurally the mine lies on the south limb of the Rand Anticline and the west limb of the Bank Anticline. The geological structure is dominated by faults and dykes. Folding is absent (Fig 3-3). Generally, the faults have a downthrow movement of less than 40 m. However, the Pretorius and Big Boy Faults have vertical displacements of 80 m and up to 50 m, respectively. A few reverse faults are observed and are associated with the near EW-trending Georgette and Peggy Dykes (McWha, 1994) (Fig. 3-2). Most of the faults postdate the VCR and have displaced strata and ore bodies within the mine. Dykes mainly strike E-W and NNE and intrude the VCR (Fig.3-3). They are basic in composition. The Bank Dyke is exposed on the surface and formed during Karoo times (Madams, 1991).

3.3.3 The VCR conglomerate and quartzite

Ore bodies in the VCR comprise two types: the terrace type and the slope or riser type. They formed in response to the geographic evolution of the terrace prior to and during VCR deposition (McWha, 1994; Henning et al., 1994). The terrace type occurs in river channels and is characterized by thicknesses of 50 to 200 cm and by high gold concentrations. The slope type is preserved along palaeo-river banks (slopes), and consists of thin, unstable conglomerate sheets

of less than 30 cm thickness, and is characterized by low gold grades. The VCR ore bodies generally dip to the southeast at 18 to 24°, have a thickness of 20 to 200 cm, and rest unconformably on the footwall at an average angle of 4° (Henning, 1994). The orebodies are mainly comprised of conglomerates with internal quartzites. The conglomerates are auriferous, oligomictic, poorly sorted, clast- to matrix-supported. The clasts of the conglomerates comprise mainly white and smoky vein quartz with minor chert. The size of vein quartz ranges from 1 to 10 cm in diameter, whereas the chert is usually much smaller than the vein quartz in size. The matrix of the conglomerates is chloritic, micaceous, quartzitic, and sulphidic with dark grey to yellowish green colour. The conglomerates host major gold ore bodies.

Two types of the quartzites occur in the VCR: an apple-green fine-grained immature quartzite, and a fine- to medium-grained dark-grey mature quartzite. Gold concentrations in the quartzites are very low.

3.3.4 Hanging wall and footwall of the VCR

As discussed above, the Klipriviersberg Group comprises the Westonaria, Alberton, Orkney, and Edenville Formations. The Alberton Formation of this Group constitutes the direct hanging wall of the VCR at WDLSM (McWha, 1994), and consists of basaltic-andesitic lavas (see Chapter 5 bulk rock geochemistry), characterized by pillow textures at the base, and amygdaloidal textures in lava in contact with the VCR. The Westonaria Formation, as described elsewhere, is absent at WDLSM.

The footwall of the VCR is composed of the Johannesburg and Turffontein Subgroups of the Central Rand Group. In the mine, the direct footwall of the VCR consists of Elsburg quartzite in

the west, then successively Dennys Quartzite, Kimberley Quartzite, Booysens Shale, Krugersdorp Quartzite, and Bird Conglomerate Formations and Luipaardsvlei Quartzite Formation towards the east (McWha, 1994, Henning et al., 1994) (Fig. 3-2). The footwall strata strike about N-S in contrast to the VCR which is southeast striking. This is caused by the effect of the pre-VCR Bank Anticline on the footwall strata, and the post-VCR Rand Anticline on the VCR. The reef types (terrace reef and slope reef) are controlled by palaeomorphology, as shown by the distinctive footwall bedding-plane truncation angles of risers and terraces against placer palaeodips, and placer thickness (Henning et al., 1994). The palaeomorphology is, in turn, affected by the footwall rock types. For example, it is common that palaeoslopes merge with the ridge formed by Booysens Shale at Western Deep Levels South Mine (McWha, 1994).

3.4 Summary

In summary, the VCR was developed at the contact between the Klipriviersberg Group lavas and the underlying Central Rand Group in the WWL. It is a well preserved, gold-rich conglomerate horizon. The VCR strata formed in a dominantly fluvial fan environment, and consists of three units. Two conglomerate types characterize the VCR, namely the stable, low angle, footwall strata-affected Western Deep Levels (WDL) type; and the high angle, unstable, active fault-influenced South Deep (SD) type. The VCR formed at about 2714 Ma, and was mainly disturbed by the post-VCR Rand Anticline and the related faults. The VCR at WDL SM is a typical WDL type, characterized by an unconformity with the footwall strata consisting of thick, stable terrace reefs and thin unstable slope reefs, which were controlled by the palaeomorphology of the footwall. The Alberton Formation and Central Rand Group comprise the hanging wall and the footwall of the VCR. The VCR lies on a monocline and its structures are characterized by post-VCR faults, and dykes.

4 MINERALOGY OF ALTERATION AT WESTERN DEEP LEVELS SOUTH MINE

4.1 Introduction

Alteration is produced by the interaction of hydrothermal fluids with host rocks and is controlled by the compositions of both the original wall rocks and the fluid compositions. In this chapter, alteration zones within and around the VCR, as well as associated with dykes, and pseudotachylite are described, and the major alteration types are presented. Alteration stages are interpreted and summarized.

4.2 Previous work on alteration mineralogy in the Witwatersrand Basin

4.2.1 Alteration mineralogy in the Klipriviersberg Group lavas

Petrography, mineralogy and geochemistry have been studied by various workers (Winter, 1976; Wyatt, 1976; Bowen et al., 1986; Westhuizen et al., 1991; Linton, 1992). Volcanic rocks of this group comprise fine-grained to aphanitic basic to intermediate lavas, occasionally porphyritic, as well as tuffs and agglomerates. The primary mineral assemblages can be seen in all formations of the group and are mainly plagioclase, augite, epidote, and sphene while the primary minerals are partially altered and replaced by actinolite, epidote, chlorite, and quartz during post-depositional events (Bowen et al., 1986). Amygdales of the lavas represent post-lava mineral growth and consist mainly of quartz, calcite, epidote, chlorite, chalcedony and in rare cases haematite, pyrite and chalcopyrite (Linton, 1992).

At least two types of alteration have been identified: (1) poorly developed purple alteration zones

in places with enrichment of minute chlorite amygdales; and (2) bleaching dark green alteration with enrichment of secondary epidote.

4.2.2 Alteration mineralogy in the Witwatersrand conglomerates, quartzites and meta-pelites

A vast amount of literature has been published concerning the primary, synsedimentary and authigenic mineralogy of the Witwatersrand reefs (e.g. Coetzee, 1965; Viljoen, 1964; Hallbauer, 1972; Liebenberg, 1973; Feather & Koen, 1975; Pretorius, 1977; Hallbauer, 1986; MacLean & Fleet, 1989; Law, 1990).

For example, Coetzee (1965) described the vertical distribution of the heavy mineral assemblage in meta-conglomerates of the Dominion Reef, Witwatersrand reefs, VCR, and the Black Reef in the Transvaal Supergroup. The spatial distribution and compositional variation within a single reef horizon were first described by Viljoen (1964). Feather and Koen (1975) summarized the mineralogy of the Witwatersrand reefs largely based on the observation of polished sections. Based on the use of the scanning-electron microscope, microprobe and refined techniques in atomic absorption spectrophotometry, and neutron activation analysis together with the previous work, Hallbauer (1986) summarized detailed mineralogy of pyrite, gold, uranium and carbonaceous matter in the Witwatersrand. The results from pyrite, gold, and uranium and carbonaceous matter support the following ideas: (1) different provenance areas for various fans in the Witwatersrand Basin; (2) the majority of the provenance areas was geochemically different from the Archaean Barberton Mountain Land; (3) a large proportion (up to 90%) of the gold is detrital, retaining its detrital features; (4) validity of the modified placer theory in principle; (5) no major solution transportation of gold or uranium; (7) an oxygen-deficient depositional environment; and (8) the important role of organic matter in the concentration of gold and

uranium in distal facies and locally, in low-energy environments of certain reefs, such as the Carbon Leader Reef and Vaal Reef. MacLean and Fleet (1989) studied compact round pyrite from the Basal reef, Vaal reef and VCR in the Witwatersrand Basin and suggested the compact rounded pyrite does represent a detrital origin due to the truncation of original oscillatory as zonation. Zhou et al. (1995) studied pyrrhotite in the Witwatersrand gold fields and suggested that pyrrhotite is widespread in all lithologies of the Witwatersrand Supergroup due to regional metamorphism instead of intrusion of sills and dykes.

Recently, Law (1990) carried out a detailed study on the alteration mineralogy of rock-forming minerals (e.g. silicates, phyllosilicates, carbonate) in quartzites and meta-pelites in the Witwatersrand Supergroup in the Welkom Goldfield and suggested that argillic alteration has affected quartzites of the entire Central Rand Group and the present mineral assemblages reflect the syn-metamorphic modification and re-equilibration of the pre-existing diagenetic assemblage. Moreover, mineralogical and compositional differences between the West Rand Group and Central Rand Group are present. Enhanced alteration of Central Rand Group lithologies has destroyed initial detrital variation in phyllosilicates and resulted in widespread, secondary mineral assemblages due to significant fluid influx, particularly along conglomeratic aquifers in the Witwatersrand Basin. Fluids leached Na, K, Fe and Mg from quartzites and this resulted in the destruction of the pre-existing detrital assemblage in quartzites and meta-pelites in the Witwatersrand Supergroup. However, the West Rand Group preserved some labile detrital minerals (e.g. feldspar) due to its limited amount of fluid influx during rapid burial processes.

In the same study (Law, 1990), detrital rock-forming minerals in quartzites and meta-pelites were determined to be mainly quartz, feldspar, muscovite, zircon, rutile and chromite. Moreover,

authigenic mineral assemblage was quartz - muscovite - kaolinite - pyrophyllite - chlorite - chloritoid - leucoexene - pyrite - zircon.

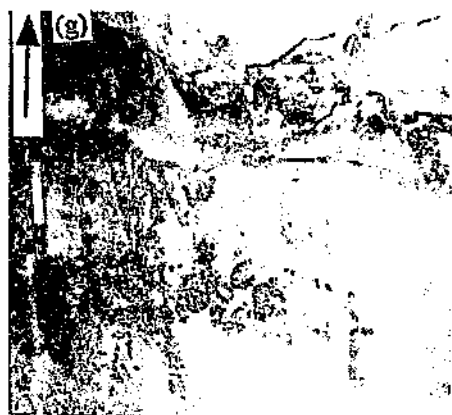
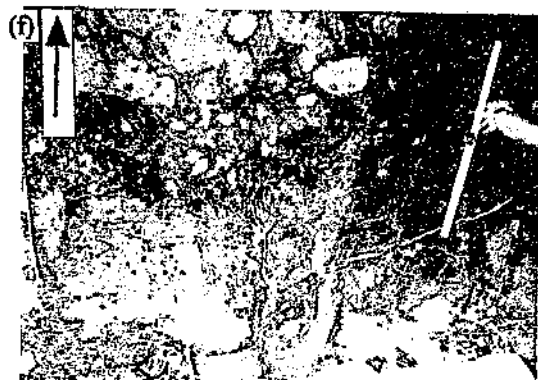
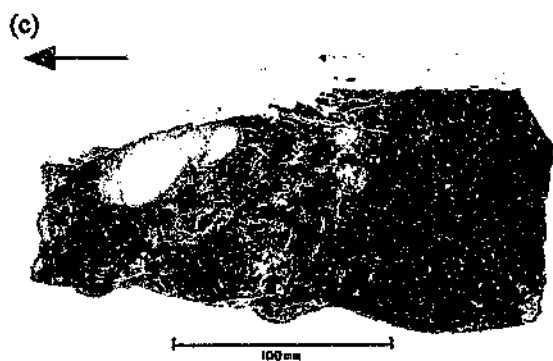
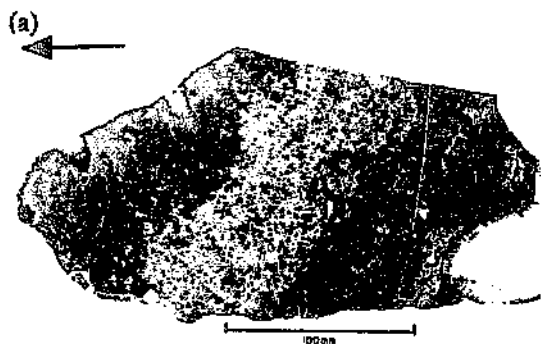
4.3 Alteration zones associated with the VCR

Alteration in the VCR occurs mainly around the conglomerate reef, as well as around faults and dykes that cut across it. Little alteration around pseudotachyllite is found. Details of the alteration around the VCR are described below. In addition, brief descriptions of the alteration around dykes, faults and pseudotachyllite are presented.

4.3.1 Alteration within and around the VCR

Seven alteration zones in the VCR were recognized ranging from the hanging wall to the footwall, based on mineral assemblages and alteration colours (Fig. 4-1, Table 4-1). In the hanging wall (lavas), three alteration zones, namely Dark Green (DG), Whitish Grey (WG), and MultiColour (MC) zones, were identified in terms of different mineral assemblages, and distinct colours with certain areas (Fig. 4-1a). The DG zone is typically 100 to 200 cm in width. The mineral assemblage is chlorite-albite-muscovite-calcite-epidote-quartz, and is characterized by a dark grey colour and enrichment of chlorite. The WG zone is about 30 to 50 cm wide. The mineral assemblage here is calcite-chlorite-muscovite-quartz-sulphides, and is characterized by a whitish grey colour and enrichment of calcite. Cubic pyrite is enriched relative to pyrrhotite and other sulphides in the DG zone. The MC zone is narrow, typically about 20 to 50 cm wide and comprises a mineral assemblage of sphene-chlorite-quartz-(muscovite-calcite). This zone is characterized by multicolours and enrichment of sphene. The alteration in the hanging wall lava extends from 150 to 300 cm.

Fig. 4-1 Distinctive alteration zones within and around the VCR. (a) Alteration zones in lava (from left to right): DG zone is characterized by dark grey colour and enrichment of quartz amygdales; WG zone is characterized by enrichment of carbonates, and by whitish colour; MC zone is characterized by enrichment of sphene (white); a large quartz pebble at right marks top of the reef. (b) RA zone conglomerate is cut by quartz veinlets and characterized by dark grey colour. (c) RA zone conglomerate and DGG zone quartzite is characterized by dark grey colour. (d) at left, LDG zone quartzite is characterized by scattered secondary pyrite pervading into the footwall quartzite; in the middle, DGG zone quartzite is characterized by enrichment of chlorite, pyrrhotite, sphalerite, galena, and chalcopyrite. (e) GG zone quartzite, characterized by enrichment of muscovite and light green colour. Alteration is developed along microfractures, and foresets. (f) slope reef in RA zone (middle) with hanging wall lava (upper), and footwall quartzite (below). (g) pebble lags of conglomerate (RA) with quartzite. (h) Terrace Reef in RA zone (middle) with hanging wall lava (upper), and footwall quartzite (below). Arrow shows way up.



The reef alteration zone (RA) within the VCR is about 20 to 200 cm wide depending on reef thickness, and consists of a mineral assemblage of chlorite-muscovite-quartz-sulphides-calcite-albite and possible rutile. This zone is characterized by a dark grey colour and enrichment of chlorite, muscovite, and sulphides. Apple green quartzites in the VCR are not grouped into this zone due to their very different mineral and chemical characteristics.

In the footwall, three alteration zones, namely Dark Grey zone (DGG), Lighter Dark-Grey zone (LDG), and Greenish Grey zone (GG), were recognized (Fig. 4-1c, d). The DGG zone occurs immediately below the VCR and is about 20 to 50 cm wide. The zone comprises a mineral assemblage of chlorite-muscovite-quartz-sulphides-albite-(rutile), and is characterized by a dark grey colour and enrichment of chlorite, muscovite, albite and pyrrhotite, sphalerite, galena and chalcopyrite. The LDG zone occurs directly below the DGG zone and is about 20 to 100 cm wide. The zone comprises a mineral assemblage of muscovite - chlorite - quartz - pyrite - pyrrhotite - albite, and is characterized by enrichment of muscovite and pyrite. The GG zone occurs below the LDG zone and is widely distributed throughout the mine. This zone is composed of a mineral assemblage of muscovite - (chlorite - quartz) - talc, and is characterized by enrichment of muscovite. The alteration in this zone is developed along microfaults and foresets (Fig. 4-1e). The alteration in the GG zone extends from 100 to 200 cm, and is related to faults, microfractures and foresets.

4.3.2 Alteration around dykes

The alteration around dykes is developed in all lithologies, and is termed the "chilled zone" at WDLMS and "burnt zone" at Deelkraal Gold Mine. Mineral assemblages of the alteration in the sediments (VCR conglomerates and quartzites) consist of zoned mineral assemblages of chlorite,

quartz, muscovite, and sulphides. The alteration is characterized by distinctive mineral assemblages, recrystallization textures, and colouration as well as gold remobilization (Table 4-2). Five alteration zones are distinguished and named the Lava contact alteration Zone (LZ), self-metamorphosed Dyke Zone (DZ), the Inner Zone (IZ), Middle Zone (MZ), and Outer Zone (OZ) in the VCR conglomerates and quartzites.

The LZ zone occurs immediately around dykes and is a narrow zone of 20-50 cm width. This zone is composed of a mineral assemblage of chlorite-quartz-sphene-pyrite-(muscovite-calcite), and is characterized by a dark grey colour, enrichment of chlorite and pyrite. Pyrite veinlets are abundant in direct contact with the dykes. The DZ is defined as a self-metamorphosed zone and is 20-200 cm wide. This zone comprises a mineral assemblage of chlorite-muscovite-quartz-sulphides-calcite-albite and is characterized by chlorite, muscovite and quartz. Pyrrhotite is enriched relative to pyrite and other sulphides. The IZ zone occurs on the inside of alteration haloes around dykes and is characteristically dark grey in colour and 20 to 100 cm in width. This zone consists of a mineral assemblage of chlorite-quartz-muscovite-pyrrhotite-pyrite and is characterized by recrystallisation of quartz, brecciation of the rocks, and by enrichment of quartz veinlets. The width of the alteration zone is strongly related to the physical properties of the wall rocks, dyke width and fracture intensity. Based on mining experience, the gold grades in reefs are generally low in this alteration zone due to remobilization of gold.

The MZ zone is from light to dark grey in colour and from 100 to 200 cm in thickness. This zone comprises a mineral assemblage of muscovite-chlorite-quartz-pyrrhotite and is characterized by enrichment of muscovite and quartz. Quartz veinlets often occur in this zone. The OZ zone is light green in colour and 20-500 cm in width. This zone is composed of muscovite-(chlorite-quartz)-pyrrhotite and is characterized by discontinuous alteration and enrichment of muscovite.

Table 4-1 Summary of alteration characteristics within and around the VCR at WDLMS

Lithology	Zone name	Mineral assemblage	Colours	Width (cm)	Qz	Ch	Ms	Ab	Ep	Sp	Cc	Ga+Sph+Cpy	Py	Po	Au	Rt
Hanging wall Lavas	DG	Ch-Ab-Ms-Cc-Ep-Qz	Light grey	100-200	○	■	○	■	○	+	○	+		+	-	-
	WG	Co-Ch-Ms-Qz-Sf	Whitish grey	30-50	○	■	○	○	+	+	■	○	○	○	-	-
	MC	Sp-Ch-Qz-(Ms-Cc)	Multi-colour	20-50	■	■	+	○	+	■	+	+	+	+	(+)	○
VCR conglomerates	RA	Ch-Ms-Qz-Sf-Cc-Ab-(Rt)	Dark grey, green	20-200	■	■	■	○	+	○	+	○	○	○	-	○
Footwall Quartzites	DGG	Ch-Ms-Qz-Sf (Fe/Pb/ Zn/Cu)-Ab-Rt	Dark grey	20-50	■	■	■	○	-	-	+	○	+	○	(+)	○
	LDG	Ms-Ch-Qz-Py-Ab	Lighter dark grey	20-100	■	■	■	○	-	-	+	+	○	+	-	+
	GG	Ms-(Ch-Qz)	greenish grey	100-200	○	+	■	+	-	-	-	-	-	+	-	-

Qz-quartz; Ch-chlorite; Ms-muscovite; Ab-albite; Ep-epidote; Sp-sphene; Cc-calcite; Ga+Sph+Cpy-galena+sphalerite+chalcocopyrite; Py-pyrite; Po-pyrrhotite; Au-gold; Rt-rutile; Sf-sulphides.
■—Major minerals; ○—minor minerals; and +—trace elements, (+)—possible Au

Table 4-2 Summary of alteration characteristics within and around dykes at Deelkraal Gold Mine

Lithology	Zone name	Mineral assemblages	Colours	Width (cm)	Macrofeatures	Au	Qz	Ch	Ms	Ab	Ep	Sp	Cc	Ga+Sph+Cpy	Py	Po
Lava	LZ	Ch-Qz-Sp-Py (Ms-Cc)	Dark grey	20-50	Py veins	Enrichment	■	■	+	○	+	■	+	+	○	+
Dyke	DK	Ch-Ms-Qz-Sf-Cc-Ab	Dark grey	20-2000	Qz veins	Enrichment	■	■	■	○	+	○	○	+	+	○
Conglomerates Quartzites	IZ	Ch-Ms-Qz-Po-Py	Dark grey	20-100	Qz veins, brecciations, Qz recrystallisation	Depletion	■	■	■	○	-	-	+	○	+	○
	MZ	Ms-Ch-Qz-Po	Lighter dark grey	100-200	Qz veinlets	-	■	○	■	○	-	-	+	+	+	+
	OZ	Ms-(Ch-Qz)-Po	greenish grey	100-500	Rare	-	○	+	■	+	-	-	-	-	-	+

Microfractures and foresets in the VCR and quartzites played a major role during alteration. The alteration within and around dykes is from 0,6 to 10m wide depending on the scale of dykes and the nature of the host rocks.

4.3.3 Alteration related to pseudotachylite

The alteration zone related to the pseudotachylite is not as prominent as the above-mentioned alteration zones within and around the VCR and dykes, but it is visible in some pseudotachylites. The alteration is limited to a narrow zone of from 5 to 30 cm wide and is characterized by a mineral assemblage of quartz - chlorite - muscovite - pyrite - pyrrhotite within and around pseudotachylites.

4.4 Alteration types

Eight major alteration types are identified including albitization, chloritization, muscovitization, silicification, sulphidization, epidotization, carbonatization, and talc alteration. Their characteristics are described below.

4.4.1 Albitization

Secondary albite was determined by microscopy, XRD, and Electron Microprobe analysis. It is commonly present in veins or veinlets in the hanging wall lavas (Fig. 4-2a), but also occurs in the conglomerates and footwall quartzites (Fig. 4-2b, c and e). Hydrothermal albite is typically fresh and characterised by albite twinning. Coexistence of albite with calcite and quartz in quartz-calcite-albite veins suggests a genetic relationship between these phases. Grains of albite usually replace sulphides and in turn, are replaced by chlorite and muscovite (Fig. 4-2c, e). Calcite genetically coexists with albite and pyrite (Fig. 4-2d). Secondary albite was also reported at Kloof

Fig. 4-2 Photomicrographs of secondary rock-forming minerals and textures. (a) vein of albite (ab), calcite (cal), and quartz (q) occurring in lava. (b) typical euhedral secondary albite with a fresh albite twin replacing secondary euhedral pyrite and is reversely replaced by muscovite around its edges. (c) in quartzite, the coexistence of secondary albite, muscovite and pyrite with micaceous matrix indicates a paragenetic sequence of pyrite $\rightarrow$ albite $\rightarrow$ chlorite-muscovite. (d) in quartzite, secondary euhedral cubic pyrite is replaced by albite, calcite, and muscovite which implies a genetic sequence of: pyrite $\rightarrow$ albite-calcite $\rightarrow$ muscovite. Quartz grain is overgrown by muscovite. (e) shows fine-grained matrix chlorite and muscovite. Detrital muscovite is bent, and recrystallized. (f) chlorite replacing a large (>2 mm) detrital grain of muscovite along its cleavage planes.

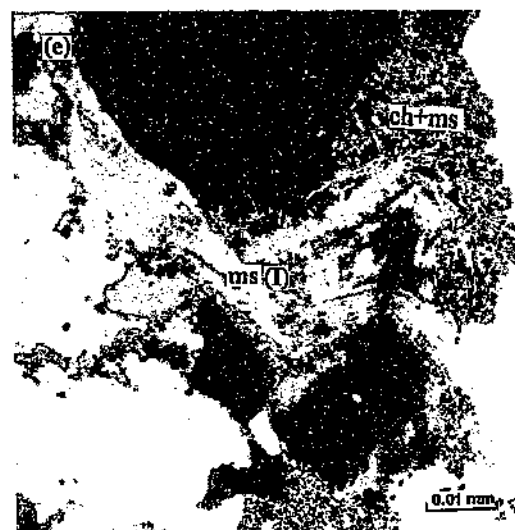
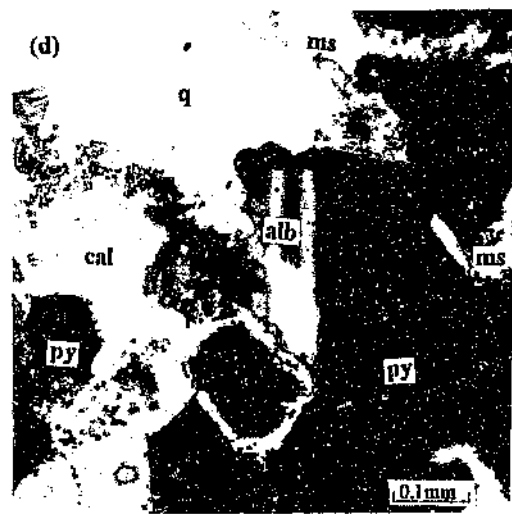
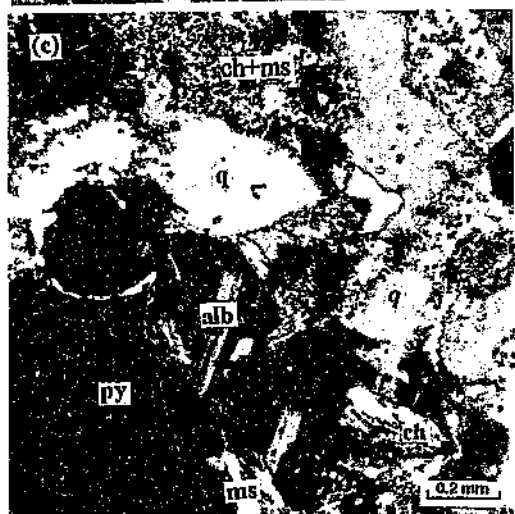
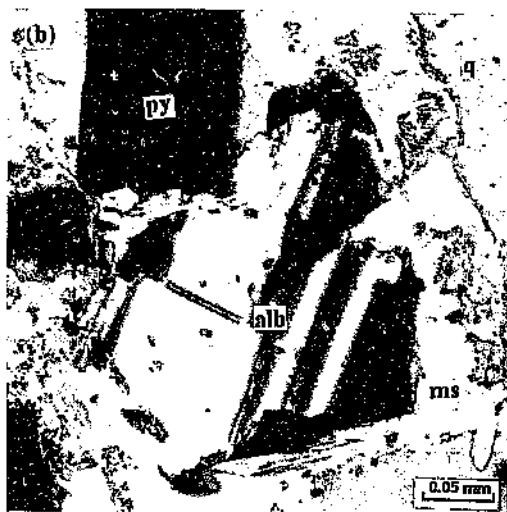


Fig. 4-2 (continued) Photomicrographs of secondary rock-forming minerals and textures. (g) porphyritic lava consisting of primary plagioclase phenocrysts and groundmass which are replaced by chlorite, and muscovite. (h) amygdaloidal lava: an amygdale consisting of quartz, chlorite and calcite, which displays a genetic sequence of quartz, chlorite, muscovite, and calcite. (I) chlorite nodules: together with muscovite and, possibly, replacing garnet, this assemblage normally indicates high gold concentrations. (j) quartzite: chlorite flakes (ch_m) coexisting with fine-grained chlorite (ch_n). Chlorite also replacing quartz grains and pyrite. (k) VCR conglomerates: muscovite and secondary quartz (q_m) overgrew quartz pebbles. (q_n) and (l) muscovite flakes formed by replacement of quartz grains, matrix, and recrystallisation, which seems foliated.

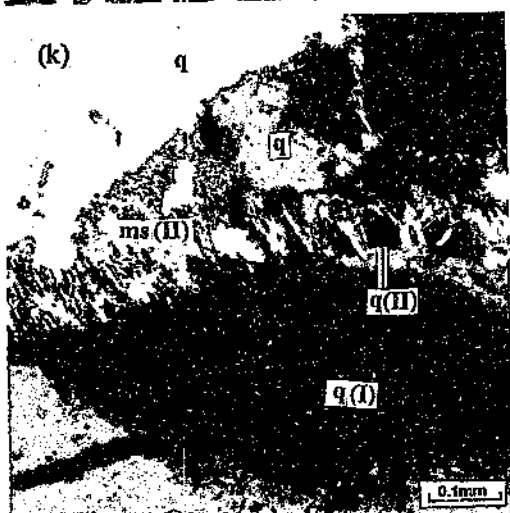
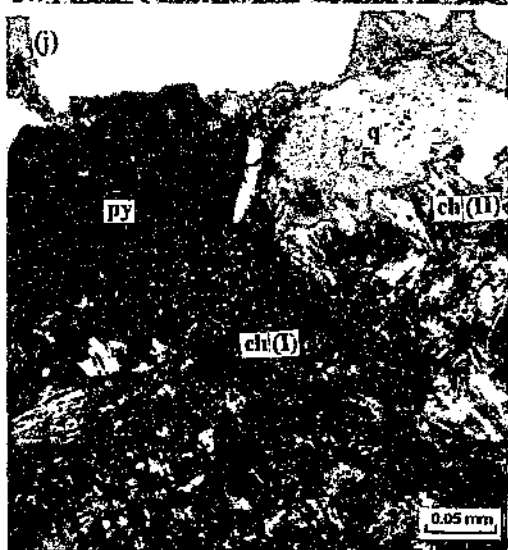
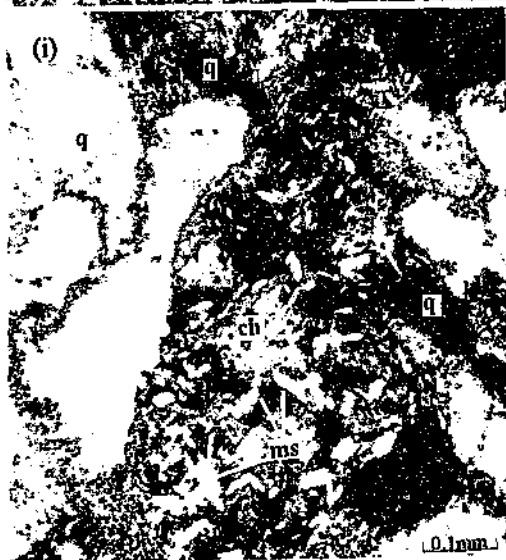
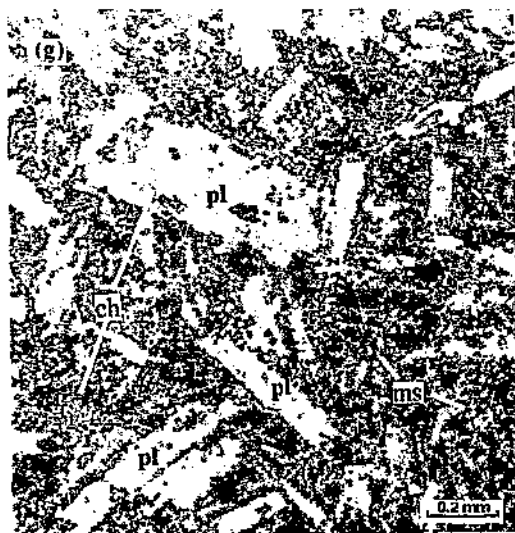
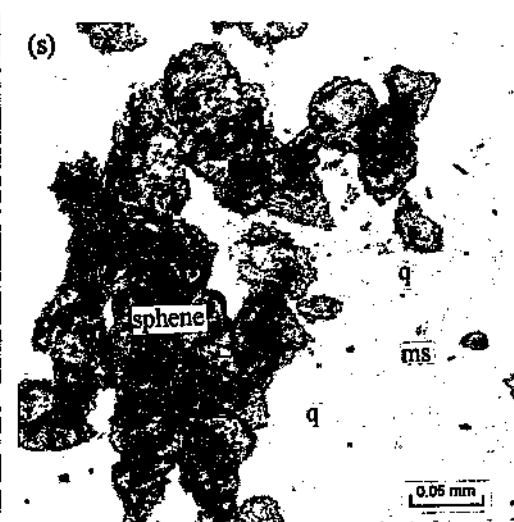
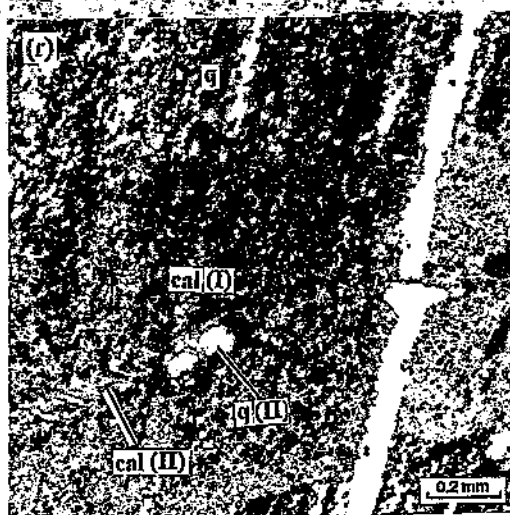
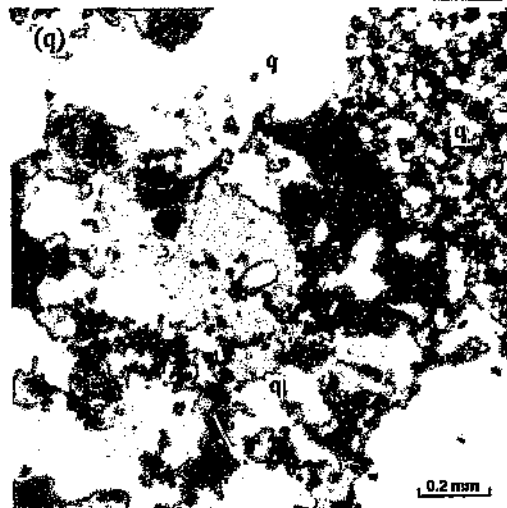
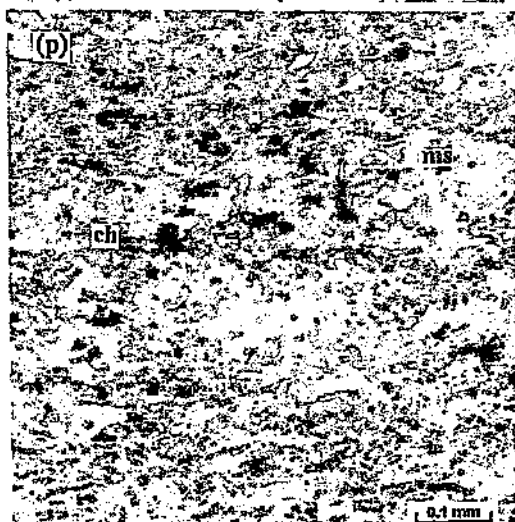
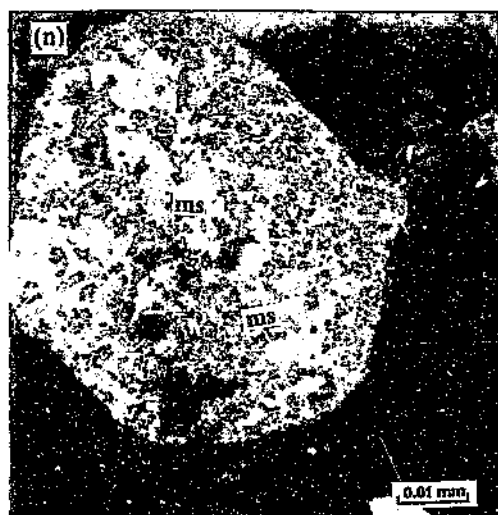
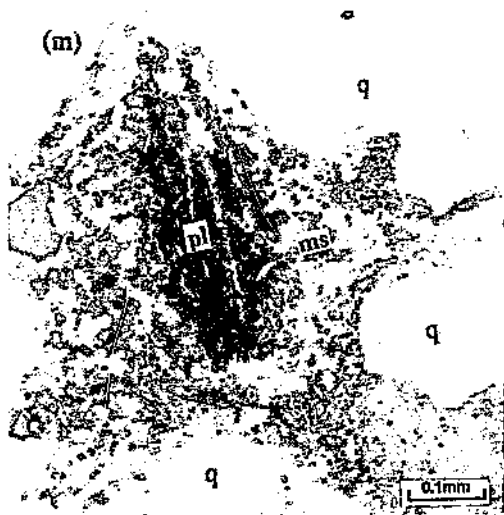


Fig. 4-2 (continued) Photomicrographs of secondary rock-forming minerals, and secondary textures. (m) remnant of possible detrital plagioclase grain. (n) rounded muscovite assemblage may indicate a replacement of plagioclase inclusion within the quartz pebble. (p) in shale, muscovite coexists with chlorite and opaque minerals. (q) recrystallized quartz grains. (r) VCR conglomerate: early generation of calcite veinlets cutting through cherty quartz, cut by secondary veinlets of calcite. This shows a multiple generation of fluids. (s) in AGNQ (apple green quartzite): sphene is enriched.



Gold Mine by Smits (1994) and at Western Deep Levels South Mine in this study by Zhao et al., (1994) and Zhou et al. (1995). The replacement of sulphides by albite, and the presence of vein albite suggest saturation of Na at some stage during the hydrothermal alteration.

4.4.2 Chloritization

Chloritization is marked by a dark colour in alteration zones. Five types (occurrences) of chloritization were identified in alteration zones: (1) chlorite occurring as fine-grained matrix-like massive aggregates (Fig. 4-2e) in the matrix of conglomerates and quartzites; (2) chlorite replacing detrital muscovite along cleavage planes (Fig. 4-2 f); (3) chlorite occurring as fine-grained aggregates replacing phenocrysts of plagioclase in lavas (Fig. 4-2 g); (4) chlorite infilling amygdalae and coexisting with quartz, and calcite (Fig. 4-2h); (5) chlorite nodules found mainly in altered conglomerates (Fig. 4-2i) which are usually characterized by high gold concentrations in the VCR. Three processes appear to have given rise to the formation of the five types of chlorite: (1) replacement of detrital muscovite and garnet by chlorite in sediments; (2) precipitation from hydrothermal fluids in lava amygdalae; (3) recrystallization of early-formed chlorite in the matrix.

4.4.3 Muscovitization

At least four types of muscovite were distinguished in the sediments based on grain sizes, mineral morphology and genesis. (1) deformed, coarse-grained ($>200\text{ }\mu\text{m}$) detrital muscovite (Fig. 4-2 e,f) is frequently replaced by secondary chlorite along its cleavages (Fig. 4-2d); (2) flaky hydrothermal muscovite overgrows quartz grains with secondary quartz crystals (Fig. 4-2k), and replaces albite together with chlorite (Fig. 4-2c). Size of grains is between 100 and 200 μm ; (3) recrystallized flaky fine-grained (10 μm) muscovite coexists with fine-grained chlorite in the

matrix of the sediments (Fig. 4-2c,e), and (4) possibly replaces feldspar as shown by pseudomorphs of albite twins (Fig. 4-2m, n). In shale samples, flaky muscovite coexists with chlorite (Fig. 4-2p).

4.4.4 Silicification

Silicification is commonly observed in the alteration zones. Four types of silicification were identified. (1) Recrystallisation of quartz was usually found in quartz grains in the conglomerates and strongly replaces early quartz (Fig. 4-2q); (2) hydrothermal quartz overgrowing detrital quartz in the conglomerates (Fig. 4-2k); (3) quartz occurring as fillings in amygdaloids together with chlorite, carbonates and sulphides in the lavas (Fig. 4-2 h) and in quartz-carbonate veins (Fig. 4-1b; 4-2r) and (4) euhedral sphene aggregates (Fig. 4-2s). Two samples from the quartzites were analysed by cathodoluminescence (CL) to determine the generations and genesis of quartz following the method described by Miller (1991). Authigenic infilling quartz is typically blue-luminescing, which suggests that most of the authigenic quartz has high Ti/Fe ratios; and is formed at relatively high temperature (Zingernagel, 1978). The blue CL feature excludes any possibility of a diagenetic origin for this quartz (Zingernagel, 1978; Matter and Ramseyer, 1995). Detrital quartz shows bluish-black luminescence, which suggests that the quartz was affected by strong metamorphism (Zingernagel, 1978). Frimmel et al. (1993) reported that authigenic quartz in Basal Reef showed yellow cathodoluminescence (rather than blue cathodoluminescence) due to enrichment of calcite inclusions.

4.4.5 Carbonatization

Calcite and siderite alteration are important alteration types within and around the VCR. Strong carbonatization has been found in the WC zone (Fig.4-1a), and occurs in veins (Fig.4-2a), in

quartzite and conglomerate (Fig.4-2d, r).

4.4.6 Epidotization

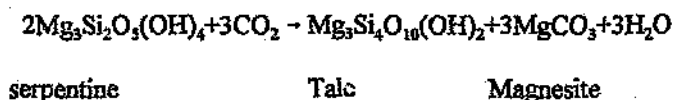
Epidote mainly occurs in vugs and veinlets in the lavas and less commonly in the conglomerates and quartzites. Epidotization is affected by the chemical composition of the lavas which have high concentrations of Ca and Fe.

4.4.7 Sphene alteration

Sphene is enriched in AGNQ quartzites (Fig.4-2s) and is also found in the MC of the Klipriviersberg group lavas (Fig.4-1 r).

4.4.8 Talc

Talc was identified along shear planes in immature light grey quartzites at Deelkraal Gold Mine, but it is not a common mineral. Formation of talc can be: (1) hydrothermal alteration of ultrabasic rocks; (2) low grade thermal metamorphism of siliceous dolomite; (3) hydrothermal fluid solutions from an original ultrabasic body, and external source (Deer, et al., 1992). Serpentinization of ultramafic fragments from the immature quartzites and the basaltic dykes could generate high Mg fluids. However no stronger talc alteration has been found near the dykes so that the former source is favoured. Conversion of serpentine to talc may occur by the addition of silica and removal of magnesium or by addition of CO₂ (Deer et al., 1992):



Temperatures of formation of talc are at about 300-320 °C (Browne, 1991).

4.4.9 Sulphidization

Sulphidization is widespread in the VCR package and occurs in the conglomerates, lavas and quartzites. Sulphides in the conglomerates include mainly pyrite and pyrrhotite with minor sphalerite, chalcopyrite, galena, and pentlandite.

4.4.9.1 *Pyrite*

The occurrence of pyrite in the Witwatersrand reefs and its relationship to the gold mineralization have been reviewed by Feather and Koen (1975) and Hallbauer (1986). Pyrite is the most conspicuous ore mineral (3 to 5 mole%) and often accounts for more than 90% of the ore minerals in the Witwatersrand reefs. There are three basic paragenetic types in the Witwatersrand reefs: (1) detrital pyrite; (2) syngenetic pyrite; and (3) authigenic, post-depositional pyrite (Hallbauer, 1986). Detrital pyrite has normally a compact rounded feature and varying amount of solid fluid inclusions of orthoclase, biotite, gold, quartz, molybdenite, chalcopyrite, sphalerite, pyrrhotite, rutile, garnet and micaceous materials (Hallbauer, 1986). MacLean & Fleet have studied detrital pyrite from the Basal Reef, Vaal Reef and the VCR in the Witwatersrand Basin and revealed that the compacted rounded detrital pyrite is characterized by an original oscillatory zonation in As. The syngenetic pyrite has a varying high porosity and is fine-grained and has been identified in six textural types: (1) oolitic; (2) radial, concretionary; (3) mudball; (4) rounded, layered; (5) coarse-grained aggregates of quartz and pyrite; and (6) possible organic framboidal type (Hallbauer, 1986). The authigenic pyrite typically occurs in the Witwatersrand sediments as idiomorphic-to-hypidiomorphic grains (Hallbauer, 1986) and has been termed hydrothermal pyrite (Ramdohr, 1955), and reconstituted authigenic pyrite (Saager, 1970; Hirdes, 1979; Utter, 1978).

In this study, detrital pyrite in the VCR is compact rounded and coexists with detrital arsenopyrite (Fig.4-3a), and is replaced by authigenic pyrrhotite (Fig. 4-3b). Mudball pyrite in the VCR is the most common type and actually consists of aggregates of small grained cubic pyrite inclusions, later cemented by hydrothermal chalcopyrite (Fig.4-3c) and pyrrhotite ((Fig.4-3f). Authigenic pyrite is euhedral cubic in the VCR and footwall sediments.

4.4.9.2 *Pyrrhotite*

The intrusion of sills and dykes in Witwatersrand sediments frequently caused local temperature increases and a resulting replacement of pyrite by pyrrhotite, based on the hydrothermal pseudomorphs of pyrrhotite after pyrite in Middle Elsburg Reef in Cook II Shaft and the VCR (Hallbauer, 1986). Zhou et al. (1995) suggest a metamorphic origin of pyrrhotite instead of due to the effects of magmatic activities based on their study on pyrrhotite from different gold fields in the Witwatersrand Basin. The above authors emphasised the widespread distribution of pyrrhotite in the Witwatersrand Supergroup and noted that it is not restricted to environments immediately below Ventersdorp lavas or adjacent to mafic dykes.

In this study, pyrrhotite is the dominant sulphide in the Ventersdorp Supergroup lavas, pseudotachylites and dykes cutting the VCR conglomerates and footwall quartzites while pyrite only occurs as hydrothermal veins or veinlets in the Ventersdorp Supergroup lavas and dykes or in the intermediate contact with VCR conglomerates and other sediments. However, local enrichment of pyrrhotite in the VCR conglomerates and footwall quartzites and shales is common in the VCR. Therefore, this feature of the distribution of pyrrhotite and pyrite most probably represents its close relationship to the intrusion of post-VCR sills and dykes as suggested by Hallbauer (1986).

Fig. 4-3 Photomicrographs of primary and secondary ore-minerals and textures. (a) in the VCR, rounded detrital pyrite (py) coexists with arsenopyrite (aspy), and secondary euhedral cubic pyrite can also be seen. (b) in the VCR, replacement of detrital pyrite by pyrrhotite (po). (c) in the VCR, euhedral cubic pyrite grains are included in chalcopyrite (cpy). (d) in quartzite, pyrrhotite inclusions occur in galena (ga). (e) in the VCR, pyrite is replaced by chalcopyrite (cpy) from the inside. (f) in quartzite, replacement of secondary pyrrhotite by euhedral cubic pyrite.

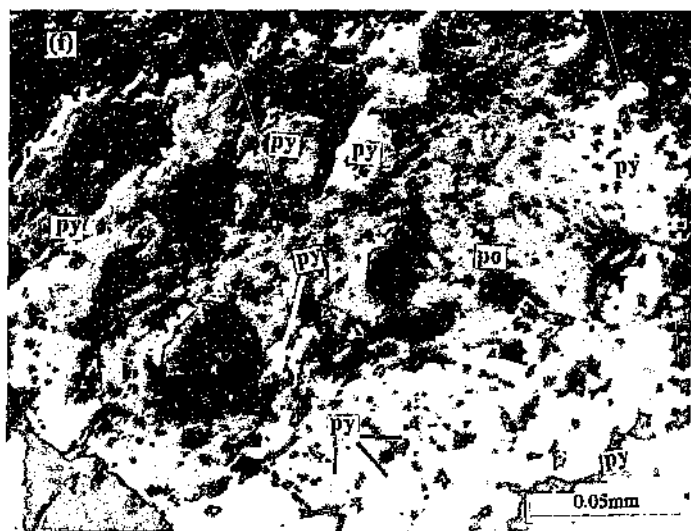
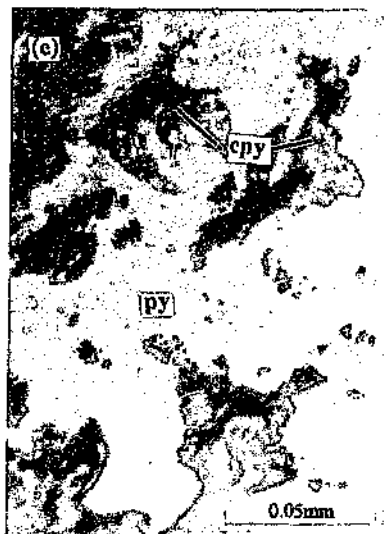
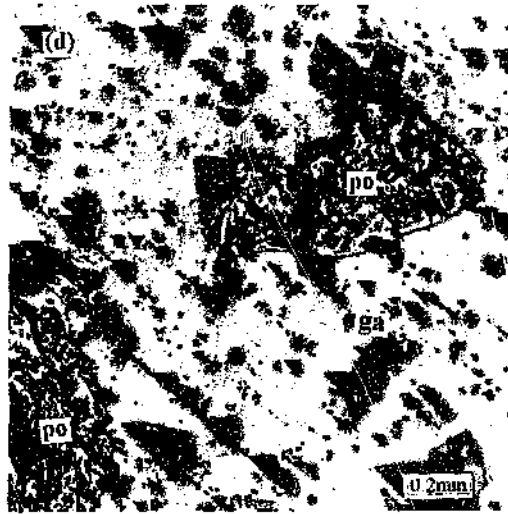
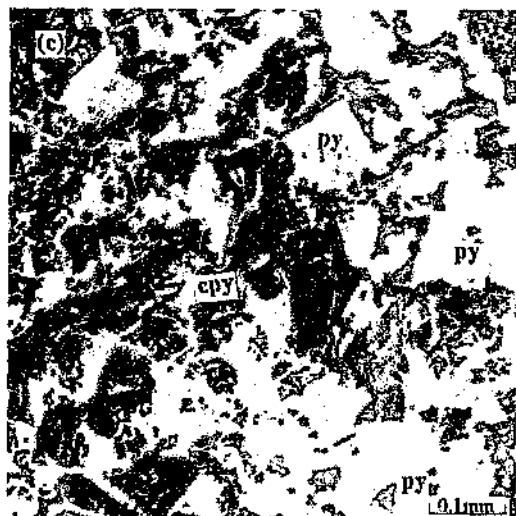
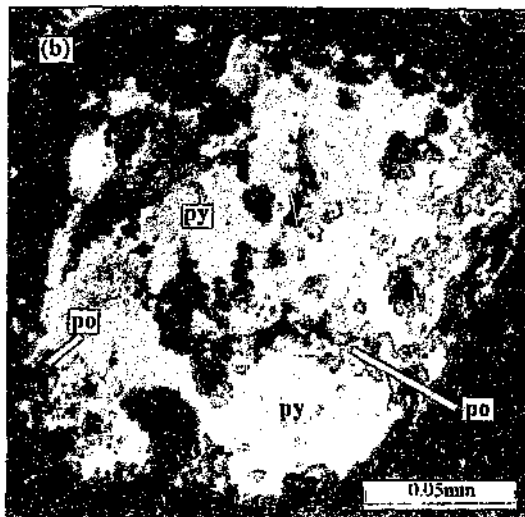
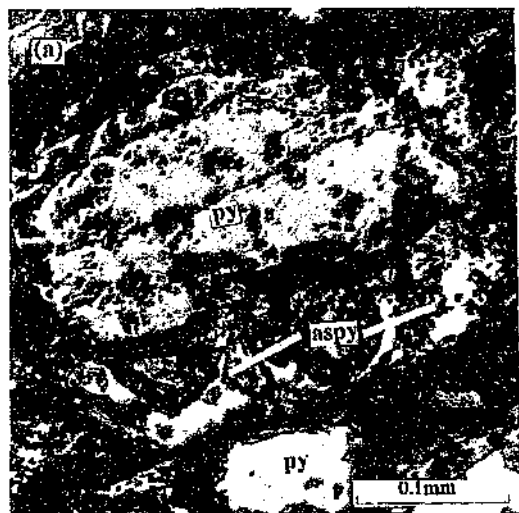
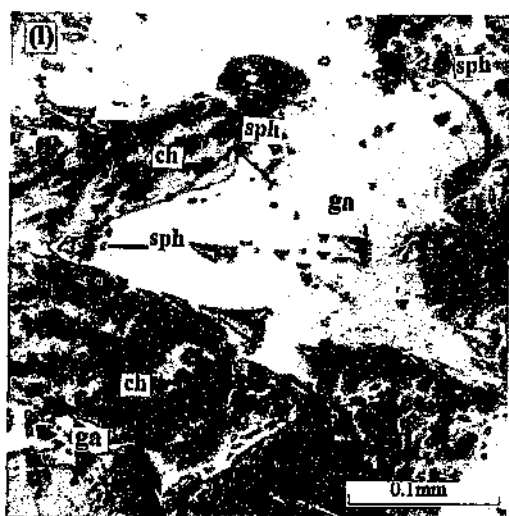
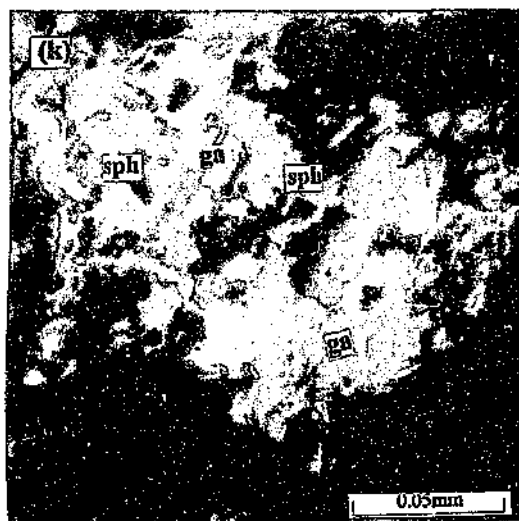
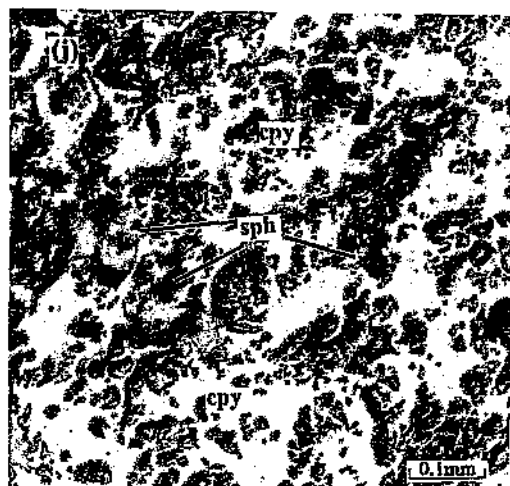
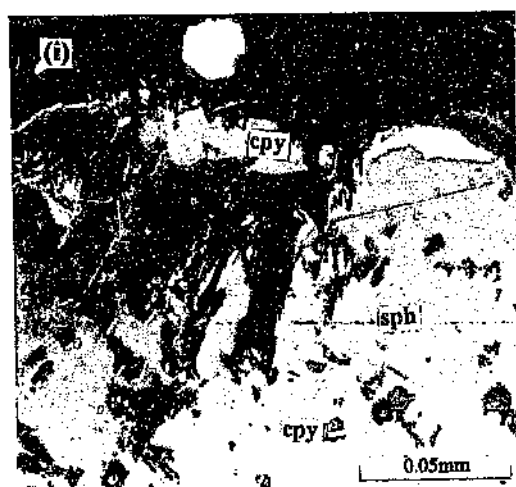
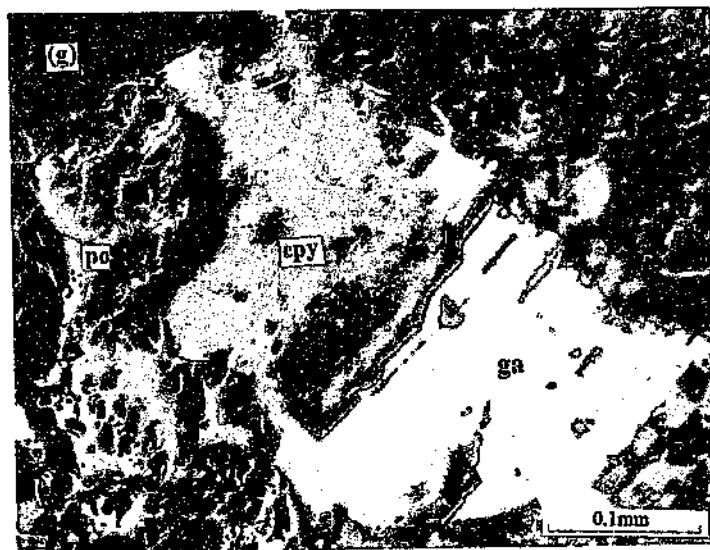


Fig. 4-3 (continued) Photomicrographs of secondary ore-minerals and textures. (g) in quartzite, galena, coexisting with chalcopyrite replacing pyrrhotite. (h) replacement of detrital pyrite by pyrrhotite (po). (i) in a lava amygdale, exsolution texture of sphalerite and chalcopyrite in sphalerite (sph). (j) exsolution texture of sphalerite grains in chalcopyrite. (k) galena coexisting with sphalerite. (l) in the VCR conglomerate, galena and sphalerite coexist with chlorite (ch).



Three types of textures of pyrrhotite have been identified in the VCR: (1) pyrrhotite occurring as inclusions in galena (Fig. 4-3d) and formed earlier than the host (galena); (2) replacing detrital pyrite and coexisting with authigenic cubic pyrite grains (Fig. 4-3f); and (3) pyrrhotite replaced by both chalcopyrite and galena in lava amygdaloids (4-3g). This indicates a paragenetic order for pyrrhotite relative to other sulphides: detrital pyrite $\rightarrow$ pyrrhotite+pyrite $\rightarrow$ chalcopyrite and galena.

4.4.9.3 *Sphalerite, galena and chalcopyrite*

Mudball sphalerite has been identified in one sample and probably represents an origin of either synsedimentary or diagenetic as for the mudball pyrite, but no detrital sphalerite and chalcopyrite have been identified. Sphalerite, galena and chalcopyrite are the common authigenic sulphides in the VCR. They are genetically related and show the following relationship: (1) coexistence of galena with sphalerite (Fig. 4-3h, k); (2) exsolution texture between sphalerite and chalcopyrite (Fig. 4-3i, j), and coexistence of galena, and sphalerite with chlorite (Fig. 4-3l).

A paragenetic sequence of sulphides is summarized as follows: detrital arsenopyrite and pyrite (I) $\rightarrow$ pyrite (II)+pyrrhotite (II) $\rightarrow$ chalcopyrite+sphalerite+galena (III).

4.4.10 Gold mineralisation

4.4.10.1 *Gold mineralisation in the Witwatersrand Basin*

Hallbauer (1986) distinguished four major types of gold in the Witwatersrand deposits: (1) detrital gold particles and primary gold in detrital allochthonous sulphides; (2) biochemically redistributed gold in carbonaceous matter; (3) gold redistributed by metamorphic or diagenetic processes; and (4) gold in post-depositional quartz veins.

The detrital gold particles in diameter range from 10 μm to rarely 500 μm with an average of 50 to 100 μm (Hallbauer, 1986) with rounded, distorted textures, and are intergrown with inclusions of sphalerite, gersdorffite, cobaltite and chalcopyrite mainly in detrital pyrite. Chemically, the gold particles contain 5 to 30% Ag with an average of 10%; 1 to 4% Hg; usually traces of Cu, Sb, Co, and Ni. Detrital gold grains are associated with a heavy metal mineral assemblage of pyrite - rutile - uraninite and show ovoid, flattened and edge-overturned morphologies (Robb & Meyer, 1995). Minter et al. (1993) have reported similar detrital gold grains (from 38 to 473 μm) with a mean of 136 μm based on a detailed investigation on the morphology of detrital gold grains from the Basal Reef in the Welkom gold field.

Biochemically redistributed gold grains are fine filaments, bundles and agglutinated aggregates in texture and range from 0,5 to 2 μm in diameter due to the digestion of the organisms (Hallbauer, 1986). This type of gold is distributed widely in the Carbon Leader Reef, Vaal Reef, Steyn Reef, Basal Reef and "B"-Reef.

Recrystallized gold occurs as (1) irregular rounded gold particles and nuggets (Feather & Koen, 1975); (2) irregular jagged flaky particles with porous surfaces; (3) octahedral crystal faces in places (Utter, 1979); (4) finer grained (0,7 to 1,1 mm) (Minter et al., 1993); (5) fineness of 770 to 980 which does not vary between different types of gold particles but changes in different stratigraphic horizons (Hallbauer, 1986); (6) more complicated metal mineral assemblage: pyrite-pyrrhotite-galena-sphalerite-uranite-rutile-gold (high fineness); (7) close relationship of gold with detrital pyrite (Meyer et al., 1994); and (8) its close relationship with authigenic quartz (Frimmel et al., 1993).

Gold occurs, in places, in post-depositional quartz veins in the Witwatersrand Basin and in a large range of sizes up to 2 cm. Hirdes (1979) has observed a depletion of gold in reefs near the gold-bearing veins.

4.4.10.2 *Gold mineralisation in the VCR*

Several studies on gold mineralization in the VCR have been carried out at Venterspost (e.g. De Kock, 1964; Von Rahden, 1964, 1970;), West Driefontein (e.g. De Kock, 1964; Stefan & Martin, 1992) and Elandsrand Gold Mines (e.g. Henckel & Schweitzer, 1994). De Kock (1964) suggests that the gold in the VCR is coarse and occurs generally in later sequences than detrital sulphides, uraninite, and carbon. Based on the above studies, gold mineralization is characterised by: (1) gold-pyrite-sphalerite-pyrrhotite-sphalerite assemblage. Pyrite is still the major gold host in all minerals together with sphalerite, pyrrhotite and chalcopyrite. Gold is mainly hosted by neoformed idiomorphic pyrite, but it is also related to secondary sphalerite, pyrrhotite and chalcopyrite in veinlets. The gold is characterized by overall very coarse grains (e.g. De Kock, 1964) between 8 and 110 μm (Stefan & Martin, 1992). Henckel and Schweitzer (1994) described hydrothermally altered areas at Elandsrand Gold Mine and found them to be enriched in gold, with areas being rich in secondary pyrite, sphalerite, galena and chalcopyrite.

(2) Gold-chlorite assemblage. Stefan and Martin (1992) studied different reef facies of the VCR at West Driefontein Gold Mine and reported that the gold-chlorite assemblage is very common in the different facies of the VCR. Gold is characteristically fine-grained from 7,5 to 40 μm , associated with coarse hydrothermal chlorite. Two types of chlorite are matrix chlorite and coarse-grained buckshot chlorite. Gold mineralisation is mainly related to the latter. Gold in the chlorite assemblage occurs in (1) hydrothermal veinlets in pyrrhotite and pseudo rutile; (2) in

chlorite along the recrystallized quartz boundaries and (3) gold disseminated in hydrothermal chlorite as very fine grained disaggregated gold. Stefan and Martin (1992) emphasized the influence of the gold-hosting chlorites as the main reason for the higher residue values (0,35 g/t). They referred to a hydrothermal overprint that caused development of an Fe-rich chlorite with significant pyrrhotite, chalcopyrite, sphalerite, galena, gersdorffite and authigenic gold.

(3) Gold-bitumen assemblage. Nodules of black hydrocarbon also occur in the VCR (De Kock, 1964; Stefan & Martin, 1992). In the VCR, the gold grains occur along the edge of the kerogen nodules and are very fine-grained (Stefan & Martin, 1992). Robb et al. (1994) have suggested that carbonaceous matter generally heralds the presence of high values of gold and uranium in the Witwatersrand reefs.

(4) Gold-uranium-bearing mineral assemblage. Based on an optical study of polished sections from the VCR conglomerate at West Driefontein Gold Mine, Stefan and Martin (1992) suggest that gold, in places, is related to uraninite. In the Witwatersrand Basin, uraninite is normally found along the footwall contact associated with other heavy minerals and ranges in size from 75 to 100 μm with an rounded, oval, and muffin-shaped outline in polished sections (Liebenberg, 1955; Feather & Koen, 1975).

4.5 Paragenetic sequences of alteration

Based on the relationships of replacement among alteration minerals, four sequences of alteration are identified in this study (Table 4-3).

Table 4-3 Paragenetic sequences of secondary minerals within and around the VCR at WDLMS

	Py-Po-Sph	Ab-Cc	Ch-Ms-Sf	Qz-Cc vein
	Stage I	Stage II	Stage III	Stage IV
Quartz		-----	-----	-----
Chlorite		-----	-----	-----
Muscovite		-----	-----	-----
Albite	-----	-----	-----	
Epidote		-----	-----	
Talc		-----	-----	
Sphene	-----	-----		
Carbonate	-----	-----	-----	
Native gold	-----	-----	-----	
Pyrite	-----	-----	-----	-----
Pyrrhotite	-----	-----	-----	
Sphalerite		-----	-----	-----
Galena		-----	-----	-----
Chalcopyrite		-----	-----	-----

Py - pyrite; Po - pyrrhotite; Sph - sphalerite; Ab - albite; Cc - calcite; Ch - chlorite; Ms - muscovite; Sf - sulphides; Qz - quartz.

At Stage I, the mineral assemblage is characterized by enrichment of pyrite and pyrrhotine with possible occurrence of native gold and sphene. No data are available to determine the exact relationship between gold mineralization and the alteration mineral assemblage at this stage in the study, however, enrichment of secondary sulphides in the VCR might be a good indicator for gold mineralisation based on above-described relationship between gold mineralisation and sulphidization (e.g. Stefan & Martin, 1994; Henckel & Schweizer, 1994). At Stage II, the mineral assemblage is characterized by enrichment of albite and carbonates. However, replacement of the primary and secondary pyrite and pyrrhotite proves a remobilization of base metals. Remobilization of gold together with base metals can be deduced based on the close relationship between gold and sulphides.

At Stage III, the mineral assemblage is characterized by enrichment of chlorite, muscovite, quartz, chalcopyrite, sphalerite and galena. Epidote and talc may occur at this stage. Alteration associated with this stage is well-developed in the VCR. The close relationship between gold and chlorite (Stefan & Martin, 1992), together with enrichment of chalcopyrite, sphalerite, and galena is a good indicator for gold mineralisation. Moreover, enrichment of authigenic quartz may be also related to remobilization of gold as described by Frimmel et al. (1993) in the Basal Reef, Welkom gold field.

At Stage IV, the mineral assemblage mainly consists of quartz and carbonate in a quartz-calcite vein system. At this stage, few sulphides or gold were precipitated.

4.6 Summary

Alteration zones within and around the VCR, dykes, faults and pseudotachylite are characterized

by distinctive mineral assemblages and colouration. Seven alteration zones associated with the VCR and five alteration zones related to dykes have been identified. Alteration extends in width from 2 to 10 m both related to the VCR and dykes, whereas alteration within and around pseudotachylite is of very limited extent. Formation of albite, chlorite, muscovite, carbonate, and sulphides are the most important alteration types, whereas epidote, talc, rutile and sphene are limited to specific zones. The mineral assemblage of the peak hydrothermal alteration in the research area is chlorite - muscovite - quartz - calcite - siderite - albite - sulphides (pyrite - pyrrhotite - sphalerite - galena - chalcopryite) - sphene - rutile, which is a typical greenschist facies assemblage at medium temperature and low pressures. Another possible mineral assemblage is muscovite (1M) - chlorite (Ch2), which formed at lower temperature and pressure. Four alteration stages have been presented as: pyrite - pyrrhotite - sphene - (gold) - quartz (I) → albite - calcite (II) → chlorite - muscovite - quartz - sphalerite - galena - chalcopryite (III) → quartz - calcite - pyrite - pyrrhotite. The major gold mineralisation and mobilisation during metamorphism and hydrothermal alteration is associated with Stage I, Stage II and Stage III.

5 WHOLE ROCK GEOCHEMISTRY

5.1 Introduction

5.1.1 Geochemistry of the Klipriviersberg Group lavas

The Ventersdorp Supergroup comprises three groups, namely the Klipriviersberg Group at the base overlain by the Platberg Group, and the Priel Sequence. The Klipriviersberg Group comprises the hanging wall stratigraphy of the VCR at WDLMS. The geochemistry of lavas from the Klipriviersberg Group was studied by Horwood as early as in 1910. Geochemistry and isotopes of whole rocks indicate that the lava flows were mainly of a mantle origin (e.g., Crow and Condie, 1988, Nelson et al., 1990; Van Der Westhuizen et al, 1991), with crustal contamination during the evolution of the Ventersdorp volcanics (Bowen, 1984; Van Der Westhuizen et al, 1991) during crustal extension in the Kaapvaal Craton (McIver et al., 1982, Crow and Condie, 1988, Schweitzer and Kröner, 1985). The lavas are basically grouped into compositional types, namely tholeiitic basalt and basaltic andesite (Wyatt, 1976; Crow and Condie, 1988).

The Klipriviersberg Group is depleted in incompatible elements such as Ti, P, Y and Zr as well as Fe, V and Ca, but is enriched in Ni (Linton, 1992). The volcanic rocks of the Klipriviersberg Group can be geochemically discriminated from those of Dominion Group and Crown lavas by Ti, Y, U, Mg, P, Zr and V (Bowen et al., 1986).

5.1.2 Geochemistry of the Witwatersrand Reefs

Geochemical analyses of major reefs in the Wits Basin have been undertaken by Pretorius (1974b), who summarized the average chemical data in tables from previous workers (e.g., Liebenberg, 1973) and reached the following results : (1) Cr/Zr ratios decrease upwards; (2) high

correlation between Au and Ag; Au, Ag and U; Au, U and Cr; U and Zr; Cr and Zr; U and Pb; and Ni and Co; (3) chronite, zircon and leucoxene are the three most persistent and abundant heavy minerals.

5.1.3 Geochemistry of the VCR

Geochemical studies of zircon and bulk rocks from the VCR at Elandsrand Gold Mine indicated that the Upper Unit (see Chapter 3) is enriched in Ti, Mg, P, Zr, Cr, and V, relative to the Lower Unit. Based on this, Henckel and Schweitzer (1994) suggested that the provenance areas were different from each other for the two reef bands.

5.1.4 Geochemistry of the Witwatersrand Supergroup sediments

Law (1990) studied quartzites and metapelites of the Witwatersrand Supergroup, and concluded that the major units of the Central Rand Group experienced significant meteoric fluid influx which leached Na, K, Fe and Mg from the quartzites and destroyed the pre-existing detrital assemblage, while rapid burial of West Rand Group quartzites resulted in limited meteoric fluid influx and the preservation of labile minerals (e.g. feldspar). Moreover, further alteration occurred in response to diagenetic fluids generated by compaction and mineral devolatilization reactions. Gold and uranium are concentrated in association with a suite of chalcophile metals (Ni, Co, As, Sb).

5.1.5 Aims of this chapter

The aims of this chapter are to investigate the following subjects: (1) the overall geochemical characteristics of the hanging wall lavas, the VCR conglomerates, footwall quartzites, and shales; (2) enrichment and depletion of major and trace elements in different alteration zones associated

with the VCR; and (3) reconstruction of the geochemical processes involved in hydrothermal alteration.

5.2 Sample descriptions and analytical methods

Samples were taken from underground stopes and boreholes. A total of 116 samples were collected and analysed for the Klipriviersberg Group lavas (21), VCR (25), DGG zone footwall quartzite (36), GG zone footwall quartzite (21), AGNQ (apple green) quartzite (8) and Kimberley Shale (5). Of these, forty eight samples were from boreholes (e.g. BH1169, BH1170) and 68 samples from underground stopes.

Chemical analyses were undertaken by XRF in the Department of Geology, University of the Witwatersrand. XRF analyses of major elements were completed on a glass bead made from the powdered sample fused with lithium tetraborate using an automatic XRF spectrometer, and following the procedure given by Norrish and Hutton (1968). Loss on ignition was determined after heating powdered samples to 1110 °C. Major oxides determined include SiO_2 , TiO_2 , Al_2O_3 , $\text{Fe}_2\text{O}_{3(\text{total})}$, MnO , MgO , CaO , Na_2O , K_2O , and P_2O_5 . Average errors are between 0,6 and 3,8 wt% for the major oxides except for K_2O and Na_2O that have an error range of between -5,2 and 11,2 wt%. Most analytic totals are between 99 and 101 wt%. Trace elements of V, Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, and Ba were determined by XRF spectrometer using pressed powder pellets, and following the procedures given by Feather and Willis (1976). Uncertainties in analyses of the trace elements are between 1,1 and 10 wt% except for Rb, Nb, and Ba which have errors between 19,5 and 40,5 wt%.

5.3 Analytical results

Chemical compositions of the hanging wall lavas at WDL SM are tabulated in Table 5-1 in terms of major oxides (wt%) and trace elements (ppm).

5.3.1 Lavas

5.3.1.1 *Classification*

The lavas from twenty-one samples from WDL SM are classified in Fig. 5-1, using a plot of total alkalis versus SiO_2 after Cox et al. (1979), and using another plot of Zr/TiO_2 against Nb/Y , of Winchester and Floyd (1977). As shown in Fig. 5-1a, the hanging wall lavas in the study area plot in the basalt and andesite categories with a few exceptions. Average data for the Alberton, Loraine-Edenville, and Orkney Formations (Bowen et al., 1986) also plot in the basalt and andesite fields. With respect to the exceptions, the six samples are projected out of the fields with low $\text{Na}_2\text{O/K}_2\text{O}$ against high SiO_2 . This may be related to mobilization of Na_2O (see later) and enrichment of K_2O . The former is mainly related to albitization while the later is connected with muscovitization.

In terms of Zr/TiO_2 against Nb/Y (Fig. 5-1b), the WDL SM lavas are further classified chiefly into subalkaline basalt. They are a little different from the Klipriviersberg Group lavas (Bowen et al., 1986) due to their higher ratios of Nb/Y , which may be due to alteration (e.g. albitization, carbonatization, cf., Liu et al., 1980) during hydrothermal alteration (see later).

5.3.1.2 *Major oxides*

Major oxides (>1 wt%) in the lava samples are SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaO , TiO_2 , and K_2O in descending order, with minor MnO , Na_2O , and P_2O_5 (their total amount less than 1.5%).

Table 5-1 Bulk rock chemistry of lavas from the Alberton Formation of the Klipriviersberg Group from WDLSM (total of 21 samples)

	bb01	bb02	bb05	bb20	bbb6	bhc9	bb11	bb13	bb14	bb13	bhm1	bhm2	bhm3	b701	b711	b102	b110	b382	b391	x441	1650a	AVG	STD
wt%																							
SiO ₂	48.53	36.58	50.65	62.68	50.34	53.70	52.97	49.02	55.03	53.08	53.67	58.32	56.97	74.66	48.05	54.94	59.41	59.03	48.58	56.50	53.62	54.11	7.0
TiO ₂	1.44	12.03	1.32	1.35	1.19	1.37	1.33	1.34	1.57	1.36	1.25	1.45	1.32	0.25	2.17	1.46	1.32	1.32	1.32	1.46	1.35	1.86	2.3
Al ₂ O ₃	13.34	20.92	12.65	13.96	12.74	13.72	13.51	13.66	15.57	14.70	14.49	14.36	14.33	14.00	17.25	14.27	13.42	13.11	14.36	15.10	13.64	14.43	1.8
Fe ₂ O ₃	12.93	21.67	11.87	11.05	17.65	14.93	11.75	11.25	12.84	13.91	12.15	12.68	14.65	1.93	17.66	15.07	13.58	14.25	17.07	13.82	16.57	13.77	3.7
MnO	0.21	0.22	0.13	0.10	0.09	0.16	0.16	0.22	0.16	0.17	0.14	0.19	0.22	0.22	0.20	0.18	0.15	0.17	0.18	0.14	0.23	0.17	0.0
MgO	4.97	7.96	4.27	3.22	2.32	7.12	4.11	4.64	4.79	5.51	4.14	4.79	5.56	1.10	5.17	4.73	4.38	5.13	8.08	4.50	7.46	4.95	1.7
CaO	7.34	0.81	9.74	0.79	4.42	1.29	8.81	7.59	1.34	2.17	5.84	1.57	0.51	0.27	1.69	2.17	1.05	0.60	1.90	0.32	2.32	2.98	2.9
Na ₂ O	0.72	0.24	2.95	0.16	3.99	0.16	2.60	0.00	0.00	2.21	3.37	0.00	0.11	0.18	0.00	0.14	0.00	1.33	0.00	0.59	0.00	0.89	1.3
K ₂ O	1.19	2.47	0.07	2.29	0.32	1.23	0.09	1.89	2.40	0.64	0.05	1.86	1.28	3.97	1.99	1.71	1.91	1.38	0.99	1.96	0.93	1.46	0.9
P ₂ O ₅	0.18	0.32	0.19	0.20	0.16	0.20	0.16	0.19	0.23	0.18	0.20	0.21	0.20	0.49	0.29	0.20	0.18	0.23	0.39	0.21	0.18	0.23	0.1
L.O.I.	9.42	7.03	6.16	3.58	5.90	4.79	3.39	8.48	4.42	5.30	4.10	4.85	4.61	2.29	5.19	4.64	4.08	4.28	6.24	4.75	1.83	5.02	1.8
Totals	100.26	100.51	100.04	99.37	99.12	98.67	98.88	98.28	98.35	98.79	99.60	100.26	99.76	98.57	99.67	99.51	99.48	100.83	99.11	99.35	98.12	99.36	0.7
ppm																							
V	35	283	166	170	163	217	179	197	240	207	206	223	204	57	251	210	184	192	185	206	26	181	64
Cr	147	220	146	140	119	147	149	142	159	148	163	156	136	171	233	154	130	149	140	150	587	176	96
Co	6	60	38	47	67	46	39	24	38	42	40	22	30	10	45	45	51	28	54	39	52	39	15
Ni	11	122	90	77	103	109	108	80	66	122	115	76	88	31	111	94	153	84	300	95	102	102	53
Cu	0	173	71	91	443	59	121	33	99	153	131	56	114	0	189	86	259	67	44	110	83	113	95
Zn	2	295	99	115	68	644	96	200	197	293	90	420	290	65	317	242	245	184	177	203	293	216	139
Rb	122	132	7	110	24	65	14	91	114	38	14	86	65	159	94	90	98	68	53	88	58	76	40
Sr	48	17	451	17	413	16	508	65	29	72	454	37	25	40	22	30	21	28	57	31	27	115	167
Y	7	25	18	18	22	23	19	27	24	23	21	25	19	14	39	25	17	17	30	18	13	21	6
Zr	153	195	141	142	136	157	146	149	168	154	161	159	152	96	208	156	142	148	146	163	251	158	30
Nb	6	10	6	7	8	10	9	9	10	10	10	10	10	7	12	9	8	9	10	10	8	9	1
Ba	371	1201	105	1029	136	635	55	382	453	169	65	461	293	1108	635	811	814	688	209	477	440	502	335

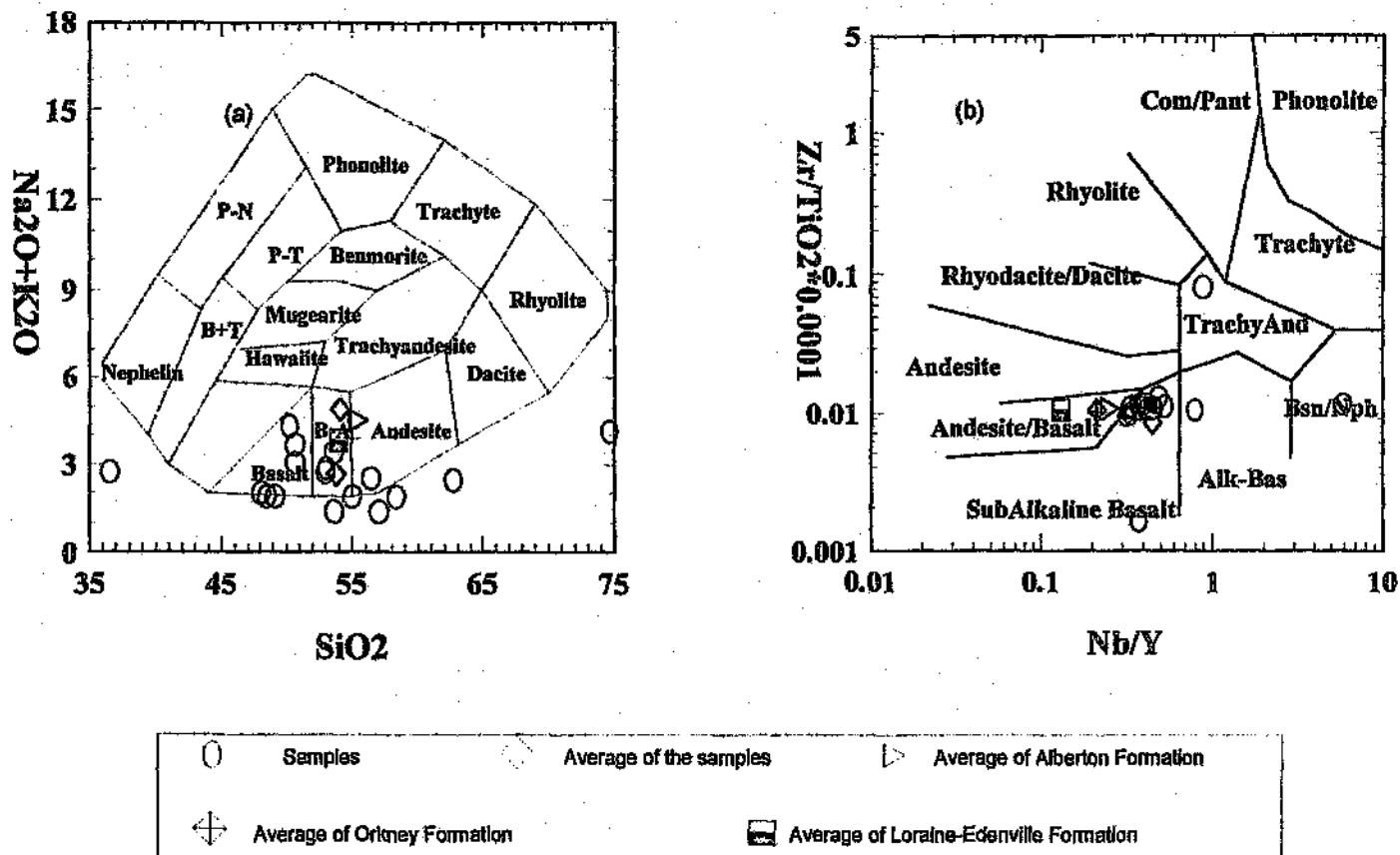


Fig. 5-1 Classification of lava samples from the research area on plots of (a) SiO_2 vs $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ (after Cox et al., 1979), and of (b) $\log \text{Nb/Y}$ vs $\log \text{Zr/TiO}_2$ (after Winchester & Floyd, 1977). Average chemical compositions of the Klipriviersberg Group lavas (Bowen et al., 1986) are also shown for reference.

Oxides are plotted against SiO_2 (Fig. 5-2), which demonstrates that the lavas in the research area are obviously enriched in TiO_2 (Fig. 5-2a), Fe_2O_3 (Fig. 5-2c), P_2O_5 (Fig. 5-2i) and SiO_2 (Fig. 5-2), while they are depleted in CaO (Fig. 5-2f) and possibly Na_2O (Fig. 5-2g). More-over, Al_2O_3 , and K_2O are similar to the average Klipriviersberg Group lavas (Bowen et al., 1986). Some of the results are consistent with those of Linton (1992). For example, the author suggests that the Klipriviersberg Group is depleted in incompatible elements such as Ti, P, and Fe.

As described in Chapter 4, sphene and rutile are enriched, in particular, in the MC zone (multiple colour zone) relative to the other alteration zones in the lavas and contribute to the high concentration of TiO_2 . Enrichment of Fe_2O_3 is most probably related to the strong sulphidization (pyrrhotite with minor pyrite) in the altered lavas, which has been described in Chapter 4. Both the enrichments of MnO and P_2O_5 are probably related to Fe (see later). Moreover, it seems that some of the lava samples are enriched in SiO_2 relative to the Klipriviersberg Group lavas (Bowen et al., 1986) (Fig. 5-2a), which is clearly related to silicification occurring in lava amygdalae and quartz veinlets.

Depletion of CaO in the lava samples in the research area suggests that Ca may be remobilized into sediments during the hydrothermal alteration. This has been supported by carbonatization in the VCR and DGG zone quartzite relative to the Klipriviersberg Group lavas (Fig. 5-2c). The lack of strong carbonatization in the Witwatersrand quartzites (Law, 1992) probably gives indirect evidence for the assumption. Slight depletion of Na_2O suggests that minor amounts of Na were locally remobilised from the altered lavas and probably introduced to the adjacent alteration zones in VCR and footwall quartzites. As discussed in Chapter 4, albitization has been seen in the RA (VCR) zone and DGG zone quartzites, but not identified in the Witwatersrand quartzites (Law,

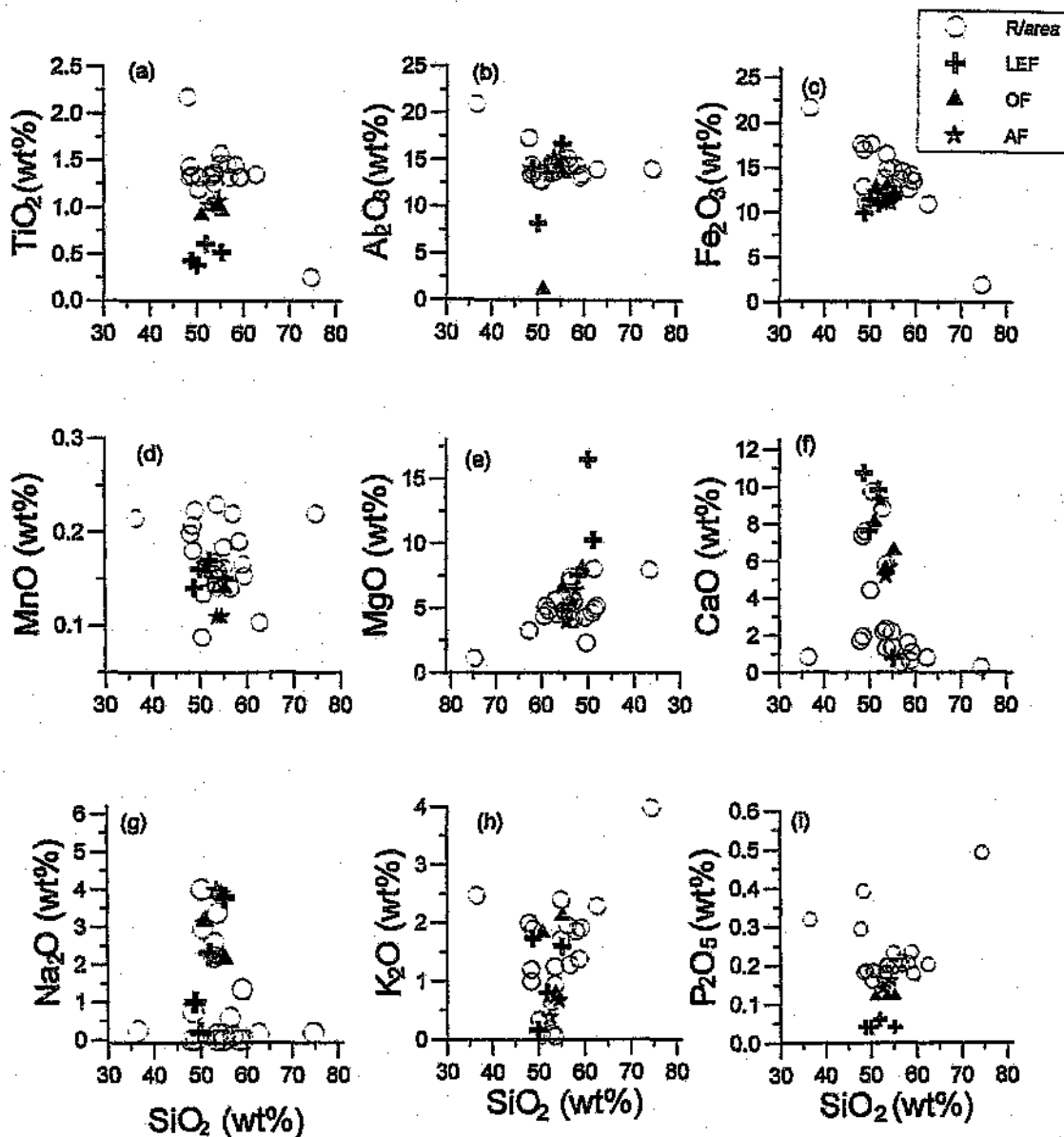


Fig.5-2 Plots of TiO_2 , Fe_2O_3 , MnO , MgO , CaO , Na_2O , K_2O , P_2O_5 vs SiO_2 for the lava samples, in the research area, together with the Kilpriviersberg Group lavas for reference. Average compositions of oxides of the Kilpriviersberg Group lavas are from Bowen et al. (1986), R/area—the research area; LEF—Lorraine-Edenville Formation; OF—Orkney Formation; and AF—Alberton Formation.

1992). This suggests mobilization of Na during fluid circulation in the hydrothermal alteration processes. Slight depletion of MgO and K₂O (Fig. 5-2e, h) may be related to their mobilization during fluid circulation (see later). However, Al₂O₃ in the research area is not obviously different from those of the Klipriviersberg Group lavas (Bowen et al., 1986) (Fig. 5-2b, e, g, h), due to its immobile characteristics.

The selected oxides are plotted against Fe₂O₃, Al₂O₃, and TiO₂ respectively in bivariate diagrams (Fig. 5-3) in order to examine the relationship of these elements in the hanging wall lava samples in the research area. It is suggested that strong correlations exist between Al₂O₃ and TiO₂ ($r = 0.73$), and between MgO and Fe₂O₃ ($r=0.50$); and weakly between TiO₂ and Fe₂O₃ ($r=0.32$) (Fig. 5-3b, c, h). The strong correlations between Al₂O₃ and TiO₂ may be attributed to sphene mineralisation, while correlation of TiO₂ and Fe₂O₃ may indicate either replacement of Fe by Ti or the existence of ilmenite. Moreover, correlations of MgO and Fe₂O₃ is attributed to chloritization. Furthermore, it seems that there are some correlations of MnO and MgO with Fe₂O₃. However, no obvious correlations are shown between CaO, K₂O, Na₂O and Al₂O₃, and MnO and TiO₂, and FeO (Fig. 5-3a, d, e, f, g).

The data are further plotted in an AFM diagram (cf., Rollinson, 1993), together with the average of the Loraine-Edenville, Alberton, and Orkney Formations of the Klipriviersberg Group (Bowen et al., 1986) (Fig. 5-4). The end members are represented by the following (cf., Rollinson, 1993):

$$F = (\text{FeO} + 0.8998\text{Fe}_2\text{O}_3)$$

$$A = (\text{Na}_2\text{O} + \text{K}_2\text{O})$$

$$M = \text{MgO}.$$

The oxide compositions are used as weight percentage (wt%). In the research area, the major

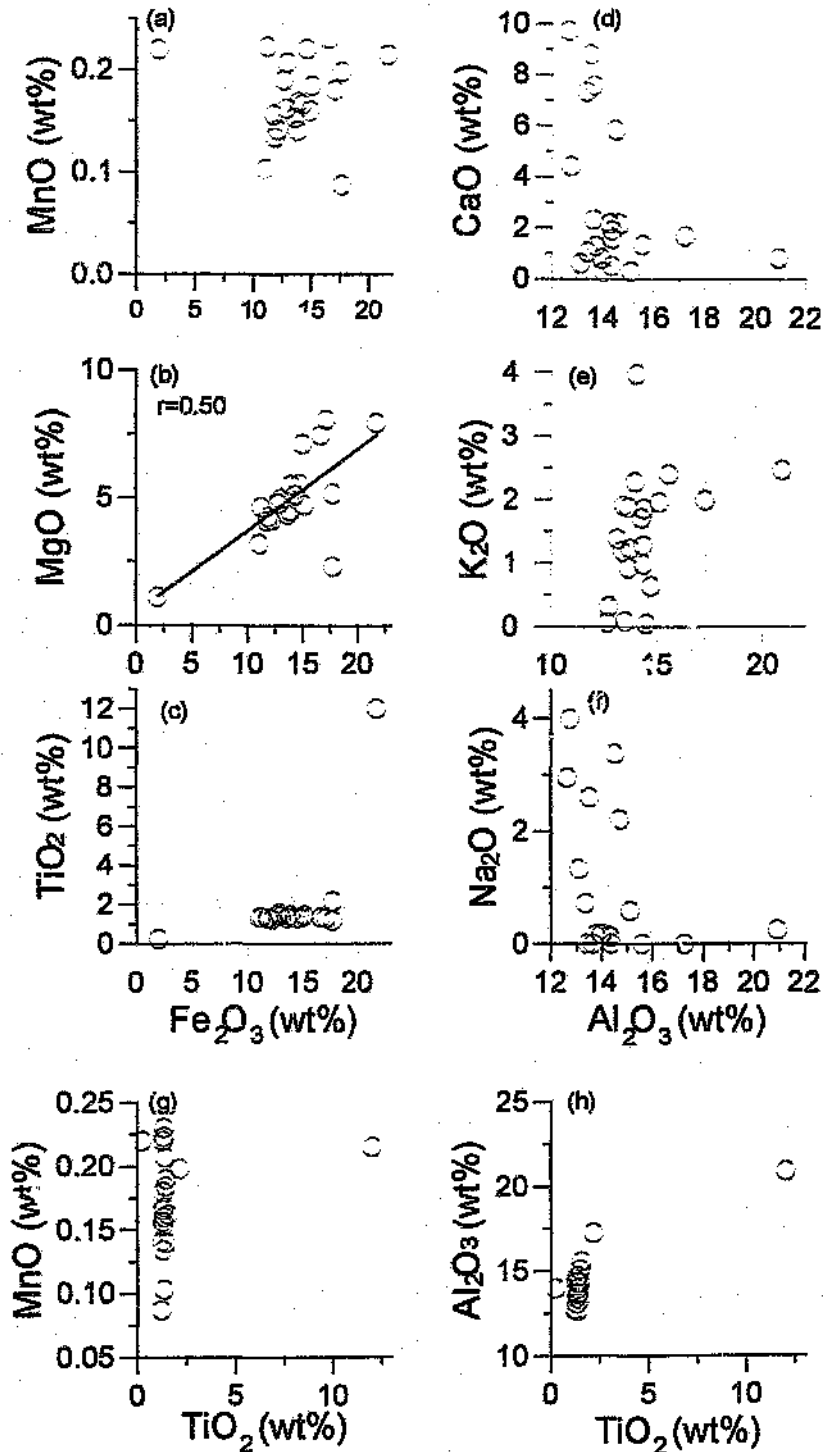


Fig. 5-3 Plots of MnO, MgO, TiO_2 vs Fe_2O_3 , and K_2O , Na_2O , CaO vs Al_2O_3 and MnO and Al_2O_3 vs TiO_2 for the lava samples in the research area.

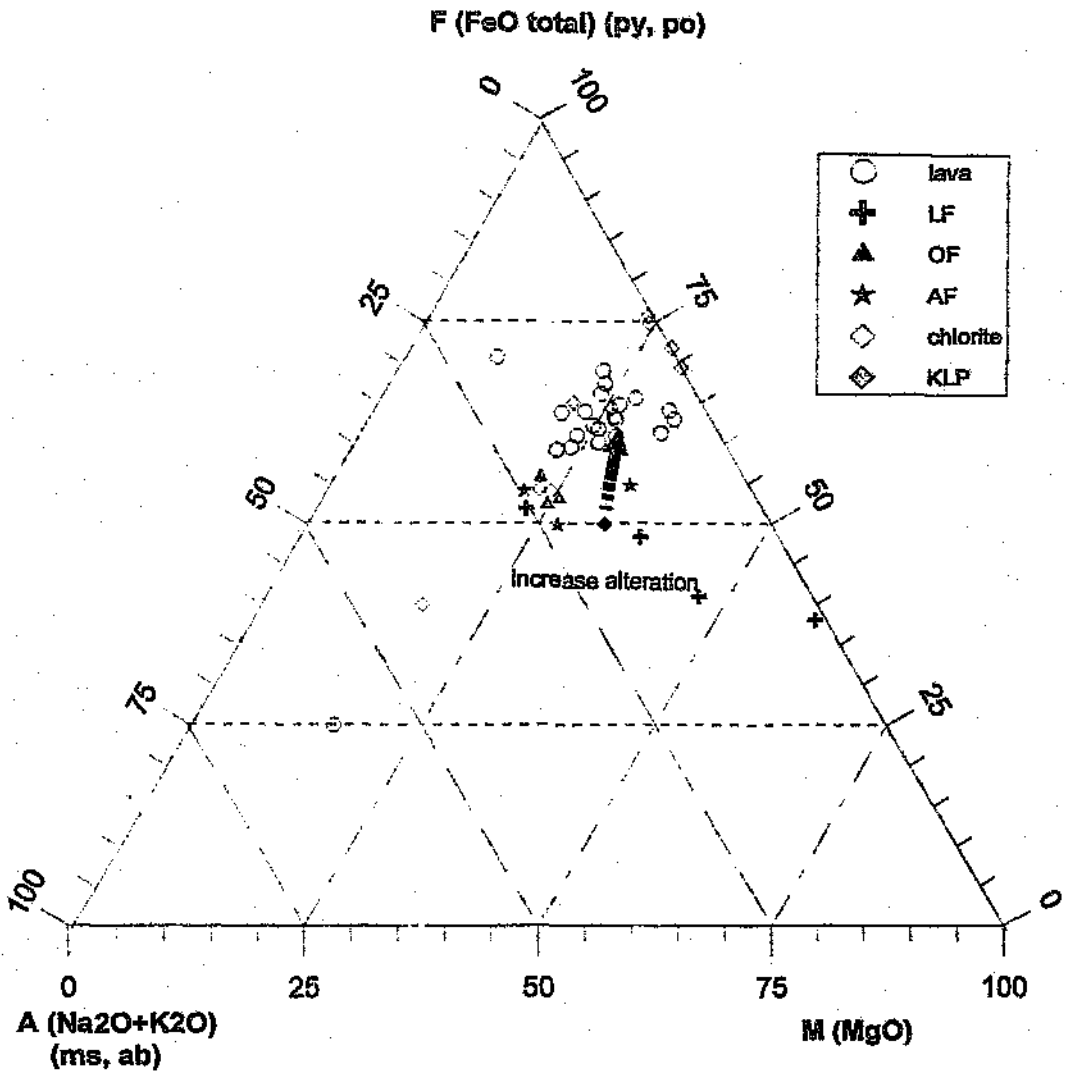


Fig. 5-4 AFM diagram showing deviation of the lava samples in the research area with the Kilprivierberg Group lavas (Bowen et al., 1986). Py—pyrite; po—pyrrhotite; ms—muscovite; KLP—average compositions of the Kilpriviersberg Group lavas; and others as in Fig. 5-2.

authigenic minerals are also projected in the diagram based on the same principle in order to help interpret the rock geochemical data. Pyrite (py) and pyrrhotite (po) are represented at the F-apex member, and muscovite and albite in the A-end member, while chlorite from the hanging wall lavas in the research area is plotted as actual points. The results demonstrate the existence of deviation of the lava samples in the research area from the Klipriviersberg Group lavas (Bowen et al., 1986) (Fig. 5-2a) and enrichment of FeO, which is in a good agreement with the bivariate plot of Fig. 5-2c. It is suggested that the hanging wall lavas in the research area were involved in strong alteration of the original Klipriviersberg Group lavas. Moreover, a close correlation between the samples and chlorite is also demonstrated in the diagram so that an evolution line can be drawn towards chloritization and sulphidization (pyrite, pyrrhotite).

5.3.1.3 Trace elements

The analysed trace elements of the rocks include V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, and Ba (Table 5-1). Of the analysed trace elements, the concentrations of V, Cr, Ni, Cu, Zn, Sr, Zr, and Ba are higher than 100 ppm with lesser amounts of Co, Rb, Y, and Nb (<100 ppm). The selected trace elements are plotted against TiO_2 (Fig. 5-5), which is thought to be one of the typical immobile elements, except under extreme oxidizing and acidic/alkaline conditions. The results demonstrate that Zr is the only element that correlates with TiO_2 ($r=0.4$) in these elements (V, Cr, Co, Ni, Cu, Zn, Y, Zr, Nb). It is suggested that Zr is present as zircon or replacement of Ti in sphene or rutile, while the others are not related to TiO_2 .

The further selected trace elements are plotted against some major elements for the hanging wall lava samples (Fig. 5-6). Both Cu and Zn are weakly related to Fe_2O_3 (Fig. 5-6a, b), which suggests that they occur as sulphides (chalcopyrite and sphalerite) independently and

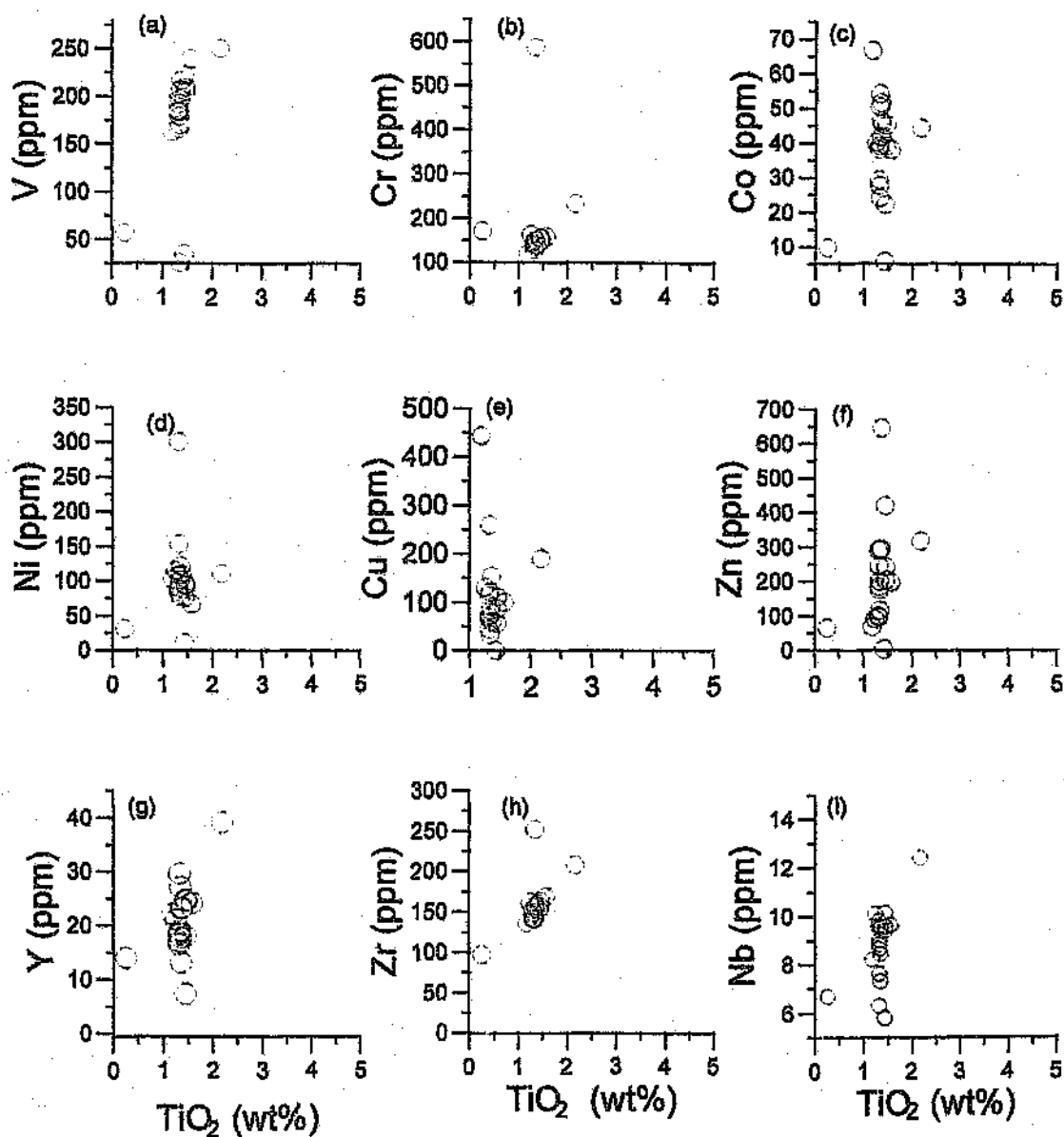


Fig.5-5 Plots of V, Cr, Co, Ni, Cu, Zn, Y, Zr and Nb (ppm) vs TiO_2 (wt%) for the lava samples in the research area.

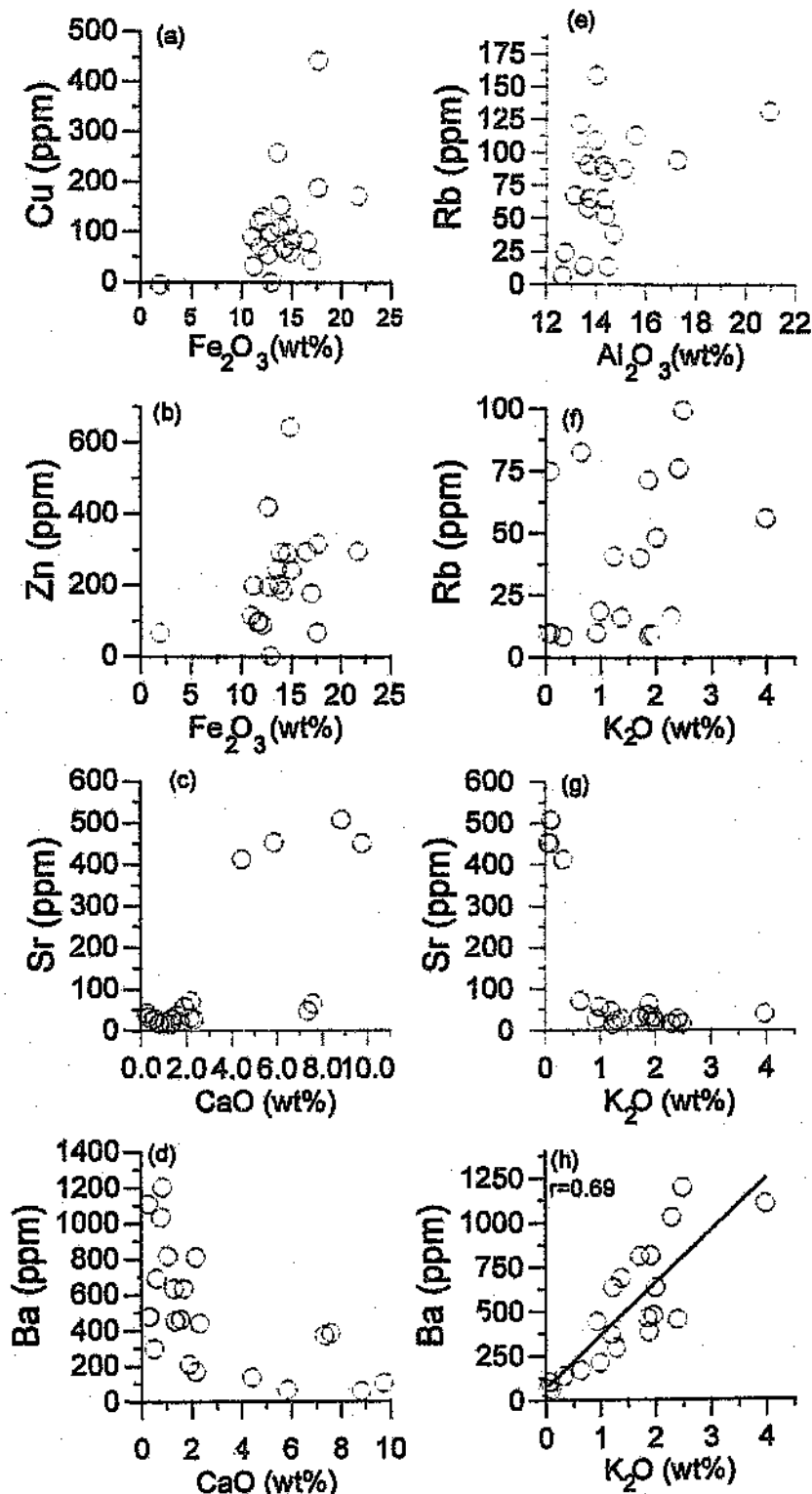


Fig. 5-6 Plots of Cu, Zn vs Fe_2O_3 and Sr, Ba vs CaO, Rb vs Al_2O_3 and Rb, Sr, Ba vs K_2O for the lava samples in the research area.

possibly coincide with pyrite and pyrrhotite mineralization. CaO is moderately correlated with Sr ($r=0.55$), but not with Ba (Fig. 5-6c, d). Rb is not correlated with Al_2O_3 (Fig. 5-6e), and Rb and Ba are strongly correlated with K_2O . It is suggested that muscovitization contributed to the correlation of Rb and Ba with K_2O .

A further plot of Rb, Sr and Ba in a triangular diagram (Fig. 5-7) demonstrates that Ba is enriched in some samples, but Sr in the others in comparison with the Klipriviersberg Group. As presented in Fig. 5-6c, h and discussed previously, the deviation of enrichment of Sr and Ba is due to carbonatization (calcite) and muscovitization, respectively.

Fig. 5-8 shows patterns of transition elements (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) for the WDLSM lavas, together with those of the Klipriviersberg Group lavas. These elements are normalized to their corresponding primitive mantle values (Sun, 1982). The normalized patterns of the trace elements for the lavas are characterized by strong depletion of Cr and Ni, and they are very similar to that of MORB lavas (Langmuir et al., 1977; Rollinson, 1993). In addition, the WDLSM lavas are enriched in Ti, Cu and Zn, relative to the Klipriviersberg Group. It is suggested that enrichment of Cu and Zn is related to hydrothermal activity, while enrichment of Ti is probably related to the original chemical character due to its immobile behaviour.

5.3.1.4 Summary of the lava geochemistry

The hanging wall lavas in the research area are of basalt-andesite type, weakly subalkaline due to Ti-rich alteration. Hydrothermal alteration is suggested as the cause of the shift in the classification. The lava samples are enriched in TiO_2 , Fe_2O_3 , MnO, P_2O_5 , K_2O , which are related to sulphidization, sphene and rutile mineralization, and muscovitization, but depleted in CaO,

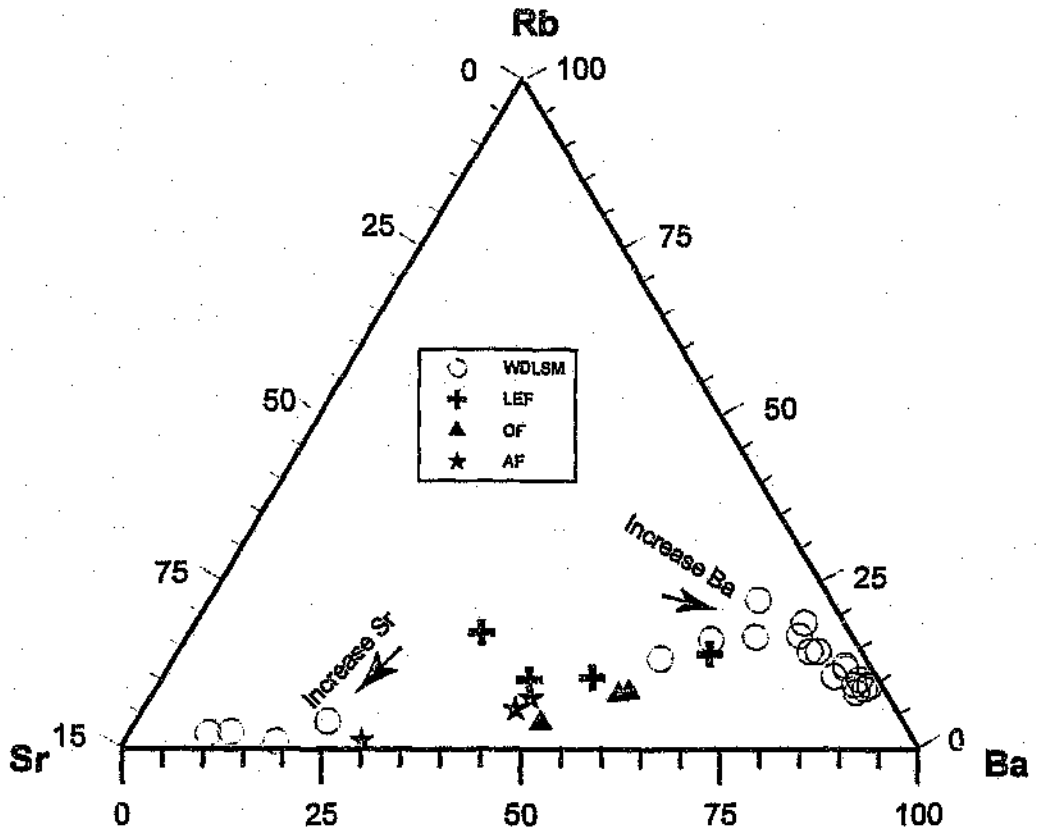


Fig. 5-7 A triangular diagram of Rb, Sr and Ba for the lava samples in the research area, together with the Kilpriviersberg Group lavas. The diagram illustrates two trends of enrichment of Ba and Sr for the samples, relative to the Kilpriviersberg lavas compiled from Bowen et al. (1986). Abbreviations as in Fig. 5-2.

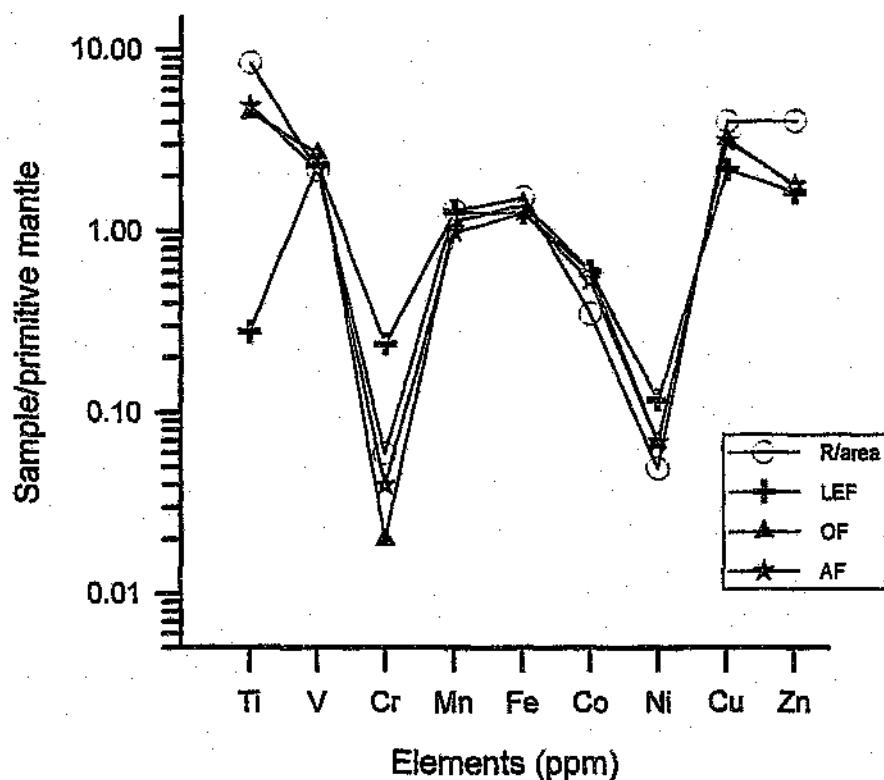


Fig. 5-8 Primitive mantle-normalized transition element patterns of the lava samples in the research area, together with the Klipriviersberg Group lavas. The data of the Klipriviersberg Group lavas are from Bowen et al. (1986), and those of the primitive mantle from Sun (1982). Abbreviations as in Fig. 5-2.

MgO and Na₂O which is due to their removal from the altered lavas by hydrothermal fluids during hydrothermal alteration. There is a clear trend towards increasing MgO and FeO which is attributed to Fe-sulphidization and chloritization of the lavas in the research area. The lava samples in the research area are enriched in Cu and Zn, which are attributed to sulphidization. Muscovitization and carbonatization contributed to the deviation of Sr and Ba compositions from the Klipriviersberg Group lavas.

5.3.2 Conglomerates of the VCR

Chemical compositions of the VCR conglomerates are tabulated in Table 5-2 in the same format as those of the hanging wall lavas.

5.3.2.1 *Major oxides*

SiO₂, Al₂O₃, and Fe₂O₃ constitute the major oxides of the VCR, with minor amounts of K₂O, MgO, CaO, TiO₂, MnO, Na₂O, and P₂O₅. All major oxides are plotted against SiO₂ together with other Witwatersrand reefs (Fig. 5-9), which include the North Reef (NR), Main Reef (MR), South Reef (SR), Upper and Lower bands of the Livingstone Reef (ULR, LLR), Boulder Reef (BR) and White Reef (WR) (Pretorius, 1974). The results show that the VCR conglomerates are obviously enriched in (MnO), MgO, CaO, (Na₂O), K₂O (Fig. 5-9d, e, f, g, h) and depleted in TiO₂ with no change in Al₂O₃, Fe₂O₃, and P₂O₅. The enrichments of these major oxides are attributed to chloritization (MgO, MnO), carbonatization (CaO, FeO), albitization (Na₂O) and muscovitization (K₂O). The VCR samples are also plotted in an AFM diagram to demonstrate the evolution of the major oxides during hydrothermal alteration (see later).

In order to determine the relationships between the major elements, the selected oxides are plotted against Fe₂O₃, Al₂O₃, and TiO₂ (Fig. 5-10). The results show that some of the elements are

Table 5-2 Bulk rock chemistry of the VCR conglomerates at WDLSM (total of 25 samples)

	bb19	bb22	bb25	bb26	bb25	bb22	bb21	bb22	ref	1701	1710	5358	1364	1365a	1378	1395	1402	x423	x442a	1608a	1620a	1630a	1638a	bb21b	bb22e	AVG	STD
wt%																											
SiO ₂	94.92	86.03	86.58	91.71	88.04	92.46	90.08	96.03	97.35	74.66	89.65	88.20	97.25	89.78	93.53	84.60	92.88	92.54	93.57	52.67	63.93	85.67	81.28	94.36	97.85	87.66	10.51
TiO ₂	0.03	0.22	0.16	0.07	0.10	0.03	0.12	0.03	0.09	0.25	0.20	0.12	0.03	0.23	0.05	0.33	0.10	0.08	0.03	0.49	0.06	0.06	0.03	0.07	0.04	0.12	0.11
Al ₂ O ₃	0.56	8.38	6.48	1.49	2.83	0.57	3.81	0.86	0.58	14.00	5.94	6.14	0.52	8.02	0.89	5.54	3.30	2.94	0.82	5.63	2.68	2.32	1.09	1.12	0.56	3.48	3.27
Fe ₂ O ₃	2.55	1.56	1.82	3.19	4.66	1.25	2.20	1.49	1.54	1.93	1.43	1.79	1.58	4.12	3.09	5.54	0.75	1.67	2.77	8.69	9.79	7.06	11.19	2.31	1.14	3.40	2.82
MnO	0.02	0.10	0.02	0.03	0.05	0.01	0.02	0.02	0.03	0.02	0.02	0.01	0.00	0.07	0.03	0.04	0.00	0.03	0.02	0.80	0.09	0.04	0.01	0.00	0.02	0.06	0.15
MgO	0.13	0.30	0.56	0.82	1.06	0.00	0.48	0.04	0.00	1.10	0.02	0.22	0.00	2.18	0.42	1.33	0.12	0.00	0.02	3.61	0.13	1.18	0.19	0.30	0.00	0.57	0.82
CaO	0.19	0.09	0.09	0.10	0.13	0.05	0.12	0.03	0.09	0.27	0.13	0.09	0.08	0.15	0.12	0.13	0.11	0.13	0.07	0.13	8.70	0.06	0.06	0.14	0.06	0.45	1.68
Na ₂ O	0.00	0.00	0.00	0.19	0.00	0.00	0.00	0.00	0.00	0.02	0.43	0.00	0.00	0.00	0.11	0.00	0.00	0.00	0.00	0.12	0.00	0.00	0.51	0.00	0.07	0.06	0.13
K ₂ O	0.13	2.52	1.92	0.06	0.33	0.16	0.97	0.24	0.18	3.97	1.85	1.92	0.17	1.61	0.11	1.32	1.21	0.97	0.18	0.05	0.93	0.23	0.24	0.15	0.18	0.86	0.96
P ₂ O ₅	0.01	0.03	0.03	0.02	0.01	0.01	0.03	0.01	0.01	0.05	0.04	0.03	0.01	0.01	0.01	0.04	0.01	0.03	0.02	0.05	0.01	0.01	0.01	0.01	0.04	0.02	0.01
LOI	0.48	1.57	1.13	0.50	1.14	0.04	0.88	0.82	0.09	2.29	0.92	0.98	0.27	2.02	0.61	1.33	52.00	0.88	1.17	29.20	11.98	2.21	5.32	0.36	0.03	4.73	11.31
Totals	99.00	100.71	98.78	98.19	98.34	99.57	98.72	99.56	99.96	98.57	100.63	99.49	99.92	99.18	98.96	93.19	99.00	99.27	98.67	100.71	98.29	98.84	99.66	98.80	99.98	99.24	0.75
ppm																											
V	23	47	24	17	24	14	19	10	12	57	18	21	12	37	18	52	24	19	9	72	13	18	13	11	12	24	16
Cr	132	181	152	315	101	77	153	48	69	171	214	82	82	245	125	272	72	58	73	67	75	100	51	128	57	124	72
Co	24	10	12	34	25	12	24	15	9	10	18	19	16	20	25	11	8	15	23	31	66	45	42	12	9	21	13
Ni	35	55	44	54	44	73	54	41	11	31	39	70	19	58	35	62	18	31	32	99	77	132	157	25	17	53	34
Cu	25	14	n.d.	16	94	0	76	6	0	0	23	24	2	15	94	1	n.d.	16	0	93	68	99	146	12	12	33	41
Zn	12	21	29	36	117	1005	32	38	17	65	25	15	12	99	21	26	6	50	28	109	1030	1562	83	58	29	181	387
Rb	0	100	75	6	17	9	41	10	9	159	76	82	10	72	0	56	49	40	10	10	57	16	19	10	10	30	38
Sr	4	21	15	10	13	12	22	13	13	40	24	22	12	23	2	6	3	14	12	13	39	9	10	12	13	16	12
Y	6	11	8	6	4	1	5	2	3	14	9	11	4	7	7	6	8	10	13	38	13	15	6	4	1	9	7
Zr	60	105	120	196	48	25	172	47	40	96	110	90	36	129	73	87	76	46	60	89	53	73	36	134	53	82	42
Nb	2	6	5	6	4	4	6	3	4	7	6	10	4	7	2	4	5	7	4	7	2	3	3	4	5	5	2
Ba	42	392	496	20	73	40	185	29	32	1108	444	527	56	307	32	305	292	222	57	19	168	53	49	62	31	210	251

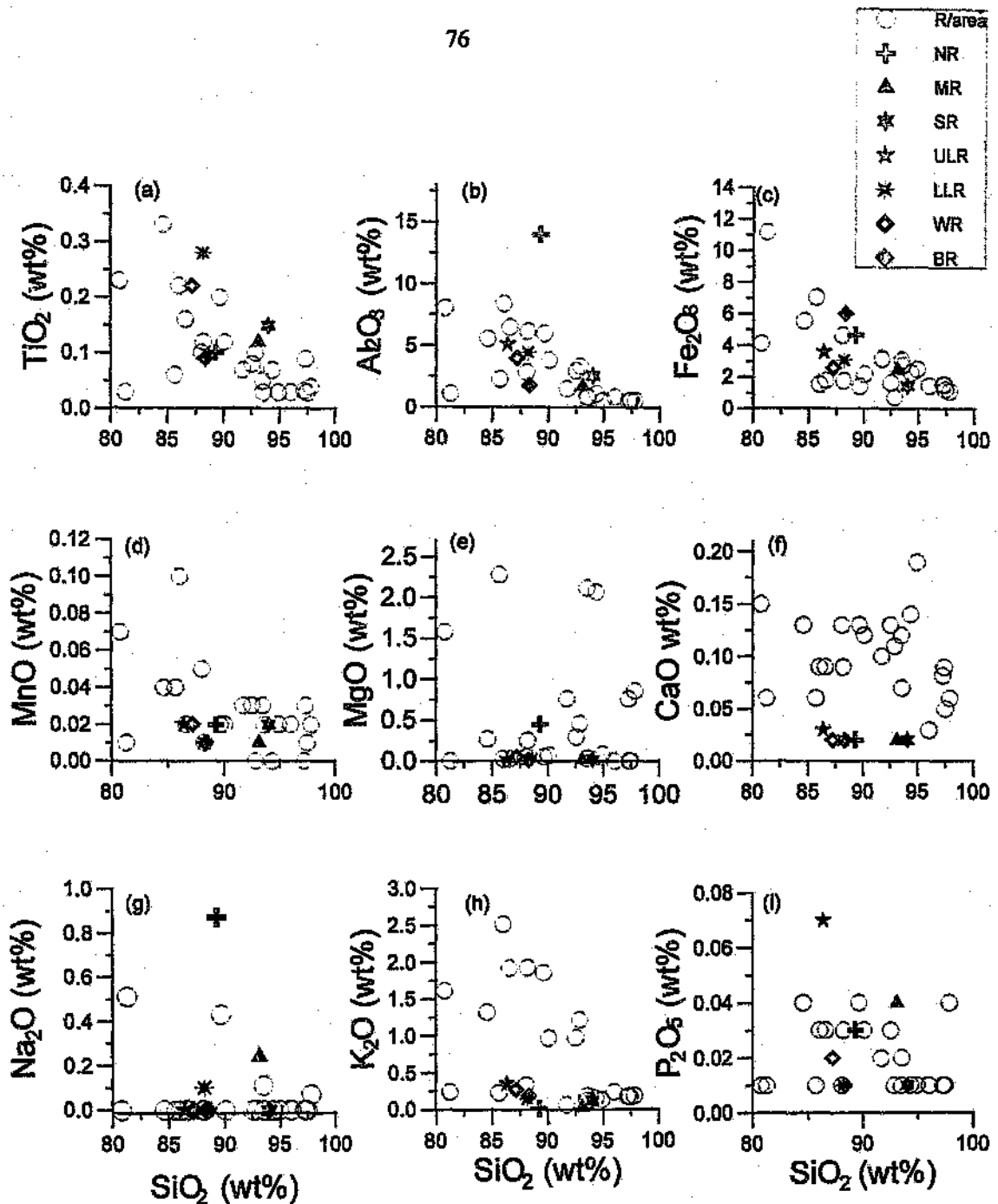


Fig. 5-9 Plots of TiO_2 , Fe_2O_3 , MnO , MgO , CaO , Na_2O , K_2O , P_2O_5 vs SiO_2 for the VCR in the research area, together with the average compositions of the other Wits reefs for reference. The data for the Wits reefs are from Pretorius (1974). R/area—the research area; NR—North Reef; MR—Main Reef; SR—South Reef; ULR—Upper Band of the Livingstone Reef; LLR—Lower Band of the Livingstone Reef; WR—White Reef; and BR—Boulder Reef.

strongly correlated: (1) K_2O and Al_2O_3 ($r=0.74$); (2) Al_2O_3 and TiO_2 ($r=0.73$) and (3) MnO and TiO_2 ($r=0.30$) (Fig. 5-10e, h, g), which separately correspond to (1) muscovitization, and (2) detrital assemblage of ilmenite and clay minerals in the matrix of the VCR or post-depositional alteration processes (see later) and (3) replacement of Ti by Mn. The strong correlation of TiO_2 with Al_2O_3 is consistent with the results of Law (1991). The correlation of TiO_2 with Al_2O_3 exists in both Central and West Rand Group quartzites and the Leader Reef. This has been interpreted to be due to post-depositional mixing processes rather than any detrital control on the ratios. No obvious correlation is identified for the following: (1) MnO and Fe_2O_3 ; (2) TiO_2 and FeO_3 ; (3) Na_2O and Al_2O_3 (Fig. 5-10a, c, f). It is suggested that Mn and Ti are not related to Fe, and Na is fairly scattered and may be related to albitization.

5.3.2.2 Trace elements

The trace element contents of the VCR are dominated by higher concentrations of Ba, Cr, and Zn (>100 ppm), with lesser Rb, V, Co, Ni, Zr, Cu, Sr, Y, and Nb (<100 ppm) (Table 5-2). Selected trace elements are plotted against TiO_2 (Fig. 5-11) and the plots demonstrate the relationship between these elements and TiO_2 . There is a close positive correlation of V and Cr with TiO_2 and weak positive correlation of Zr and Nb with TiO_2 (Fig. 5-11a, b, h, i). The correlation of Nb with TiO_2 is consistent with the results of Law (1991). No correlations have been identified between chalcophile elements (Cu and Zn) and Co, and with TiO_2 (Fig. 5-11e, f), which suggests that the former (Cu, Zn) is more related to hydrothermal activity.

Selected trace elements are plotted against Fe_2O_3 , CaO , Al_2O_3 and K_2O (Fig. 5-12). The results suggest that Cu in the VCR is more correlated with Fe_2O_3 than in the hanging wall lavas, but Zn shows no correlation with Fe_2O_3 , as was the case in the hanging wall lavas. Rb, Sr, and Ba are correlated with Al_2O_3 , and K_2O , but not with CaO . Sr in the VCR behaves differently compared

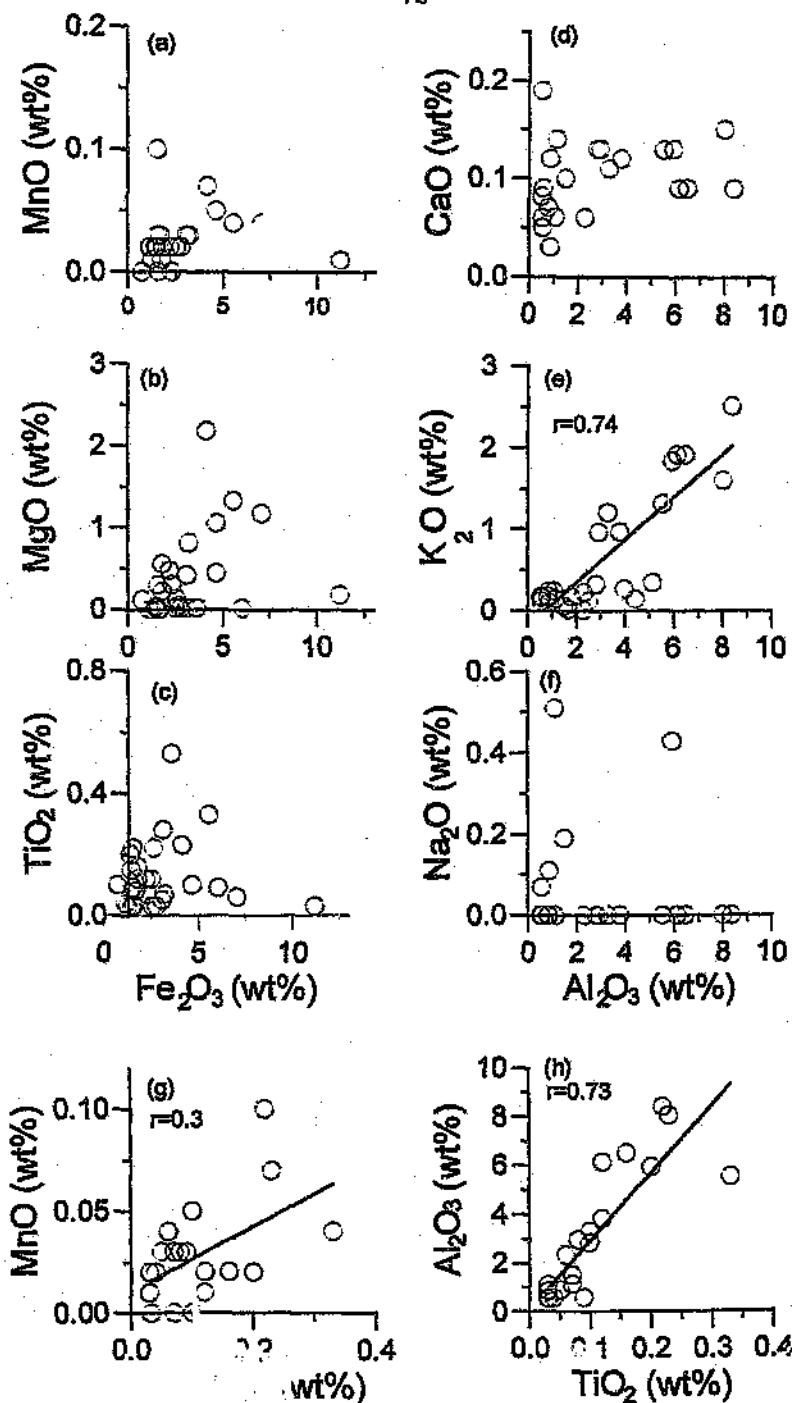


Fig. 5-10 Plots of MnO, MgO, TiO_2 vs Fe_2O_3 , and CaO, K_2O , Na_2O vs Al_2O_3 , and MnO and Al_2O_3 vs TiO_2 for the VCR samples in the research area.

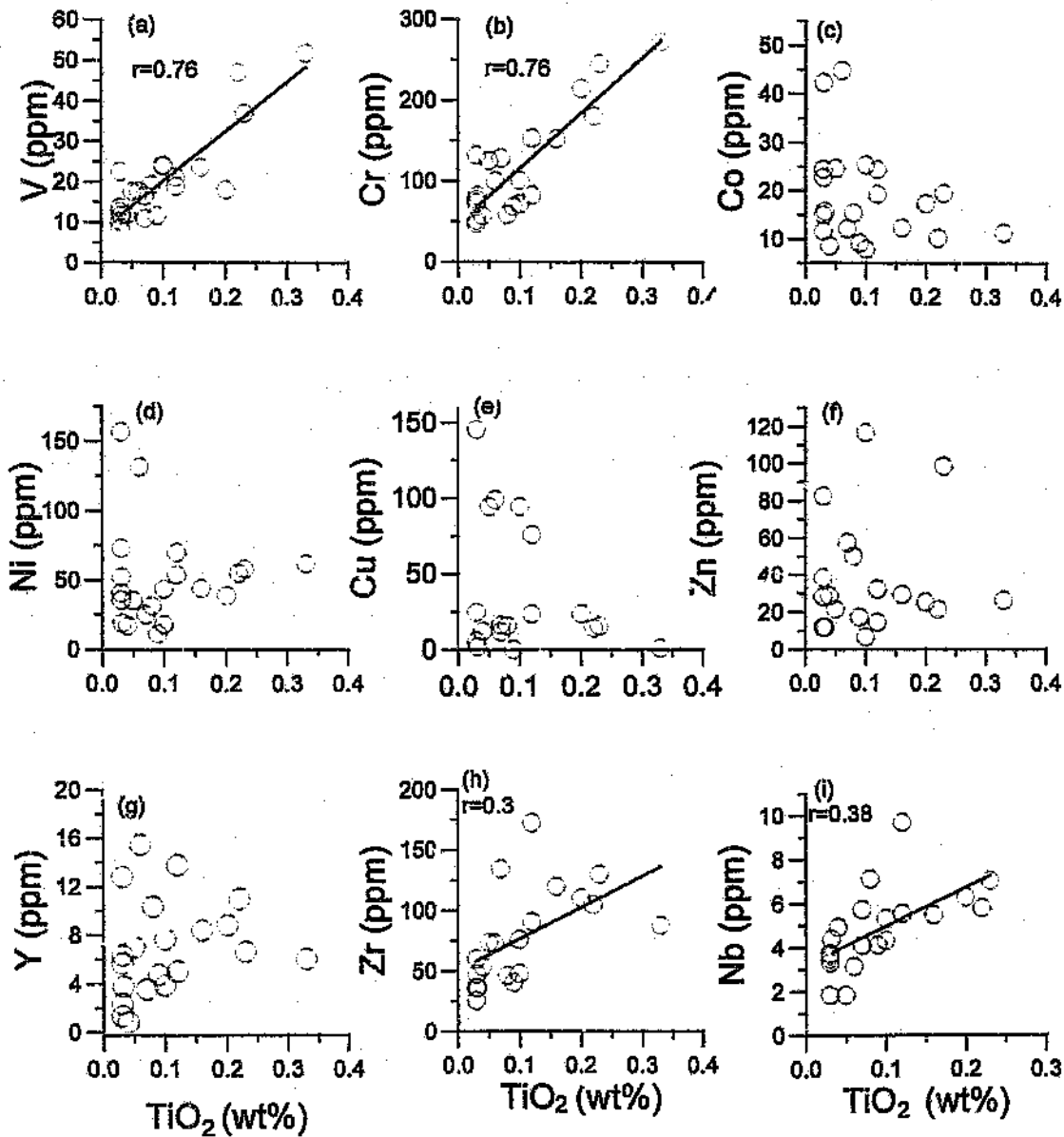


Fig.5-11 Plots of V, Cr, Co, Ni, Cu, Zn, Y, Zr and Nb (ppm) vs TiO_2 (wt%) for the VCR samples in the research area.

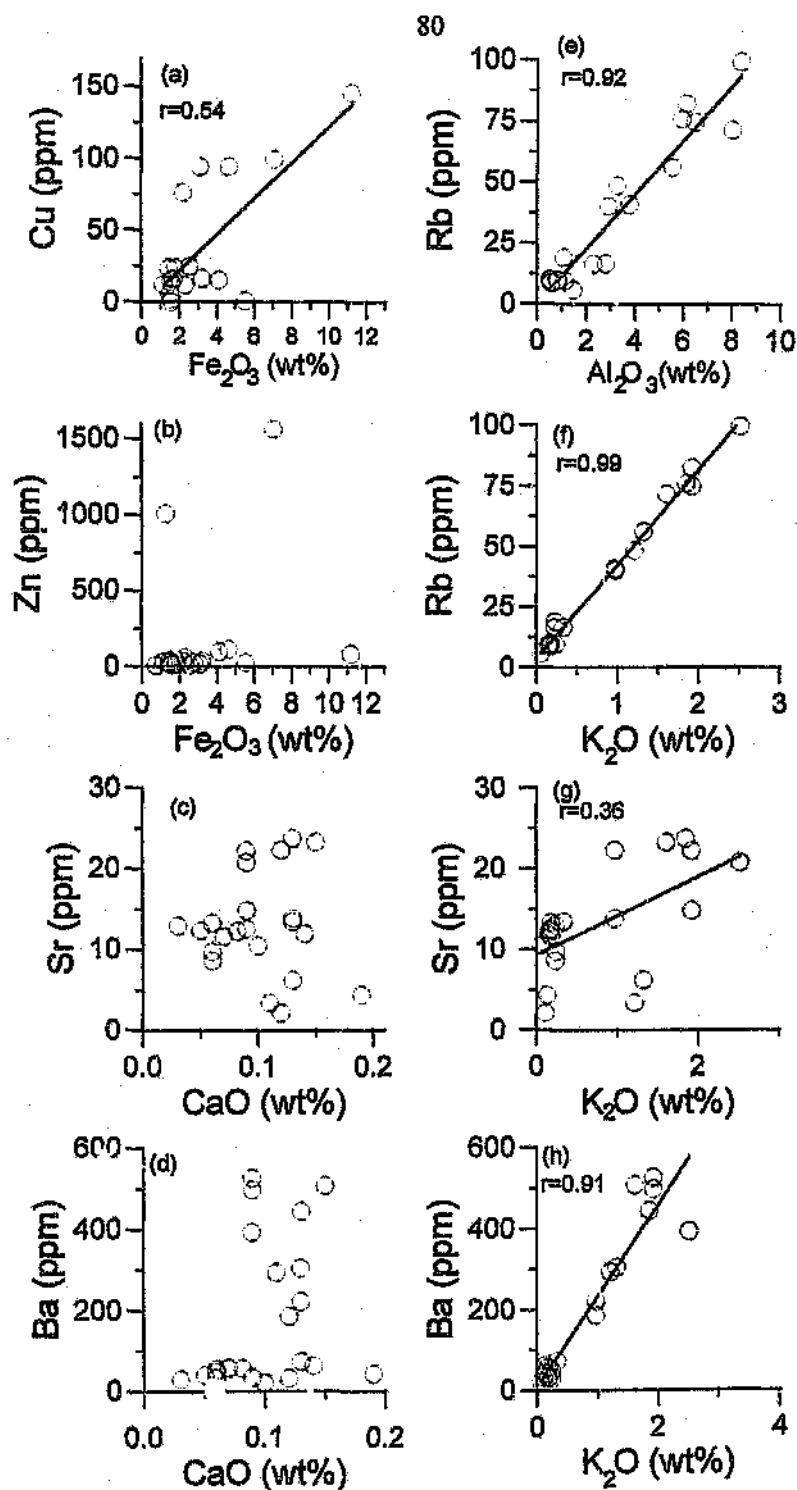


Fig. 5-12 Plots of Cu, Zn vs Fe_2O_3 and Sr, Ba vs CaO, and Rb vs Al_2O_3 , and Rb, Sr, Ba vs K_2O for the VCR samples in the research area.

to the hanging wall lavas due to predominant muscovitization rather than carbonatization in the VCR. The pattern of the transition elements from the VCR at WDLMS is similar to those of the VCR at Elandsrand Gold Mine (Henckel & Schweitzer, 1994), but is characterized by stronger depletion of Cr and by enrichment of Zn (Fig. 5-13). Moreover, the Upper Unit of the VCR at Elandsrand is enriched in Ti, V, Cr, Mn, Ni relative to the lower unit. This may be related to the incorporation of mafic volcanics due to direct contact with the hanging wall lavas rather than due to different source areas as suggested by Henckel and Schweitzer (1994).

5.3.2.3 Summary of the VCR geochemistry

Enrichment of alkalis (K_2O , Na_2O) and alkali earth metals (MgO , CaO) are attributable to post-depositional hydrothermal activity and corresponds to muscovitization, albitization, chloritization and carbonatization. Enrichment of the chalcophile elements (Cu, Zn) is due to hydrothermal circulation in the Witwatersrand Basin and circulation around the VCR conduit and corresponds to the mineralization of chalcopyrite, sphalerite and galena. Siderophile elements of V, Cr, Zr, Ti, and (Nb) are correlated with TiO_2 and Al_2O_3 , which is consistent with the enrichment of the three persistent and most important heavy minerals (chromite, zircon) in the Witwatersrand reefs (Pretorius, 1974). The III elements (Rb, Sr, and Ba) are correlated with K_2O and Al_2O_3 , related to predominant muscovitization rather than carbonatization in the VCR. Differences in the Upper Unit and Lower Unit VCR in siderophile elements (Ti, V, Cr, Mn, Fe and Ni) indicate the local chemical effect of incorporated hanging wall lava materials.

5.3.3 Quartzites

Chemical compositions of the DGG zone and GG zone footwall quartzites and AGNQ internal quartzite are tabulated in Table 3-3, 4, 5 in terms of major oxides (wt%) and trace elements

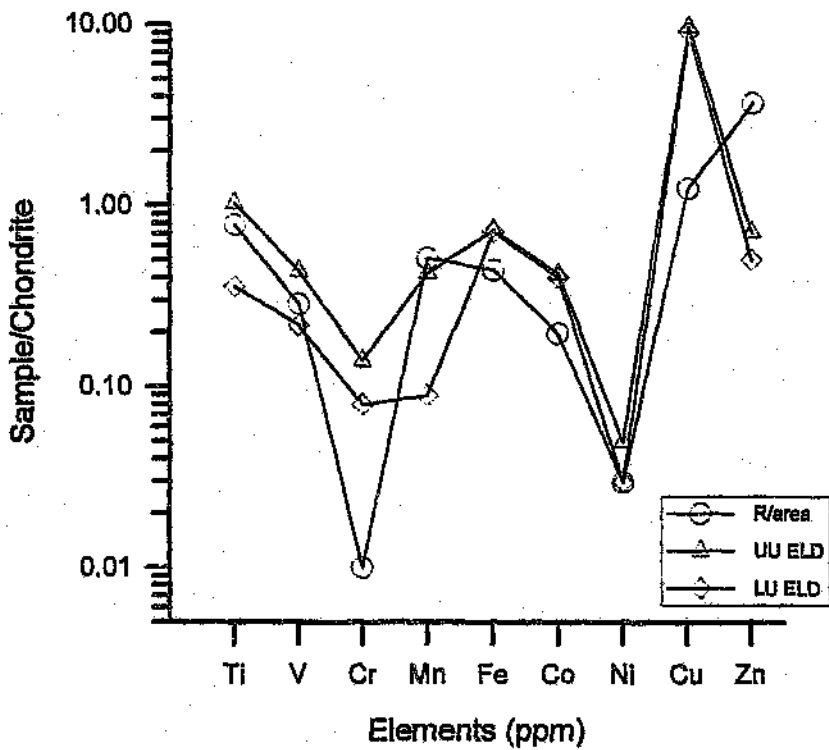


Fig.5-13 Chondrite-normalized transition element patterns for the VCR samples in the research area (R/area), together with the VCR samples from Elandsrand Gold Mine. The data for Elandsrand Gold Mine are from Henckel and Schweitzer (1994). UU ELD—Upper Unit of the VCR, Elandsrand; LU ELD—Lower Unit of the VCR, Elandsrand.

Table 5-3 Bulk rock chemistry of the DGG zone footwall quartzite at WDL SM (total of 36 samples)

	1005	1006	1007	1008	1009	1010	1011	1012	1013	1014	1015	1016	1017	1018	1019	1020	1021	1022	1023	1024	1025	1026	1027	1028	1029	1030	1031	1032	1033	1034	1035	1036	1037	1038	1039	1040	1041	1042	1043	1044	1045	1046	1047	1048	1049	1050	1051	1052	1053	1054	1055	1056	1057	1058	1059	1060	1061	1062	1063	1064	1065	1066	1067	1068	1069	1070	1071	1072	1073	1074	1075	1076	1077	1078	1079	1080	1081	1082	1083	1084	1085	1086	1087	1088	1089	1090	1091	1092	1093	1094	1095	1096	1097	1098	1099	1100	1101	1102	1103	1104	1105	1106	1107	1108	1109	1110	1111	1112	1113	1114	1115	1116	1117	1118	1119	1120	1121	1122	1123	1124	1125	1126	1127	1128	1129	1130	1131	1132	1133	1134	1135	1136	1137	1138	1139	1140	1141	1142	1143	1144	1145	1146	1147	1148	1149	1150	1151	1152	1153	1154	1155	1156	1157	1158	1159	1160	1161	1162	1163	1164	1165	1166	1167	1168	1169	1170	1171	1172	1173	1174	1175	1176	1177	1178	1179	1180	1181	1182	1183	1184	1185	1186	1187	1188	1189	1190	1191	1192	1193	1194	1195	1196	1197	1198	1199	1200	1201	1202	1203	1204	1205	1206	1207	1208	1209	1210	1211	1212	1213	1214	1215	1216	1217	1218	1219	1220	1221	1222	1223	1224	1225	1226	1227	1228	1229	1230	1231	1232	1233	1234	1235	1236	1237	1238	1239	1240	1241	1242	1243	1244	1245	1246	1247	1248	1249	1250	1251	1252	1253	1254	1255	1256	1257	1258	1259	1260	1261	1262	1263	1264	1265	1266	1267	1268	1269	1270	1271	1272	1273	1274	1275	1276	1277	1278	1279	1280	1281	1282	1283	1284	1285	1286	1287	1288	1289	1290	1291	1292	1293	1294	1295	1296	1297	1298	1299	1300	1301	1302	1303	1304	1305	1306	1307	1308	1309	1310	1311	1312	1313	1314	1315	1316	1317	1318	1319	1320	1321	1322	1323	1324	1325	1326	1327	1328	1329	1330	1331	1332	1333	1334	1335	1336	1337	1338	1339	1340	1341	1342	1343	1344	1345	1346	1347	1348	1349	1350	1351	1352	1353	1354	1355	1356	1357	1358	1359	1360	1361	1362	1363	1364	1365	1366	1367	1368	1369	1370	1371	1372	1373	1374	1375	1376	1377	1378	1379	1380	1381	1382	1383	1384	1385	1386	1387	1388	1389	1390	1391	1392	1393	1394	1395	1396	1397	1398	1399	1400	1401	1402	1403	1404	1405	1406	1407	1408	1409	1410	1411	1412	1413	1414	1415	1416	1417	1418	1419	1420	1421	1422	1423	1424	1425	1426	1427	1428	1429	1430	1431	1432	1433	1434	1435	1436	1437	1438	1439	1440	1441	1442	1443	1444	1445	1446	1447	1448	1449	1450	1451	1452	1453	1454	1455	1456	1457	1458	1459	1460	1461	1462	1463	1464	1465	1466	1467	1468	1469	1470	1471	1472	1473	1474	1475	1476	1477	1478	1479	1480	1481	1482	1483	1484	1485	1486	1487	1488	1489	1490	1491	1492	1493	1494	1495	1496	1497	1498	1499	1500	1501	1502	1503	1504	1505	1506	1507	1508	1509	1510	1511	1512	1513	1514	1515	1516	1517	1518	1519	1520	1521	1522	1523	1524	1525	1526	1527	1528	1529	1530	1531	1532	1533	1534	1535	1536	1537	1538	1539	1540	1541	1542	1543	1544	1545	1546	1547	1548	1549	1550	1551	1552	1553	1554	1555	1556	1557	1558	1559	1560	1561	1562	1563	1564	1565	1566	1567	1568	1569	1570	1571	1572	1573	1574	1575	1576	1577	1578	1579	1580	1581	1582	1583	1584	1585	1586	1587	1588	1589	1590	1591	1592	1593	1594	1595	1596	1597	1598	1599	1600	1601	1602	1603	1604	1605	1606	1607	1608	1609	1610	1611	1612	1613	1614	1615	1616	1617	1618	1619	1620	1621	1622	1623	1624	1625	1626	1627	1628	1629	1630	1631	1632	1633	1634	1635	1636	1637	1638	1639	1640	1641	1642	1643	1644	1645	1646	1647	1648	1649	1650	1651	1652	1653	1654	1655	1656	1657	1658	1659	1660	1661	1662	1663	1664	1665	1666	1667	1668	1669	1670	1671	1672	1673	1674	1675	1676	1677	1678	1679	1680	1681	1682	1683	1684	1685	1686	1687	1688	1689	1690	1691	1692	1693	1694	1695	1696	1697	1698	1699	1700	1701	1702	1703	1704	1705	1706	1707	1708	1709	1710	1711	1712	1713	1714	1715	1716	1717	1718	1719	1720	1721	1722	1723	1724	1725	1726	1727	1728	1729	1730	1731	1732	1733	1734	1735	1736	1737	1738	1739	1740	1741	1742	1743	1744	1745	1746	1747	1748	1749	1750	1751	1752	1753	1754	1755	1756	1757	1758	1759	1760	1761	1762	1763	1764	1765	1766	1767	1768	1769	1770	1771	1772	1773	1774	1775	1776	1777	1778	1779	1780	1781	1782	1783	1784	1785	1786	1787	1788	1789	1790	1791	1792	1793	1794	1795	1796	1797	1798	1799	1800	1801	1802	1803	1804	1805	1806	1807	1808	1809	1810	1811	1812	1813	1814	1815	1816	1817	1818	1819	1820	1821	1822	1823	1824	1825	1826	1827	1828	1829	1830	1831	1832	1833	1834	1835	1836	1837	1838	1839	1840	1841	1842	1843	1844	1845	1846	1847	1848	1849	1850	1851	1852	1853	1854	1855	1856	1857	1858	1859	1860	1861	1862	1863	1864	1865	1866	1867	1868	1869	1870	1871	1872	1873	1874	1875	1876	1877	1878	1879	1880	1881	1882	1883	1884	1885	1886	1887	1888	1889	1890	1891	1892	1893	1894	1895	1896	1897	1898	1899	1900	1901	1902	1903	1904	1905	1906	1907	1908	1909	1910	1911	1912	1913	1914	1915	1916	1917	1918	1919	1920	1921	1922	1923	1924	1925	1926	1927	1928	1929	1930	1931	1932	1933	1934	1935	1936	1937	1938	1939	1940	1941	1942	1943	1944	1945	1946	1947	1948	1949	1950	1951	1952	1953	1954	1955	1956	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100	2101	2102	2103	2104	2105	2106	2107	2108	2109	2110	2111	2112	2113	2114	2115	2116	2117	2118	2119	2120	2121	2122	2123	2124	2125	2126	2127	2128	2129	2130	2131	2132	2133	2134	2135	2136	2137	2138	2139	2140	2141	2142	2143	2144	2145	2146	2147	2148	2149	2150	2151	2152	2153	2154	2155	2156	2157	2158	2159	2160	2161	2162	2163	2164	2165	2166	2167	2168	2169	2170	2171	2172	2173	2174	2175	2176	2177	2178	2179	2180	2181	2182	2183	2184	2185	2186	2187	2188	2189	2190	2191	2192	2193	2194	2195	2196	2197	2198	2199	2200	2201	2202	2203	2204	2205	2206	2207	2208	2209	2210	2211	2212	2213	2214	2215	2216	2217	2218	2219	2220	2221	2222	2223	2224	2225	2226	2227	2228	2229	2230	2231	2232	2233	2234	2235	2236	2237	2238	2239	2240	2241	2242	2243	2244	2245	2246	2247	2248	2249	2250	2251	2252	2253	2254	2255	2256	2257	2258	2259	2260	2261	2262	2263	2264	2265	2266	2267	2268	2269	2270	2271	2272	2273	2274	2275	2276	2277	2278	2279	2280	2281	2282	2283	2284	2285	2286	2287	2288	2289	2290	2291	2292	2293	2294	2295	2296	2297	2298	2299	2300	2301	2302	2303	2304	2305	2306	2307	2308	2309	2310	2311	2312	2313	2314	2315	2316	2317	2318	2319	2320	2321	2322	2323	2324	2325	2326	2327	2328	2329	2330	2331	2332	2333	2334	2335	2336	2337	2338	2339	2340	2341	2342	2343	2344	2345	2346	2347	2348	2349	2350	2351	2352	2353	2354	2355	2356	2357	2358	2359	2360	2361	2362	2363	2364	2365	2366	2367	2368	2369
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Table 5-4 Bulk rock chemistry of the GG zone footwall quartzite at WDLMS (total of 21 samples)

	bh14	bh15	bh16	bh17	bh18	bh19	bh20	015	b104	b357	b360	b366	b368	b373	b374	b379	b380	K7-65c	x419a	1620c	1639	AVG	STD
wt%																							
SiO2	85.08	72.80	78.95	83.24	89.51	84.09	87.96	85.95	89.23	87.00	81.22	85.90	79.05	80.49	84.56	75.68	84.10	81.41	76.24	81.86	75.24	82.45	4.74
TiO2	0.12	0.60	0.32	0.18	0.09	0.22	0.15	0.30	0.09	0.15	0.12	0.16	0.55	0.30	0.21	0.32	0.26	0.23	0.10	1.17	0.46	0.25	0.15
Al2O3	9.14	17.45	13.56	6.97	7.71	8.60	6.52	8.57	5.91	6.17	11.73	6.20	9.61	12.00	9.60	14.95	9.42	10.88	5.17	6.94	4.91	9.47	3.41
Fe2O3	0.45	0.88	0.42	3.37	0.58	0.80	0.83	0.69	0.89	0.57	0.45	2.53	4.49	0.56	0.45	0.75	0.52	1.09	4.32	0.53	0.53	1.22	1.25
MnO	0.02	0.02	0.01	0.02	0.03	0.00	0.02	0.01	0.01	0.00	0.01	0.03	0.03	0.00	0.00	0.02	0.01	0.02	0.15	0.05	0.00	0.02	0.03
MgO	0.05	0.03	0.14	0.21	0.00	0.40	0.70	0.15	0.14	0.00	0.16	0.63	0.76	0.39	0.13	0.53	0.32	0.50	0.27	0.14	0.09	0.27	0.23
CaO	0.06	0.05	0.06	0.39	0.12	0.15	2.06	0.25	0.08	0.09	0.09	0.17	0.28	0.05	0.07	0.08	0.05	0.13	4.01	2.17	0.06	0.58	1.21
Na2O	0.30	0.35	0.57	0.19	0.00	0.14	0.02	0.00	0.00	0.00	0.32	0.00	0.25	0.14	0.00	0.20	0.34	0.00	0.10	0.00	0.00	0.14	0.16
K2O	2.58	4.66	3.67	1.98	1.69	2.78	0.94	2.14	1.84	1.87	3.77	1.64	2.82	3.68	2.83	4.33	2.83	3.18	1.69	2.44	4.75	2.80	1.03
P2O5	0.03	0.01	0.01	0.02	0.01	0.02	0.00	0.02	0.01	0.02	0.01	0.02	0.03	0.02	0.03	0.02	0.02	0.03	0.03	0.00	0.00	0.02	0.01
LOI	1.14	2.55	1.76	1.87	0.97	1.30	0.00	1.20	0.83	0.80	1.60	1.26	1.95	1.69	1.33	2.03	1.32	1.64	5.71	3.61	2.06	1.74	1.13
Total	98.95	99.38	99.48	98.65	98.69	98.51	99.20	99.87	99.01	98.64	99.47	98.53	99.31	99.22	99.21	98.91	99.18	99.14	98.58	96.80	99.11	99.06	0.39
ppm																							
V	32	66	64	35	17	31	25	36	24	24	22	28	47	41	28	67	39	54	19	19		38	18
Cr	85	488	229	385	56	153	63	327	95	128	87	129	557	195	138	156	140	190	73	55	228	191	137
Co	6	12	6	26	9	10	10	11	6	11	6	16	38	13	12	6	10	10	24	9	11	13	11
Ni	13	21	24	86	22	18	12	13	16	43	15	36	105	26	30	33	29	28	72	13	19	32	25
Cu	0	14	4	76	0	1	0	0	0	0	0	29	98	7	9	0	6	0	79	0	15	16	29
Zn	4	1	4	8	20	21	18	14	3	16	11	658	39	52	34	43	45	139	623	202	34	95	103
Rb	79	141	119	88	58	110	78	114	73	70	151	68	116	145	113	173	114	128	75	108	170	109	34
Sr	18	39	28	28	16	22	21	39	11	23	34	17	27	48	41	43	38	38	42	32	46	30	10
Y	8	13	9	20	6	11	5	11	7	10	9	8	16	11	8	19	17	11	12	8	12	11	4
Zr	67	372	119	176	68	112	67	158	100	90	60	99	284	115	94	89	98	101	67	39	163	122	75
Nb	2	9	5	7	5	6	5	7	3	5	6	4	10	8	6	6	7	6	7	5	8	6	2
Be	242	448	264	544	191	1052	325	719	513	443	919	485	797	984	747	1403	822	579	338	463	965	681	287

Table 5-5 Bulk rock chemistry of the AGNQ internal quartzite at WDLSM
(total of 8 samples)

	bhb-3a	bhb-4	x0416a	x0416b	x0416c	x0417a	x0444	x0612a	AVG	STD
SiO ₂	93.65	82.62	73.62	76.61	80.35	46.97	75.04	70.79	74.96	10.30
TiO ₂	0.3	0.81	11.28	0.97	0.45	4.75	0.91	0.95	2.53	3.46
Al ₂ O ₃	3.47	8.4	2.29	8.99	7.56	22.01	14.1	12.8	9.95	5.40
Fe ₂ O ₃	0.89	2.06	0.04	1.81	1.71	2.36	2.17	4.5	1.94	1.14
MnO	0.02	0.02	0.72	0.03	0.06	0.04	0	0.74	0.12	0.23
MgO	0.2	0.55	2.26	0.55	0.31	1.38	0.15	0.72	0.77	0.64
CaO	0.25	0.72	0.12	2.23	2.78	4.65	0.15	0.76	1.46	1.45
Na ₂ O	0	0.14	4	0.14	0	3.99	0	0	1.03	1.67
K ₂ O	1.29	3.03	0.03	3.19	2.65	7.92	4.2	4.64	3.37	2.07
P ₂ O ₅	0.02	0.08	1.42	0.03	0.04	0.03	0.03	0.01	0.21	0.45
L.O.I	0.55	1.69	3.15	4.53	2.89	4.83	2.18	2.85	2.83	1.00
Totals	100.64	100.1	98.93	99.09	98.8	98.95	98.93	98.06	99.19	0.32
V	49	121	191	471	74	416	135	140	191	121
Cr	399	1148	2237	5937	813	6842	1291	1197	2446	2113
Co	32	25	24	29	28	30	34	27	29	3
Ni	73	209	399	45	250	365	440	932	339	242
Cu	0	45	24	33	26	7	59	22	27	15
Zn	15	18	19	31	23	31	13	19	21	6
Rb	59	97	157	341	129	395	164	219	196	98
Sr	13	15	28	38	37	36	44	18	29	9
Y	4	6	33	66	47	73	14	23	33	22
Zr	56	114	199	308	404	385	156	159	223	102
Nb	9	6	11	34	5	45	12	12	17	13
Ba	343	735	1876	3484	1189	3468	565	1256	1652	1020

Table 5-6 Bulk rock chemistry of the footwall shale from the Booyens
Shale Formation (Kimberley Shale) at WDLSM (total of 5 samples)

	b0388	b0392	b0393	b0389	b0394	AVG	STD
SiO ₂	54.59	54.30	54.72	55.87	57.63	55.42	1.23
TiO ₂	0.65	0.65	0.69	0.70	0.60	0.66	0.04
Al ₂ O ₃	20.34	21.19	20.34	20.72	18.52	20.14	0.88
Fe ₂ O ₃	8.52	7.50	9.25	8.21	9.32	8.56	0.68
MnO	0.09	0.05	0.08	0.09	0.082	0.06	0.03
MgO	4.65	4.15	4.91	4.43	4.84	4.60	0.28
CaO	0.46	0.36	0.19	0.28	0.178	0.26	0.16
Na ₂ O	0.10	0.13	0.73	0.10	0.60	0.33	0.28
K ₂ O	5.44	6.19	4.85	5.54	4.29	5.26	0.65
P ₂ O ₅	0.07	0.04	0.08	0.07	0.102	0.05	0.03
L.O.I	4.70	4.48	4.44	4.48	4.19	4.46	0.16
Totals	99.59	99.04	100.26	100.09	100.34	99.86	0.49
V	150	137	156	159	136	147	10
Cr	786	796	793	857	723	791	43
Co	32	29	34	35	32	32	2
Ni	305	232	260	269	319	277	31
Cu	1	9	18	1	12	8	7
Zn	143	77	108	489	93	182	155
Rb	224	257	211	225	176	219	26
Sr	38	37	26	34	29	33	5
Y	22	24	19	25	20	22	2
Zr	50	183	147	141	131	150	17
Nb	11	12	10	11	12	11	1
Ba	1188	1129	998	1142	773	1046	151

5.3.3.1 *Chemical classification*

The chemical classification of quartzites is shown in the plot of $\log \text{SiO}_2/\text{Al}_2\text{O}_3$ vs $\log(\text{Fe}_2\text{O}_3/\text{K}_2\text{O})$ (Fig. 5-14) (after Herron, 1988). Samples of the DGG zone plot in a wide range from the arkose-subarkose to Fe-bearing sand and have the highest $\text{Fe}_2\text{O}_3/\text{K}_2\text{O}$ ratio that probably represents iron-related alteration, e.g. chloritization and sulphidization, while some others have higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, which are due to silicification. However, quartzites of the GG zone and AGNQ cover a smaller range from the arkose-subarkose to litharenite-sublitharenite and probably display less chemical effects due to hydrothermal alteration.

5.3.3.2 *Major oxides*

The major oxides are plotted against $\log(\text{Fe}_2\text{O}_3/\text{K}_2\text{O})$ (Fig. 5-15). The DGG zone quartzite represents the strong alteration in the VCR footwall quartzite and is enriched in Fe_2O_3 , MgO , Na_2O , MnO and SiO_2 (Fig. 5-15c, e, g), and depleted in TiO_2 , Al_2O_3 , CaO , and K_2O relative to other alteration zones in the quartzites (Fig. 5-15a, b, f, h). The enrichment of the above element oxides is most probably attributable to chloritization, albitization and silicification.

In contrast, the GG zone quartzite represents the least altered footwall quartzite and is depleted in Fe_2O_3 , MgO , Na_2O and SiO_2 , but enriched in Al_2O_3 , and K_2O . This is clearly ascribed to muscovitization, but less to chloritization and silicification (Fig. 5-15).

AGNQ quartzite (apple green quartzite) represents a very different rock type in the VCR and is enriched in alkali (K_2O), alkaline earth elements (MgO) and siderophile elements (TiO_2 , Fe_2O_3 , MnO), and has both the chemical characteristics of major oxides of the DGG zone (enrichment of Fe_2O_3 , MgO , CaO , Na_2O) and of the GG zone (TiO_2 , K_2O). Enrichment of TiO_2 is attributable to enrichment of Ti-rich minerals, e.g. sphene, rutile, and enrichment of MgO and Fe_2O_3 is related

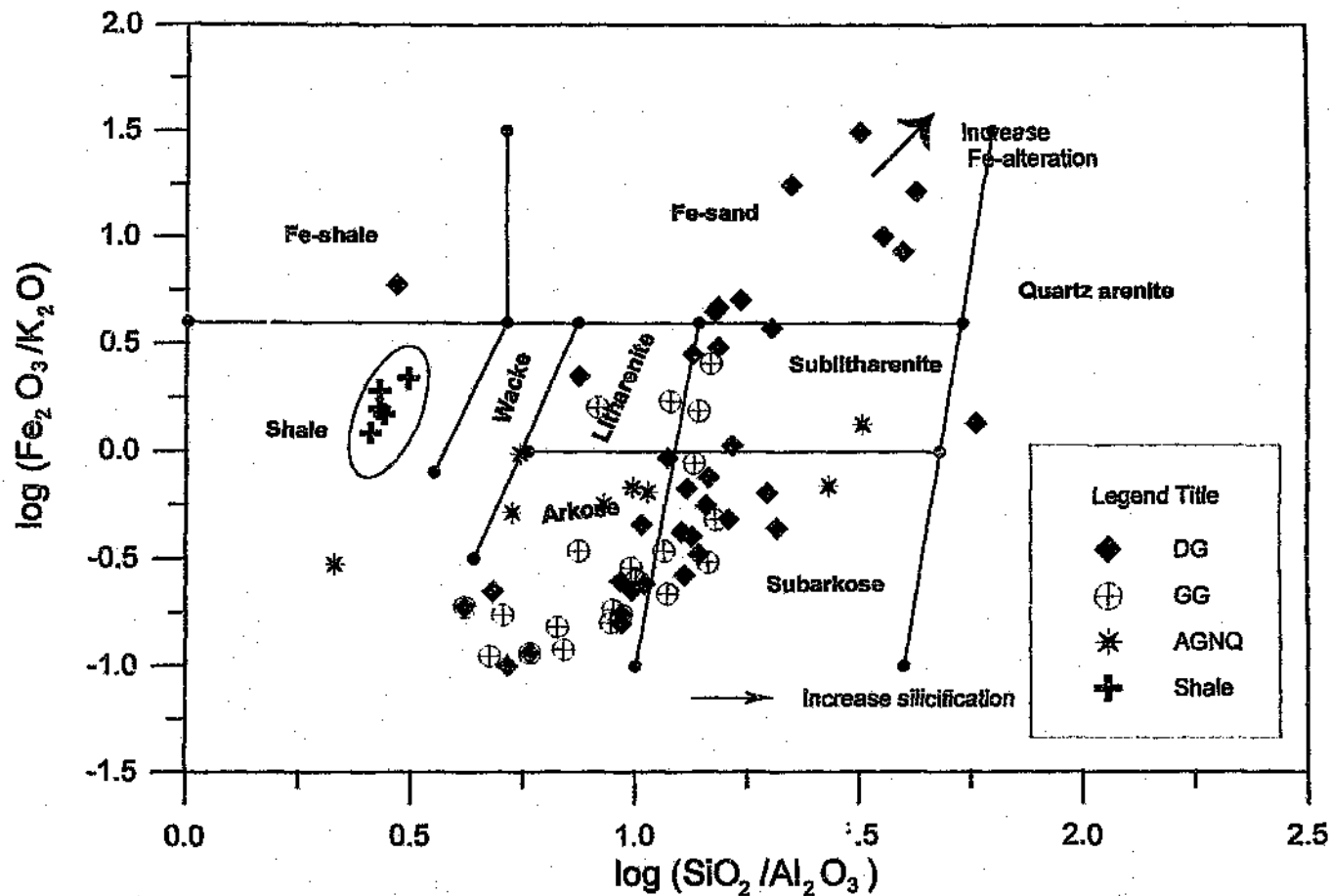


Fig. 5-14 Chemical classification of the quartzites and shale using $\log (\text{Fe}_2\text{O}_3/\text{K}_2\text{O})$ vs $\log (\text{SiO}_2/\text{Al}_2\text{O}_3)$ (after Herron, 1988). Alteration vectors are also indicated.

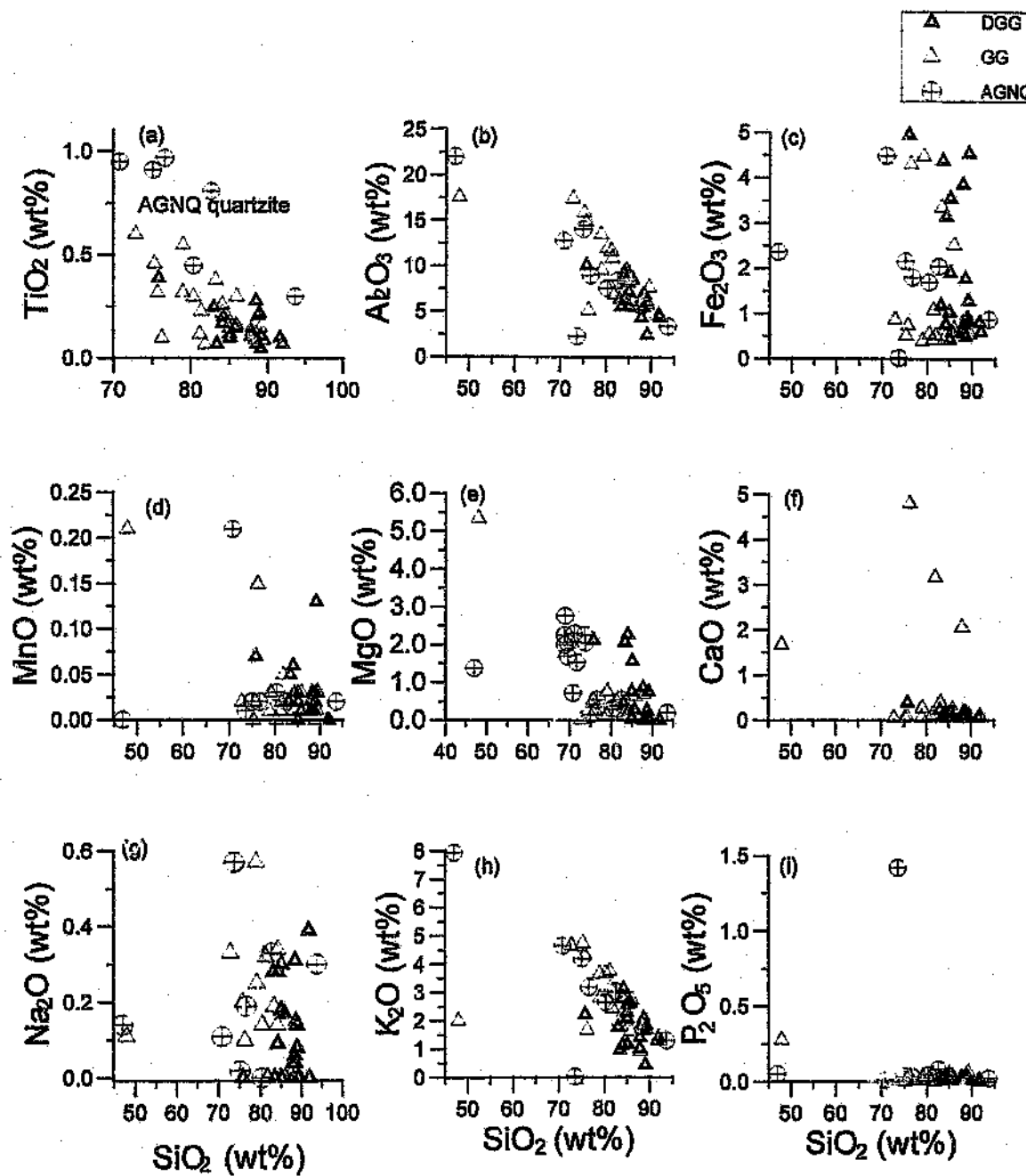


Fig.5-15 Plots of TiO_2 , Fe_2O_3 , MnO , MgO , CaO , Na_2O , K_2O , P_2O_5 vs SiO_2 for DGG zone, GG zone, and AGNQ (apple green) quartzites in the research area.

to chloritization, while enrichment of K_2O is attributed to fine-grained muscovitization.

MnO , MgO and TiO_2 are plotted against Fe_2O_3 (Fig. 5-16a, b, c), which demonstrates a close correlation between MgO and Fe_2O_3 , not for MnO , and TiO_2 . However, the quartzites from different alteration zones are distinguishable in MnO versus Fe_2O_3 (Fig. 5-16b). CaO , K_2O and Na_2O are plotted against Al_2O_3 , demonstrating a close correlation of K_2O with Al_2O_3 (Fig. 5-16f), but not for CaO and Na_2O (Fig. 5-16d, e, f). Al_2O_3 and MnO are plotted against TiO_2 and this demonstrates a similar correlation for the former (Al_2O_3) as shown in the VCR (Fig. 5-16g, h), but not for the later (MnO).

An AFM diagram is plotted for the VCR and footwall quartzites from different alteration zones, which is similar to Fig. 5-4 for the hanging wall lava. Chlorites from all lithologies are chiefly projected on the F-M axis with a wide range in FeO and MgO compositions, together with the lavas shown in Fig. 5-17. There is an obvious trend to increase FeO and MgO with increase of hydrothermal alteration although the strongly altered DGG zone footwall quartzite largely overlaps the GG zone footwall quartzite and the VCR. Enrichments of FeO and MgO are attributable to sulphidization and chloritization. This is consistent with the mineralogical characteristics of the alteration zones of the VCR described in Chapter 4. For example, sulphides (pyrite, pyrrhotite) are enriched in the DGG zone quartzite and depleted in the GG zone quartzite. It seems that the lava in the research area has a similar trend in alteration geochemistry to the altered quartzite (DGG zone footwall quartzite) (Fig. 5-17).

5.3.3.3 *Trace elements*

The selected trace elements are plotted against TiO_2 (Fig. 5-18) and demonstrate that the DGG

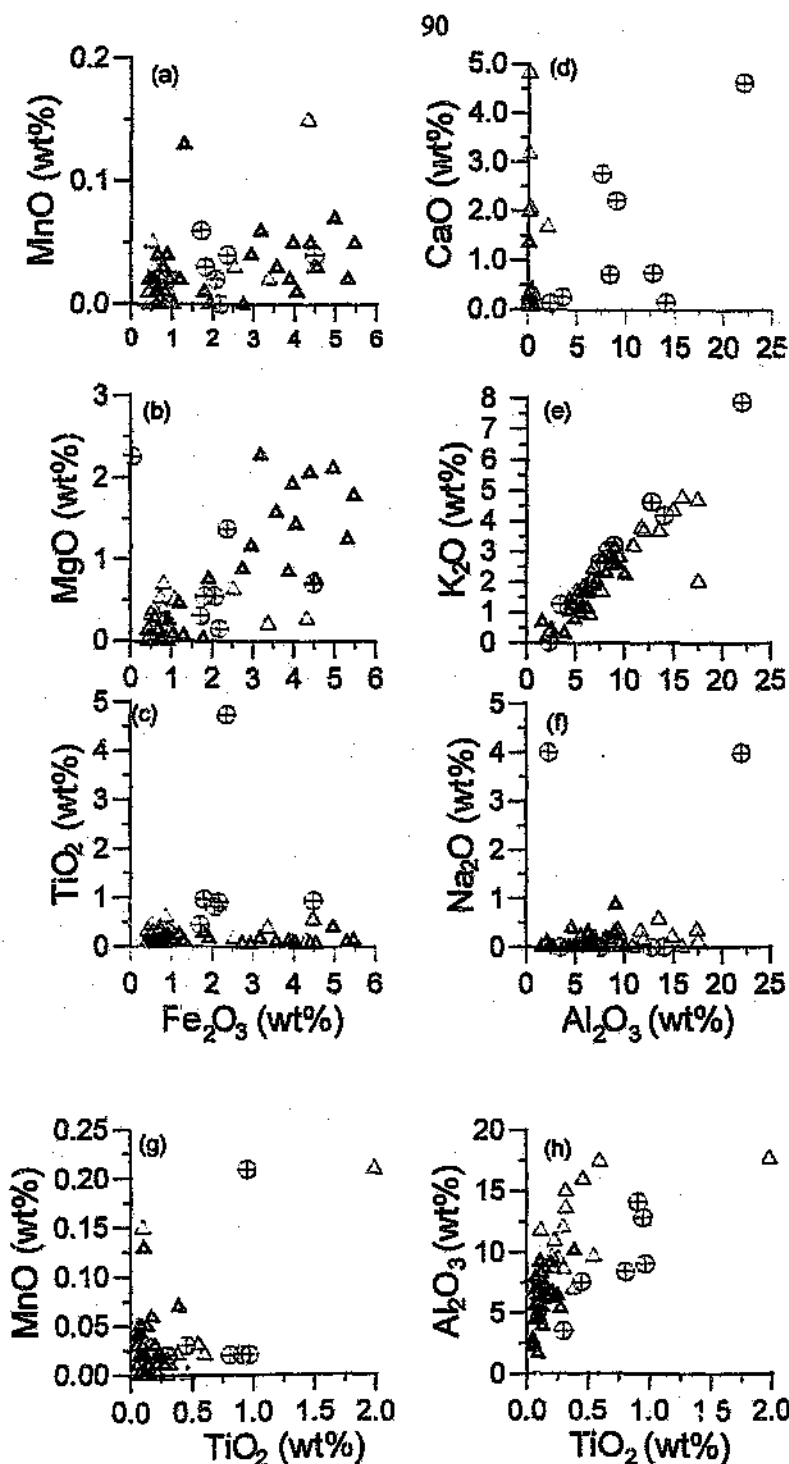


Fig. 5-16 Plots of MnO, MgO, TiO_2 vs Fe_2O_3 , and CaO, K_2O , Na_2O vs Al_2O_3 , and MnO, Al_2O_3 vs TiO_2 for the DGG zone, GG zone, and AGNQ quartzites in the research area.

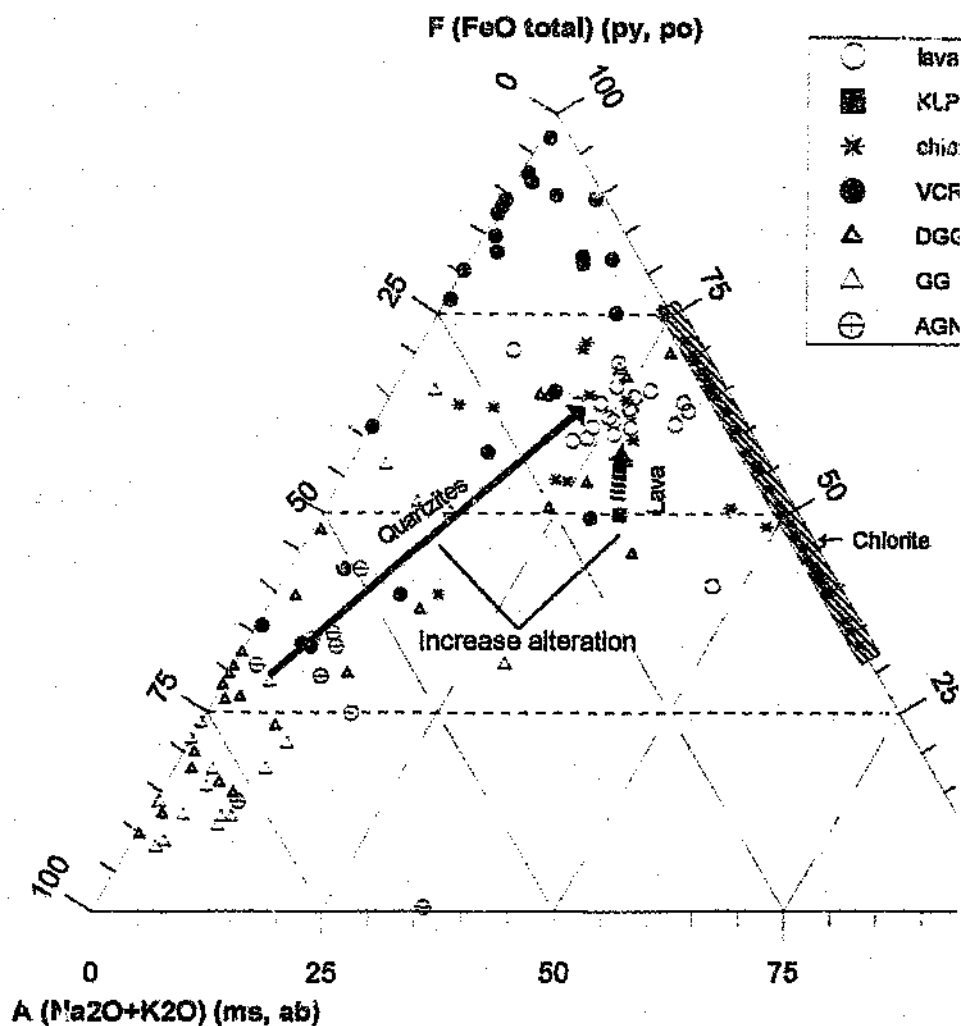


Fig. 5-17 AFM diagram showing alteration trends in the alteration zones associated with 1. Legend as in Fig. 5-4, 15.

zone is enriched in chalcophile elements (Cu, Zn), while the GG zone quartzite is enriched in V, Ni, Y and Zr. Moreover, the AGNQ is extremely enriched in the siderophile elements (V, Co, Cr, Ni, Zr) and rare earth elements (Y, Nb), but obviously depleted in chalcophile elements (Cu, Zn). It is suggested that the AGNQ may be strongly affected by detrital chemical assemblage or by volcanic ashes which was blowing from a long distance. Furthermore, V, Cu, Cr, Co, Y, Zr and Nb are correlated with TiO_2 . This suggests that the immobile trace elements are related to heavy minerals such as zircon, and rutile.

Plots of Cu and Zn against Fe_2O_3 and Rb, Sr, Ba against CaO, Al_2O_3 , K_2O for DGG zone, GG zone and AGNQ quartzites demonstrate a very similar relationship for the former two zones to that as shown in the VCR (see Fig. 5-12), i.e., correlations of Cu with Fe and of Rb, Sr and Ba with Al and K. However, the AGNQ internal quartzite is dramatically deviated from the trends, indicating its difference in the elements from the mentioned quartzites (Fig. 5-19).

5.3.3.4 Summary of the quartzite geochemistry

Quartzite types are principally arkose to litharenite types, but they are strongly affected by two factors of hydrothermal alteration, namely, Fe alteration (pyrite, pyrrhotite, chlorite) and SiO_2 (silicification). The enrichments of alkali elements (Na_2O), alkaline earth elements (MgO , CaO), siderophile elements (Fe_2O_3 , MnO), and chalcophile elements (Cu, Zn) in the DGG zone quartzite represent strong hydrothermal alteration during post-depositional events which is attributable chiefly to albitization, chloritization, sulphidization (pyrite, pyrrhotite, chalcopyrite, sphalerite and galena). In contrast, enrichments of alkali elements (K_2O) and Al_2O_3 , trace siderophile elements (V, Cr, Ni, Zr) and rare earth elements (Y) in the GG zone quartzite are typically representative

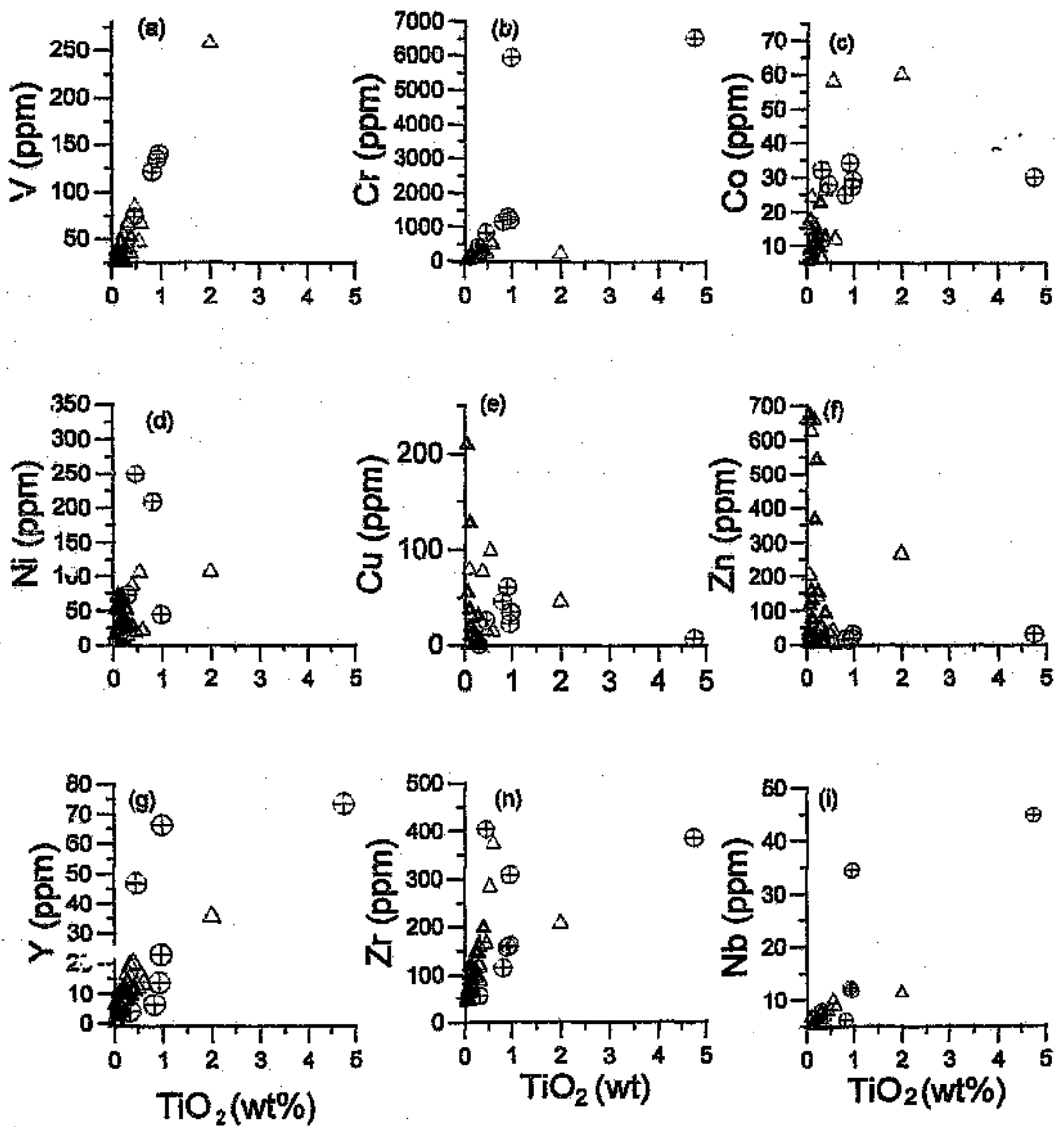


Fig.5-18 Plots of V, Cr, Co, Ni, Cu, Zn, Y, Zr and Nb (ppm) vs TiO_2 (wt%) for the DGG zone, GG zone, and AGNQ quartzites in the research area.

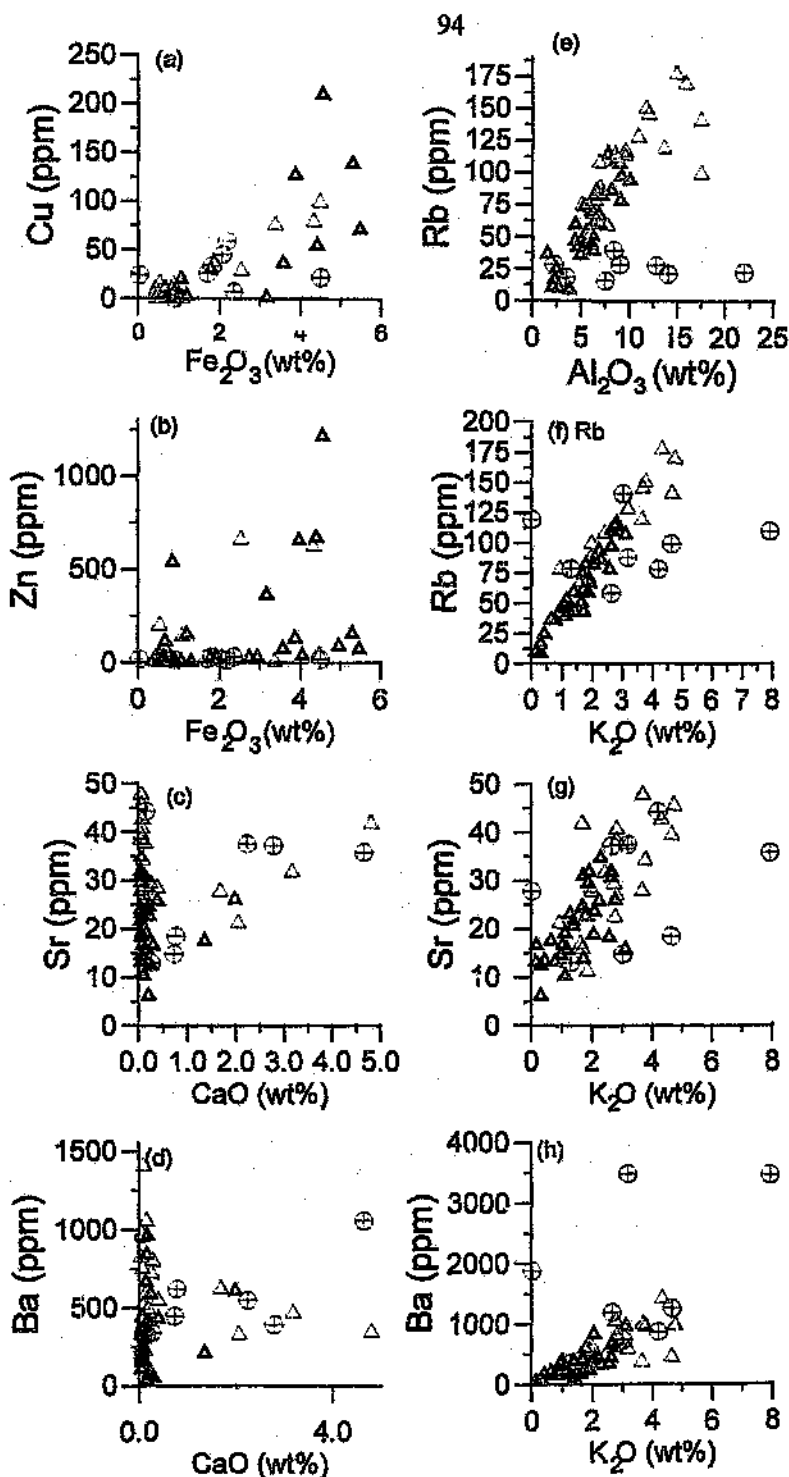


Fig. 5-19 Plots of Cu, Zn vs Fe_2O_3 , and Sr, Ba vs CaO, Rb vs Al_2O_3 , and Rb, Sr, Ba vs K_2O for the DGG zone, GG zone and AGNQ quartzites in the research area.

of a detrital chemical assemblage, and attributable chiefly to muscovitization, and heavy minerals (leucoxene, zircon, rutile, chromite, cobaltite). The AGNQ is characterized by enrichment of Fe_2O_3 , MgO , Na_2O , which is similar to the DGG zone quartzite and enrichment of TiO_2 , Al_2O_3 , K_2O , and the siderophile elements (V, Cr, Co, Ni, Zr) and rare earth elements (Y, Nb), which is similar to the GG zone quartzite, but the concentrations of the siderophile elements are much higher. This is probably due to enrichment of fine-grained heavy minerals and/or incorporation of volcanic ashes.

Three alteration trends characterize the major evolution of major alteration types: (1) sulphidization; (2) chloritization and (3) muscovitization and (4) albitization in the quartzites and the hanging wall lava.

5.3.4 Shale

Major oxides of shale include SiO_2 , Al_2O_3 , and Fe_2O_3 , MgO , K_2O with minor amounts of TiO_2 , CaO and Na_2O (Table 5-6). These are consistent with muscovitization (Al_2O_3 and K_2O), chloritization (MgO , Fe_2O_3) and silicification (SiO_2). The patterns of the transition elements (Ti, V, Cr, Mn, Fe, Co, Ni) of the shale in the research area, together with the shales of the Witwatersrand Basin (Kimberley Shale) and the Nsuze Group in Pongola Sequence are shown in Fig. 5-20. The footwall shale shows almost the same pattern as those of the Witwatersrand shale (Kimberley Shale) and of Pongola Nsuze Group shale. They are all enriched in V, Cr, Mn, Fe, and Ni. However, the WDLMS shales are almost in between the Kimberley Shale and the Pongola Nsuze Group shale (Fig. 5-20). It is suggested that the shale in the research area has not been subjected to strong hydrothermal alteration, if the Kimberley Shale and the Pongola Nsuze Group shale are assumed not to be strongly exposed to hydrothermal alteration.

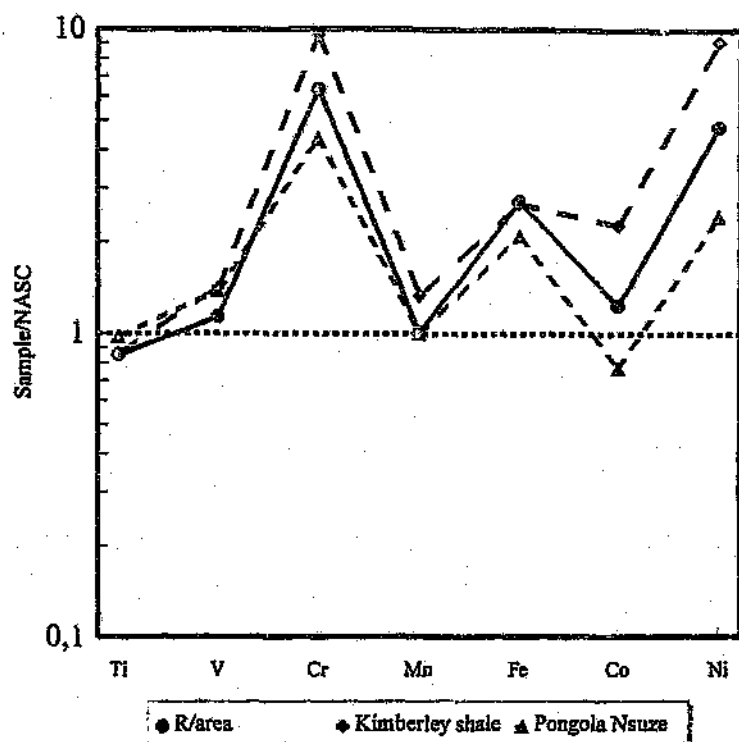


Fig. 5-20 NASC-normalized transition element patterns of the footwall shales in the research area, together with the Kimberley shale (Wronkiewicz & Condie, 1987) and Pongola Nsuze Group shale (Laskowski & Kroner, 1985).

5.4 Distribution pattern of trace elements of the VCR and related lithologies

Trace element concentrations of the VCR and related lithologies are normalized to the compositions of upper crust of the earth (Taylor & McLennan, 1981) (Fig. 5-21). The elements are logically divided into two fields: (1) mobile element field on the left hand side; and (2) the immobile element field on the right hand side. The former includes the low field strength elements (LFS) or large ion lithophile elements (LIL) (Sr, Rb, Ba), and chalcophile elements (Cu, Zn), while the latter is involved in the high field strength elements (HFS) (Nb, Zr, Ti, Y) and siderophile elements (V, Cr, Co and Ni). The results show that the VCR has a very similar pattern to, but lower concentrations than the lavas (Fig. 5-21a). This suggests that the VCR is strongly affected by the hanging wall lava in terms of the trace elements either due to exchange during hydrothermal alteration and/or incorporation of the original lava materials into the VCR.

The AGNQ quartzite shows a rather different pattern than the lavas and the VCR, specifically, strongly enriched in Rb, Sr, Cr and Ni. This suggests that the AGNQ quartzite is less strongly affected by the lava chemical composition in terms of trace elements. The footwall DGG zone shows a very similar pattern to the VCR, but is slightly different from the GG zone quartzite, which is due to the stronger alteration of the DGG zone quartzite than the GG zone quartzite (Fig. 5-21b). The latter is more likely to be an original feature in trace elements than the strong alteration zone (DGG zone). AGNQ quartzite shows almost the same pattern as the footwall shale (Kimberley Shale) and a similar pattern to the GG zone quartzite. The enrichment of the trace elements in the AGNQ quartzite, as identified previously, is more likely to be an original feature due to its fine-grained texture (absorption of trace elements) or fine volcanic dust. The immobile trace elements are possibly absorbed by clay minerals and enrichments of heavy minerals (chromite, zircon, ilmenite, cobaltite) during sedimentation.

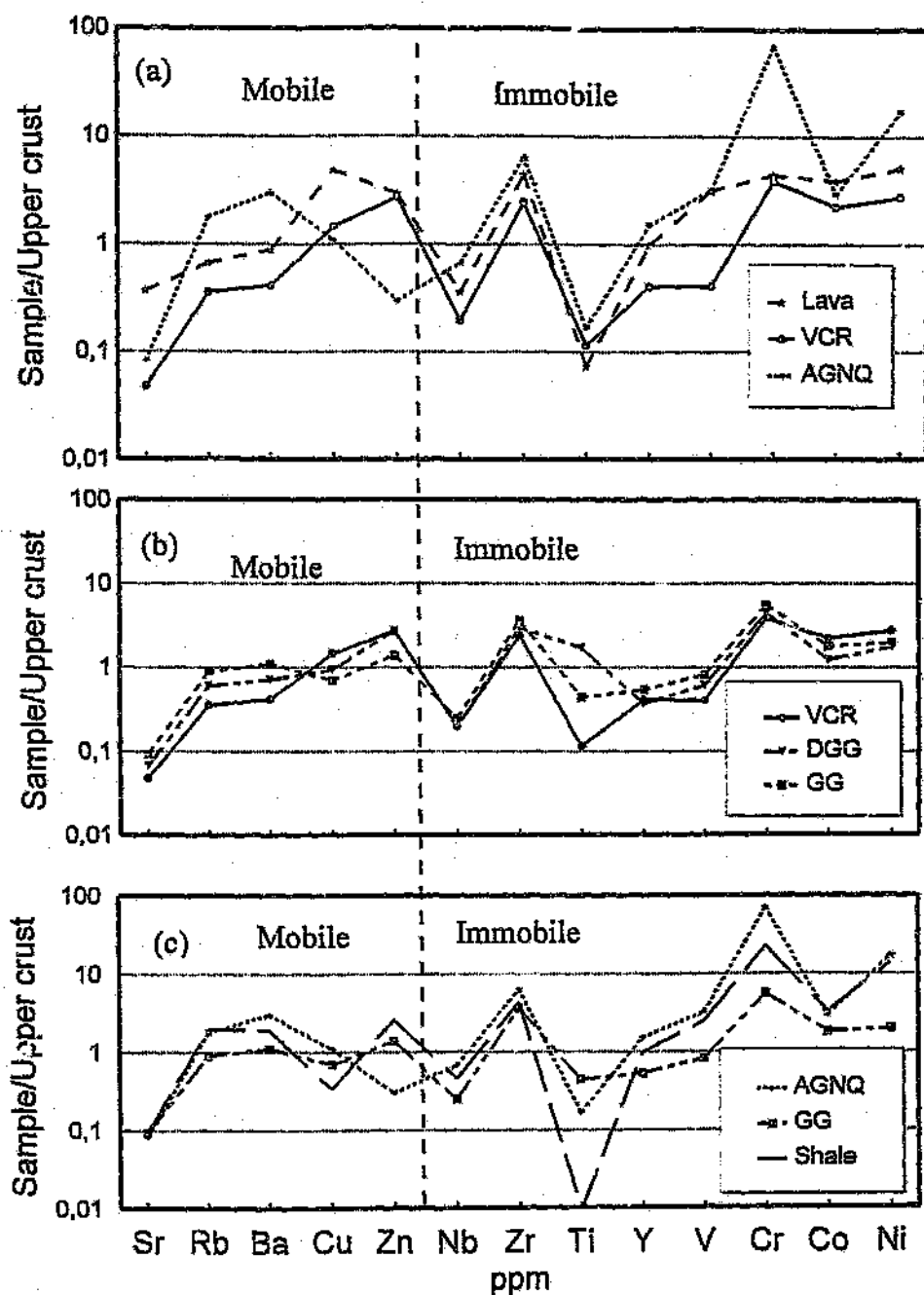


Fig. 5-21 Trace element concentrations of the hanging wall lavas, VCR, footwall DGG zone, GG zone quartzites, AGNQ quartzites and footwall shale in the research area, normalized to the composition of average upper crust (Taylor & McLennan, 1981).

In summary, the similar pattern in the trace element compositions between the VCR and its hanging wall lavas is likely to be due to both hydrothermal alteration and direct incorporation of the lava materials. The DGG zone quartzite shows similar trends to the VCR in terms of trace element chemical composition due to stronger hydrothermal alteration. Similar trace element chemical compositions of the AGNQ quartzite and the footwall shale are attributable to their original fine-grained texture, strongly absorbing trace elements, rather than a post-depositional hydrothermal alteration feature as suggested by Law (1991).

5.5 Relative gains and losses of chemical elements

5.5.1 Major oxides

Relative gain and loss of major mobile elements for the altered rocks were presented using an enrichment and depletion diagram (cf. Rollinson, 1993), and plotted in Fig. 5-22. The WDL SM lavas are normalized to the least altered Klipriviersberg Group lavas (Bowen et al. 1986), and characterized by gains of SiO_2 , Fe_2O_3 , K_2O , and losses of MgO , CaO , Na_2O (Fig. 5-22). The VCR, normalized to the average Witwatersrand conglomerates (Pretorius, 1974) shows gains of MgO , CaO , K_2O , and losses of SiO_2 , Fe_2O_3 , and Na_2O . The normalized DGG quartzite to the relatively fresh GG zone quartzites is characterized by gains of SiO_2 , Fe_2O_3 , MgO , Na_2O , and P_2O_5 , and by losses of CaO , and K_2O (Fig. 5-15c).

5.5.2 Trace elements

Relative gains and losses for the mobile trace elements are shown in Fig. 5-23. The hanging wall lavas at WDL SM are characterized by gains of Ba, Cu, and Zn, and by losses of Rb, Sr (Fig. 5-

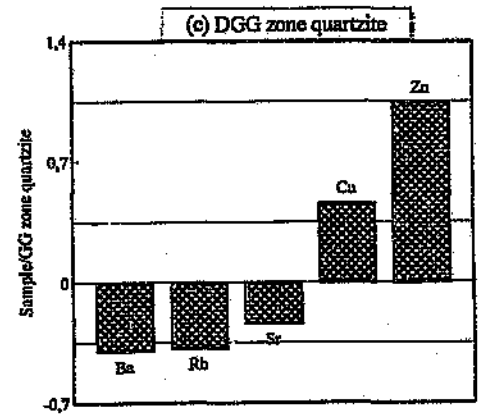
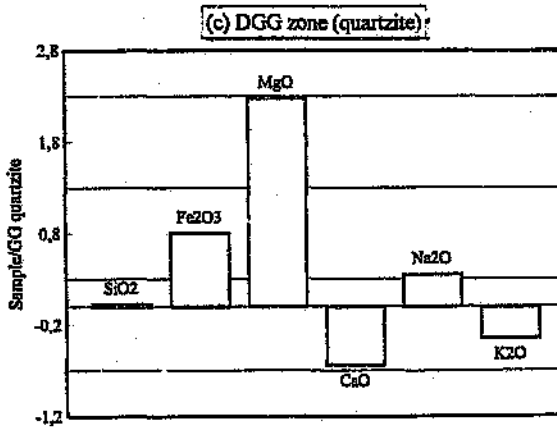
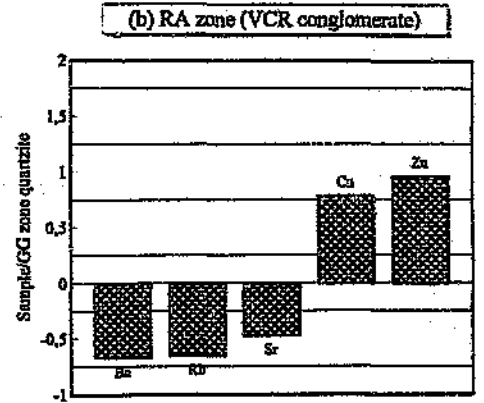
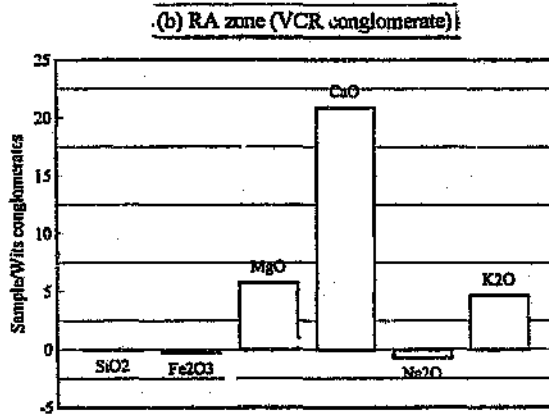
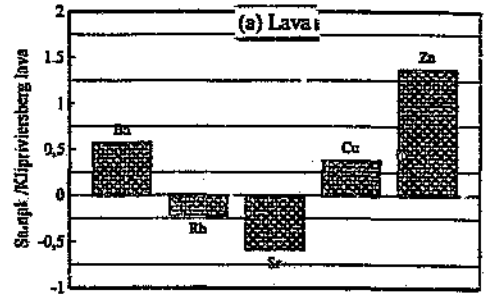
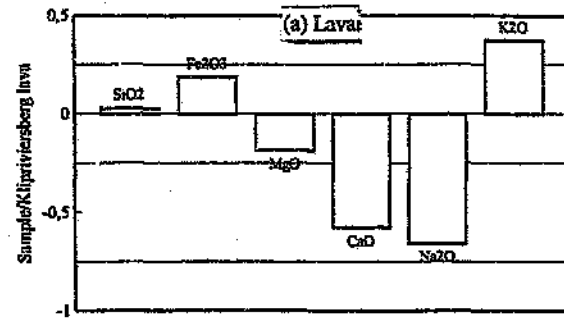


Fig. 5-22 Enrichment-depletion diagrams demonstrating the extent of major element mobilization in alteration zones within the a) hanging wall lavas; b) RA zone conglomerate of the VCR; and c) DGG zone footwall quartzite.

Fig. 5-23 Enrichment-depletion diagrams showing the extent of trace element mobilization in alteration zones with the a) hanging wall lavas; b) RA zone conglomerate of VCR; and c) DGG zone footwall quartzite.

23a). The normalized DGG quartzite to the least altered GG zone quartzites is marked by gains of Cu and Zn, and by losses of Ba, Rb and Sr (Fig. 5-23c). Due to lack of a complete data set of the above trace elements for the other Witwatersrand reefs, used as a standard, the VCR conglomerates in the research area are also normalized to the least altered GG zone footwall quartzites. In this case, the VCR is characterized by gains of Cu and Zn, and by losses of Ba, Rb, Sr (Fig. 5-23b).

If it is geologically valid to use the least altered GG zone footwall quartzite as a standard for the VCR conglomerates, it is suggested that Cu and Zn, for example, are enriched in all the three alteration zones (hanging wall lavas, the VCR, the DGG zone footwall quartzite). This suggests that Cu and Zn (Pb? and Au?) were introduced by hydrothermal fluids. By contrast, if it is argued that Cu and Zn as mineralizing elements are two times richer in the VCR than in the GG zone footwall quartzite (Table 5-2, 4), they are rather representative of local circulation of Cu and Zn around the VCR during post-depositional hydrothermal alteration than being directly introduced by hydrothermal fluids. Automatically, the enrichments of Cu and Zn in the hanging wall lavas and the DGG zone footwall quartzite are derived from the VCR conglomerates. If this is the case, the mobile trace elements, in particular, Cu and Zn, together with the major mobile elements circulated around the VCR in a relatively closed fluid system.

5.5.3 Summary of the relative gains and losses

Fluids responsible for the alteration assemblages have circulated in a relatively closed system, in particular, for the major elements (Si, Fe, Mg, Ca, Na, K, Cu, Zn) in and around the VCR conduit.

5.6 Chemical profiles through an underground borehole and section

5.6.1 Ratios of major oxides over Al_2O_3

Underground borehole BH1169 was drilled from footwall quartzite, through the VCR, into the hanging wall lavas. It was sampled through all lithologies and alteration zones. In order to study the alteration zones and possible palaeoweathering, a profile from the VCR as base is plotted in terms of element ratios of major oxide and trace elements. The ratios of major oxides/ Al_2O_3 are plotted versus the location in metres above the VCR which is assumed to be the base of the profile (note distances are not corrected into true thickness) (Fig. 5-24). The results show that MgO , and CaO dramatically decrease downwards in the borehole, while Na_2O decreases downwards also, but less markedly. It is suggested that the mobile elements (Mg , Ca , Na) are enriched in the strong alteration zone and circulated with hydrothermal fluids around the VCR conduit. Enrichments of MgO , CaO and Na_2O are attributable to chloritization, carbonatization and albitization, which are consistent with the mineral assemblages in the alteration zones as described in Chapter 4. However, SiO_2 is overall depleted near the VCR in the DGG zone footwall quartzite. Moreover, TiO_2 and Fe_2O_3 are also enriched in the DGG zone immediately below the reef. It is suggested that Fe_2O_3 and TiO_2 are originally from the detrital assemblage concentrated on the erosion surface.

A section has been sampled from the VCR and down to the footwall quartzites in an underground section from panel 87-53-3W. The section is approximately 4m thick and the samples are assumed to be at about one metre distance in the profiles. The results show that MgO and Na_2O , Fe_2O_3 , have the similar patterns as in the borehole profile, while CaO , TiO_2 display no obvious change in the profile. Variation of SiO_2 concentrations is fairly flattened (Fig. 5-25).

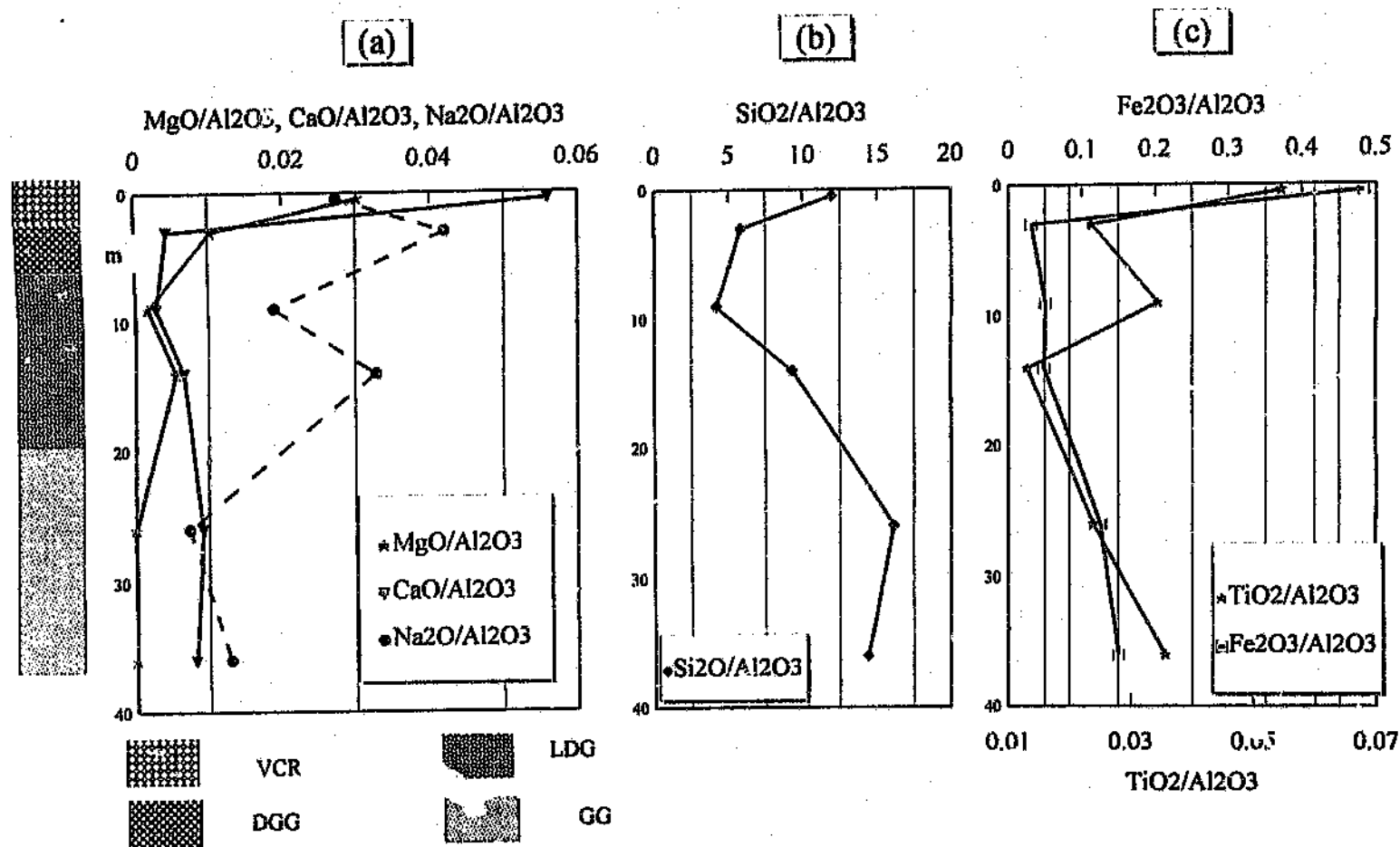


Fig. 5-24 Chemical profiles of major oxides over Al_2O_3 (wt%) ratios for BH1169. (a) mobile elements (MgO , CaO , Na_2O); (b) SiO_2 ; and (c) immobile elements (Fe_2O_3 , TiO_2). The distance (m) is based on VCR (0 m) and is not corrected to true stratigraphic thickness.

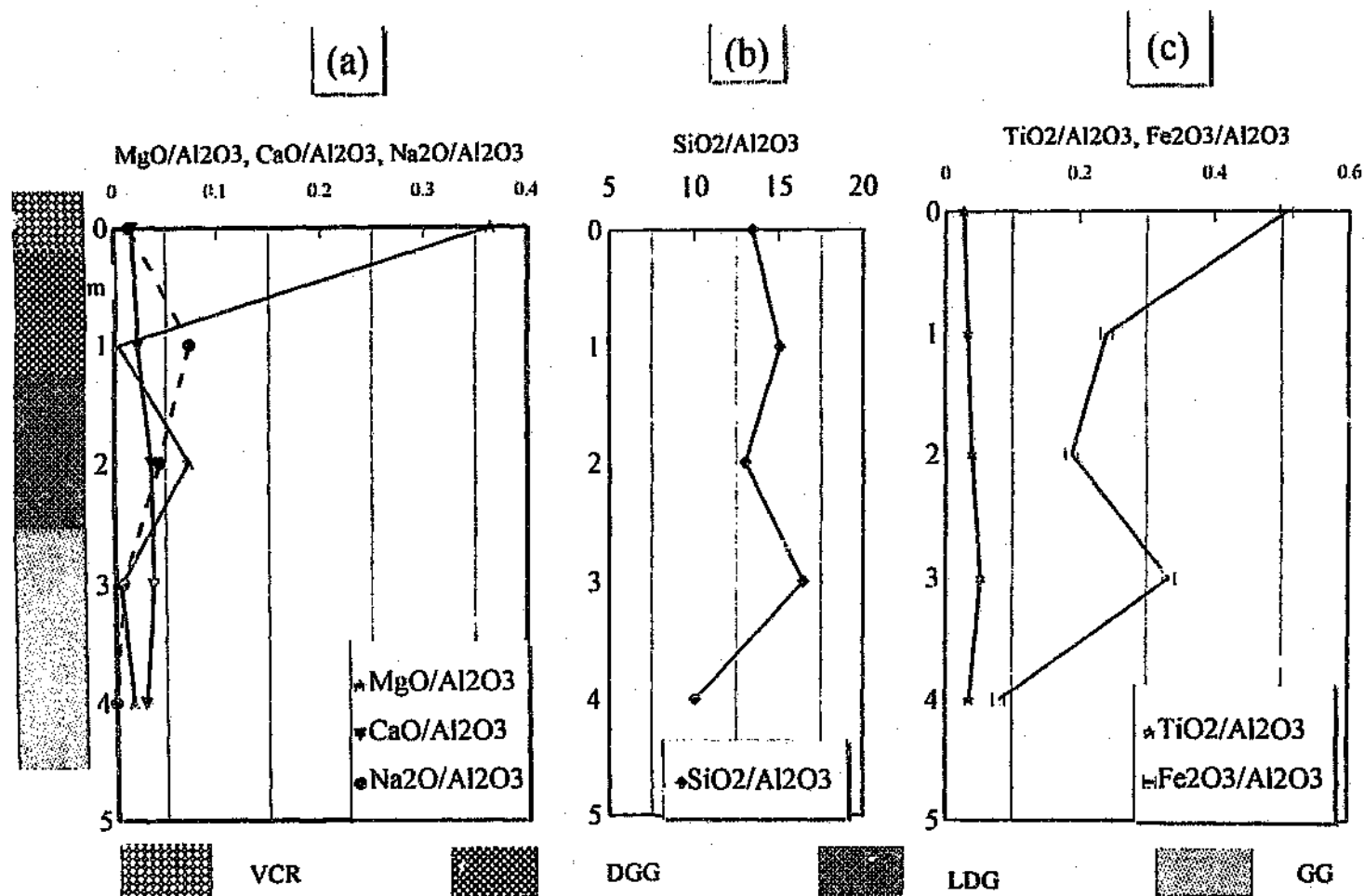


Fig. 5-25 Chemical profiles of selected oxides over Al_2O_3 (wt%) ratios for an underground section (87-53-3w). (a) mobile elements (MgO, CaO, Na2O); (b), SiO_2 ; (3) immobile elements (TiO2, Fe2O3). The distance is based on VCR (0 m) and sampled at an assumed interval of 1 m.

5.6.2 Ratios of trace elements over V

As shown in Fig. 5-26, Cu has a similar pattern as Zn, and decreases dramatically downwards in the borehole, but Zn is strongly depleted at about 2-10m. With respect to the alteration zones, it is suggested that Cu and Zn are enriched in the DGG zone which is immediately below the VCR, and depleted in the LDG zone (described in Chapter 4) and further becomes constant in the GG zone (Fig. 5-26). It seems that Rb, Sr and Ba are less variable and no pattern can be followed. Immobile elements, Cr, Co, Zr, Ni, Y, and Nb have very similar patterns and are enriched in the DGG and LDG zones and become normal very quickly. It is suggested that they were probably enriched in a palaeoweathering zone (Fig. 5-26).

In the underground section profile, Zn decreases dramatically towards the least altered quartzite and no obvious change in different alteration zones has been identified for Rb, Sr, Ba, Cr, Co, Zr, Ni, Y, Nb which display flattened profiles (Fig. 5-27).

5.6.3 Summary of the chemical profile information

Mobile elements (e.g. Mg, Ca, Na) are enriched in the strong alteration zones around the VCR conduit and enrichments of these elements are attributable to the hydrothermal alteration, in particular, chloritization, carbonatization and albitization. Moreover, immobile trace elements of Cr, Ni, Zr, Y, and Nb are more closely related to the original detrital features and were occasionally concentrated on the original erosion surface, which may be an indication of existence of a paleoweathering zone (e.g. indicated by Palmer et al., 1986; Ritger, 1990), but it is clearly altered in geochemistry by hydrothermal fluids. Mobile trace elements, such as Rb, Sr and Ba are more related to muscovitization as discussed previously.

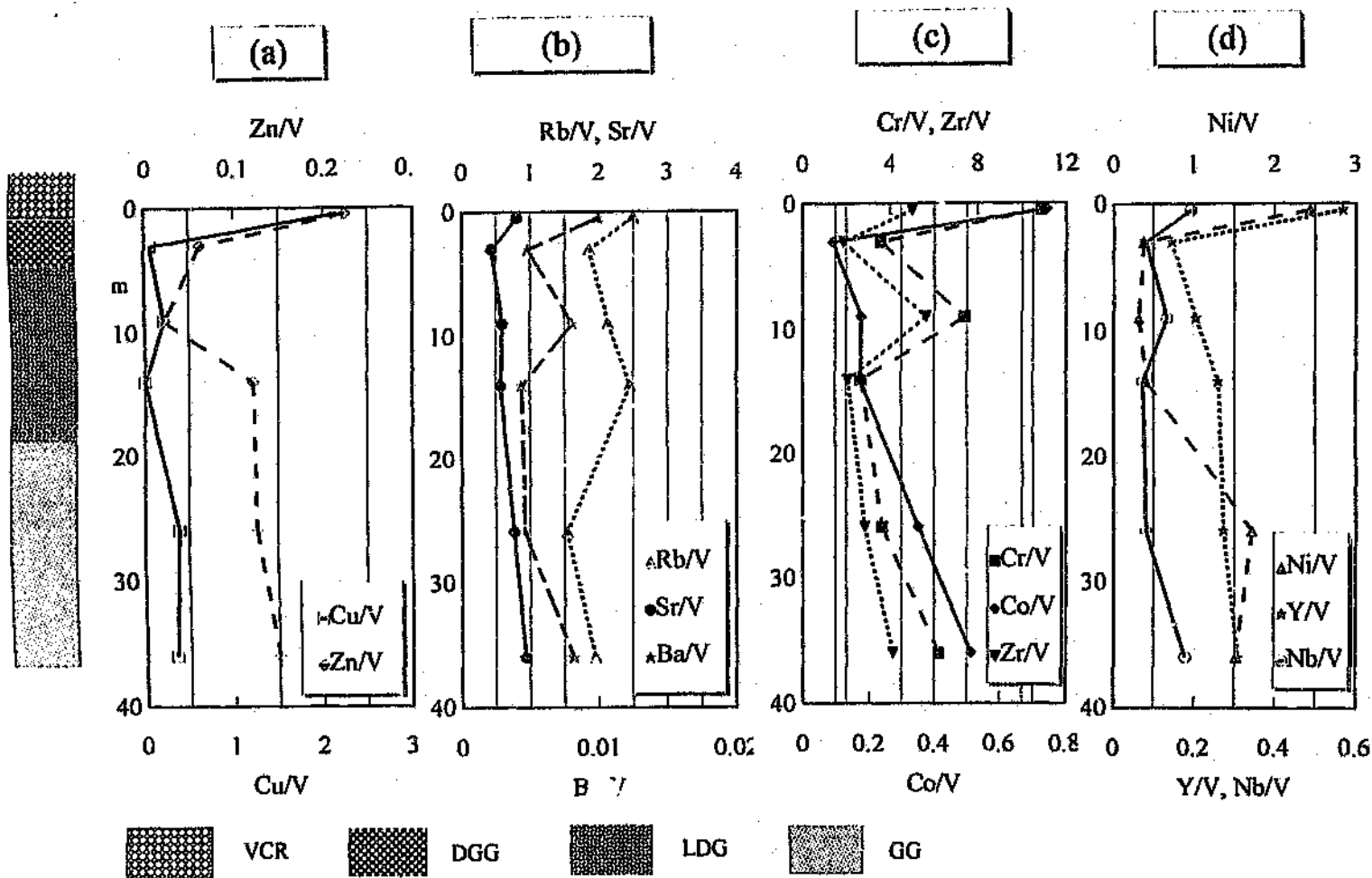


Fig. 5-26 Chemical profiles of selected trace elements over V (ppm) ratios for BH1169. (a) Cu/V and Zn/V; (b) Rb/V, Sr/V, Ba/V; and (c) Cr/V, Co/V, Zr/V; (d) Ni/V, Y/V, Nb/V. The distance (m) is based on VCR (0 m), being not corrected for true stratigraphic thickness..

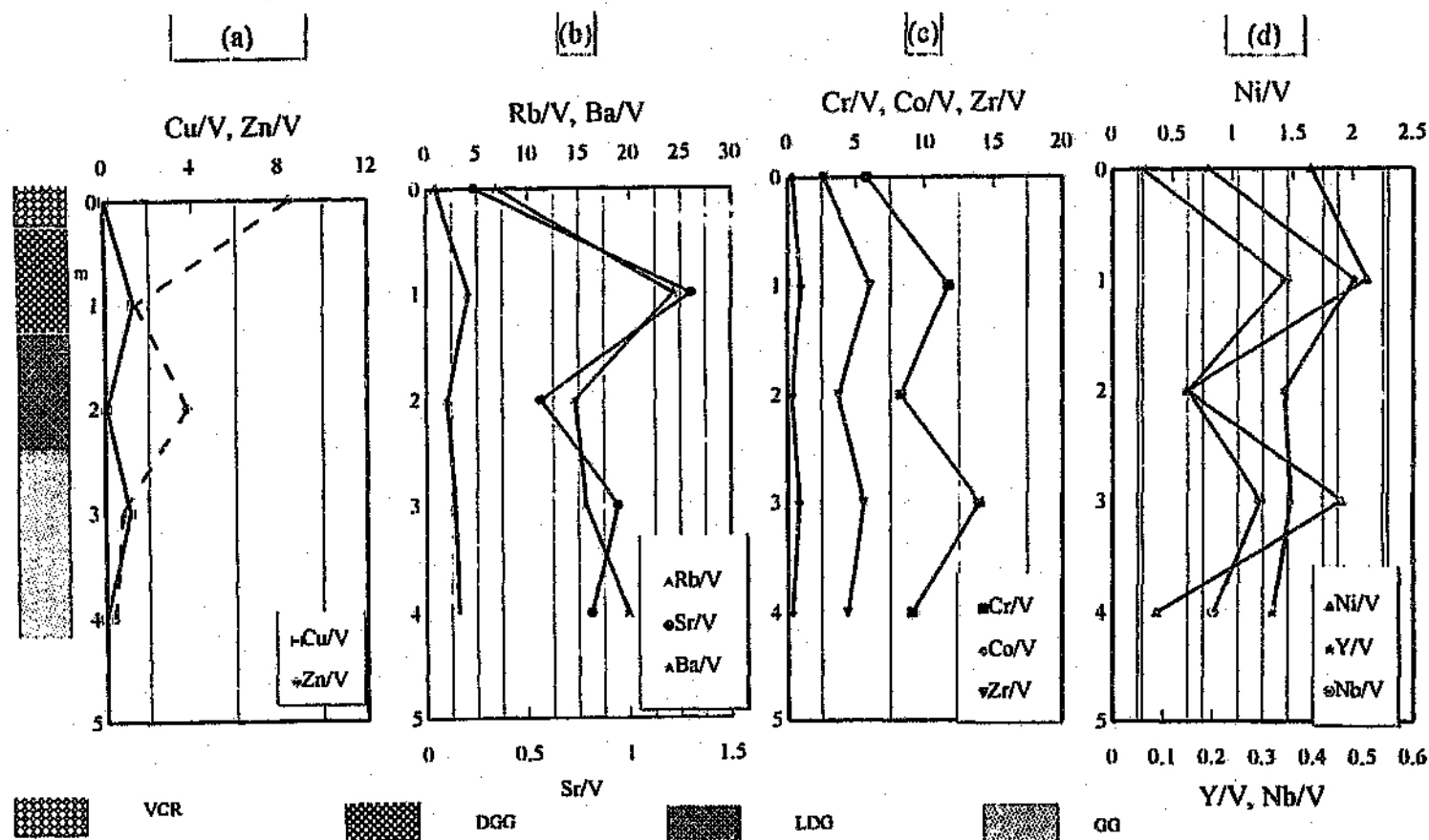


Fig. 5-27 Chemical profiles of selected trace elements/V (ppm) ratios for an underground section (87-53-3w). (a) Cu/V, and Zn/V, (b) Rb/V, Sr/V, Ba/V; (c) Cr/V, Co/V, and Zr, (d) Ni/V, Y/V, Nb/V. The distance is based on VCR (0 m) and sampled at an assumed interval of 1 m.

5.7 Summary

Fluids responsible for alteration assemblages in and around the VCR at WDLSM have remobilised the elements in such a way that this system appears to have remained relatively closed because depletion in certain elements of one alteration zone is matched by concomitant enrichments in adjacent alteration zones, and vice versa. The elements remobilised include the LIL elements (Na, Rb, Sr, Ba, K) which are exchanged among the hanging wall lavas, the VCR, footwall quartzite and are attributable to strong hydrothermal alteration. They include chloritization (Fe, Mg), albitization (Na), muscovitization (K, Rb, Sr, Ba), carbonatization (Ca, Sr), epidotization (Ca, Fe) and sulphidation (pyrrhotite, chalcopyrite, sphalerite, galena) (Fe, Cu, Zn, Pb). Major element geochemistry and the FM diagram suggests that the major alteration around and within the VCR was along an important trend of increasing sulphidization (Fe, Cu, Pb, Zn) and chloritization (Fe, Mg) and remobilization of alkalis (Na, K) in the hanging wall lava and the footwall quartzites.

Immobile trace elements, in particular, Nb, Zr, Ti, Y, V, Cr, Co, Ni, are indicative of the original chemical feature of the rocks rather than due to the post-depositional effects. However, strong remobilisation of some major elements occurred as discussed above. The VCR has been affected by hydrothermal alteration and incorporation of lava materials, while the DGG zone quartzite represents the results of strong alteration around the VCR. The similarity of trace elements in the AGNQ quartzite to the footwall shale (Kimberley Shale) suggests that the AGNQ quartzite displays the original characteristics of immobile trace elements inherited during deposition. Enrichments of immobile elements (Cr, Ni, Zr, Y, Nb) may indicate existence of palaeoweathering zone in the footwall quartzites, in particular, the DGG zone.

6 MINERAL GEOCHEMISTRY

6.1 Introduction

6.1.1 Mineral geochemistry of the Witwatersrand reefs

Extensive studies of chlorite geochemistry have been carried out for the calibration of chlorite forming temperatures (e.g., Meyer et al., 1990a; Wallmach & Meyer, 1990; Zhao et al., 1994; Frimmel, 1994, 1997; Drennan, 1997). Geochemical results also indicate that sudoite is a common chlorite type in the Witwatersrand Basin (Zhou & Phillips, 1994; Frimmel, 1997). Due to the relationship between authigenic chlorite and gold mineralization, chlorite geochemistry has also been analysed for economic purposes.

Due to the close relationship between sulphides, particularly pyrite and gold, the geochemistry of sulphides has been extensively investigated in the Witwatersrand Basin. Studies of detrital pyrite geochemistry has been carried out by various workers (Saager, 1973; Pretorius, 1974b; Hirds, 1979; Hallbauer, 1980, 1986; Meyer et al., 1990b). For example, Hallbauer (1980, 1986) compared Ni/Co ratios of detrital pyrite in the Witwatersrand with those of other Archaean pyrite (Saager, 1973) and concluded that a number of provenance areas are responsible for providing pyrite to the basin.

Meyer et al. (1990b) compared the Co/Ni ratios of different pyrite types (compact round, porous round and recrystallized) in the Witwatersrand reefs with the pyrite from various sources (e.g., Murchison and Pietersburg greenstone belts, Moodies Group, Pongola Supergroup, Uitenhage).

Formation) and concluded that it is doubtful to trace the origin of the detrital pyrite due to its extensive post-depositional chemical redistribution/homogenization.

The mineral chemistry of gold grains in detrital and authigenic forms has been extensively examined (e.g., Strasheim & Jackson, 1971; Feather & Koen, 1975; Utter, 1978; Hallbauer, 1986). The trace elements in gold grains are: (1) Ag, Fe; (2) Cu, Mo, Co, Bi, Pb, Sn, As, Hg (trace); (3) V, Ni, Mn, Sb (small trace). Hg and Ag chemistry has been examined by various workers (e.g., Erasmus, 1977; Watling, 1978), which suggests that Hg and Ag can be discriminated by localities although no correlation of the two elements is present (Hallbauer, 1986).

In addition to the above minerals (chlorite, pyrite, gold), the geochemistry of uraninite and carbonaceous matter has also been examined (Smits, 1992, 1994; Hallbauer, 1986).

Hallbauer (1986) suggested that the fine grained detrital pyrite (<1 mm) in the VCR contains much higher concentrations of Ni and Co than coarse-grained pyrite (>1mm), which suggests the presence of at least two sedimentary components within the VCR of the Carletonville Goldfield, together with occurrence of two types of quartz pebbles within the VCR.

6.1.2 Aims of this chapter

The aims of this chapter are to examine the geochemistry of the major rock forming minerals (chlorite, muscovite, albite, carbonates) and sulphides (pyrite, pyrrhotite, chalcopyrite, sphalerite, galena, pentlandite) from the hanging wall Klipriviersberg Group lavas, the VCR, and the footwall

quartzites (DGG and GG zones) as well as AGNQ internal quartzite in the research area.

6.2 Methodology of electron microprobe

Mineral chemical analyses were performed on carbon coated polished sections by electron microprobe (EM). Rock forming minerals and sulphides were analysed at the Rand Afrikaans University and Anglo American Research Laboratory, Johannesburg, and the Institut für Mineralogie und Lagerstättenlehre, RWTH, Aachen Germany, respectively. Chemical analyses of sulphides were performed at working conditions of 20kv (sphalerite) and 25kv (pyrite, pyrrhotite, galena, pentlandite) and 20nA current. The reproducibility of the analyses of the sulphides is $\pm 2\%$. The data are presented as either single analyses for chlorite, muscovite, albite, carbonates, pyrite and average values of samples for pyrrhotite, chalcopyrite, galena, sphalerite and pentlandite. Average (arithmetic mean) (AVG) and standard deviation (STD) of mineral compositions in the host rock types, alteration zones and total samples are presented in a summary sheet in the same tables (see later).

6.3 Rock-forming minerals

6.3.1 Chlorite

6.3.1.1 General

Chemical analyses of chlorite were obtained from the hanging wall Klipriviersberg lavas (2), the VCR (2) and DGG zone footwall quartzite (6). The analytical totals for the determined elements (oxides) excluding volatile elements (OH, H₂O, F) were always better than 86%. The element oxides, together with the calculated numbers of ions in the formula, are tabulated in Table 6-1. As described in the mineralogical study (see Chapter 4), two types (CH1, CH2) of chlorite were

Table 6-1 Chemical composition of chlorite in the VCR

	Rock	Lava												VCR												DGG zone quartzite														Rock
	Sample	H0002			0711	VCR-			B0378										10705				B0415			10713		B0361				Sample								
		6	10	67	43	30	31	33	34	35	38	39	40	7	8	12	15	27	31	42	44	46	61	52	35	37	41	42												
wt%	SiO2	23.99	26.23	29.87	26.32	24.57	23.48	25.16	25.47	25.05	25.54	24.34	25.31	27.17	27.20	25.58	26.52	24.64	26.35	26.16	25.08	24.38	26.66	26.68	35.29	25.83	26.39	25.01	SiO2											
	TiO2	0.04	0.10	0.12	0.09	0.03	0.02	0.05	0.00	0.00	0.00	0.00	0.19	0.00	0.00	0.03	0.11	0.00	0.00	0.00	0.01	0.60	0.01	0.00	0.70	0.02	0.02	0.00	TiO2											
	Al2O3	20.20	20.64	26.45	19.71	21.67	21.11	22.10	22.05	22.29	22.84	22.77	21.87	22.97	22.22	22.66	22.50	21.17	23.21	21.88	21.33	20.16	23.42	22.58	26.27	22.94	22.77	22.86	Al2O3											
	FeO	29.59	29.08	19.82	18.95	27.79	27.87	27.62	27.92	26.68	26.53	26.99	27.28	18.33	15.88	25.25	12.23	20.03	15.14	23.99	28.21	25.34	13.92	16.07	12.43	22.07	24.44	23.86	FeO											
	MnO	0.32	0.36	0.26	0.53	0.46	0.49	0.43	0.47	0.54	0.34	0.45	0.48	0.51	0.85	0.39	0.63	0.20	0.66	0.39	0.37	0.34	0.57	0.44	0.00	0.35	0.34	0.29	MnO											
	MgO	11.66	12.86	6.51	19.88	13.19	12.26	14.16	13.17	14.15	14.46	13.21	13.64	20.36	21.46	16.34	22.40	17.63	21.33	15.65	11.99	13.09	22.11	20.08	6.05	17.85	16.00	15.54	MgO											
	CaO	0.11	0.10	0.00	0.05	0.07	0.13	0.11	0.13	0.07	0.09	0.07	0.02	0.04	0.02	0.05	0.08	0.10	0.06	0.05	0.12	0.21	0.11	0.12	1.22	0.04	0.08	0.02	CaO											
	Na2O	0.00	0.00	0.21	0.00	0.04	0.06	0.02	0.00	0.01	0.02	0.00	0.01	0.00	0.00	0.03	0.00	0.00	0.00	0.01	0.04	0.04	0.03	0.02	0.04	2.43	0.03	0.01	0.00	Na2O										
	K2O	0.00	0.01	4.00	0.00	0.03	0.07	0.08	0.01	0.03	0.02	0.01	0.00	0.03	0.05	0.02	0.02	0.01	0.03	0.00	0.02	0.01	0.00	0.09	0.06	0.02	0.02	0.00	0.00	K2O										
	Cr2O3	0.00	0.10	0.00	1.30	0.28	0.25	0.23	0.17	0.08	0.17	0.30	0.18	0.11	0.09	0.12	0.41	0.87	0.07	0.18	0.58	0.52	0.14	0.07	0.00	0.07	0.13	0.01	0.00	Cr2O3										
	NiO	0.00	0.03	0.06	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.07	0.01	0.03	0.00	0.03	0.09	0.08	0.06	0.13	0.12	0.10	0.00	0.00	0.00	NiO										
	Total	85.91	89.51	87.30	86.87	88.13	85.74	90.44	89.92	88.90	90.10	88.14	88.98	89.53	87.79	90.54	84.93	84.68	86.86	88.37	87.84	84.61	89.02	84.30	84.57	89.05	90.20	87.70	Total											
Ion	SiT	2.61	2.73	3.11	2.73	2.59	2.56	2.59	2.63	2.59	2.60	2.55	2.62	2.67	2.70	2.57	2.69	2.62	2.63	2.69	2.67	2.69	2.62	2.70	3.60	2.59	2.65	2.58	SiT											
	AlT	1.13	1.08	0.73	1.10	1.17	1.19	1.18	1.14	1.18	1.18	1.22	1.15	1.18	1.16	1.21	1.20	1.20	1.23	1.15	1.12	1.15	1.28	1.17	0.32	1.22	1.15	1.21	AlT											
	FeT	0.26	0.20	0.14	0.17	0.24	0.25	0.24	0.23	0.23	0.22	0.24	0.23	0.16	0.14	0.21	0.11	0.18	0.13	0.16	0.22	0.16	0.10	0.13	0.08	0.19	0.20	0.21	FeT											
	AlO	1.47	1.45	2.30	1.31	1.52	1.52	1.30	1.55	1.53	1.56	1.39	1.53	1.48	1.44	1.47	1.49	1.46	1.50	1.5	1.56	1.47	1.43	1.52	2.84	1.50	1.54	1.56	AlO											
	FeO	0.27	0.27	0.20	0.17	0.25	0.25	0.24	0.25	0.23	0.23	0.24	0.24	0.16	0.14	0.21	0.11	0.18	0.13	0.22	0.26	0.26	1.10	0.15	0.13	0.19	0.21	0.21	FeO											
	Fe2O	2.17	2.06	1.39	1.31	1.96	2.03	1.90	1.94	1.84	1.80	1.89	1.89	1.19	1.04	1.70	0.82	1.42	1.00	1.68	2.03	1.92	0.11	1.09	0.86	1.48	1.64	1.64	Fe2O											
	Mg+Mn	1.92	2.02	1.03	3.12	2.11	2.03	2.21	2.07	2.22	2.22	2.10	2.15	3.02	3.25	2.48	3.44	2.81	3.23	2.43	1.93	2.18	3.29	3.07	0.92	2.70	2.42	2.41	Mg+Mn											

	Rock	DGG zone quartzite												CH2				SUMMARY SHEET												Rock
	Sample	B0361			B0368			B0368			Lava (3)			VCR (5)			DGG (27)			Total (35)			CH2 (DGG) (3)			Sample				
		47	49	83	84	86	5	6	13	14	15	23	24	28	34	76	79	80	AVG	STD	AVG	STD	AVG	STD	AVG	STD	AVG	STD	AVG	STD
wt%	SiO2	25.26	24.33	26.70	25.45	27.25	25.88	26.26	25.52	25.33	26.18	25.91	25.23	25.51	25.51	24.64	26.43	29.02	26.70	2.42	25.03	0.77	26.18	1.89	25.97	1.83	26.70	1.80	SiO2	
	TiO2	0.00	0.00	0.01	0.11	0.00	0.00	0.08	0.19	0.38	0.10	0.15	0.08	0.09	0.00	0.11	0.11	0.22	0.09	0.03	0.04	0.06	0.07	0.14	0.07	0.13	0.15	0.05	TiO2	
	Al2O3	22.52	21.86	23.71	23.07	22.38	21.94	22.17	22.19	21.85	21.21	21.41	21.65	22.02	21.56	22.76	24.24	26.55	22.43	2.85	21.82	0.90	22.36	1.06	22.25	1.27	24.52	1.56	Al2O3	
	FeO	22.34	26.63	17.40	18.86	15.15	19.00	17.37	21.28	21.56	21.39	14.32	19.99	24.80	17.17	18.50	17.42	17.18	26.16	4.49	26.40	2.68	19.88	4.27	21.77	4.96	17.70	0.57	FeO	
	MnO	0.20	0.49	0.40	0.46	0.45	0.42	0.41	0.40	0.42	0.44	0.48	0.42	0.28	0.45	0.30	0.45	0.44	0.31	0.04	0.47	0.06	0.42	0.15	0.42	0.14	0.40	0.07	MnO	
	MgO	16.37	13.95	20.61	18.76	22.54	18.07	19.08	16.91	15.71	16.70	21.09	15.81	14.78	19.27	18.36	17.60	14.86	10.34	2.75	14.24	2.09	17.50	3.55	16.26	3.87	16.94	1.50	MgO	
	CaO	0.05	0.08	0.12	0.02	0.18	0.10	0.05	0.07	0.04	0.00	0.07	0.07	0.03	0.03	0.08	0.05	0.04	0.07	0.05	0.08	0.03	0.11	0.21	0.10	0.18	0.06	0.02	CaO	
	Na2O	0.02	0.00	0.00	0.03	0.02	0.01	0.04	0.00	0.02	0.02	0.00	0.01	0.02	0.00	0.02	0.04	0.11	0.07	0.10	0.02	0.02	0.10	0.44	0.08	0.37	0.06	0.04	Na2O	
	K2O	0.04	0.01	0.01	0.00	0.03	0.00	0.04	0.00	0.00	0.00	0.00	0.01	0.00	0.04	0.15	0.94	1.76	1.34	1.88	0.03	0.03	0.02	0.02	0.12	0.61	0.95	0.66	K2O	
	Cr2O3	0.20	0.03	0.62	0.41	0.43	0.60	0.66	0.09	0.36	0.10	1.01	0.69	0.44	0.69	0.06	0.00	0.00	0.03	0.05	0.33	0.33	0.33	0.28	0.31	0.30	0.02	0.03	Cr2O3	
	NiO	0.01	0.00	0.05	0.00	0.00	0.08	0.00	0.09	0.01	0.02	0.03	0.12	0.03	0.09	0.01	0.00	0.14	0.03	0.02	0.00	0.01	0.04	0.04	0.03	0.04	0.05	0.06	NiO	
	Total	87.01	87.38	89.63	87.17	88.43	86.10	86.16	86.74	85.68	86.16	84.47	85.08	88.00	84.81	84.99	87.28	90.32	87.57	1.48	88.58	1.46	86.99	1.85	87.38	1.86	87.53	2.18	Total	
Ion	SiT	2.61	2.56	2.62	2.59	2.69	2.68	2.69	2.64	2.67	2.72	2.69	2.7	2.65	2.66	2.7	2.67	2.84	2.82	0.21	2.60	0.05	2.68	0.18	2.68	0.17	2.74	0.07	SiT	
	AlT	1.19	1.21	1.23	1.24	1.18	1.16	1.16	1.19	1.15	1.11	1.18	1.13	1.15	1.18	1.15	1.18	1.05	0.98	0.17	1.17	0.03	1.15	0.16	1.14	0.15	1.12	0.06	AlT	
	FeT	0.2	0.23	0.15	0.16	0.13	0.17	0.15	0.17	0.18	0.17	0.13	0.17	0.21	0.15	0.15	0.15	0.11	0.20	0.05	0.23	0.02	0.16	0.04	0.18	0.04	0.14	0.02	FeT	
	AlO	1.55	1.51	1.52	1.53	1.42	1.52	1.53	1.52	1.57	1.49	1.45	1.6	1.55	1.47	1.57	1.71	2.02	1.81	0.49	1.51	0.08	1.55	0.25	1.56	0.26	1.77	0.19	AlO	
	FeO	0.2	0.23	0.15	0.17	0.13	0.17	0.16	0.19	0.2	0.2	0.13	0.19	0.22	0.16	0.17	0.16	0.16	0.25	0.03	0.23	0.02	0.21	0.17	0.22	0.15	0.16	0.00	FeO	
	Fe2O	1.54	1.88	1.13	1.28	0.99	1.3	1.18	1.48	1.51	1.49	0.98	1.43	1.72	1.19	1.24	1.17	1.13	1.87	0.35	1.84	0.20	1.33	0.39	1.48	0.43	1.18	0.05	Fe2O	
	Mg+Mn	2.34	2.23	3.05	2.89	3.35	2.82	2.95	2.64	2.5	2.63	3.31	2.56	2.31	3.04	2.8	2.69	2.20	1.66	0.45	2.25	0.31	2.70	0.51	2.53	0.56	2.57	0.26	Mg+Mn	

classified based on their paragenetic features. The former is the major chlorite type (CH1), and the latter only occurs as the replacement of detrital muscovite and represents a low temperature assemblage associated with 1M muscovite (see Chapter 4, 7). The chemical characteristics of chlorite can be categorized into major and trace elements by concentration:

Major (wt%): SiO_2 (25,97), Al_2O_3 (22,25); $\text{FeO}_{\text{total}}$ (21,77); MgO (16,26).

Trace (wt%): TiO_2 (0,07), MnO (0,42), CaO (0,10), Na_2O (0,08), K_2O (0,12),

Numbers of ions in the formula are also presented as tetrahedral sites (SiT , AlT , Fe^{+3}T) and octahedral sites (AlO , Fe^{+3}O , Fe^{+2}O , $\text{Mg}+\text{Mn}$) (Table 6-1). Based upon 36 oxygen atoms, a formula for the two types of chlorite in the VCR can be presented as follows:

CH1: $((\text{Mg}+\text{Mn})_{5,06}, \text{Al}_{3,12}, \text{Fe}^{+2}_{2,96}, \text{Fe}^{+3}_{0,44})_{11,58}(\text{Si}_{5,36}, \text{Al}_{2,28}, \text{Fe}^{+3}_{0,36})_{\text{T}} \text{O}_{20}(\text{OH})_{16}$,

CH2: $((\text{Mg}+\text{Mn})_{3,14}, \text{Al}_{3,54}, \text{Fe}^{+2}_{2,36}, \text{Fe}^{+3}_{0,32})_{11,36}(\text{Si}_{5,48}, \text{Al}_{2,24}, \text{Fe}^{+3}_{0,28})_{\text{T}} \text{O}_{20}(\text{OH})_{16}$.

6.3.1.2 *Classification of chlorite*

In the plot of the chemical classification of chlorite (Hey, 1954), the analysed samples mostly fall in the ripidolite field, except for three samples, of which one sample falls in the pycnochlorite, one in diabantite and another in the talc-chlorite field (Fig. 6-1). Chlorite from WDLMS has moderate Fe ($\text{Fe}^{+2}+\text{Fe}^{+3}$) from 2 to 6 mole of Fe and moderate silica from 5 to 5,5 mole.

Stilpnomelane has been reported in the VCR at West Driefontein Gold Mine by Stefan and Martin (1992) and is characterized by enrichment of Fe and depletion of Mg and Al. Sudoite and chloritoid have been documented in the Khaki shale in Basal Reef, Welkom Goldfield by Zhou and Phillips (1994). The former is characterized by enrichment of Al and Mg and depletion of Fe, but the latter is characterized by enrichment of Al and Fe and depletion of Mg. Chemical compositions of the different chlorite types and chloritoid in the VCR and the Witwatersrand

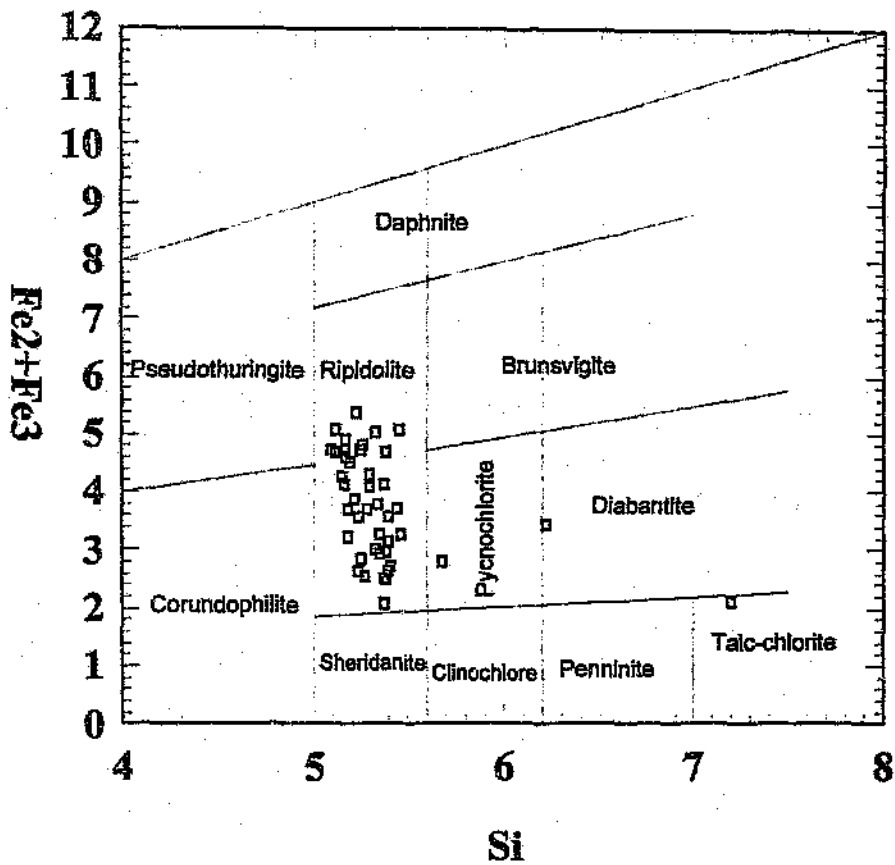


Fig. 6-1 Classification of chlorite in the VCR, using a bivariate plot of $(\text{Fe}^{2+} + \text{Fe}^{3+})$ vs Si (mole). The original fields of chlorite are from Hey (1954)

Basin are plotted in an A'FM diagram (Fig. 6-2), which demonstrates their chemical relationship.

The end members of the A'FM plot are represented by following:

$$A' = Al_2O_3 \text{ (wt\%)}$$

$$F = (FeO + 0.8998Fe_2O_3) \text{ (wt\%)}$$

$$M = MgO \text{ (wt\%)}$$

It seems that there is an absence of obvious solid solution in the three minerals. Of them, ripidolite in this study is documented in the VCR. However, sudoite and chloritoid may exist in the VCR footwall quartzite and footwall reef bands which are enriched in Khaki shale fragments.

6.3.1.3 *Mineral geochemistry in different host rocks and alteration zones*

The selected elements of the major chlorite type (CH1) and of minor chlorite type (CH2) are plotted against FeO (wt%) in terms of host rocks, i.e., lava, VCR, and DGG zone footwall quartzite (Fig. 6-3). The results indicate that the major components are variable in different host rock types and alteration zones. For example, Fe is enriched in chlorites from the VCR and the hanging wall lava, but depleted in chlorites from the DGG zone quartzite. Mg, Cr, Ni are enriched in the DGG zone quartzite, but depleted in the lava and the VCR. It seems that CH2 has higher Al, and lower Cr, Ni concentrations with moderate Fe concentration (Fig. 6-2a, b, c, d). Al_2O_3 , Cr_2O_3 , Na_2O and FeO are enriched in lava chlorite, but depleted in sample from the VCR and the DGG zone footwall quartzite. It is suggested that the major chlorite compositions reflect affinities of chemical compositions between the chlorite and its host rocks (Fig. 6-2).

6.3.2 Muscovite

A total of forty five analyses from eight rock samples were analysed for muscovite chemical

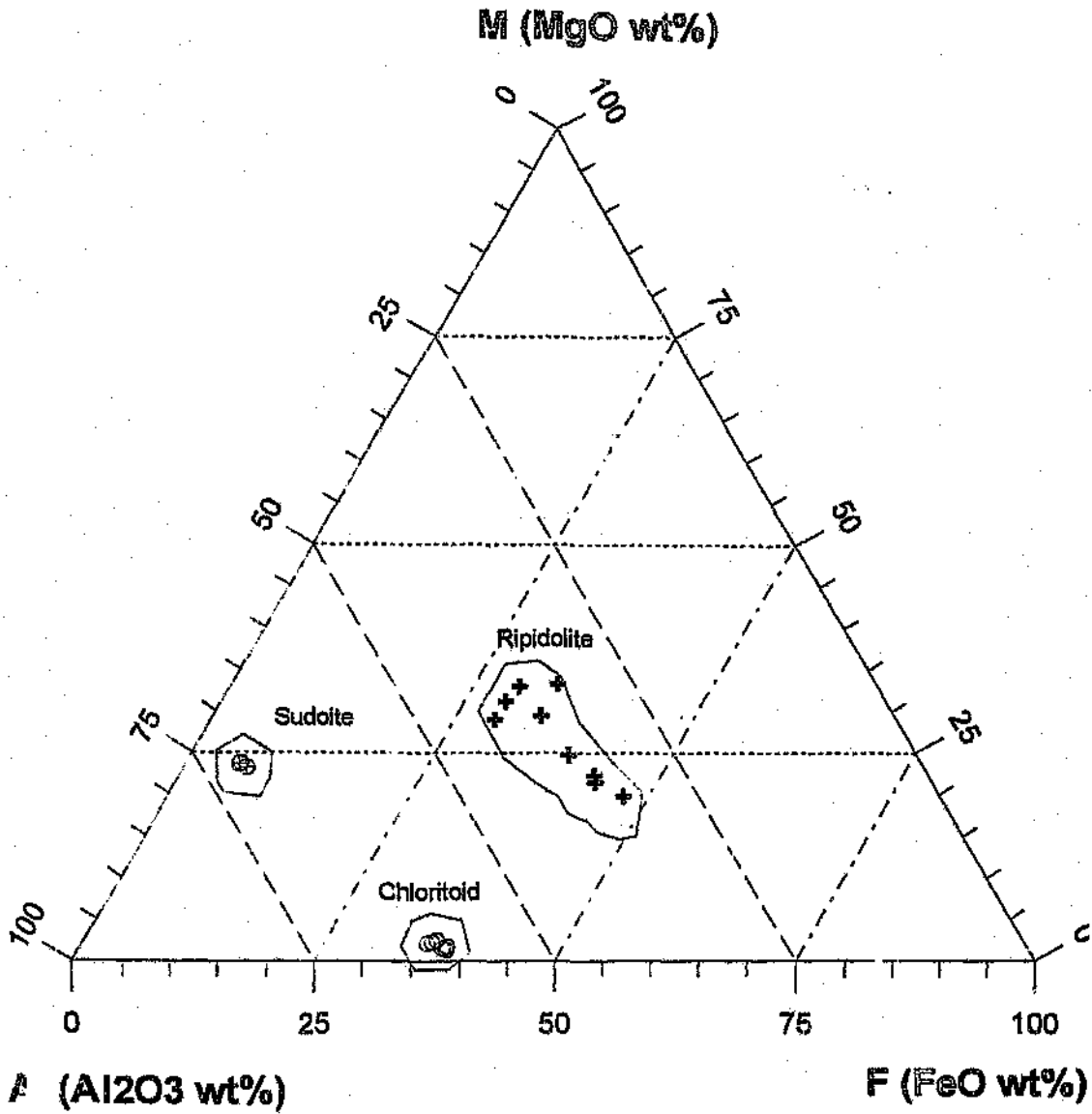


Fig. 6-2 A'FM diagram of chlorite types and chloritoid in the VCR and the Witwatersrand Basin. Data source: sudoite and chloritoid (Zhou & Phillips, 1994)

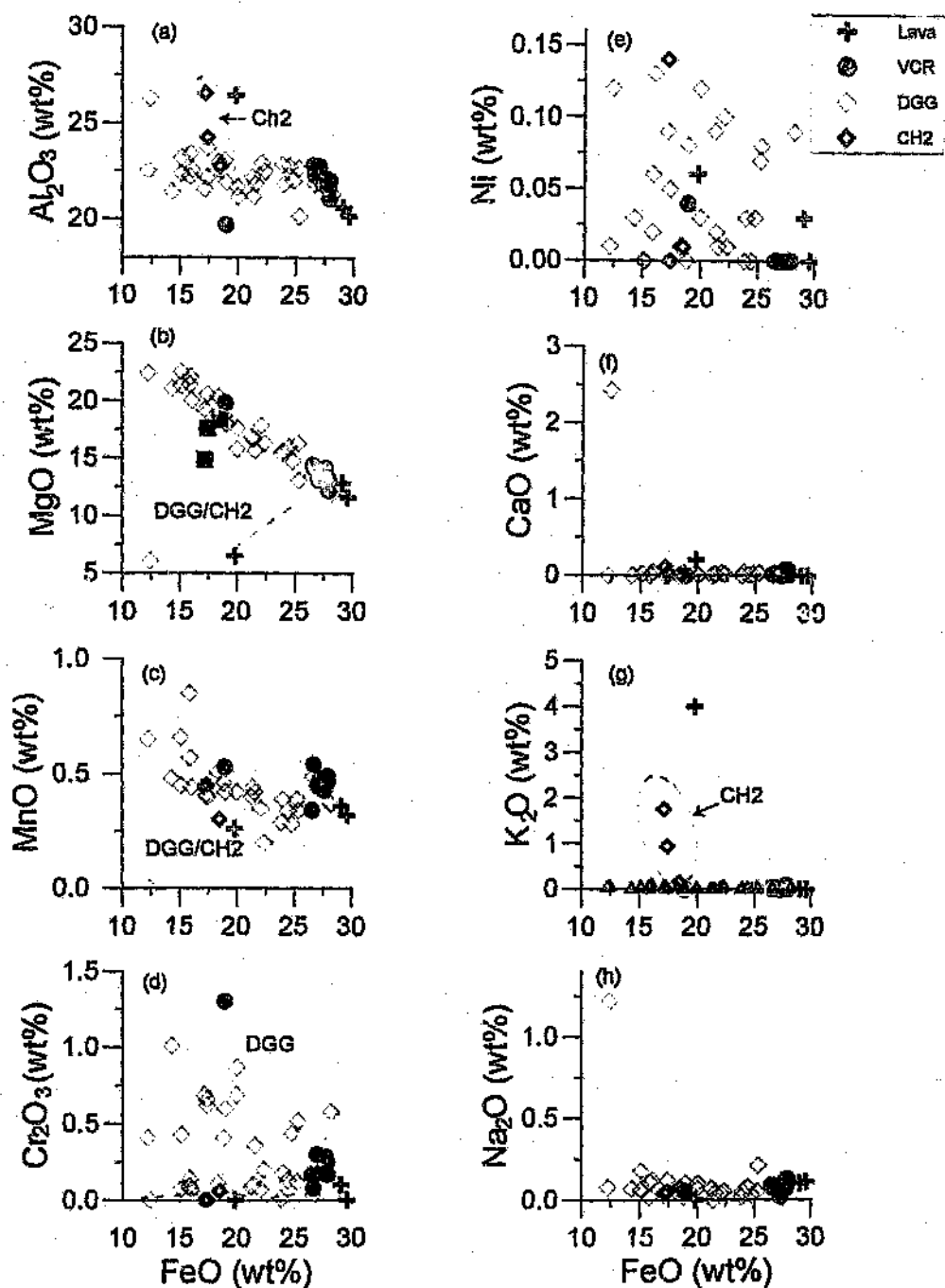


Fig. 6-3 Plots of selected oxides vs $\text{FeO}_{\text{total}}$ (wt%) for authigenic chlorite in the different host rocks from the VCR. DGG-DGG zone footwall quartzite; CH2-replacement-type of chlorite.

composition using the electron microprobe. The rock samples include lavas (2), the VCR (1), DGG zone footwall quartzite (4) and AGNQ internal quartzite (1). The chemical compositions of muscovite are tabulated in Table 6-2, listing analyses in different samples, rock types and alteration zones. Numbers of ions in the formula are also presented in the table. Average chemical compositions of muscovite for different host rocks and alteration zones, and totals for all the samples are summarized in Table 6-3.

The totals of the major oxides, excluding water, were always better than 87 wt%. The chemical components on average are as follows:

Authigenic muscovite:

Major (> 1,0 wt%): SiO_2 (44,96), Al_2O_3 (31,89), K_2O (9,81),

Trace (<0,5 wt%): FeO (0,69), MgO (0,93), Cr_2O_3 (0,55), TiO_2 (0,11), MnO (0,03),

Na_2O (0,38).

Detrital muscovite:

Major (> 1,0 wt%): SiO_2 (44,85), Al_2O_3 (31,86), FeO (2,68), MgO (1,04), K_2O (10,22),

Trace (< 1 wt%): TiO_2 (0,94), MnO (0,01), Na_2O (0,44), Cr_2O_3 (0,03), NiO (0,03).

Based on the numbers of ions, the structural formula for muscovite can be represented as follows:

Authigenic: $(\text{K}_{1,79}, \text{Na}_{0,11})(\text{Al}_{3,81}, \text{Cr}_{0,05})[\text{Si}_{6,42}\text{Al}_{1,58}\text{O}_{20}](\text{OH},\text{F})_4$.

Detrital: $(\text{K}_{1,82}, \text{Na}_{0,12})(\text{Al}_{3,74})[\text{Si}_{6,24}\text{Al}_{1,76}\text{O}_{20}](\text{OH},\text{F})_4$.

There is minor difference in the chemical composition between detrital muscovite and authigenic muscovite (see later).

Table 6-2 Chemical composition of muscovite in the VCR

Rock	Sample	VCR																												Rock	Sample		
		Leve														DOQ meto quabdo																	
		B0002						B0711						B0718						B0713						B0768							
		7	8	11	66	68	72	36	37	14	21	24	54	55	56	64	9	11	12	16	17	18	21	22	23	24.00	25	26					
wt%	SiO ₂	36.03	35.76	38.26	57.00	43.57	44.87	45.51	45.44	47.32	44.26	43.28	43.64	48.44	43.38	43.59	47.58	46.10	47.09	46.28	44.73	47.85	43.80	46.62	47.96	47.58	46.96	47.29					
	TiO ₂	0.09	0.07	0.29	0.09	0.05	0.22	0.30	0.07	0.28	n.d.	0.07	0.18	0.26	0.27	0.09	0.16	0.05	0.22	0.05	0.24	0.81	0.07	0.18	0.13	0.22	0.08	0.12					
	Al ₂ O ₃	21.93	22.79	22.08	22.16	33.04	33.40	33.81	33.54	33.60	34.20	33.54	34.38	33.07	33.66	32.74	32.71	32.57	31.22	31.37	32.02	32.56	33.93	32.50	32.94	32.62							
	FeO	20.37	14.40	13.99	5.13	2.77	1.38	0.86	0.85	0.43	0.61	0.72	1.02	0.94	0.77	0.46	0.54	0.61	0.63	0.43	0.60	0.00	0.59	0.62	0.55	0.45	0.70	0.43					
	MnO	0.27	0.18	0.23	0.00	0.05	0.03	0.00	0.03	0.00	0.01	n.d.	0.05	0.03	0.05	0.01	0.05	0.02	0.00	0.01	0.00	1.24	0.02	0.00	0.02	0.00	0.01						
	MgO	8.13	6.50	5.93	2.28	1.20	0.91	0.86	0.84	0.84	0.44	0.68	0.85	1.05	0.92	1.19	0.87	0.79	0.87	0.60	0.82	0.00	0.80	0.84	1.00	1.30	0.99	1.0					
	CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.21	0.00	0.00	0.00	0.00	0.00						
	Na ₂ O	0.11	0.16	0.22	0.19	0.35	0.30	0.66	0.64	0.50	0.53	0.49	0.33	0.45	0.37	0.38	0.41	0.38	0.36	0.38	0.37	0.44	0.38	0.42	0.42	0.36	0.41	0.45					
	K ₂ O	3.08	5.61	5.63	5.28	10.58	10.56	10.37	10.18	10.75	9.71	9.95	10.41	10.22	9.81	10.34	9.86	9.92	9.69	9.78	10.28	9.51	10.25	10.17	9.84	10.17	9.50	9.72					
	Cr ₂ O ₃	0.13	0.04	0.14	0.05	0.07	0.06	0.11	0.29	0.22	0.51	0.57	0.04	0.09	0.03	0.02	0.63	0.77	0.64	0.28	0.64	0.04	0.71	0.61	0.62	0.95	0.66	0.64					
	NiO	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.03	0.10	0.00	0.09	0.03	0.08	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.07	n.d.	0.04	0.00	0.10					
	Totals	90.14	91.29	91.86	92.26	93.69	91.50	94.17	92.79	94.18	89.21	89.36	90.91	87.05	92.05	89.15	93.84	91.38	92.12	90.38	93.55	91.47	88.64	92.09	94.47	93.37	92.24	92.41					
ions	Si	5.56	5.54	5.63	8.16	6.84	6.72	6.26	6.22	6.35	6.23	6.14	6.10	5.93	6.21	6.19	6.37	6.36	6.42	6.43	6.37	6.51	6.27	6.39	6.38	6.43	6.39	6.43					
	Al	2.44	2.46	2.37	0.00	1.16	1.20	1.74	1.72	1.65	1.77	1.36	1.90	2.07	1.79	1.81	1.63	1.64	1.58	1.57	1.63	1.49	1.73	1.61	1.62	1.57	1.61	1.57					
	Al	1.55	2.39	2.32	3.96	4.60	4.72	3.68	3.77	3.69	3.79	4.25	3.73	3.73	3.61	3.72	3.68	3.68	3.68	3.76	3.61	3.60	3.67	3.65	3.70	3.57	3.68	3.66					
	Ti	0.01	0.01	0.03	0.00	0.00	0.00	0.03	0.01	0.03	0.00	0.01	0.01	0.03	0.03	0.01	0.02	0.01	0.02	0.01	0.03	0.01	0.01	0.02	0.01	0.02	0.01	0.01					
	Fe+3	2.63	1.78	1.72	0.60	0.36	0.12	0.10	0.10	0.05	0.07	0.09	0.12	0.12	0.09	0.05	0.06	0.07	0.07	0.05	0.17	0.09	0.07	0.07	0.06	0.05	0.08	0.05					
	Mn	0.04	0.02	0.03	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00					
	Mg	1.87	1.44	1.30	0.48	0.24	0.24	0.17	0.17	0.17	0.09	0.14	0.20	0.23	0.19	0.25	0.17	0.16	0.16	0.12	0.17	0.25	0.17	0.17	0.20	0.26	0.20	0.21					
	Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00					
	Na	0.03	0.05	0.06	0.00	0.12	0.12	0.17	0.17	0.11	0.14	0.13	0.09	0.13	0.10	0.10	0.11	0.10	0.10	0.10	0.10	0.11	0.08	0.11	0.11	0.10	0.11	0.12					
	K	0.61	1.06	1.06	0.89	2.04	2.04	1.84	1.78	1.84	1.74	1.80	1.86	1.91	1.71	1.87	1.69	1.75	1.67	1.73	1.67	1.65	1.87	1.78	1.67	1.75	1.65	1.69					
	Cr+3	0.02	0.00	0.00	0.01	0.01	0.01	0.01	0.03	0.02	0.06	0.06	0.00	0.01	0.00	0.00	0.07	0.08	0.07	0.03	0.07	0.05	0.08	0.07	0.07	0.10	0.07	0.07					
	Ni	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01					

Rock	Sample	SUMMARY SHEET																																				Rock	Sample																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																						
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		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																								
wt%	SiO ₂	45.76	42.39	42.39	44.23	45.70	45.15	45.54	46.12	44.87	44.87	45.74	47.26	47.97	48.46	45.48	44.22	47.05	7.25	45.88	0.03	45.34	2.01	46.22	1.76	44.96	3.70	44.85	0.63	SiO ₂	32.18	29.79	31.72	32.30	31.63	33.87	33.76	35.91	31.18	37.18	29.30	29.81	28.02	36.21	32.22	31.50	27.73	4.38	35.09	1.06	32.69	1.05	33.47	3.362	31.89	2.98	31.86	0.36	Al ₂ O ₃	0.64	1.11	1.01	0.63	0.50	2.66	2.73	0.31	0.28	0.28	0.81	2.85	3.64	0.30	2.39	2.97	9.67	6.98	0.86	0.00	0.62	0.23	1.54	1.315	0.69	4.65	2.68	0.02	FeO	0.07	0.09	0.00	0.00	0.01	0.05	0.03	0.01	0.02	0.02	0.00	0.00	0.02	0.02	0.01	0.00	0.13	0.10	0.03	0.00	0.07	0.25	0.019	0.014	0.03	0.22	0.01	0.01	MnO	0.88	1.10	0.95	0.67	0.92	0.54	0.58	0.21	0.19	0.19	1.71	1.68	1.92	0.21	1.08	1.00	4.16	2.81	0.85	0.01	0.85	0.25	0.803	0.7	0.93	1.79	1.04	0.01	MgO	0.00	0.00	0.00	0.00	0.00	0.03	0.02	0.02	0.01	0.01	0.06	0.04	0.02	0.03	0.00	0.00	0.01	0.03	0.00	0.00	0.01	0.04	0.027	0.015	0.00	0.64	0.00	0.00	CaO	0.17	0.31	0.37	0.37	0.40	0.36	0.37	0.48	0.55	0.55	0.20	0.16	0.50	0.44	0.43	0.43	0.22	0.08	0.65	0.01	0.40	0.05	0.374	0.147	0.38	0.11	0.44	0.00	Na ₂ O	9.61	9.34	10.77	9.82	9.92	10.10	9.16	9.73	9.85	9.85	9.61	9.03	8.43	9.20	10.26	10.17	6.79	2.81	10.28	0.09	9.77	0.7	9.44	0.495	9.81	1.77	10.22	0.04	K ₂ O	0.72	0.61	0.16	0.33	0.53	0.00	0.00	0.11	0.11	0.11	1.16	1.15	1.08	0.00	0.03	0.03	0.08	0.04	0.20	0.09	0.47	0.27	0.422	0.503	0.53	0.20	0.03	0.00	Cr ₂ O ₃	0.00	0.06	0.00	0.01	0.00	0.00	0.02	0.00	0.01	0.01	0.00	0.02	0.00	0.03	0.03	0.03	0.03	0.04	0.00	0.00	0.03	0.04	0.01	0.011	0.03	0.64	0.03	0.00	NiO	90.30	84.80	88.43	88.76	89.73	92.82	92.28	93.08	92.27	92.21	91.29	92.91	92.09	95.20	93.02	91.10	92.01	1.18	92.28	0.89	90.85	2.33	92.91	1.013	89.52	2.21	92.06	0.96	Totals	6.38	6.34	6.72	6.29	6.42	6.20	6.27	6.25	6.34	6.05	6.43	6.47	6.67	6.47	6.25	6.23	6.41	0.95	6.24	0.02	6.14	0.15	6.35	0.172	6.42	0.43	6.24	0.01	Si	1.62	1.66	1.78	1.71	1.58	1.80	1.73	1.75	1.66	1.95	1.57	1.58	1.73	1.77	1.62	0.90	1.73	0.01	1.69	0.16	1.66	0.165	1.58	0.41	1.76	0.01	Al	3.67	3.59	4.72	3.71	3.66	3.68	3.78	3.71	3.91	3.96	3.29	3.24	3.24	3.47	3.66	3.26	1.22	3.73	0.04	3.74	0.24	3.563	0.291	3.81	0.60	3.47	0.00	Al	0.02	0.00	0.00	0.02	0.01	0.00	0.01	0.01	0.01	0.00	0.03	0.04	0.02	0.04	0.11	0.09	0.01	0.01	0.02	0.01	0.01	0.01	0.010	0.015	0.01	0.01	0.10	0.01	Ti	0.05	0.14	0.12	0.07	0.06	0.31	0.32	0.31	0.03	0.03	0.33	0.33	0.42	0.33	0.27	0.35	1.20	0.90	0.10	0.00	0.08	0.03	0.268	0.131	0.08	0.59	0.31	0.00	Fe+2	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0	0	0.00	0.01	0.00	0.00	Mn	0.18	0.25	0.24	0.14	0.19	0.11	0.11	0.12	0.04	0.04	0.36	0.35	0.40	0.35	0.22	0.21	0.93	0.64	0.17	0.00	0.19	0.04	0.209	0.143	0.20	0.40	0.22	0.01	Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	Ca	0.10	0.09	0.12	0.10	0.11	0.10	0.07	0.10	0.13	0.14	0.06	0.06	0.05	0.06	0.12	0.12	0.06	0.04	0.17	0.00	0.11	0.01	0.086	0.031	0.11	0.03	0.12	0.00	Na	1.71	1.78	2.16	1.78	1.78	1.77	1.41	1.60	1.53	1.69	1.72	1.59	1.50	1.59	1.80	1.81	1.28	0.56	1.81	0.03	1.78	0.11	1.6	0.107	1.79	4.32	1.82	0.02	K	0.03	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.03	0.13	0.12	0.13	0.00	0.00	0.01	0.02	0.01	0.05	0.03	0.057	0.05	0.03	0.00	0.00	0.00	Cr+3	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0	0	0.00	0.00	0.00	0.00	Ni

Table 6-3 Calculated solid solution components of muscovite in the VCR (mole%)

Rock	Lava		VCR		DGG zone quartzite																							
	10711		B0378		10715			10713				B0366						B0368										
	68	72	36	37	14	23	24	54	55	56	64	87	7	8	9	11	12	16	17	18	21	22	23	24	25	26		
Celadonite	0.28	0.16	0.12	0.13	0.09	0.08	0.11	0.15	0.16	0.13	0.15	0.10	0.10	0.12	0.11	0.11	0.11	0.09	0.11	0.09	0.12	0.11	0.12	0.15	0.14	0.12		
Muscovite	0.64	0.76	0.75	0.75	0.81	0.79	0.78	0.77	0.78	0.71	0.78	0.78	0.78	0.76	0.72	0.75	0.71	0.78	0.81	0.69	0.81	0.77	0.70	0.72	0.68	0.71		
Pyrophyllite	0.00	0.00	0.00	0.00	0.08	0.03	0.00	0.00	0.00	0.00	0.00	0.05	0.05	0.09	0.07	0.06	0.09	0.13	0.08	0.02	0.02	0.08	0.06	0.07	0.05	0.09		
Paragonite	0.05	0.04	0.09	0.08	0.07	0.07	0.08	0.04	0.06	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.06	0.05	0.05	0.05	0.06		
Hydromica	0.03	0.02	0.03	0.03	0.00	0.03	0.03	0.03	0.00	0.10	0.01	0.01	0.01	0.00	0.03	0.01	0.03	0.00	0.00	0.13	0.00	0.00	0.06	0.00	0.07	0.01		

Rock	AGNQ quartzite												Detrital	
Sample	B0368		B0407										B0368	
	32	36	1a	2a	3a	5a	6a	1	2	3	5	77	78	
Celadonite	0.11	0.20	0.21	0.21	0.04	0.03	0.03	0.21	0.32	0.40	0.04	0.19	0.24	
Muscovite	0.73	0.69	0.67	0.58	0.80	0.81	0.81	0.64	0.45	0.33	0.73	0.65	0.63	
Pyrophyllite	0.75	0.00	0.00	0.00	0.07	0.00	0.00	0.03	0.00	0.00	0.13	0.00	0.00	
Paragonite	0.05	0.04	0.05	0.05	0.06	0.07	0.07	0.03	0.03	0.02	0.06	0.06	0.06	
Hydromica	0.02	0.07	0.07	0.15	0.03	0.08	0.08	0.07	0.19	0.24	0.03	0.04	0.03	

SUMMARY SHEET											
Authigenic (32)										Detrital (2)	
Lava (2)		VCR (2)		DGG (24)		AGNQ (9)		Total		DGG (2)	
AVG	STD	AVG	STD	AVG	STD	AVG	STD	AVG	STD	AVG	STD
0.22	0.06	0.13	0.00	0.12	0.03	0.17	0.13	0.14	0.07	0.22	0.03
0.70	0.06	0.75	0.00	0.75	0.04	0.65	0.16	0.72	0.10	0.64	0.01
0.00	0.00	0.00	0.00	0.08	0.14	0.03	0.04	0.05	0.12	0.00	0.00
0.05	0.01	0.09	0.01	0.05	0.01	0.05	0.02	0.05	0.01	0.06	0.00
0.03	0.01	0.03	0.00	0.03	0.03	0.10	0.07	0.05	0.05	0.04	0.01

The selected elements are plotted against K_2O (wt%) (Fig. 6-4). It clearly demonstrates a similar picture to the chlorite geochemistry as previously described. Chemical components of the muscovite are variable among different host rock types and alteration zones. Muscovite from lavas and AGNQ internal quartzite is distinguishable from the VCR and DGG zone footwall quartzite in almost all the elements (Al, Fe, Mn, Cr, Mg, Ni, Ti) (Fig. 6-3a, b, c, d, e, f, g, h). Detrital muscovite is only distinguishable from CHI in TiO_2 . It is suggested that the detrital muscovite has been chemically reconstructed during hydrothermal alteration.

Mineral compositions of muscovite were calculated by the solid solution model of Loucks (1991) in terms of muscovite (pure end-member)-hydromica-pyrophyllite-muscovite-celadonite (Cr-celadonite+Al-celadonite)-paragonite solid solutions. The calculated results are tabulated in Table 6-3. It is suggested that muscovite has various solid solutions and muscovite and celadonite are the two predominant components. They are:

Muscovite $(KAl_2[Si_3AlO_{10}](OH,F)_2)$: 72 mole%,

Celadonite $(K(Mg,Mn,Fe^{2+},Zn)(Cr,Al,Ti,Fe)Si_4O_{10}(OH)_2)$: 14 mole%

Pyrophyllite $(H_3O)Al_2Si_4O_{10}$: 0,05 mole%,

Paragonite $(NaAl_2AlSi_3O_{10}(OH)_2)$: 0,07 mole%.

Hydromica $(H_3O)Al_2AlSi_3O_{10}(OH)_2$: 0,05 mole%.

The variation of chemical compositions in different host rocks has also been shown in the calculated muscovite solid solution components, which are plotted in bivariate diagrams (Fig. 6-5). Lines have been drawn on the plots to emphasize the distribution fields of muscovite solid solution components. For example, the majority of the analyses in the DGG zone footwall quartzite and VCR have moderate celadonite concentrations (Fig. 6-5a). The DGG zone footwall

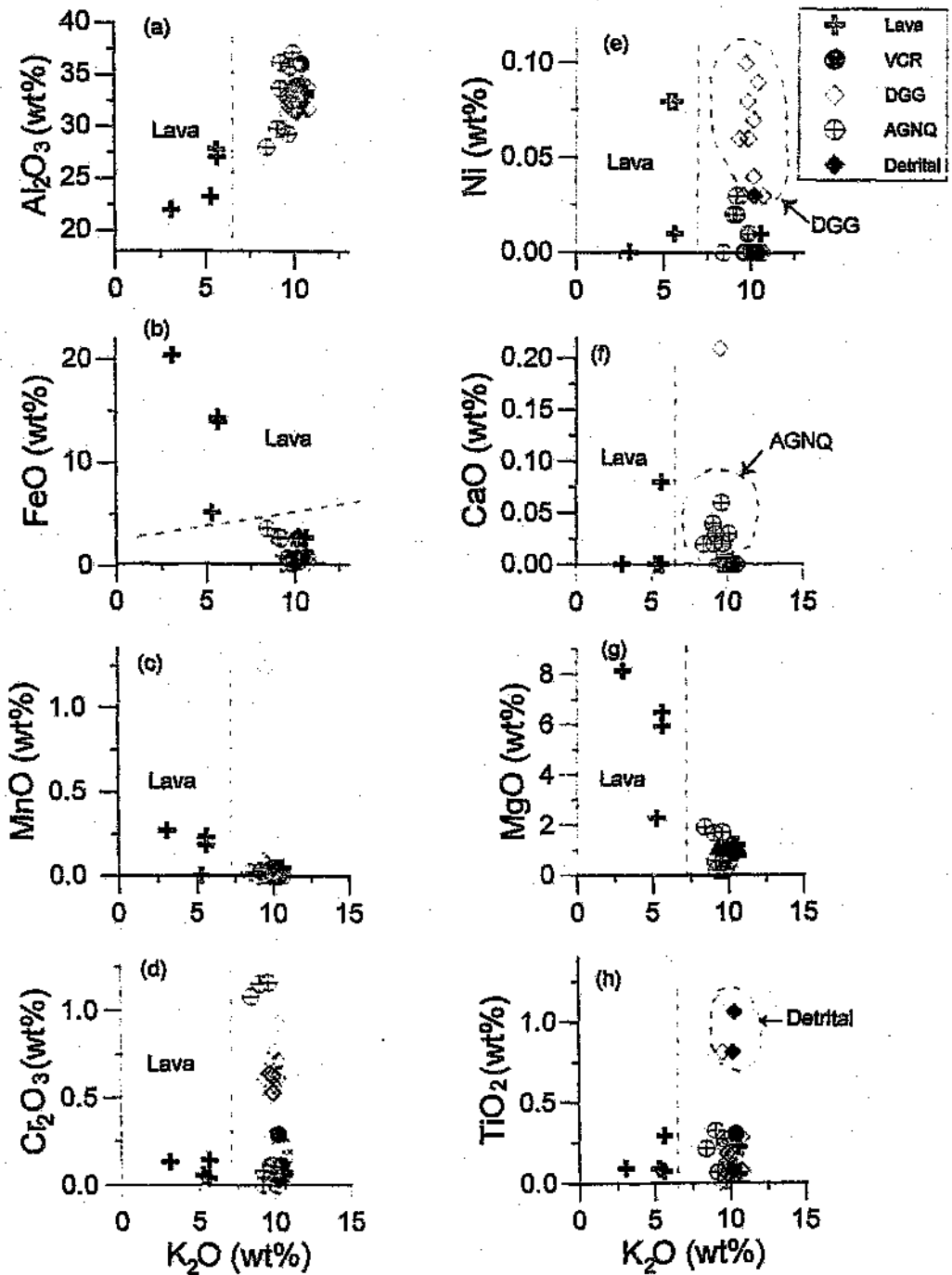


Fig. 8-4 Plots of selected elements vs K_2O for the authigenic muscovite, together with minor detrital muscovite in different host rocks from the VCR.

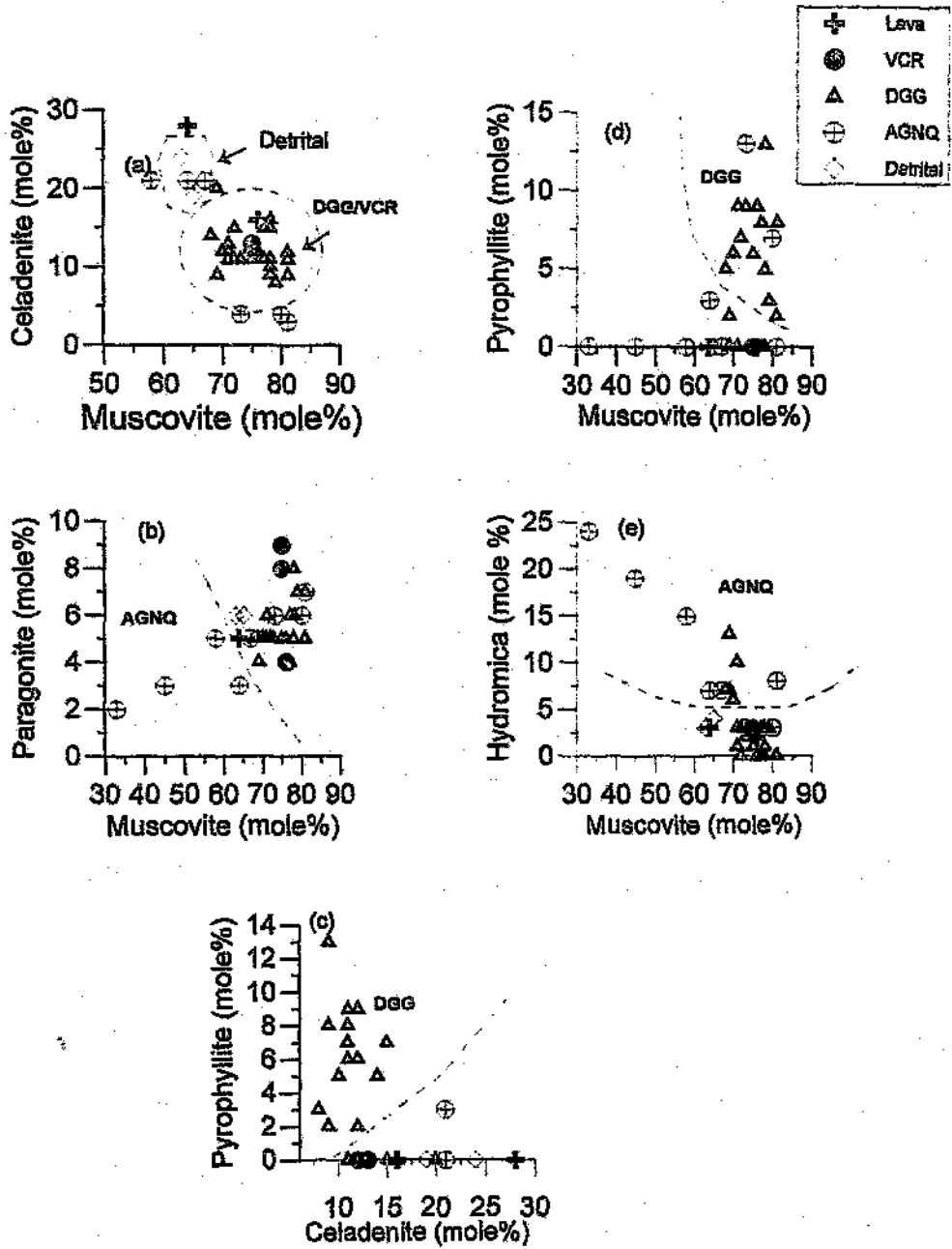


Fig. 6-5 Bivariate plots of the individual end-members of muscovite (mole%) in the VCR.

quartzite has a high pyrophyllite concentration (Fig. 6-5e, c). AGNQ internal quartzite has low muscovite concentration and high hydromica concentration (Fig. 6-5a, c).

6.3.3 Albite

A total of thirty two analyses were obtained for albite from five rock samples, including lava (1), VCR (1) and DGG zone footwall quartzite (3). Chemical compositions of albite and the numbers of ions are tabulated in Table 6-4. The chemical components are presented as follows:

Major (>1 wt%): SiO_2 (67,15), Al_2O_3 (21,04), Na_2O (11,87),

Trace (<1 wt%): FeO (0,16), MgO (0,01), MnO (0,07), K_2O (0,03), CaO (0,07).

Very little chemical change can be seen in the table for different host rocks and alteration zones due to the internal texture. However, when the selected elements are plotted against Na_2O in terms of different host rocks and alteration types (Fig. 6-6), it can be seen that Ca is clearly enriched in the DGG zone quartzite, and Mn and K trend to be enriched in the lava and DGG zone footwall quartzite (Fig. 6-5d, c, d), but some variations also occur in the others (Fig. 6-6a, b). The lines are drawn to emphasize the distinctive distribution fields of the albite compositions in different host rocks and alteration zones (Fig. 6-6c, d, e) similar to muscovite plots (Fig. 6-4, 5).

6.3.4 Carbonate

Limited analyses of carbonates were obtained from lava (1), VCR (1) and DGG zone footwall quartzite (1). The chemical compositions of the carbonates are tabulated in Table 6-5. Two end-members of the carbonates were identified to be calcite and siderite. Except for the major oxides of Ca, Fe, and Mg, minor elements (Si, Na, Al, Mn, Ti, K) also exist in the calcite and siderite.

Table 6-4 Chemical composition of albite in the VCR

Rock	Lava				VCR			DGG zone quartzite										B0368					Rock
Sample	bb002				B0378			B0366										B0368					Sample
	33	34	37	38	40	45	49	50	51	52	10	11	13	14	5	6	8	9	17				
wt%																							
SiO ₂	67.67	68.43	68.06	68.48	67.48	65.38	67.43	67.21	67.73	66.74	66.95	67.70	66.80	66.66	67.78	65.72	65.56	69.71	67.62				SiO ₂
Al ₂ O ₃	21.28	21.23	21.02	21.27	20.80	21.23	21.01	21.15	21.05	21.15	21.31	21.18	20.88	20.61	21.22	20.93	20.82	22.37	21.24				Al ₂ O ₃
FeO	0.17	0.00	0.00	0.16	0.09	0.44	0.83	0.22	0.41	0.22	0.00	0.03	0.13	0.36	0.06	0.09	0.00	0.16	0.17				FeO
MgO	0.00	0.04	0.01	0.01	0.00	0.01	0.01	0.05	0.01	0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.00	0.02	0.01				MgO
MnO	0.12	0.00	0.10	0.00	0.00	0.00	0.00	0.07	0.14	0.02	0.00	0.67	0.03	0.00	0.00	0.00	0.00	0.01	0.28				MnO
CaO	0.00	0.30	0.04	0.01	0.03	0.05	0.11	0.03	0.00	0.11	0.09	0.08	0.21	0.38	0.17	0.12	0.13	0.24	0.00				CaO
Na ₂ O	12.23	11.97	12.07	11.81	12.25	12.96	12.19	12.02	12.17	12.41	11.21	11.46	11.11	11.13	11.60	11.95	11.94	7.69	11.72				Na ₂ O
K ₂ O	0.00	0.03	0.00	0.03	0.05	0.00	0.06	0.00	0.05	0.00	0.06	0.10	0.03	0.04	0.06	0.00	0.06	0.00	0.00				K ₂ O
Total	101.30	101.87	101.20	101.69	100.70	100.70	101.64	100.75	101.57	100.65	99.62	100.63	99.21	99.18	100.89	98.81	98.51	100.20	101.14				Total
ions																							
Si	11.71	11.76	11.77	11.77	11.75	11.54	11.68	11.70	11.71	11.66	11.73	11.76	11.77	11.77	11.75	11.67	11.94	11.74	11.73				Si
Al	4.34	4.30	4.28	4.31	4.27	4.42	4.29	4.34	4.29	4.35	4.40	4.34	4.33	4.29	4.34	4.38	4.52	4.23	4.33				Al
Fe+2	0.00	0.00	0.00	0.02	0.00	0.06	0.12	0.03	0.06	0.03	0.00	0.00	0.02	0.05	0.01	0.01	0.02	0.00	0.02				Fe+2
Mn	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00				Mn
Mg	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00				Mg
Na	4.10	3.99	4.05	3.94	4.14	4.44	4.10	4.06	4.08	4.20	3.81	3.86	3.79	3.81	3.90	4.11	2.55	4.03	3.93				Na
Ca	0.00	0.00	0.01	0.00	0.01	0.01	0.02	0.00	0.03	0.00	0.02	0.01	0.04	0.07	0.03	0.02	0.04	0.01	0.00				Ca
K	0.00	0.01	0.00	0.01	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.02	0.01	0.01	0.01	0.00	0.00	0.01	0.00				K

													SUMMARY SHEET								Rock
Rock	DGG zone quartzite												Authigenic (32)								Rock
Sample	B0368									I0705			Lava (4)		VCR (3)		DGG (24)		Total		Sample
	18	19	20	23	24	26	27	28	29	33	36	37	AVG	STD	AVG	STD	AVG	STD	AVG	STD	
SiO2	66.86	68.11	66.58	67.46	67.05	66.53	68.15	68.03	68.32	65.88	65.42	64.25	68.16	0.33	66.76	0.98	67.03	1.13	67.15	1.12	SiO2
Al2O3	21.17	20.77	20.85	20.77	20.87	20.59	20.97	21.00	20.68	20.72	20.96	21.16	21.20	0.11	21.01	0.18	21.02	0.35	21.04	0.32	Al2O3
FeO	0.27	0.17	0.05	0.25	0.13	0.45	0.06	0.00	0.03	0.00	0.13	0.00	0.08	0.08	0.45	0.30	0.1	0.13	0.16	0.18	FeO
MgO	0.00	0.01	0.00	0.00	0.00	0.01	0.03	0.01	0.00	0.00	0.00	0.02	0.02	0.02	0.01	0.00	0.01	0.01	0.01	0.01	MgO
MnO	0.07	0.11	0.00	0.08	0.19	0.27	0.00	0.12	0.10	0.15	0.15	0.10	0.06	0.06	0.09	0.00	0.08	0.08	0.07	0.08	MnO
CaO	0.00	0.00	0.15	0.00	0.00	0.00	0.00	0.16	0.00	0.00	0.02	0.05	0.01	0.02	0.06	0.03	0.08	0.10	0.07	0.09	CaO
Na2O	12.08	11.90	12.06	12.09	12.32	11.86	12.05	12.01	12.01	12.12	12.98	12.80	12.02	0.15	12.47	0.35	11.78	0.96	11.88	0.88	Na2O
K2O	0.02	0.01	0.03	0.06	0.08	0.00	0.00	0.03	0.07	0.00	0.00	0.05	0.02	0.02	0.04	0.03	0.03	0.03	0.03	0.03	K2O
Total	100.47	101.08	99.72	100.71	100.55	99.71	101.26	101.36	101.12	98.87	99.67	98.43	101.54	0.27	101.01	0.44	100.17	0.94	100.43	0.98	Total
Si	11.68	11.80	11.71	11.75	11.71	11.72	11.78	11.76	11.81	11.69	11.58	11.52	11.75	0.02	11.66	0.09	11.73	0.08	11.72	0.08	Si
Al	4.36	4.24	4.32	4.26	4.30	4.28	4.27	4.28	4.22	4.33	4.73	4.47	4.31	0.02	4.33	0.07	4.34	0.11	4.34	0.10	Al
Fe+2	0.04	0.02	0.01	0.04	0.02	0.07	0.01	0.00	0.00	0.00	0.02	0.00	0.01	0.01	0.06	0.05	0.02	0.02	0.02	0.03	Fe+2
Mn	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	Mn
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	Mg
Na	4.05	4.00	4.11	4.08	4.17	4.05	4.04	4.03	4.03	4.17	4.45	4.45	4.02	0.06	4.23	0.15	3.99	0.34	4.02	0.31	Na
Ca	0.00	0.02	0.00	0.01	0.02	0.05	0.00	0.02	0.02	0.03	0.03	0.02	0.00	0.00	0.01	0.00	0.02	0.02	0.02	0.02	Ca
K	0.00	0.00	0.01	0.01	0.02	0.00	0.00	0.01	0.02	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	K

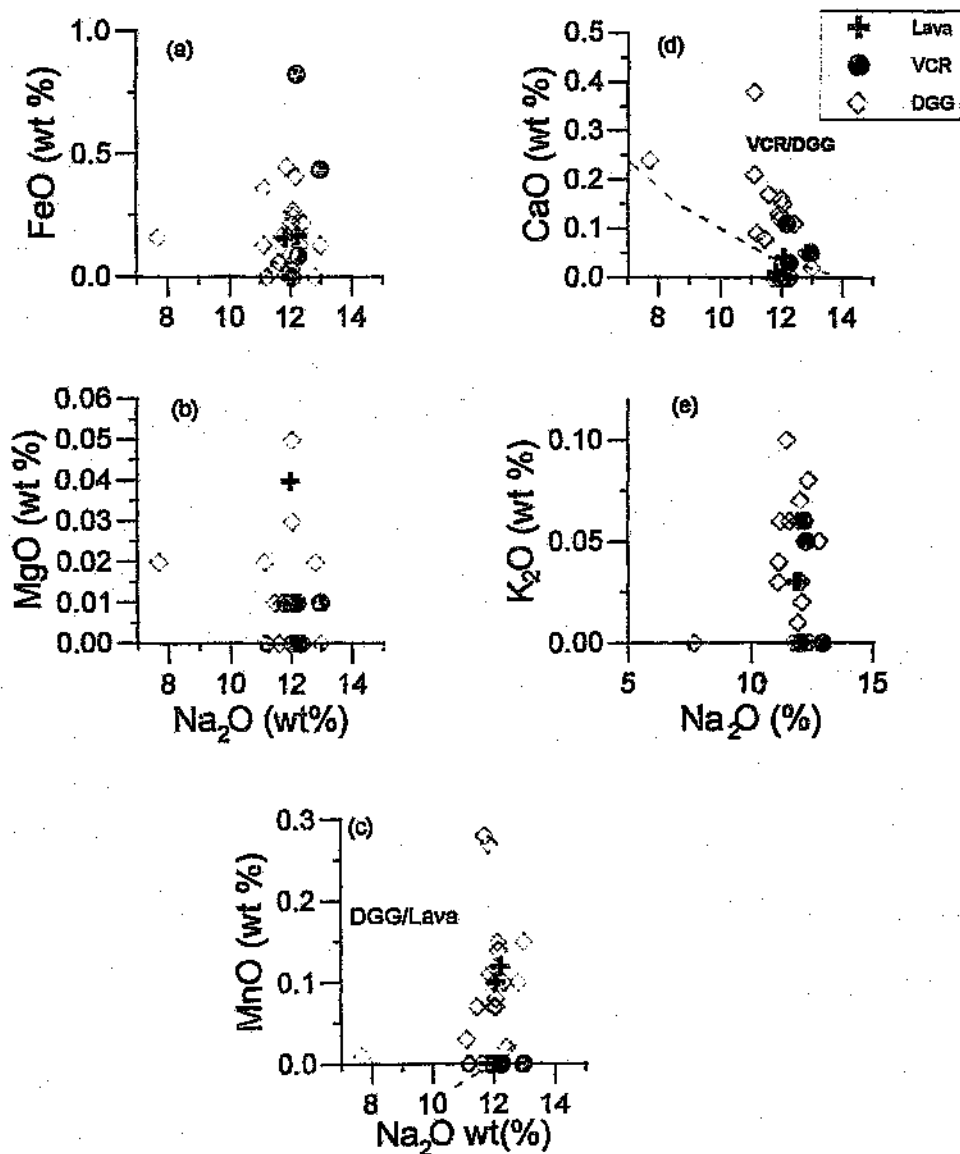


Fig. 6-6 Plots of selected oxides vs Na_2O (wt%) for authigenic albite in the different host rocks from the VCR.

Table 6-5 Chemical composition of calcite and siderite in the VCR

Mineral	Calcite							Siderite							
	Rock (sample)	Lava (Bh002)	Quartzite (B0361)				AVG	STD	VCR-1					AVG	STD
			9	40	43	44			46	47	48	49	50		
wt%	SiO2	1,31	0,00	0,03	0,00	0,34	0,56	0,22	0,01	0,03	0,00	0,03	0,06	0,08	
	TiO2	0,00	0,03	0,06	0,13	0,06	0,05	0,09	0,03	0,05	0,00	0,10	0,05	0,04	
	Al2O3	0,24	0,01	0,00	0,01	0,07	0,10	0,03	0,00	0,00	0,01	0,01	0,01	0,01	
	FeO	0,11	0,23	0,29	0,12	0,19	0,08	58,26	60,85	57,96	54,32	60,44	58,37	2,32	
	MnO	0,23	0,20	0,32	0,33	0,27	0,06	0,01	0,26	0,22	0,28	0,04	0,16	0,11	
	MgO	0,03	0,00	0,01	0,00	0,01	0,01	2,14	1,66	1,98	3,15	2,36	2,26	0,50	
	CaO	58,10	58,08	60,54	60,99	59,43	1,35	0,10	0,14	0,07	1,76	0,28	0,47	0,65	
	Na2O	0,16	0,00	0,00	0,00	0,04	0,07	0,07	0,00	0,02	0,00	0,09	0,04	0,04	
	K2O	0,02	0,00	0,01	0,00	0,01	0,01	0,03	0,03	0,01	0,04	0,01	0,02	0,01	
	Cr2O3	0,00	0,00	0,11	0,02	0,03	0,05	0,00	0,00	0,00	0,00	0,02	0,00	0,01	
	NiO	0,03	0,02	0,00	0,00	0,01	0,01	0,01	0,00	0,00	0,00	0,00	0,00	0,00	
	Total	60,23	60,23	58,57	61,60	60,16	1,07	60,96	62,98	60,34	59,56	63,30	61,43	1,47	

6.4 Sulphides

Authigenic pyrite, pyrrhotite, chalcopyrite, galena, sphalerite and pentlandite were analysed using the electron microprobe.

6.4.1 Pyrite

A total of seventy chemical analyses of pyrite were obtained from eight rock samples, including the hanging wall lava (2), VCR (1), DGG zone footwall quartzite (4) and AGNQ internal quartzite (1). About ten analyses were performed for each rock sample. The chemical compositions of the pyrite are tabulated in Table 6-6 in terms of analyses in different rock types and alteration zones, and the numbers of ions in the formula and Co/Ni ratios. The totals of the analysed chemical compositions are highly accurate and are between 99 and 101 wt%. The principal substitutions are thus:

Fe: Co, Ni,

S: Se, As.

The average Co/Ni ratios are variable between 1,8 and 10,4 with an average of 3,5. This is much higher than those of detrital pyrite from the VCR at East Driefontein Gold Mine (0,5 to 1,0 with average of 0,8) and that of the Elsburg Reef at the Loraine Mine (0,01 and 0,3 with average of 0,2) (Hallbauer, 1986) (Table 6-6).

In order to determine the variation and relationship between the elements in pyrite, bivariate plots of the selected elements were constructed against Co/Ni ratio (Fig. 6-7). The results show that the selected elements are variable in pyrite from host rock types and alteration zones. For example, Fe is enriched in the lava pyrite (Fig. 6-7a), while Co, Ni, S are enriched in those of the AGNQ internal quartzite (Fig. 6-7b, f).

Table 6-6 Chemical composition of pyrite from the VCR

	Rock	Lava																								
		BHL-3												BHL-2												
wt%	Sample																									
	Fe	46.04	46.28	46.08	45.98	46.18	46.21	46.37	46.09	46.81	45.27	46.80	46.82	46.51	46.41	46.40	47.88	46.76	46.64	46.51	46.71	46.50	46.92	45.17	46.97	46.51
	Co	0.07	0.07	0.05	0.09	0.04	0.05	0.03	0.06	0.02	0.06	0.07	0.05	0.07	0.02	0.05	0.05	0.04	0.07	0.07	0.09	0.02	1.46	0.03	0.07	
	Ni	0.65	0.13	0.13	0.17	0.17	0.14	0.14	0.09	0.17	1.08	0.02	0.03	0.03	0.04	0.02	0.03	0.01	0.03	0.02	0.00	0.06	0.00	0.04	0.01	0.04
	Se	0.02	0.06	0.65	0.00	0.00	0.00	0.05	0.00	0.04	0.00	0.02	0.11	0.06	0.04	0.02	0.00	0.00	0.01	0.06	0.04	0.00	0.06	0.00	0.03	0.06
	As	0.15	0.38	0.00	0.00	0.11	0.23	0.23	0.00	0.27	0.23	0.12	0.00	0.08	0.08	0.08	0.00	0.12	0.20	0.00	0.06	0.00	0.24	0.28	0.43	0.24
	S	53.49	53.61	52.94	52.63	52.84	52.76	52.99	52.48	52.22	52.41	53.38	53.25	53.34	53.10	52.99	53.03	53.08	53.05	52.68	52.36	52.97	52.77	53.03	52.99	52.37
Total	100.45	100.53	99.25	98.79	99.34	99.39	99.42	98.72	98.73	99.65	100.39	100.26	100.10	99.69	99.47	100.19	100.02	99.98	99.35	99.19	99.62	100.01	99.98	100.46	99.29	
mole	Fe	0.82	0.83	0.83	0.82	0.83	0.83	0.83	0.83	0.82	0.81	0.84	0.84	0.83	0.83	0.84	0.84	0.84	0.83	0.84	0.83	0.84	0.81	0.84	0.83	
	Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	Ni	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	Se	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	As	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	
	S	1.67	1.67	1.65	1.64	1.65	1.65	1.64	1.64	1.63	1.63	1.67	1.66	1.66	1.66	1.65	1.65	1.65	1.65	1.64	1.63	1.65	1.65	1.65	1.65	1.63
	Co/Ni	0.1	0.5	0.4	0.5	0.2	0.4	0.2	0.7	0.1	0.1	3.5	1.7	2.3	0.5	2.0	1.7	3.0	1.3	3.5	-	1.5	-	36.4	3.0	1.7
	Rock	DGG zone quartzite																								
		DQ110b												XR1646												
wt%	Sample																									
	Fe	47.15	46.54	46.89	46.02	46.52	46.30	46.28	46.36	45.99	46.11	46.14	45.97	46.05	45.37	46.19	46.48	46.29	46.56	46.54	46.36	46.36	46.42	46.55	46.37	46.42
	Co	0.02	0.04	0.05	0.09	0.03	0.04	0.04	0.05	0.06	0.04	0.04	0.13	0.04	0.37	0.03	0.08	0.03	0.02	0.06	0.08	0.12	0.02	0.04	0.05	0.05
	Ni	0.02	0.02	0.05	0.20	0.03	0.16	0.04	0.02	0.01	0.03	0.03	0.06	0.17	0.34	0.02	0.03	0.01	0.04	0.03	0.05	0.07	0.06	0.01	0.05	0.02
	Se	0.04	0.01	0.00	0.06	0.01	0.02	0.00	0.00	0.02	0.00	0.01	0.01	0.00	0.00	0.05	0.02	0.00	0.02	0.06	0.07	0.01	0.00	0.00	0.00	0.00
	As	0.13	0.42	0.32	0.28	0.21	0.42	0.57	0.25	0.17	0.08	0.26	0.29	0.47	0.68	0.00	0.00	0.12	0.00	0.00	0.43	0.00	0.2	0.00	0.00	0.03
	S	53.00	53.39	53.04	53.51	53.54	53.68	53.45	53.18	53.17	53.38	53.57	53.17	53.35	53.31	53.43	53.02	52.79	52.58	52.68	52.89	52.84	52.86	52.90	52.96	52.97
Total	100.36	100.42	99.55	100.16	100.34	100.62	100.38	99.86	99.42	99.44	100.05	99.63	100.28	100.07	99.72	99.63	99.24	99.21	99.37	99.88	99.40	99.62	99.50	99.51	99.46	
mole	Fe	0.84	0.83	0.83	0.82	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.82	0.82	0.81	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83
	Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	Se	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	As	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	
	S	1.65	1.67	1.65	1.67	1.67	1.67	1.67	1.66	1.66	1.67	1.67	1.66	1.67	1.66	1.67	1.65	1.65	1.64	1.64	1.65	1.65	1.65	1.65	1.65	1.65
	Co/Ni	1.0	2.0	1.0	0.4	1.0	0.2	1.0	2.5	6.0	1.3	1.3	2.1	0.2	1.1	1.5	1.7	3.0	0.5	2.0	1.6	1.7	0.3	4.0	1.0	2.5

Table 6-6 Chemical compositions of pyrite in the VCR (continued)

	Rock	VCR										DGG zone quartzite									
		B0410a										B0410b									
	Sample																				
wt%	Fe	45.53	46.17	45.88	46.41	45.63	46.43	46.32	46.43	46.68	46.10	46.14	46.13	46.27	46.19	46.19	46.24	46.21	46.55	46.48	46.16
	Co	1.07	0.03	0.04	0.03	0.03	0.04	0.02	0.15	0.14	0.03	0.06	0.05	0.03	0.03	0.03	0.04	0.02	0.04	0.03	0.04
	Ni	0.03	0.21	0.08	0.00	0.17	0.03	0.05	0.12	0.02	0.03	0.02	0.02	0.04	0.02	0.01	0.05	0.01	0.03	0.03	0.03
	Se	0.00	0.00	0.03	0.02	0.08	0.04	0.00	0.00	0.05	0.00	0.05	0.02	0.00	0.20	0.00	0.00	0.05	0.00	0.01	0.06
	As	0.00	0.04	0.00	0.00	0.27	0.00	0.00	0.00	0.00	0.36	0.06	0.60	0.59	0.36	0.26	0.28	0.17	0.32	0.32	0.21
	S	53.03	53.14	52.90	52.52	52.16	53.28	53.30	53.21	53.12	53.82	53.45	53.09	52.90	52.43	52.78	52.81	53.21	53.60	53.77	52.83
	Total	99.66	99.59	99.90	98.90	98.34	99.82	99.69	99.92	100.01	100.34	99.78	99.91	99.83	99.03	99.27	99.42	99.67	100.54	100.64	100.78
mole	Fe	0.82	0.83	0.82	0.83	0.82	0.83	0.83	0.83	0.84	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83
	Co	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Se	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	As	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	S	1.65	1.66	1.65	1.64	1.63	1.66	1.66	1.66	1.66	1.68	1.67	1.66	1.65	1.64	1.65	1.65	1.66	1.67	1.68	1.68
	Co/Ni	35.5	0.1	0.5	-	0.2	1.3	0.4	1.2	7.0	1.0	3.0	2.5	0.7	1.5	3.0	0.8	2.0	1.3	1.0	1.3
	Rock	AGNQ internal quartzite										SUMMARY SHEET									
		B0417										Lava (15)		VCR (9)		DGG (36)		AGNQ (10)		Total (70)	
	Sample											AVG	STD	AVG	STD	AVG	STD	AVG	STD	AVG	STD
wt%	Fe	46.35	46.51	44.99	46.57	46.06	45.87	44.93	44.81	46.55	46.36	46.37	0.46	46.16	0.37	46.28	0.27	45.90	0.68	45.12	7.15
	Co	0.49	0.27	1.06	0.76	0.83	0.88	1.01	0.84	0.50	0.54	0.11	0.28	0.17	0.32	3.06	0.06	0.81	0.44	0.18	0.34
	Ni	0.02	0.15	0.08	0.10	0.31	0.13	0.13	0.13	0.13	0.03	0.13	0.23	0.08	0.07	0.05	0.07	0.12	0.08	0.08	0.14
	Se	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.03	0.00	0.00	0.03	0.03	0.03	0.03	0.02	0.03	0.01	0.02	0.02	0.03
	As	0.00	0.23	0.38	0.57	0.15	0.42	0.80	0.15	0.00	0.00	0.14	0.13	0.03	0.08	0.23	0.19	0.27	0.26	0.19	0.19
	S	53.85	53.66	53.91	53.14	53.84	53.88	53.90	53.35	54.06	53.66	52.89	0.36	52.96	0.36	53.18	0.36	53.72	0.27	51.84	8.21
	Total	100.71	100.82	101.32	101.14	101.19	101.18	100.82	99.31	101.24	100.58	99.67	0.55	99.44	0.52	99.85	0.46	100.83	0.56	97.43	15.42
mole	Fe	0.83	0.83	0.81	0.83	0.82	0.82	0.80	0.80	0.83	0.83	0.83	0.01	0.83	0.01	0.83	0.00	0.82	0.01	0.81	0.13
	Co	0.01	0.00	0.03	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.01	0.00	0.01
	Ni	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Se	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	As	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	S	1.68	1.67	1.68	1.66	1.68	1.68	1.68	1.66	1.69	1.67	1.65	0.01	1.65	0.01	1.66	0.01	1.68	0.01	1.62	0.26
	Co/Ni	24.4	1.8	24.4	5.6	2.2	6.7	2.2	6.4	2.2	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

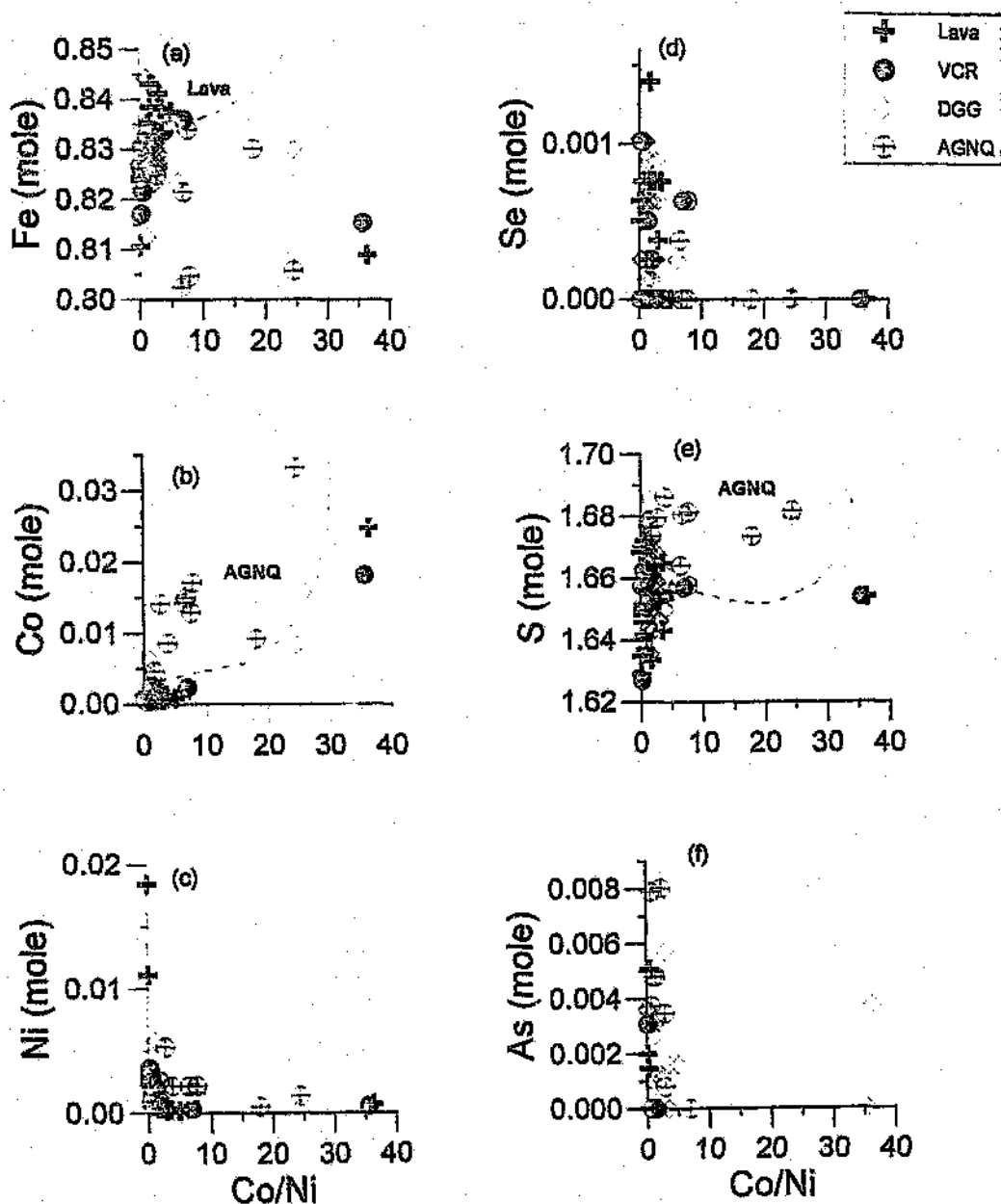


Fig. 6-7 Plots of selected elements (mole) vs Co/Ni ratios for authigenic pyrite in different host rocks from the VCR.

Co is also plotted against Ni for the pyrite from this study (Fig. 6-8), together with collected pyrite chemical data. The data collected from the literature include: (1) detrital pyrite from the VCR at East Driefontein Gold Mine; (2) detrital pyrite from Elsburg Reef EA12 at the Loraine Mine; (3) detrital pyrite and authigenic pyrite from the other Central Rand and West Rand reefs; (4) Greenstone Gold Mines and Barberton Greenstone Belt rocks, being thought to be the possible source of the Witwatersrand reefs (Robb & Meyer, 1987); (5) shale-associated gold deposits; (6) Western Transvaal basement veins in granitoid; and (7) Olifantsgeraamte Gold Mine, magmatism-related. The data for (1) and (2) are from Hallbauer (1986) and the others are from Meyer et al. (1990b).

Authigenic pyrite is distinguishable from detrital pyrite in the bivariate plot of Co and Ni (Fig. 6-8a), which indicates that the authigenic pyrite was not fully reconstructed in chemical composition during post-depositional events. This suggests that detrital pyrite geochemistry can be used to trace sources of the sulphides and related mineralisation elements. This is consistent with the results of MacLean & Fleet (1989), who suggested that the compacted rounded pyrite in the Witwatersrand Basin represents allogenic detrital grains. This suggestion contradicts the results of Meyer et al. (1990b), who suggested that the detrital pyrite has been strongly reconstructed by hydrothermal fluids due to their indistinguishable chemical features (Fig. 6 of Meyer et al., 1990b). The detrital pyrite from the VCR, the Elsburg Reef AE12 and the West Rand Promise Reefs is plotted in Fig. 6-8b. It shows that at least some detrital pyrite is indistinguishable from the Elsburg Reef EA12 and the West Rand Promise Reefs. These may be due to reworking of these reefs. However the others are clearly distinguishable and may represent other sources for detrital pyrite and other heavy metals (Au?, Ag?).

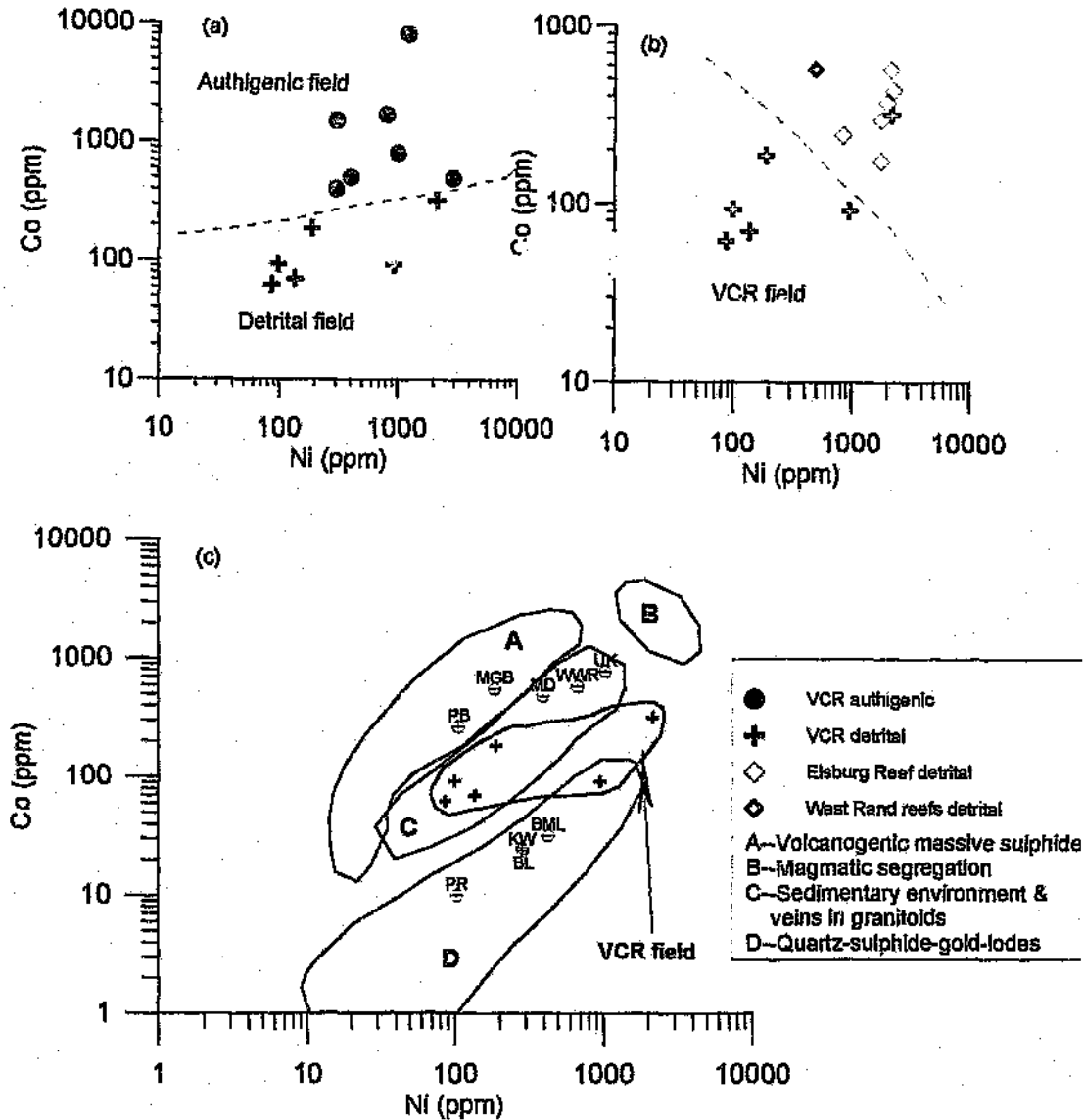


Fig. 6-8 Plots of Co vs Ni (ppm) for pyrite from the VCR, together with the collected pyrite data. (a) authigenic pyrite and detrital pyrite (Hallbauer, 1986) in the VCR; (b) VCR and other reef detrital pyrite in the Witwatersrand Basin; (c) VCR detrital pyrite in the pyrite genetic fields (after Meyer et al., 1990b). MGB-Murchison greenstone belt; PB-Pietersburg greenstone belt; WWR-Witwatersrand Supergroup; UK-Uitkyk Formation; MD-Moodies Group; PG-Pongola Supergroup; BML-Barberton greenstone belt; KW-Klipwal Gold Mine; BL-Bellingwe greenstone belt; PR-Sabie-Pilgrim's Rest Goldfield.

Furthermore, Co is plotted versus Ni for pyrite in the Witwatersrand Basin, together with the collected data from the possible source rock types, which include (A) volcanogenic massive sulphides (Murchison greenstone belt gold mine, Pietersburg greenstone gold mine), as indicated in Fig. 6-8c); (B) magmatic segregation; (C) sedimentary environment and veins in granitoid (Utiky Formation, Moodies Group, Witwatersrand Supergroup); (D) quartz-sulphide-gold-lodes (Barberton greenstone belt, Sabie-Pilgrims Rest Gold Mine). The VCR detrital field largely overlaps the sedimentary environment and veins in granitoid (C) and to a lesser extent in the quartz - sulphide - gold - lode field. It is suggested that the VCR detrital materials were mainly derived from the sedimentary environment and veins in granitoid, with minor other sources, i.e., quartz-sulphide-gold-lodes. This is consistent with the results of Hallbuaer (1984), Robb and Meyer (1985); and Hallbauer (1986) who suggested that the hydrothermally altered granitoids (HAGS) in the Witwatersrand hinterland provided the major source of sulphides and mineralization elements for the Witwatersrand Basin.

6.4.2 Pyrrhotite

Pyrrhotite was analysed from a total of twelve rock samples: lavas (2), VCR (2), DGG zone footwall quartzite (5), and GG zone footwall quartzite (3). The chemical compositions of pyrrhotite are tabulated in Table 6-7. No obvious variations of chemical components of pyrrhotite in different host rocks and alteration zone were identified. The principal substitutions of pyrrhotite are:

Fe: Co, Ni, Cu

S: Se.

The chemical formula of pyrrhotite can be presented as:



Table 6-7 Chemical composition of pyrrhotite from the VCR

														SUMMARY SHEET																							
		Lava		VCR		DGG zone quartzite								GG quartzite				AGNQ quartzite		Lava		VCR		DGG				GG				AGNQ				Total	
		R1	BHB-4	B0410a	B0378	B0415	B0361	XR164B	B0410b	B0368	B0109	BHL-1	B0379	B0417	B0407	AVG	STD	AVG	STD	AVG	STD	AVG	STD	AVG	STD	AVG	STD	AVG	STD	AVG	STD	AVG	STD				
wt%	Fe	60.34	60.28	60.90	59.35	60.23	60.13	61.07	60.25	60.07	60.02	61.24	59.39	60.06	60.35	60.51	0.28	59.79	0.44	60.38	0.40	60.22	0.77	60.21	0.40	60.26	0.52										
	Co	0.14	0.11	0.06	0.17	0.04	0.14	0.12	0.07	0.19	0.10	0.07	0.06	0.06	0.06	0.10	0.20	0.11	0.06	0.13	0.04	0.073	0.02	0.038	0.00	0.099	0.03										
	Ni	0.07	0.38	0.26	0.17	0.52	0.34	0.33	0.23	0.27	0.44	0.30	0.48	0.65	0.36	0.24	0.11	0.34	0.17	0.29	0.04	0.409	0.08	0.504	0.12	0.343	0.14										
	Cu	0.01	0.01	0.00	0.01	0.02	0.01	0.01	0.02	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.15	0.01	0.00	0.01	0.00	0.008	0.00	0.006	0.00	0.008	0.00										
	Se	0.02	0.03	0.03	0.03	0.02	0.02	0.01	0.02	0.02	0.02	0.04	0.02	0.03	0.02	0.03	0.01	0.03	0.00	0.02	0.91	0.027	0.01	0.022	0.00	0.024	0.01										
	S	39.41	39.00	38.97	38.86	38.55	39.63	38.36	38.37	38.92	38.72	38.66	38.98	39.21	38.40	39.13	19.55	38.70	0.15	38.82	0.52	38.79	0.14	38.8	0.34	38.86	0.37										
Total		99.99	99.81	100.22	98.59	99.39	100.27	99.89	98.96	99.48	99.31	100.31	98.95	100.01	99.19	100.01	30.44	98.99	0.40	99.65	0.49	99.52	0.58	99.6	0.45	99.6	0.53										
mole	Fe	1.08	1.08	1.09	1.06	1.08	1.08	1.09	1.08	1.08	1.07	1.10	1.06	1.08	1.08	1.08	49.46	1.07	0.01	1.08	0.01	1.078	0.01	1.078	0.01	1.079	0.01										
	Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.54	0.00	0.00	0.00	0.00	0.001	0.00	0.001	0.00	0.002	0.00										
	Ni	0.00	0.01	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.007	0.00	0.009	0.00	0.006	0.00										
	Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.00	0.000	0.00	0.000	0.00										
	Se	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.004	0.00	0.000	0.00	0.000	0.00										
	S	1.23	1.22	1.22	1.21	1.20	1.24	1.20	1.20	1.21	1.21	1.21	1.22	1.22	1.20	1.22	0.61	1.21	0.00	1.21	0.02	1.21	0.60	1.21	0.01	1.212	0.01										
Fe/(Fe+S)		0.47	0.47	0.47	0.47	0.47	0.47	0.48	0.47	0.47	0.47	0.48	0.47	0.47	0.47	0.47	0.60	0.47	0.00	0.47	0.00	0.471	0.00	0.471	0.00	0.471	0.00										

Table 6-7 Chemical composition of pyrrhotite from the VCR

														SUMMARY SHEET													
		Lava		VCR		DGG zone quartzite						GG quartzite		AGNQ quartzite		Lava		VCR		DGG		GG		AGNQ		Total	
		R1	BHL-3	B0410a	B0378	B0415	B0361	XR164B0410b	B0368	B0109	BHL-1	B0379	B0417	B0407	AVG	STD	AVG	STD	AVG	STD	AVG	STD	AVG	STD	AVG	STD	AVG
wt%	Fe	60.34	60.28	60.90	59.35	60.23	60.13	61.07	60.25	60.07	60.02	61.24	59.39	60.06	60.35	60.51	0.28	59.79	0.44	60.38	0.40	60.22	0.77	60.21	0.40	60.26	0.52
	Co	0.14	0.11	0.06	0.17	0.04	0.14	0.12	0.07	0.19	0.10	0.07	0.06	0.06	0.06	0.10	30.20	0.11	0.06	0.13	0.04	0.073	0.02	0.058	0.00	0.099	0.05
	Ni	0.07	0.38	0.26	0.17	0.52	0.34	0.33	0.23	0.27	0.44	0.30	0.48	0.63	0.36	0.24	0.11	0.34	0.17	0.29	0.04	0.409	0.08	0.504	0.12	0.343	0.14
	Cu	0.01	0.01	0.00	0.01	0.02	0.01	0.01	0.02	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.15	0.01	0.00	0.01	0.00	0.008	0.00	0.006	0.00	0.008	0.00
	Se	0.02	0.03	0.03	0.03	0.02	0.02	0.01	0.02	0.02	0.02	0.04	0.02	0.03	0.02	0.03	0.01	0.03	0.00	0.02	0.01	0.027	0.01	0.022	0.00	0.024	0.01
	S	39.41	39.00	38.97	38.86	38.55	39.63	38.36	38.37	38.92	38.72	38.66	38.98	39.21	38.40	39.13	19.55	38.70	0.15	38.82	0.52	38.79	0.14	38.8	0.34	38.86	0.37
	Total	99.99	99.81	100.22	98.59	99.39	100.27	99.89	98.96	99.48	99.31	100.31	98.95	100.01	99.19	100.01	30.44	98.99	0.40	99.63	0.49	99.52	0.58	99.6	0.45	99.6	0.53
mole	Fe	1.08	1.08	1.09	1.06	1.08	1.08	1.09	1.08	1.08	1.07	1.10	1.06	1.08	1.08	1.08	49.46	1.07	0.01	1.08	0.01	1.078	0.01	1.078	0.01	1.079	0.01
	Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.54	0.00	0.00	0.00	0.00	0.001	0.00	0.001	0.00	0.002	0.00
	Ni	0.00	0.01	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.007	0.00	0.009	0.00	0.006	0.00
	Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.00	0.000	0.00	0.000	0.00
	Se	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.00	0.000	0.00	0.000	0.00
	S	1.23	1.22	1.22	1.21	1.20	1.24	1.20	1.20	1.21	1.21	1.21	1.22	1.22	1.20	1.22	0.61	1.21	0.60	1.21	0.02	1.21	0.00	1.21	0.01	1.212	0.01
	Fe(Fe+S)	0.47	0.47	0.47	0.47	0.47	0.47	0.48	0.47	0.47	0.47	0.48	0.47	0.47	0.47	0.47	0.60	0.47	0.00	0.47	0.00	0.471	0.00	0.471	0.00	0.471	0.00

It is suggested that pyrrhotite in the research area shows a deficiency of iron below that required for the stoichiometric formula FeS . In the Fe-S system the pyrrhotite in equilibrium with pyrite shows an increasing iron deficit with increasing temperature (cf., Deer et al., 1992). Based on this, the equilibrium temperatures of pyrrhotite and pyrite are estimated at about 400°C (cf., Fig. 209 of Deer et al., 1992). In addition, the selected elements are separately plotted against Fe, Ni and S. The plots demonstrate that the element distributions are indistinguishable from each other in different host rocks and alteration zones, but one cluster of analyses in lava is clearly depleted in Ni content (Fig. 6-9b, c). It is suggested that pyrrhotite is not obviously controlled by its host rocks.

6.4.3 Chalcopyrite

A total of twelve rock samples were analysed for the chemical compositions of chalcopyrite from the hanging wall lava (3); VCR (2); DGG zone footwall quartzite (6), and AGNQ (1) (Table 6-8). Chalcopyrite is characterized by Ag enrichment in comparison with other sulphides. Ag concentrations in the authigenic chalcopyrite are between 0,01 and 0,02 wt% (100ppm to 200 ppm). The principal substitutions are:

Cu: Ag,

Fe: Ni,

S: As.

Selected elements of the single analyses for chalcopyrite are separately plotted versus Cu, Ni, and As (Fig. 6-10). The plots indicate that chalcopyrite is almost indistinguishable by host rocks and alteration zones except for one cluster of analyses in lavas in the plot of Ag versus Ni (Fig. 6-10e). It seems that Ag concentrations in some of the VCR and DGG zone footwall quartzite are higher than those in most of the lava samples and AGNQ internal quartzite (Fig. 6-10b, e). Moreover, it seems that there is a weak correlation between Ag and As in some of the VCR and DGG zone footwall quartzite samples (Fig. 6-10d).

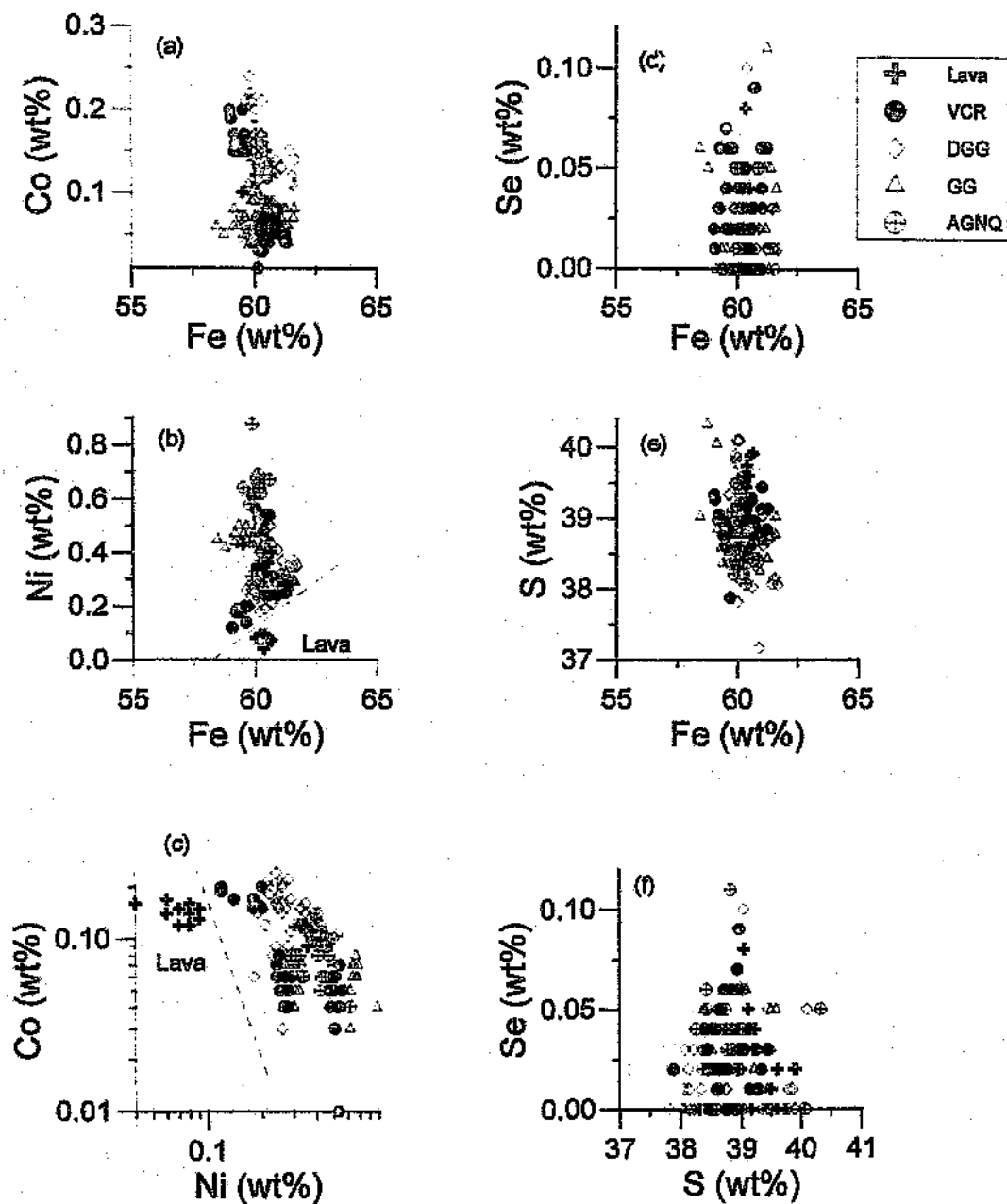


Fig. 6-9 Bivariate plots of selected elements (wt%) for authigenic pyrrhotite in the different host rocks from the VCR.

Table 6-8 Chemical compositions of chalcopyrite from the VCR

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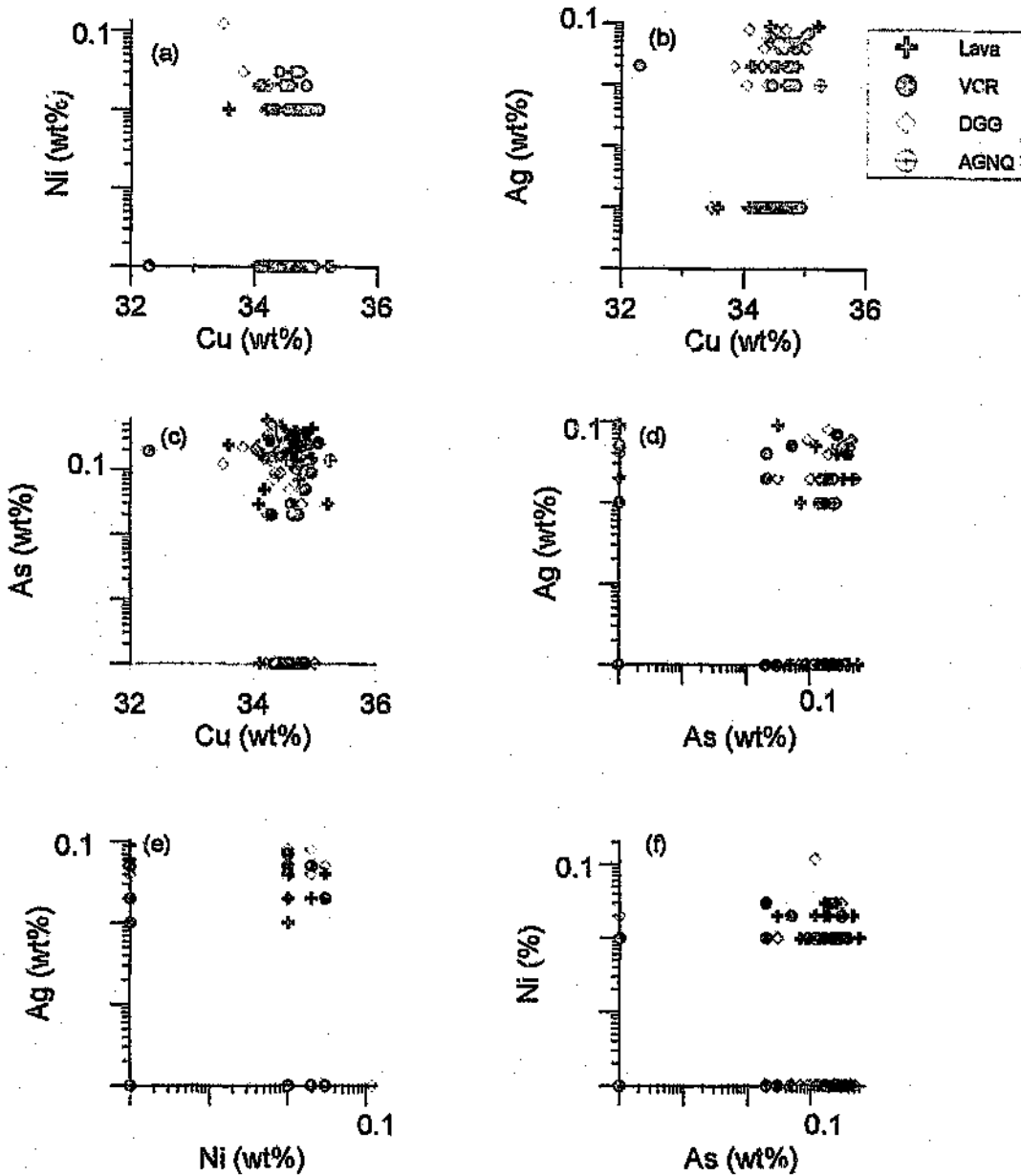


Fig. 6-10. Variate plots of selected elements (wt%) for authigenic chalcopyrite in different host rocks from the VCR.

6.4.4 Sphalerite

Analyses of sphalerite from a total of eight samples from the lavas (1), VCR (3) and DGG zone footwall quartzite (4) were completed (Table 6-9). The principal substitutions are thus:

Zn (wt%): Fe (4,58), Cu (0,31), Cd (0,18), Mn (0,03),

No replacement of S has been found in the analyses. The chemical formula for sphalerite can be constructed as:



It is suggested that Fe is enriched in sphalerite in the research area and Fe concentrations are variable in different host rocks and alteration zones. Chemical banding in sphalerite is also recorded in this study (Table 6-9).

Some elements of sphalerite from the hanging wall lava, VCR and DGG zone footwall quartzite were plotted against Zn, and Fe (Fig. 6-11). The elements are also plotted against the sample location from edge, middle and core in the same diagram (Fig. 6-11f). It clearly indicates that Zn and Cu are enriched, but Fe is depleted in the lava samples (Fig. 6-11a, b, c, d). Sphalerite compositions are not distinguishable for the VCR and DGG zone quartzite. It is suggested that the chemical concentration of sphalerite is influenced by the host rock geochemistry.

The plot of the chemical components of sphalerite versus the analytical locations shows the chemical banding from the edge to core of the sphalerite grains in the lava (Fig. 6-11f). The chemical bands are characterized by an increase of Mn, Cd, and Cu, but slight decrease of Zn and S from the edge to core. Moreover, Fe is enriched in the middle zone. The chemical banding of sphalerite in this study is probably similar to those common features in Mississippi Valley type (MVT) deposit (McLimans et al., 1980; Fowler & L'Heureux, 1996). The texture is interpreted to be due to pulses of hydrothermal fluids with variable compositions (e.g., McLimans et al.,

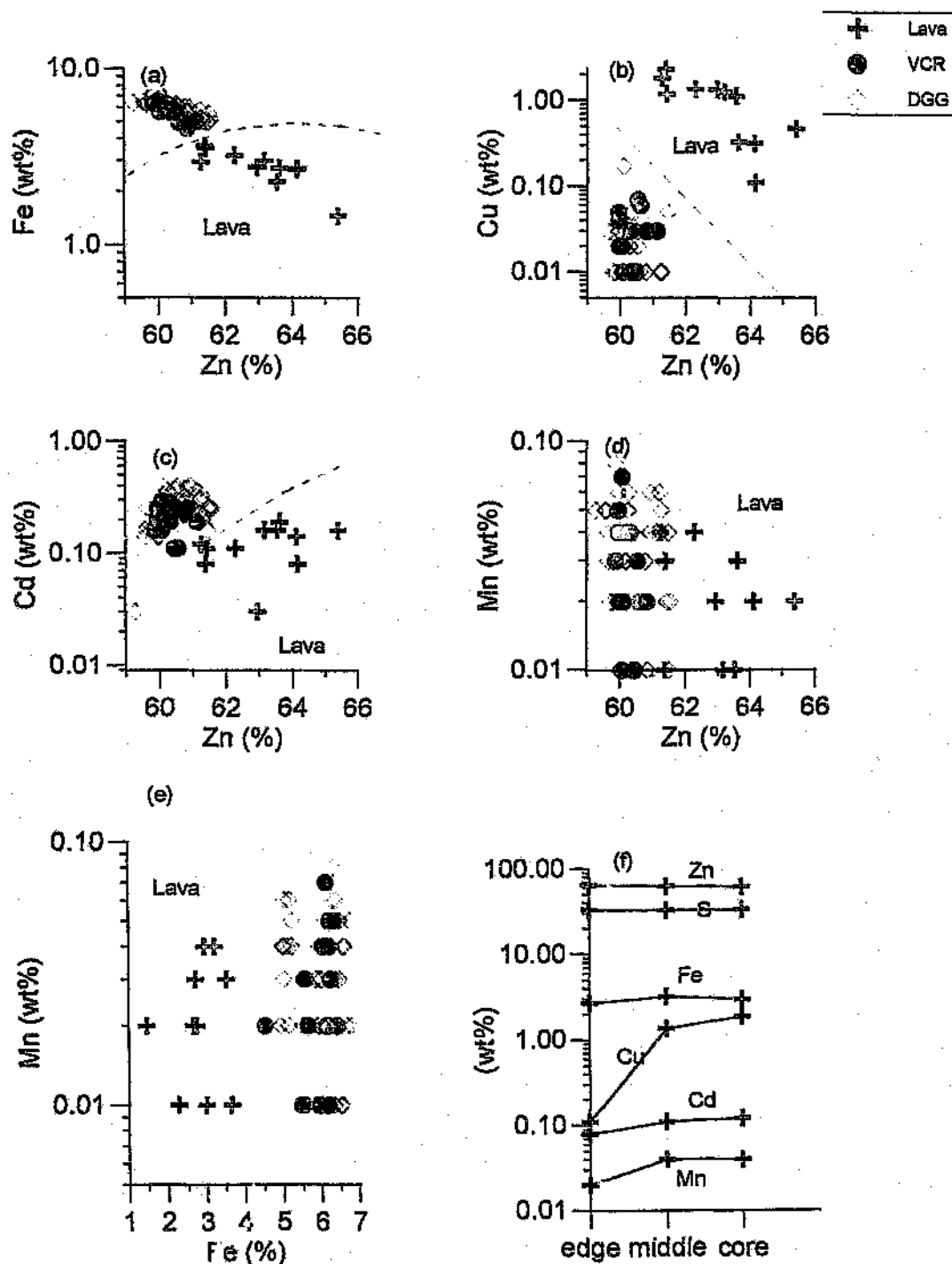


Fig. 6-11 Bivariate plots of selected elements (wt%) (a, b, c, d, e) and chemical profile from the edge, middle to core (f) for authigenic sphalerite from the VCR.

Table 6-9 Chemical composition of sphalerite from the VCR

												Summary sheet							
		Lava			VCR			DGG-zone quartzite				Lava		VCR		DGG		Total	
		BHL-3			B0410	B0415	B0384	B0361	XRJ646	B0410	B0372	AVG	STD	AVG	STD	AVG	STD	AVG	STD
		edge	middle	core															
wt%	Zn	64,15	62,28	61,26	60,48	60,06	61,24	59,69	60,82	59,99	60,29	62,56	1,20	60,27	0,21	60,41	0,56	55,48	17,59
	Fe	2,70	3,20	2,94	5,45	6,15	5,12	6,38	5,85	6,51	6,08	2,947	0,20	5,799	0,35	5,99	0,49	4,58	1,988
	Cu	0,11	1,36	1,85	0,03	0,01	0,01	0,01	0,00	0,01	0,03	1,107	0,73	0,021	0,01	0,01	0,01	0,31	0,62
	Cd	0,08	0,11	0,12	0,21	0,23	0,26	0,16	0,34	0,19	0,29	0,103	0,02	0,22	0,01	0,25	0,07	0,18	0,095
	Mn	0,02	0,04	0,04	0,02	0,03	0,04	0,05	0,02	0,02	0,03	0,033	0,01	0,026	0,01	0,03	0,01	0,03	0,013
	S	32,94	32,59	32,85	32,41	32,86	33,35	33,15	33,50	33,20	33,35	32,79	0,15	32,63	0,22	33,31	0,12	30,02	9,498
	Total	100,00	99,58	99,06	98,52	99,33	100,01	99,44	100,53	99,92	100,08	99,55	0,38	98,93	0,40	100,00	0,35	90,59	28,65
mole	Zn	0,98	0,95	0,94	0,93	0,92	0,94	0,91	0,93	0,92	0,92	0,957	0,02	0,922	0,00	0,92	0,01	0,85	0,269
	Fe	0,05	0,06	0,05	0,10	0,11	0,09	0,11	0,10	0,12	0,11	0,053	0,00	0,104	0,01	0,11	0,01	0,08	0,036
	Cu	0,00	0,02	0,03	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,017	0,01	0,000	0,00	0,00	0,00	0,00	0,01
	Cd	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,001	0,00	0,002	0,00	0,00	0,00	0,00	0,001
	Mn	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,001	0,00	0,000	0,00	0,00	0,00	0,00	0,000
	S	1,03	1,02	1,02	1,01	1,02	1,04	1,03	1,04	1,04	1,04	1,023	0,00	1,018	0,01	1,04	0,00	0,94	0,296

1980) or to non-equilibrium self-organization processes (Fowler & L'Heureux, 1996) or to fluid infiltration under supersaturated conditions during metasomatism (Yardley et al., 1991). The chemical banding of sphalerite in the VCR is most probably due to fluid infiltration under supersaturated conditions during hydrothermal alteration, evidenced by high salinity of the hydrothermal fluids (see Chapter 7).

6.4.5 Galena

A total of six galena samples from the lavas (2), the VCR (1), and DGG zone footwall quartzite (3) were analysed for galena chemistry in the research area (Table 6-10). The principal substitutions are as follows:

Pb: Ag, Bi, Cu, Zn, Sb,

S: As,

Galena is characterized by enrichment of Ag (from 700 ppm to 2000 ppm), and Bi (200 to 3000 ppm) (Table 6-7). The chemical formula of galena can be presented as:



The bivariate plots of selected elements for authigenic galena in different rocks in the VCR show that the chemical compositions vary among the host rocks and alteration zones (Fig. 6-12). For example, Bi and Ag are most enriched in the DGG zone footwall quartzite, but Zn in the VCR and DGG zone quartzite (Fig. 6-12b, c, e, f).

6.4.6 Pentlandite

Five samples of pentlandite from the lava (1), the DGG zone footwall quartzite (1), GG zone footwall quartzite (2), and AGNQ internal quartzite (2) were analysed (Table 6-11). The principal substitutions are as follows:

Fe (wt%): Ni (31,56), Co (4,323), Cu (0,124),

Table 6-10 Chemical composition of galena from the VCR

		GALENA						SUMMARY SHEET							
		Lava		VCR	DGG zone quartzite			lava		VCR		DGG		Total	
		RI	BHF-2	B0410a	B0384	XR1646	B0372	AVG	STD	AVG	STD	AVG	STD	AVG	STD
wt%	Pb	87,26	87,31	87,43	87,22	86,36	85,92	87,28	0,02	87,43	0,45	86,501	0,5381	86,916	0,5655
	Sb	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,0019	0,0015	0,0014	0,0013
	Ag	0,08	0,10	0,07	0,15	0,08	0,50	0,09	0,01	0,07	0,05	0,2433	0,1847	0,1631	0,1534
	Bi	0,04	0,01	0,07	0,01	0,02	0,79	0,02	0,02	0,07	0,06	0,2752	0,3673	0,1569	0,286
	Cu	0,00	0,00	0,01	0,00	0,01	0,00	0,00	0,00	0,01	0,02	0,0036	0,0039	0,0051	0,0041
	Zn	0,00	0,00	0,26	0,01	0,02	0,11	0,00	0,00	0,26	0,12	0,0448	0,044	0,0652	0,0925
	S	13,42	13,29	13,24	13,42	13,08	13,25	13,36	0,06	13,24	0,13	13,254	0,1388	13,286	0,1159
	As	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
	Totals	100,81	100,70	101,08	100,81	99,58	100,58	100,76	0,05	101,08	0,44	100,32	0,5336	100,59	0,478
mole	Pb	0,42	0,42	0,42	0,42	0,42	0,41	0,42	0,00	0,42	0,00	0,4175	0,0026	0,4195	0,0027
	Sb	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	2E-05	1E-05	1E-05	1E-05
	Ag	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,0023	0,0017	0,0015	0,0014
	Bi	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,0013	0,0018	0,0008	0,0014
	Cu	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	6E-05	6E-05	8E-05	6E-05
	Zn	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,0007	0,0007	0,001	0,0014
	S	0,42	0,41	0,41	0,42	0,41	0,41	0,42	0,00	0,41	0,00	0,4134	0,0043	0,4144	0,0036
	As	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00

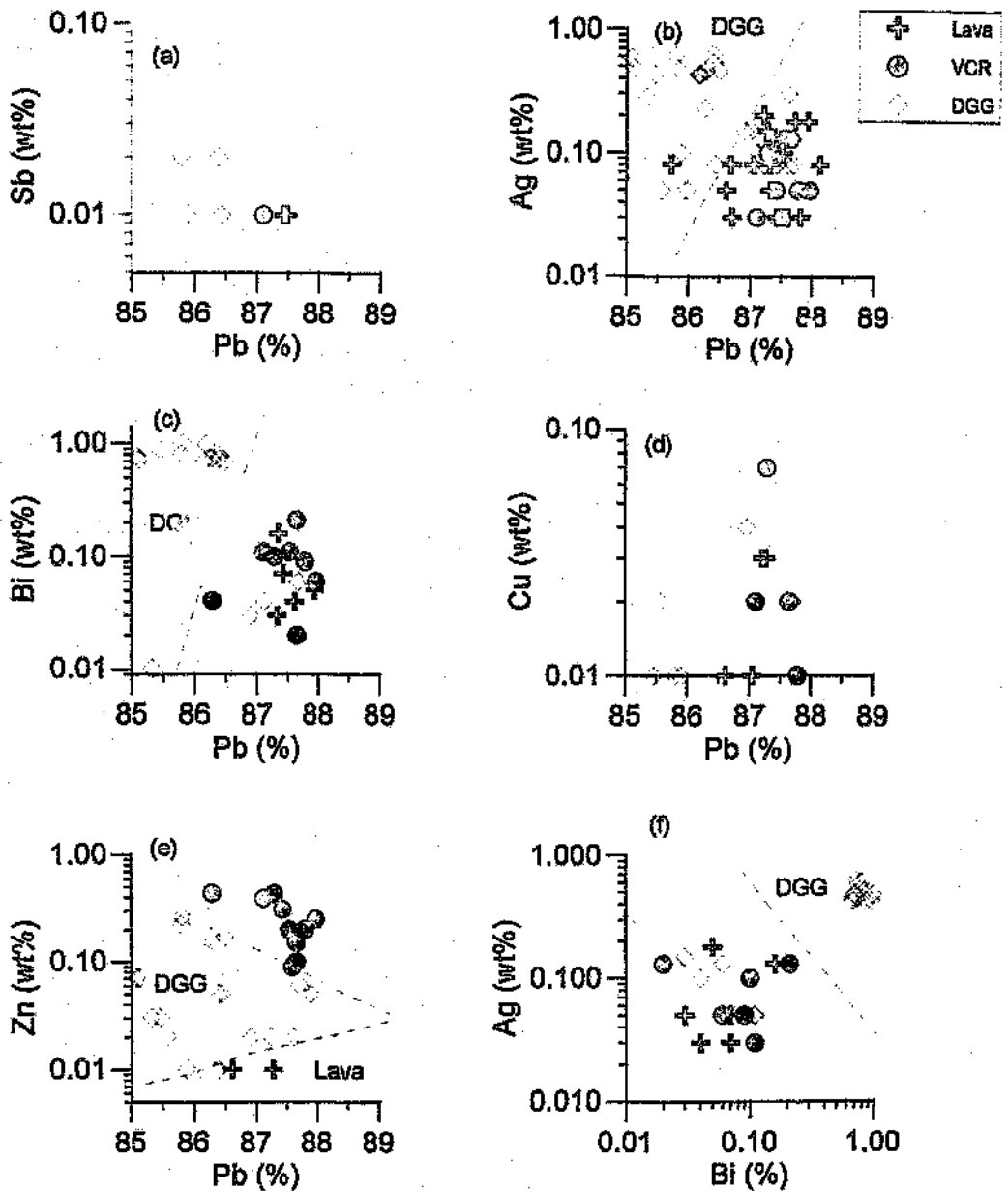


Fig. 8-12 Bivariate plots of selected elements (wt%) for authigenic galena in the different host rocks from the VCR.

										SUMMARY SHEET						
		Lava	VCR	GG zone quartz		AGNQ		Lava		VCR		AGNQ		Total		
		BHF-2	B0415	BHL-1	B0379	B0417	B0407	AVG	STD	AVG	STD	AVG	STD	AVG	STD	
wt%	Fe	20,41	31,14	30,52	30,1	30,28	31,79	20,41	1,21	31,14	0,10	31,04	0,76	29,04	3,9	
	Co	16,74	0,10	4,83	1,77	0,49	2,02	16,74	0,21	0,10	0,01	1,25	0,77	4,323	5,75	
	Ni	25,06	33,94	31,08	32,99	34,84	31,47	25,06	0,14	33,94	0,15	33,15	1,69	31,56	3,19	
	Cu	0,74	0,00	0,00	0,00	0,00	0,00	0,74	0,28	0,00	0,01	0,00	0,00	0,124	0,28	
	S	33,57	32,68	33,38	33,41	34,68	33,37	33,57	0,18	32,68	0,16	34,03	0,66	33,52	0,59	
	Se	0,02	0,01	0,02	0,02	0,04	0,02	0,02	0,02	0,01	0,01	0,03	0,01	0,02	0,01	
	As	0,00	0,00		0,39	0,04	0,00	0,00	0,00	0,00	0,00	0,00	0,02	0,02	0,085	0,15
	Total	96,54	97,86	99,83	98,66	100,36	98,66	96,54	1,17	97,86	0,32	99,51	0,85	98,65	1,25	
mole	Fe	0,37	0,56	0,55	0,54	0,54	0,57	0,37	0,02	0,56	0,00	0,56	0,01	0,52	0,07	
	Co	0,30	0,00	0,09	0,03	0,01	0,04	0,30	0,00	0,00	0,00	0,02	0,01	0,077	0,1	
	Ni	0,43	0,58	0,53	0,56	0,59	0,54	0,43	0,00	0,58	0,00	0,56	0,03	0,538	0,05	
	Cu	0,01	0,00	0,00	0,00	0,00	0,00	0,01	0,00	0,00	0,00	0,00	0,00	0,002	0,00	
	S	1,05	1,02	1,04	1,04	1,08	1,04	1,05	0,01	1,02	0,00	1,06	0,02	1,045	0,02	
	Se	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,000	0,00	
	As	0,00	0,00	0,00	0,01	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,001	0,00	

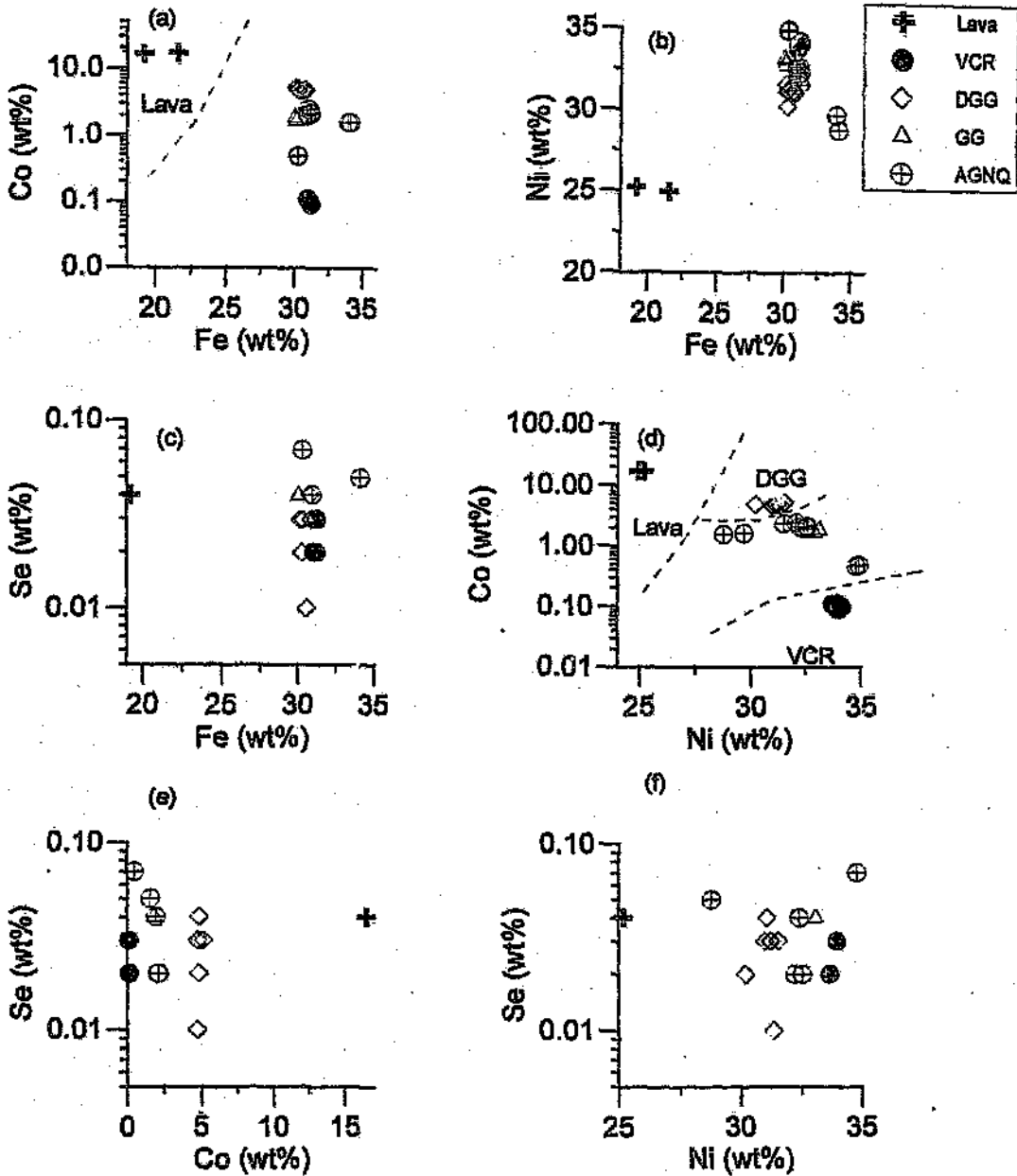


Fig. 8-13 Bivariate plots of selected elements (wt%) for pentlandite in the different host rocks from the VCR.

S: Se (0,02), As (0,085).

The chemical formula can be presented as:



Plots of the selected elements for pentlandite in different host rocks in the VCR show that Co is enriched in lava samples, but depleted in the VCR (Fig. 6-13a). Ni is enriched in the VCR and some of the AGNQ internal quartzite (Fig. 6-13b). The samples from different host rocks and alteration zones are distinctive in Co versus Ni (Fig. 6-13d). It is suggested that the Co and Ni chemistry of the pentlandite is strongly controlled by its host rocks and alteration zones.

6.5 Summary

Chemical compositions of the two phyllosilicates (chlorite, muscovite) and silicate (albite) and sulphides are, almost all, variable among different rock types and alteration zones. This is due to the influence of the original rock geochemistry. It is suggested that these authigenic minerals were formed in a rock-dominated system. At least two types of chlorite (sudoite and ripidolite) are identified in the VCR and the Witwatersrand Basin, which represent different environments and possibly different generations. Authigenic muscovite and detrital muscovite display similar major geochemistry, suggesting that the detrital muscovite was strongly effected by hydrothermal fluids during alteration. Calcite and siderite are the two types of carbonates in the VCR. Detrital pyrite is a tracer for the source of sulphides from the Witwatersrand reefs due to its clearly distinguishable chemical features compared to authigenic pyrite in terms of the Co/Ni ratio. Banding of sphalerite is probably due to fluid infiltration during hydrothermal alteration. Enrichment of Ag in authigenic galena and some chalcopyrite is indicative of remobilization of precious metals (Ag, Au?). Equilibrium temperature of pyrite and pyrrhotite is estimated to be about 400 °C using the deficit percentage of Fe in pyrrhotite and seems unrealistic.

7 PHYSICOCHEMICAL CONDITIONS OF ALTERATION IN THE VENTERSDORP CONTACT REEF

7.1 Introduction

7.1.1 General statement of metamorphism in the Witwatersrand Basin

All the rocks of the Witwatersrand Supergroup and Ventersdorp Supergroup were metamorphosed to greenschist facies (Phillips *et al.*, 1989, Frimmel, 1994, 1997) within the Witwatersrand Basin, but higher metamorphic grades (up to granulite facies) were reached in the center of the Basin and the Vredefort structure (Gibson and Stevens, 1997). Typical mineral assemblages in the marginal metamorphosed rocks of the Witwatersrand Basin are pyrophyllite-chloritoid-muscovite-quartz-rutile-tourmaline-pyrite, which implies conditions of 350 ± 50 °C and less than 3 kbar (Phillips *et al.*, 1989, Wallmach & Meyer, 1990; Law, 1990, Frimmel *et al.*, 1993; Frimmel, 1994, 1997; Phillips & Law, 1997).

Based on the experimental calibration of biotite break-down during granulite facies metamorphism maximum temperature of up to 880 to 910 °C, and a wide range of pressures of between 4,8 and 5,1 kbar are suggested for rocks in the centre of the Witwatersrand Basin (Stevens *et al.*, 1996). During peak metamorphism, a high geothermal gradient of around 35-40 °C/km, is considered to have applied (De Yoreo *et al.*, 1991, Gibson & Stevens, 1995).

7.1.2 Fluid evolution in the Witwatersrand Basin

Based on studies of geochemistry and geothermometry, and summaries of previous publications

of metamorphism and fluid conditions in the Witwatersrand Basin (e.g. Wallmach & Meyer, 1990; Robb et al., 1990, 1996; Phillips & Law, 1994; Gibson & Wallmach, 1995; Coetzee et al., 1996; Gibson & Stevens, 1995; Gartz, 1996), Frimmel (1994, 1997) categorized the metamorphism and fluid evolution in the Witwatersrand Basin into five events:

(Stage 1) thrust controlled pre-Transvaal alteration took place along the northern margin of the Witwatersrand Basin, forming a mineral assemblage of kyanite+pyrophyllite+quartz at a formation temperature of 390–400 °C and a pressure of >2,5 kbar (Coetzee et al., 1996). However, the age of the metamorphism related to thrusting is not well constrained;

(Stage 2) early Transvaal alteration took place in the Witwatersrand Basin at 300 °C and 3 kbar at a geothermal gradient of 27 °C/km. Zircon inclusions in hydrothermal gold-bearing quartz from the Basal Reef, Welkom gold field have been dated, using the SHRIMP technique, at 2,58 Ga (R. Armstrong, unpubl. data), which is similar to the age of the authigenic/hydrothermal rutile and pyrite at ca. 2,5 Ga in the Promise Reefs reported by Robb et al. (1990),

(Stage 3) basin wide burial metamorphism took place in the matrix of all the siliciclastic rocks and metabasites of the Witwatersrand and Ventersdorp Supergroup at peak T-P conditions of 300 °C and 3 kbar, with a geothermal gradient of 28 ± 7 °C/km. Available U-Pb isotopic analyses of bitumen from the Witwatersrand reefs yield an age between 2,2 and 2,3 Ga (Robb et al., 1996), which roughly coincides with the onset of deposition of the upper Transvaal Supergroup. Fluids were characterized by (1) movement upwards and towards the basin margin; (2) losses of a large amount of interstitial and structural bound waters (up to 20 vol%) (Stevens et al., 1996);

(Stage 4) thermal metamorphism in the collar of the Vredefort Dome ranged up to middle

amphibolite facies grades at 570-600 °C and $\leq 3,5$ kbar with a peak thermal gradient of 40 °C/km (Gibson & Stevens, 1995). At this stage (Stage 4) and the later stage (Stage 5), fluid flow was characterized by: (1) devolatilization reactions; (2) release of structurally bound water from clay minerals (up to 12 vol%); and (3) movement along fracture channels (Stevens et al., 1996);

(Stage 5) hydrothermal alteration related to the Vredefort Dome in the middle of the Witwatersrand Basin took place at 2023 Ma (Kamo et al., 1996) and was characterized by intense fracturing in the surrounding rocks; enrichment of pseudotachylites; and precipitation of chlorite.

7.1.3 Aims of this chapter

The aims of this chapter are to document the characteristics of metamorphism and hydrothermal alteration associated with the VCR. In order to better understand and discuss the analyzed data obtained during this study, previous publications on muscovite and chlorite geochemistry, geothermometries and fluid inclusions in the Witwatersrand Basin are briefly summarized. T-P parameters, together with f_{O_2} , f_{S_2} , $f_{H_2S(g)}$, $a_{H_2S(aq)}$, and pH of hydrothermal fluids passing through the VCR are estimated using muscovite and chlorite geothermometers and fluid inclusion microthermometric data.

7.2 Muscovite geothermometer

7.2.1 Summary of muscovite crystal chemistry

Guidotti and Sassi (1976) summarized the structure of the muscovite crystal as:

(a) a dioctahedral sheet with the octahedral sites containing Al^{+3} ; (b) sheets of $(Al_3 Si_{1.5} O_5)$ tetrahedral (in a pseudohexagonal arrangement) on both sides of the octahedral sheet forming a

"sandwich"; (c) large K^+ cations in the pseudohexagonal gaps between the tetrahedral sheets. Each K^+ ion is shared by two "sandwiches"; and serves to bond them together. The K^+ sites are called "interlayer sites" or "alkali sites" and (d) those oxygens of the dioctahedral sheet which lie almost directly below the K^+ site have an H^+ ion attached to them. Virtually all muscovites deviate from the ideal formula of $KAl_2(AlSi_3O_{10})(OH)_2$ (Deer et al., 1992) in one or more of the following fashions: (a) Na^+ can replace K^+ in the interlayer sites at least to the extent of 35% on a mole basis (Burnham & Radoslovich, 1964) and this replacement produces a decrease in the basal spacing of muscovite; and (b) Fe^{+2} and Mg^{+2} can replace Al^{+3} in octahedral sites with concomitant replacement of Al^{+3} by Si^{+4} in tetrahedral sites to balance the charges. Muscovites with significant octahedral Fe^{+2} and Mg^{+2} are described as "celadonitic" and represent partial solid-solution toward celadonite (the dioctahedral, tetrasilicic mica). Celadonite-bearing muscovites have a larger lateral spacing b_0 than celadonite-free muscovite.

7.2.2 Principle of muscovite geothermometers

Plas (1959) explained the formation of celadonitic muscovite in the following way:



It is evident that temperature has an important influence on the celadonite content of muscovite. Based on the experimental work of Velde (1965), a schematic diagram of temperature against the mole fraction of $K[(Al, Mg)Si_4O_{10}(OH)_2]$ with isobaric sections has been constructed (Guidotti & Sassi, 1976) and shows that there is a negative correlation between the celadonite content and fluid temperature for a given pressure (Guidotti & Sassi, 1976).

As described in Chapter 4, Loucks (1991) has developed a model to calculate muscovite-hydromuscovite-hydropyrophyllite solid-solutions. Estimation of mole fractions of celadonite of

muscovite makes it possible to estimate the temperatures of formation of muscovites using the experimental results of Velde (1976).

7.2.3 Sammel diagram and methodology

Phyllosilicate muscovite shows very little polymorphic variation and the most common lattice units are a 5,19Å; b 9,04Å; c 20,08Å, β 95° 30' (Deer, et al., 1992). However, the lattice parameters (b , c and β) are sensitive to temperature and pressure (Sasonov, 1995, pers. communication). Two schematic diagrams have been constructed based on experimental results on muscovite parameters (Sasonov, 1995, pers. communication).

The basic principle for measuring the lattice units (b_0 , c_0 , β_0) is very similar to ordinary XRD analysis. The prepared materials for analysis are fine-grained rock powders which are loaded on a carrier plate. Measurements were made using a Siemens D5000 diffractometer analyzer with CuK α radiation. The purpose of the XRD measurement was to examine the composition and polytypes of muscovite, to calculate lattice constants, and then to estimate temperatures and pressures for the formation of muscovite.

7.2.4 Descriptions of samples

21 samples were taken from the VCR, as well as the lavas and quartzites, and gently crushed using a laboratory jaw crusher. The samples were separated using natural precipitation techniques at the CGS in Strasbourg, France. All the samples contain mainly muscovite and chlorite with minor amounts of quartz.

7.2.5 Results

Lattice constants of muscovite were calculated from 21 samples based on qualitative XRD analyses (Table 7-1). These were plotted on the Sammel diagram to estimate temperatures and pressures of muscovite (Fig. 7-1) (Sasonov, 1995, pers. communication). Two types of muscovite were identified as the 2M1 and 1M polytypes (Fig. 7-1), of which 2M1 muscovite is the major type. The 2M1 polymorph represents the twelve-fold coordinated positions between composite layers and the stacking of successive layers (Deer et al., 1966) and forms during higher grade metamorphism than the 1M (or 1Md) structure which forms in the epithermal environment during low grade metamorphism.

In Fig. 7-1, the pressures and temperatures of formation of 2M1 polytype muscovite are estimated to range from 0,5 to 2 kbar, and 200 to 450 °C, respectively, with an average of 350 ± 55 °C. The average pressure can not be determine due to the semi-quantitative nature of the data. Pressures and temperatures of 1M type muscovite were estimated to range from 0,2 to 0,5 kbar, and 130 to 220 °C, with an average temperature of 155 ± 45 °C. Similarly the average pressure is not estimated due to the same reason cited above.

7.2.6 Interpretation of the data

As discussed in Chapter 4, three types of muscovite have been determined by optical microscopy. They are in paragenetic sequence: (Ms1) coarse-grained detrital muscovite; (Ms2) recrystallized flaky fine-grained muscovite; and (Ms3) coarse flaky hydrothermal muscovite and pseudomorphs after albite. Ms1 is relatively rare and often replaced by secondary chlorite along cleavages. It belongs to 2M1 due to its coarse grain size. But it can be ignored due to its minor amount. Ms2 is fine-grained, illite-like material and often occurs in the matrix of conglomerates and quartzites

Table 7-1 Temperatures and pressures estimated from muscovites (2M1 and 1M)

Rock type	No	Fraction	b_c	c_c	$c_c \sin \beta$	T (°C)	P (Kb)
2M1 type muscovite							
Conglomerate	730	0-0.4 μ m	9.031	20.026	19.922	380	0.5-2
		1-2 μ m	9.016	20.033	19.933	400	0.5-2
		<2 μ m	9.004	20.043	19.942	420	0.5-2
		2-6 μ m	9.008	20.055	19.954	360	0.5-2
		6-10 μ m	9.024	20.005	19.905	450	2
DGG	731	2-6 μ m	9.002	20.069	19.967	330	0.5-2
	732	<2 μ m	9.048	20.046	19.946	250	0.5
		2-6 μ m	9.023	20.039	19.936	370	0.5-2
		6-10 μ m	9.030	20.039	19.938	330	0.5-2
	733	6-10 μ m	9.004	20.066	19.961	350	0.5-2
GG	734	<2 μ m	9.011	20.083	19.980	200	0.5
		2-6 μ m	9.005	20.066	19.961	340	0.5-2
		2-6 μ m	9.002	20.072	19.970	320	0.5-2
	736	<2 μ m	9.016	20.055	19.951	340	0.5-2
		2-6 μ m	9.004	20.062	19.961	350	0.5-2
		6-10 μ m	9.011	20.055	19.951	360	0.5-2
AGNQ	737	<2 μ m	9.024	20.032	19.927	380	0.5-2
		2-6 μ m	9.043	20.011	19.909	370	0.5-2
Average $\pm 1\sigma_1$			9.017 $\pm$ 0.014	20.0473 $\pm$ 0.0209	19.9452 $\pm$ 0.0201	350 $\pm$ 55	0.5-2
1M type							
Conglomerate	729	<2 μ m	9.006	20.111	20.007	<100	0.2-0.5
DGG	020	2-10 μ m	9.017	20.081	19.974	220	0.5
GG	735	<2 μ m	9.008	20.094	19.991	130	0.2-0.5
		2-6 μ m	9.022	20.084	19.979	170	0.2-0.5
Average $\pm 1\sigma_1$			9.0133 $\pm$ 0.0065	20.0925 $\pm$ 0.0117	19.988 $\pm$ 0.013	155 $\pm$ 45	0.2-0.5

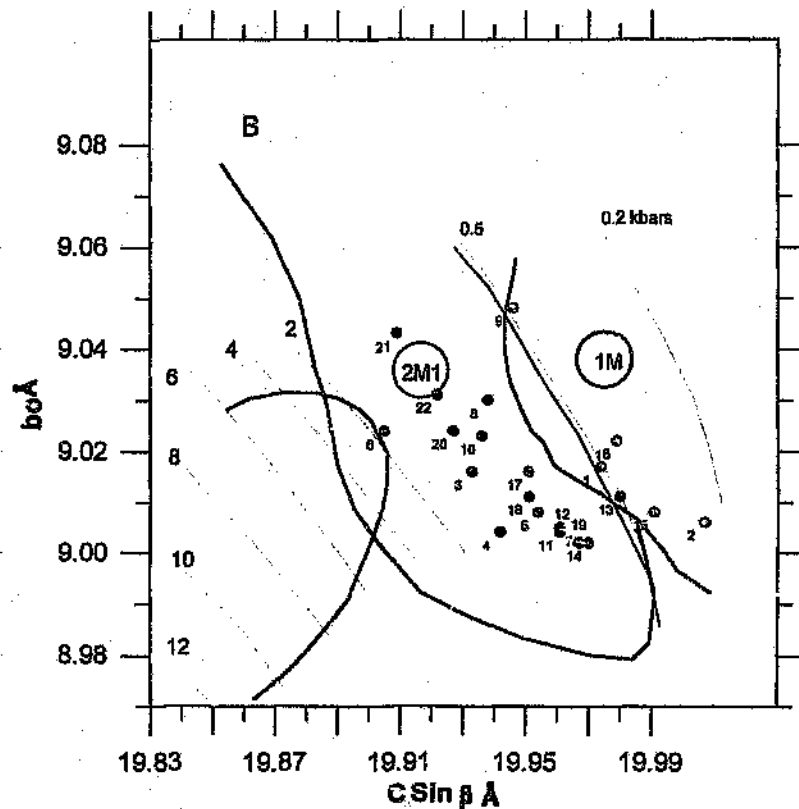
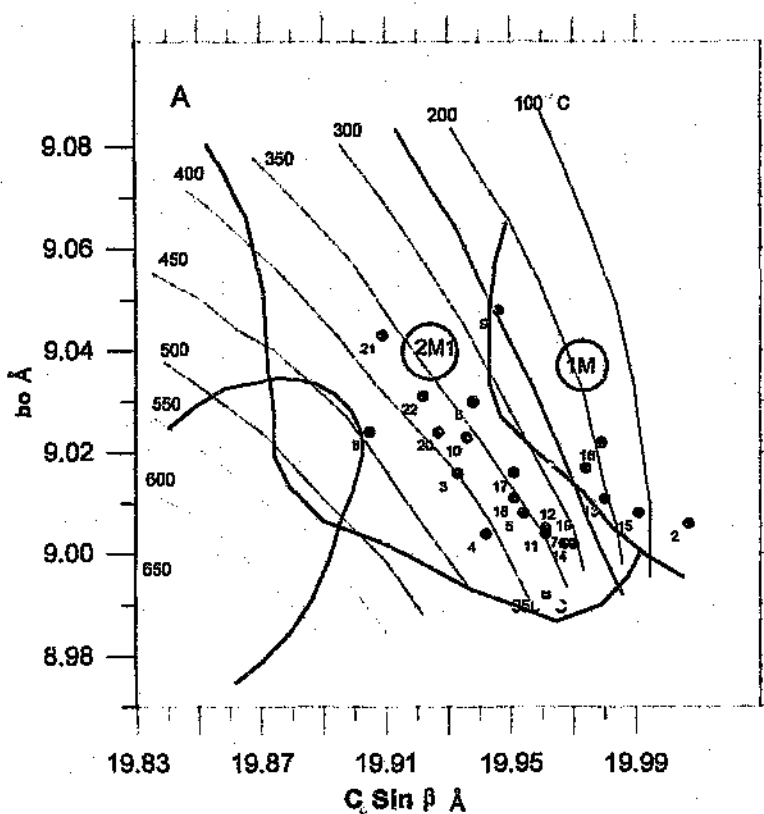


Fig. 7-1 Plots of muscovite cell parameters of $c \sin \beta$ (Å) vs b_0 (Å) with projected temperature isochores (A) and pressure isochores (B), showing the muscovite polytypes (1M and 2M1) (Sasnov, 1995, pers. communication). From these plots, muscovite formation temperatures and pressures were estimated at 350 ± 55 °C and 0,5 - 2 Kb from the 2M1 polytype, and 155 ± 45 °C and 0,2 - 0,5 Kb from 1M the polytype, respectively.

as well as in lava. It probably represents a late authigenic phase in the rocks. Based on this character, Ms2 is most probably a representative of the 1M type muscovite (illite). Ms3 is the major phase of muscovite in the sediments and in the lavas and is coarse-grained. Based on the coarse grained characteristics, it can be excluded from 1M type muscovite.

In comparison with the five stages of fluid evolution in the Witwatersrand Basin (Frimmel, 1993, 1997), the 2M1 type of muscovite probably represents the hydrothermal alteration related to the Vredefort Dome and Bushveld magmatism (Stage 4) with peak T-P conditions of 350 ± 55 °C and 0,5 to 2 kbar. The 1M type muscovite may represent either remnant of equilibration at the stage 3 or later retrograde metamorphism with lower T-P conditions of 155 ± 45 °C and 0,2-0,5 kbar (see Chapter 10).

7.3 Chlorite geothermometer

Definition of the physicochemical conditions of formation of hydrothermal minerals is commonly difficult to achieve. Recent experimental and theoretical work on chlorite solid solutions (e.g. Bryndzia, 1985; Cathelineau, 1988; Neall, 1985; Walshe, 1986) have provided activity-composition models which can be utilized as an indicator of environmental conditions. Because of its nonstoichiometry, chlorite, when fully characterized, compositionally, structurally and thermodynamically records information on physicochemical conditions. This, in turn, allows determination of fluid conditions under which the chlorite formed. Additionally, in contrast to many sulphide assemblages and compositions, chlorite has been found to preserve its peak composition and does not re-equilibrate during retrograde conditions (F. M. Meyer, 1990, pers. Communication). Moreover, chlorite is a common product of fluid-rock interaction and is present in all the Witwatersrand reefs. Therefore it should be possible to constrain the physicochemical conditions of chlorite formation during hydrothermal processes in the VCR.

Meyer et al. (1990a) pioneered the study of chlorite compositions in some of the Witwatersrand reefs, with particular emphasis on the application of the compositions to chlorite geothermometry. Using the six component chlorite solid-solution model of Walshe (1986), the authors estimated temperatures of chlorite formation in several Witwatersrand reefs. These are: (1) 290 ± 20 °C in the VCR; 310 ± 15 °C in the Elsburg Reefs; 330 ± 20 °C in the Vaal Reefs and the Main/Carbon Leader Reefs.

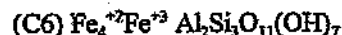
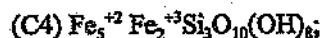
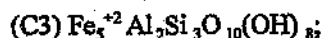
Drennan (1997) analyzed forty one chlorite samples from the edges of quartz veins, within veins and from the adjacent wall-rock matrix using the electron microprobe. She estimated the temperatures of formation of chlorites to be at 275 ± 40 °C (from 200 °C to 350 °C) using the six-component chlorite solid-solution model of Walshe (1986) and 300 ± 29 °C (uncorrected for Fe content) and 330 ± 55 °C (corrected for Fe content) using the experimental geothermometers of Cathelineau (1988).

Sudoite, with the almost ideal composition of $\text{Mg}_2\text{Al}_4\text{Si}_3\text{O}_{10}(\text{OH})_8$ has been reported in the Khaki shale of the Witwatersrand Basin by Zhou and Phillips (1994). The sudoite occurs in aggregates of elongate bundles alternating with muscovite and rarely pyrophyllite, in an assemblage of sudoite - pyrophyllite - muscovite - quartz - rutile - pyrite. Frimmel (1993, 1997) studied chlorites from various localities and stratigraphic zones and suggested that sudoite is a common and petrologically significant constituent of the Witwatersrand siliciclastic rocks. The author has constrained the fluid T-P conditions and geothermal gradient in the Witwatersrand Basin using the geothermometers of Kranidiotis & MacLean (1987), Cathelineau (1988), and Zang and Fyfe (1995) and emphasized the major differences in chlorite temperatures estimated

from different calibrations. These may be constrained by other independent methods, such fluid inclusion microthermometry and phase relations.

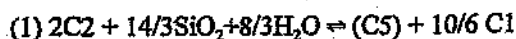
7.3.1 Principles of chlorite geothermometry and methodology

Chlorites are a group of minerals with the principle chemical composition of $(\text{Mg}, \text{Al}, \text{Fe})_{12}[(\text{Si}, \text{Al})_8\text{O}_{20}](\text{OH})_{16}$ (Deer et al., 1992). The basic structure of chlorites consists of 2:1 layers, $\text{Y}_3\text{Z}_4\text{O}_{10}(\text{OH})_2$, and interlayers, $\text{Y}_3(\text{OH})_6$. Chlorites are isochemical with both serpentine (C1) and kaolinite (C5). Based on Walshe (1986), six thermodynamic components of chlorites can be presented as follows:



Thermodynamic data for the six components (C1, C2, C3, C4, C5 and C6) were estimated making use of constraints imposed by the compositions of chlorites from the Salton Sea and Broadlands geothermal systems; the OH vein, Creede, Colorado; the Quaama granodiorite, New South Wales; and a metamorphic vein, Mt. Lyell, Tasmania.

Two geothermometers have been calibrated and these together with the constraints imposed by the Gibbs-Duhem equation allow the temperature of formation to be calculated:



Calculation of the temperatures of formation of chlorites was undertaken using the computer programmes of CH-1 (Walshe, 1987) and CHLORITE (Delpont, 1987).

7.3.2 Sample descriptions

53 samples were collected from the VCR, the lavas and quartzites at WDLMS. As described in Chapter 4, five types of chlorites were identified: (Ch1) fine-grained matrix-like massive aggregates in the matrix of conglomerates and quartzites and in the matrix and replacement of plagioclase phenocrysts in lavas; (Ch2) replacement of detrital muscovite by chlorite along its cleavage in sediments; (Ch3) chlorite nodules found mainly in altered conglomerates which are an indicator for high gold concentration in the VCR; (Ch4) chlorite occurring as fine-grained aggregates replacing phenocrysts of plagioclase in lavas (Ch5) infilling of amygdaloids with light green colour and coexisting with quartz, and calcite. Among them, only the coarse-grained varieties of chlorite (Ch2, 3) were used to estimate the temperature of formation of chlorites in different lithologies during this study. The electron microprobe data were carefully assessed based on the following conditions: (1) the absence of iron-rich chlorite and (2) the rejection of poor quality probe results.

7.3.3 Results

Based on the two geothermometers of Walshe (1986), the temperatures of formation of hydrothermal chlorites were estimated using the CHLORITE programme, developed by Delpont (1987) and the Ch-1 programme, developed by Walshe (1987). The results of the two different chlorite geothermometers (Walshe, 1986) and the petrographic characteristics of the chlorites are summarized in terms of lithology and chlorite type in Table 7-2.

Table 7-2 Temperatures estimated from the six-component chlorite solid solution model of Walshe (1986)

Rock type	No	Analysis No	T ₁ (°C)	T ₂ (°C)	Character
Conglomerate	VCR-1-33	43	282	312	Dark green colour, Ch3
	B0378-17	30	297	329	Dark green colour, Ch3
	18	31	308	345	Dark green colour, Ch3
	19	33	301	335	Dark green colour, Ch3
	20	34	281	302	Dark green colour, Ch3
	21	35	298	331	Dark green colour, Ch3
	22	38	293	323	Dark green colour, Ch3
	23	39	309	344	Dark green colour, Ch3
	24	40	285	308	Dark green colour, Ch3
	Average		295±11	325±16	
Quartzites	I0705-1	7	287	320	Dark green colour, Ch3
	2	8	283	316	Dark green colour, Ch3
	3	12	321	366	Dark green colour, Ch3
	4	15	289	326	Dark green colour, Ch3
	6	17	296	335	Dark green colour, Ch3
	10	27	305	345	Dark green colour, Ch3
	12	31	309	352	Dark green colour, Ch3
	B0415-25	42	268	290	Dark green colour, Ch3
	26	44	286	286	Dark green colour, Ch3
	27	46	269	285	Dark green colour, Ch3
	I0713-32	52	270	300	Dark green colour, Ch3
	B0361-36	36	293	324	Dark green colour, Ch3
	37	37	312	353	Dark green colour, Ch3
	38	41	279	304	Dark green colour, Ch3
	39	42	304	341	Dark green colour, Ch3
	40	47	294	327	Dark green colour, Ch3
	42	49	313	352	Dark green colour, Ch3
	52	83	305	346	Dark green colour, Ch3
	53	84	316	359	Dark green colour, Ch3
	55	86	296	334	Dark green colour, Ch3
	B0368-56	5	274	303	Dark green colour, Ch3
	57	6	270	299	Dark green colour, Ch3
	58	13	286	316	Dark green colour, Ch3
	59	14	270	294	Dark green colour, Ch3
	60	15	257	278	Dark green colour, Ch3
	61	23	288	323	Dark green colour, Ch3
	62	24	260	283	Dark green colour, Ch3
	63	28	278	301	Dark green colour, Ch3
	64	34	289	324	Dark green colour, Ch3
	Average		289±18	320±26	
	Summary		290±16	321±24	
Quartzite	B0365-48	76	262	289	Replacement of detrital muscovite, Ch2
	49	79	265	293	Replacement of detrital muscovite, Ch2
	50	80	209	230	Replacement of detrital muscovite, Ch2
	Average		245±32	271±36	
Lava	Bh002-43	6	290	310	In amygdalae, Ch4
	46	10	258	271	In amygdalae, Ch4
	15	73	311	311	In amygdalae, Ch4
	Average		286±27	297±23	

Note T₁ calculated using the CHLORITE computer programme, T₂ calculated using the CH-1 computer programme.

Using CHLORITE, the temperatures of formation of chlorite (Ch3) as nodules in the VCR ranges from 282 to 309 °C with an average of 295 ± 11 °C; in quartzites, from 257 to 313 °C with an average of 289 ± 18 °C; as replacement of detrital muscovite (Ch2) in quartzites, from 209 to 265 °C with an average of 245 ± 16 °C; as amygdales in lavas, from 258 to 311 °C with an average of 286 ± 27 °C; and 290 ± 16 °C on average in sediments (VCR conglomerates and quartzites).

Using CH-1, temperatures of formation of chlorites were determined to be systematically about 30 °C higher than the temperatures determined using CHLORITE. These are from 302 to 345 °C with an average of 325 ± 16 °C as nodules in the VCR; from 283 to 359 °C with an average of 320 ± 26 °C as nodules in quartzites; from 230 to 293 °C with an average of 271 ± 36 °C as replacement of detrital muscovite (Ch2); and from 271 to 311 with an average of 297 ± 23 °C in amygdales (Ch4) of lavas; and 271 ± 36 °C on average in sediments (VCR conglomerates and quartzites).

7.3.4 Interpretation of the data

Firstly, it can be seen that the temperature difference calculated using the two calibrations can be as much as 30 °C. This is quite similar to the results of Frimmet (1997) who stated that the difference in temperatures determined using different geothermometers, e.g. Kranidiotis and Maclean (1967), Cathelineau (1988), Zang and Fyfe (1995), can be up to 143 °C. However, the chlorite temperatures calculated from CHLORITE are in good agreement with the temperature of 290 ± 20 °C for the VCR from Meyer et al. (1990) and about 15 °C higher than those from

Drennan (1997) (275 ± 40 °C, fi. 100 °C to 350 °C) using the same model of Walshe (1986). By contrast, the temperatures estimated using CH-1 are closer to the 2M1 muscovite temperatures (350 ± 55 °C) and also to the results (330 ± 55 °C) estimated from the Fe-corrected model of Cathelineau (1988) by Drennan (1997).

Secondly, it seems that nodule chlorite (Ch3) formed at a much higher temperature in the VCR and footwall quartzites than the replacement of detrital muscovite (Ch2). Although no clear phase relationship has been identified between the two types of chlorites, it clearly indicates that the two types formed at different temperatures. The Ch2 may coexist with the low temperature phases of 1M muscovite as discussed above. If that is the case, the Ch2 represents the low temperature assemblage with the 1M muscovite.

Thirdly the average temperatures are the highest on average in the VCR while the temperatures in the hanging wall lava are the lowest. Because of the fine grain size of chlorite (Ch1) from lavas, the chemical compositions may be contaminated by fine-grained quartz and muscovite during the microprobe analysis. This may result in imprecise chemical compositions of Ch1. Therefore the data may not be reliable for the lavas. If the 5 °C difference between the VCR and footwall quartzites is geologically correct, the average temperatures of the sediments (VCR conglomerates and quartzites) are probably representative of the peak metamorphism. Therefore, the average temperature of formation of chlorites in the VCR and footwall quartzites of 290 °C estimated from CHLORITE, can be taken as the minimum temperature of peak metamorphism of the VCR, and the temperature of 321 °C estimated from CH-1, can be taken as a reference for the higher limit of the VCR because the formation temperatures (350 °C) for 2M1 muscovite indicates the highest limit for peak metamorphism as presented above.

7.4 Fluid inclusions

7.4.1 Previous work on fluid inclusions in the Witwatersrand Basin

Fluid inclusion study of the Witwatersrand reefs was carried out by Shepherd as early as 1977. He recognized five principal types of primary fluid inclusions in quartz pebbles in the Witwatersrand conglomerates. These are: (I) H_2O (L+V); (II) H_2O (L+V+S); (III) CO_2 - H_2O (L- CO_2 -L- H_2O -V); (IV) CO_2 - H_2O (L- CO_2 -L- H_2O -V-S) and (V) L or V. Total final homogenization temperatures of primary fluid inclusions were over 250 °C (Shepherd, 1977). Somewhat later, Hallbauer (1982a, b; 1983) and Hallbauer & Kable (1979; 1982) published a series of papers on pre- and post-depositional fluid inclusion types from quartz pebbles in the Witwatersrand reefs. One of the major results was the recognition of numerous solid phases in fluid inclusions of both quartz and pyrite by SEM, including orthoclase, muscovite, calcite, apatite, iron-rich phyllosilicates, barium feldspar, chlorite, rutile, corundum, anhydrite, cassiterite and various mixed chlorides, e.g. $CaCl_2$ (Hallbauer & Kable, 1979; 1982).

Frimmel et al. (1993) studied fluid inclusions in authigenic quartz in the matrix of the Basal reef placer from the Welkom gold field and recognized three different post-depositional alteration events and fluid activities: (1) regional static recrystallization at peak metamorphic temperatures of between 290 ° and 350 °C and pressures of between 2 and 3 kbar; (2) local fluid infiltration along fractures and sedimentary interfaces at temperatures of between 240 ° and 300 °C, resulting in partial mobilization of the detrital gold on a maximum scale of centimeters; and (3) local K^+ metasmatism during a later fluid infiltration event along the pre-existing zones of weakness, related to the Bushveld or Vredefort events. Both the primary and secondary fluid inclusions are mainly two-phase undersaturated liquid-rich aqueous types (L+V), with rare three-phase H_2O -

CO₂-rich (L_{H₂O}-L_{CO₂}-V) inclusions. The microthermometric data of primary fluid inclusions can be summarized as: homogenization temperature (T_h) = 134±7 °C; final ice melting temperature (T_{fm}) = -7±0,8 °C; salinity=12 wt% eNaCl and of secondary aqueous (L+V) inclusions: T_h = 137±5 °C; T_{fm} =0,9±0,8 °C (ice); salinity = 1,5 - 1,4 wt% eNaCl.

Most recently, Drennan et al. (1995) and Drennan (1997) carried out a detailed study of fluid inclusions mainly from three types of post-depositional quartz veins in the Witwatersrand conglomerates. These are (1) vein/"vug" infilling associated intrusives; (2) fault-related quartz veins; and (3) non fault-related quartz veins. The authors recognized at least four types of metamorphic/hydrothermal fluid inclusions in different veins associated with the Witwatersrand gold-bearing reefs: (F1) aqueous-rich (L+V+S); (F2) CO₂-H₂O-rich (L_{CO₂}-L_{H₂O}-V+S); (F3) CO₂+CH₄-N₂-rich; and (F4) CH₄-N₂-rich, which gave average final homogenization temperatures of fluid inclusions at 120 °C, 170 °C, 230 °C, and 230-280 °C, respectively. The above-mentioned four fluid inclusion types can be distinguished as six inclusion populations, which may represent six possible generations of the fluid inclusions: (1) < 1 µm across and forming a wispy texture to the quartz (F1 type); (2) 1-20 µm across, varying salinity (2 to 20 wt% e NaCl) (F1 type); (3) 20-40 µm across (F2 type); (4) in trail, cross-cut the early population (F3 type); (5) 10-30 µm across, predominantly fault-related (F4 type); (6) highest salinity (F1 type). Entrapment temperatures of aqueous and CO₂-rich fluid inclusions range from 230 to 590 °C and 295 to 540 °C at 2,5 kbar, respectively. Combined with stable isotope data (S, O), Drennan (1997) concluded that these fluids were derived from the dewatering of Witwatersrand shales during metamorphism.

7.4.2 Previous work on fluid inclusions in the VCR

Boer et al. (1995) studied fluid inclusions in quartz pebbles and quartz sands in footwall and reef quartzites, and hydrothermal quartz and vein quartz in the VCR. They recognized two undersaturated water-dominated aqueous (L+V) and minor CO_2 - H_2O -rich fluid inclusions. They are: type (I) F1 type (as defined above), small in size and wispy texture, with a salinity of 10 wt% eNaCl, and homogenization temperature around 210 °C; (type II) F1 type, late-stage fluid, being 9 wt% eNaCl in salinity with homogenization temperatures of between 115 °C and 190 °C; and (type III) F2 type, with variable $\text{CO}_2/\text{H}_2\text{O}$ ratios, salinity of 4 wt% eNaCl and an average homogenization temperature of 130 °C. At the assumed pressure 2,5 kbar of Wallmach & Meyer (1990) for the fluid inclusion analyzed, Boer et al. (1995) estimated average entrapment temperatures of between 220 and 370 °C. In their study, the author further analyzed the compositions of bubbles in fluid inclusions using Raman Spectroscopy and indicated that H_2O , CO_2 and CH_4 are the predominant species with total gas contents of 99 mole%. Moreover, the quadruple mass spectrometer (QMS) analyses of the type III (CO_2 -rich inclusions) indicate that there is a good correlation between gold content and elevated volatile gas content (mainly CH_4).

7.4.3 Methodology

Microthermometric measurements of fluid inclusions together with a petrographic study were carried out in the Department of Geology, University of the Witwatersrand, Johannesburg. The procedures for fluid inclusion petrographic study is similar to the description of Drennan (1997). Fluid inclusions are studied using the normal optical transmission microscope. Types, sizes, phase volume percentages and paragenetic sequences of fluid inclusions have been observed, measured and mapped on doubly polished thin sections of approximately 300 μm in thickness, using a

detailed descriptions of the fluid inclusions, the doubly polished thin sections were demarcated and broken into pieces for microthermometric measurements.

The detailed procedure for fluid inclusion microthermometry is similar to the description of Frimmel et al. (1993) and Boer et al. (1995). The measurements of fluid inclusions have been carried out, using a FLUID INC. adapted U.S.G.S gas-flow heating-freezing system, which operates by passing cooled N_2 gas, originated from liquid N_2 , or heated air directly above and beneath the chip samples. The system was calibrated using synthetic fluid inclusions in quartz provided by SYNFLINC standards for various temperatures (Sterner & Bodnar, 1984). The reproducibility of measurements during calibrations was within $0,2\text{ }^{\circ}\text{C}$ for the $-56,6\text{ }^{\circ}\text{C}$ (the triple point of CO_2) standard, within $0,1\text{ }^{\circ}\text{C}$ for the $0,0\text{ }^{\circ}\text{C}$ (the triple point of pure water) standard, and within $2\text{ }^{\circ}\text{C}$ for the $374,1\text{ }^{\circ}\text{C}$ (the critical point of pure water) standard. Therefore, the accuracy of the system is estimated to be better than $\pm 0,2\text{ }^{\circ}\text{C}$ below $0,0\text{ }^{\circ}\text{C}$, and better than $\pm 2\text{ }^{\circ}\text{C}$ on heating samples.

The ice melting temperatures were used to calculate the salinities of fluids. The P-T isochores of the fluids were determined using the computer program FLINCOR of Brown and Lamb (1989).

7.4.4 Samples and petrography

Samples for fluid inclusion analysis were collected from amygdales of the lavas and from quartzites and post-depositional quartz veins. The fluid inclusions are very small ($1\text{--}5\mu\text{m}$). As a result, only two samples, R-1 (lava amygdales in the hanging-wall) and X0449 (quartz vein cutting through the lavas, VCR and quartzites) have been successfully studied.

The amygdales in the lavas are up to 2 cm in diameter and are characterized by clean, coarse quartz. Fluid inclusions in the amygdales mainly occur as isolated single inclusions or in groups. According to Roedder (1984), it is suggested that these fluid inclusions are primary. However, some fluid inclusions may be secondary, because it is hard to identify fluid inclusions along growth zones of quartz crystals.

Fluid inclusions in vein quartz are rare and less than 5 μm in size. They occur as isolated inclusions, or in groups. These fluid inclusions are also suggested to be mainly primary. All fluid inclusions from the two samples are two phase undersaturated liquid-rich aqueous types (L+V) with the vapour bubble volume of approximately 3-5% at room temperature (about 25 °C). This fluid inclusion type is defined as the F1 type, as described above, and is petrographically similar to the primary inclusions in authigenic quartz of Frimmel et al. (1993) and in vein quartz of Drenman (1997) and secondary fluid inclusions in quartz pebbles of Boer et al. (1995). Other types of fluid inclusions, e.g. CO_2 - H_2O - rich (F2), CO_2 - CH_4 - N_2 - rich (F3), and CH_4 - N_2 - rich (F4) of Drenman (1997) were not observed in this study.

7.4.5 Results

The ice melting and final homogenization temperatures of fluid inclusions from the amygdales in the hanging wall lavas range from -23,9 to -6,6 °C and from 138 to 183 °C, respectively. The calculated salinities of inclusion fluids are between 10,0 and 23,2 wt% eNaCl (Table 7-3). The final ice melting, and homogenization temperatures of the fluid inclusions from vein quartz span a range of -11,0 to -5,4 °C, and 143 to 173 °C, respectively. The calculated salinities of inclusion fluids range from 8,4 to 11,9 wt% eNaCl (Table 7-3).

Table 7-3 Microthermometric data for primary fluid inclusions from late-stage vein and amygdale quartz in the VCR

Population	$-T_m$ (°C)	T_h (°C)	Wt%NaCl
High salinity	Quartz from lava amygdales (R-1)		
	23.9	156	23.2
	21.2	164	23.2
	18.0	152	21.0
	15.0	n.d.	19.4
Average	21.0±3	157±7	21.7±2
Moderate salinity	Quartz from lava amygdales (R-1)		
	10.9	n.d.	14.9
	10.9	183	14.9
	8.8	162	12.6
	6.6	138	10.0
	Quartz from quartz vein (X0449)		
	11.0	173	11.9
	8.2	143	11.8
	8.2	147	8.4
	8.1	143	11.8
	5.4	n.d.	11.9
Average	9.1±1.9	156±2	11.9±2.1
Total average	11.7±5.1	156±15	14.9±5.1

T_m - final melting temperature for ice at normal temperature.

T_h - Homogenization temperature of fluid inclusion.

N.d. - not determined.

Wt%NaCl - salinity assuming that all salts are NaCl, calculated using the computer software of Brown and Lamb (1989).

The final ice melting and homogenization temperatures of fluid inclusions from the samples are plotted as histograms in Fig. 7-2. All the entire homogenization temperatures of fluid inclusions from both vein and lava amygdale quartz are in a range of between 140° and 170°C with a modal temperature about 145°C in a skewed rough normal distribution (Fig. 7-2a). The total final melting temperatures of fluid inclusions from both vein and lava amygdale quartz range from -21 to -7°C and have two clusters, which possibly represent two distributions (Fig. 7-2b). One has final melting temperatures of between $-6,5^{\circ}$ and -12°C with a modal temperature of -9°C , and includes the fluid inclusions from both vein and lava amygdale quartz. The other cluster is quite scattered and only consists of the fluid inclusions from lava amygdale quartz.

The final melting temperatures, and salinities are plotted against fluid inclusion homogenization temperatures in Fig 7-3. The diagram of the final ice melting temperatures and fluid inclusion homogenization temperatures clearly shows two populations (Fig. 7-3a), which are (1) lower final ice melting temperatures from $-23,9$ to $-15,0^{\circ}\text{C}$, which consists only of the fluid inclusions from lava amygdale quartz and (2) higher final ice melting temperatures from $-10,9$ to $-5,4^{\circ}\text{C}$, which includes fluid inclusions from both vein and lava amygdale quartz (Fig. 7-3a, Table 7-3). Correspondingly, the diagram of the estimated salinities from the final ice melting temperatures and fluid inclusion homogenization temperatures indicates two distinct salinity populations (Fig. 7-3b), which are (1) a higher salinity population from $23,2$ to $19,4$ wt % eNaCl, which only consists of fluid inclusions from lava amygdale quartz and (2) a lower salinity population from $14,9$ to $10,0$ wt% eNaCl, which includes the fluid inclusions from both vein and lava amygdale quartz (Fig. 7-3b, Table 7-3).

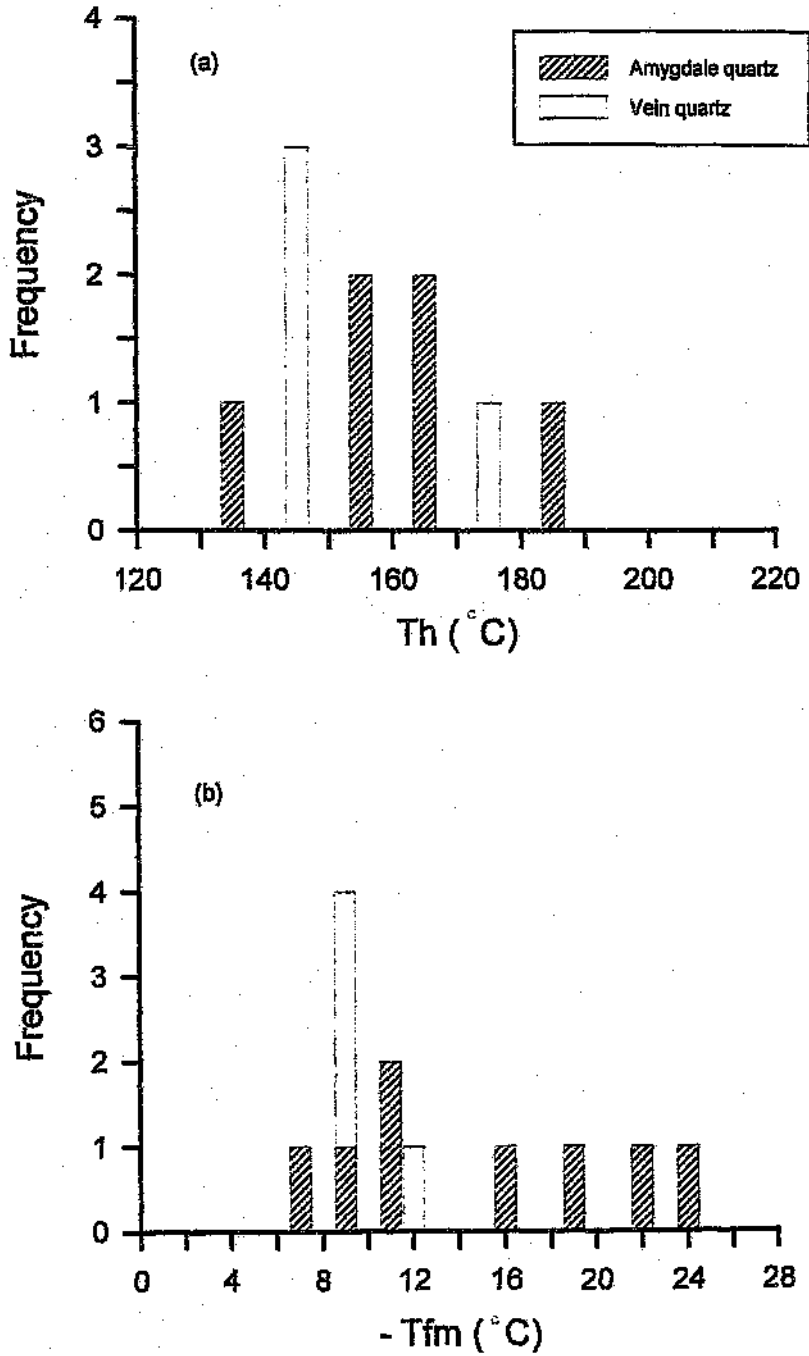


Fig. 7-2 Histograms of (a) total homogenization (Th) and (b) final ice melting (Tfm) temperatures for fluid inclusion data.

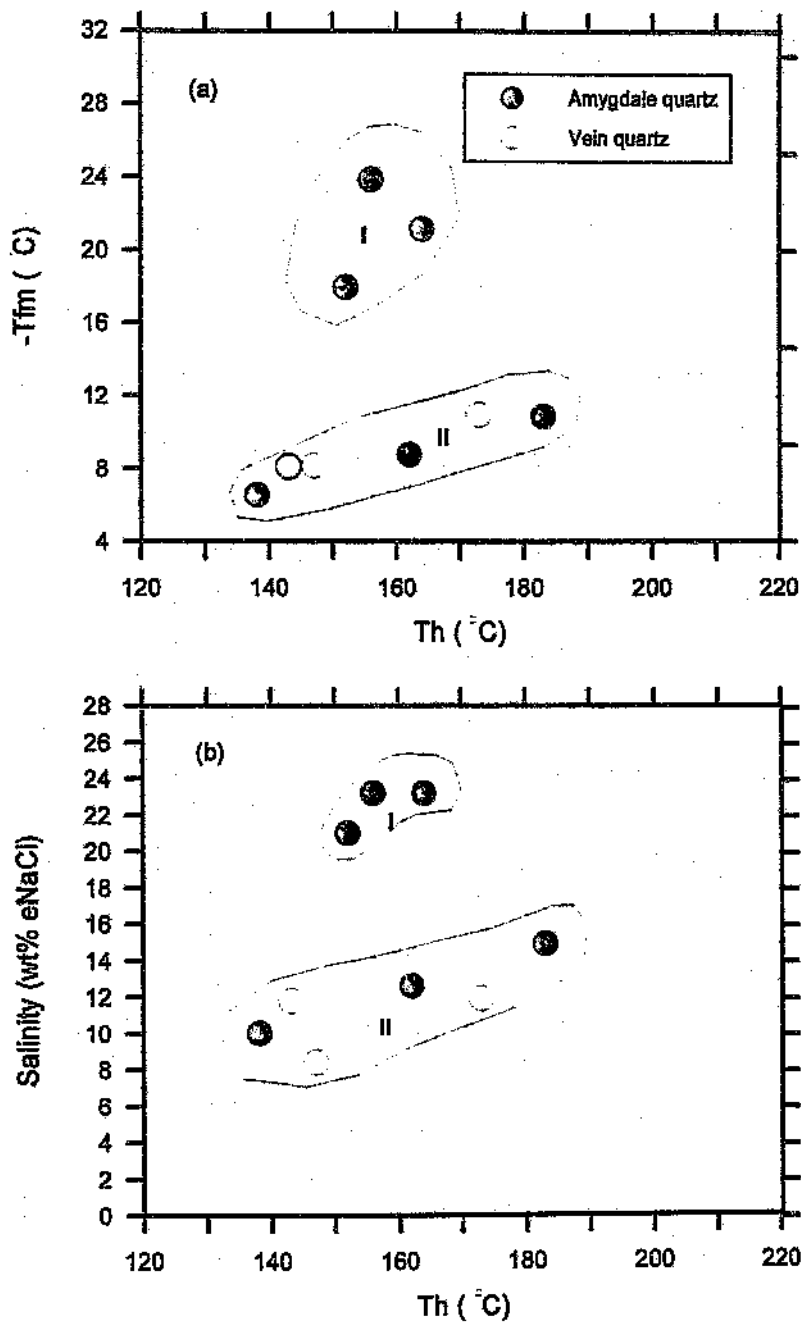


Fig. 7-3 Diagrams of final ice melting temperatures and salinity vs total homogenization temperatures for fluid inclusion data. (I) higher salinity population; (II) lower salinity population.

7.4.6 Interpretation of the fluid inclusion data

As shown in Fig. 7-2, 3 and Table 7-3, two distinct populations of T_m and salinities versus final homogenization temperatures can be clearly identified in lava amygdale quartz and only one population in vein quartz. Therefore, it is suggested that at least two different fluids have been trapped during the formation of various amygdales of lavas and only one in quartz veins. One fluid population (Type I) has a higher salinity, 19 -23 wt% eNaCl and medium T_h of 152 to 164 °C. This is similar to the secondary fluid inclusions in detrital quartz of the Basal reef in the Welkom gold field (Frimmel et al., 1993). The major one (Type II) is of moderate salinity (8,4 - 15 wt% eNaCl) with T_h of 143 to 183 °C and includes all the fluid inclusions in quartz veins and some fluid inclusions in amygdale quartz of the lavas. This can be compared with the primary inclusions (3) in authigenic quartz of Frimmel (1993) (salinity 7 to 17 wt% eNaCl, T_h of 130 to 140 °C); F1 of Drennan (1997) (salinity, 2,8 to 18,6 wt%, T_h of 145 to 290 °C) and the primary inclusions of Boer et al. (1995) (salinity, 9 wt% eNaCl, 115 - 190 °C).

If the quartz veins within and around the VCR are considered to have been produced by later fluid activity, the moderate salinity fluid population (Type II) in both lava amygdale and vein quartz probably represents a later phase of fluid activity, while the high salinity population (Type I) present only in the lava amygdales can be interpreted as possibly representative of an earlier phase of fluid activity in the Witwatersrand Basin. Therefore, the fluids of metamorphism and hydrothermal alteration represent two stages of evolution within and around the VCR: (1) early fluids with high salinity and (2) later fluid with moderate salinity.

The final homogenization temperatures are considered to represent the minimum entrapment temperatures of the fluids due to no pressure correction. However, the true entrapment

temperatures and pressures of the fluids can be estimated on the basis of fluid inclusion isochores, together with the independent geothermometers of muscovite and chlorite (see below).

7.5 Pressure and geothermal gradient

7.5.1 Previous work

Wallmach and Meyer (1990) suggested a pressure of at least 2,5 kbar, determined from fault related kyanite occurring close to the Kimberley and Monarch reefs. The pressure at peak metamorphism in the Witwatersrand Basin was less than 3 kbar, based on the basin-wide greenschist facies as also suggested by Phillips and Law (1994), except for the amphibolite facies around the Vredefort Dome in the centre of the Basin, which indicates a pressure of approximately 5 kbar (Stevens et al. 1995).

Geothermal gradient during peak metamorphism in the Witwatersrand Basin has been suggested to be between 35 and 40 °C/km during greenschist facies metamorphism (350 °C and 2-3 kbar), 40 °C/km at amphibolite facies (Gibson & Stevens, 1995), and > 45 °C/km at granulite facies metamorphism around the Vredefort Dome (Stevens et al., 1995). Frimmel (1997) estimates the geothermal gradient at 28 ± 7 °C for the Central Rand Group, corresponding to the early Transvaal hydrothermal event (Stage 3), and 38 ± 5 °C at the time of the emplacement of the Bushveld igneous Complex (Stage 4), based on the stratigraphic thickness and chlorite temperatures.

7.5.2 Results

As discussed above, at least five types of fluids corresponding to different thermal events have been proposed by Frimmel et al. (1993, 1997): (Stage 1) thrust-controlled pre-Transvaal alteration; (Stage 2) early Transvaal alteration; (Stage 3) Basin-wide burial metamorphism; (Stage 4) thermal metamorphism in the collar of the Vredefort Dome and (Stage 5) hydrothermal

alteration related to Vredefort Dome/Bushveld magmatism at about 2 Ga years. The fluids in all five stages could have affected the VCR. However, the hydrothermal alteration (Stage 5) at about 2 Ga is the most important event affecting the VCR based on the mineralogical data discussed in Chapter 4 and radiometric dating (see Chapter 9).

Taking into account the stratigraphic sequence of the Vaalian Era, the lithostatic pressure can be estimated based on the total thickness of 8 to 9 km for the Ventersdorp and Transvaal Supergroups overlying the Witwatersrand Supergroup. The average density of the rocks is about $2,75 \text{ g/cm}^3$. Therefore, the lithostatic pressures at peak metamorphism are estimated to be between 2,2 and 2,4 kbar.

Independent average temperatures from chlorite and muscovite can be used to represent entrapment temperatures of fluids due to (1) mutual contact of chlorite and muscovite with quartz in uncorroded grain boundaries (see SEM photomicrograph in Chapter 9), which proves an equilibrium of the three minerals; and (2) the chlorite and muscovite temperatures, which correspond well to the temperature conditions ($\pm 350^\circ\text{C}$) of greenschist facies metamorphism. Therefore, the entrapment pressures of fluids can be determined by the combination of fluid inclusion isochores and the muscovite and chlorite geothermometers. The entrapment pressures of the fluids were estimated to be between 2,2 and 3,2 kbar at temperatures of 290°C (chlorite) and 350°C (muscovite) with an average of 2,7 kbar (Fig. 7-4).

The lithostatic geothermal gradient at peak metamorphic conditions can be estimated from the thickness of overlying strata of the Ventersdorp and Transvaal Supergroups at a maximum depth of 9 km and a maximum temperature of 350°C (Wallmach & Meyer, 1990). The corresponding

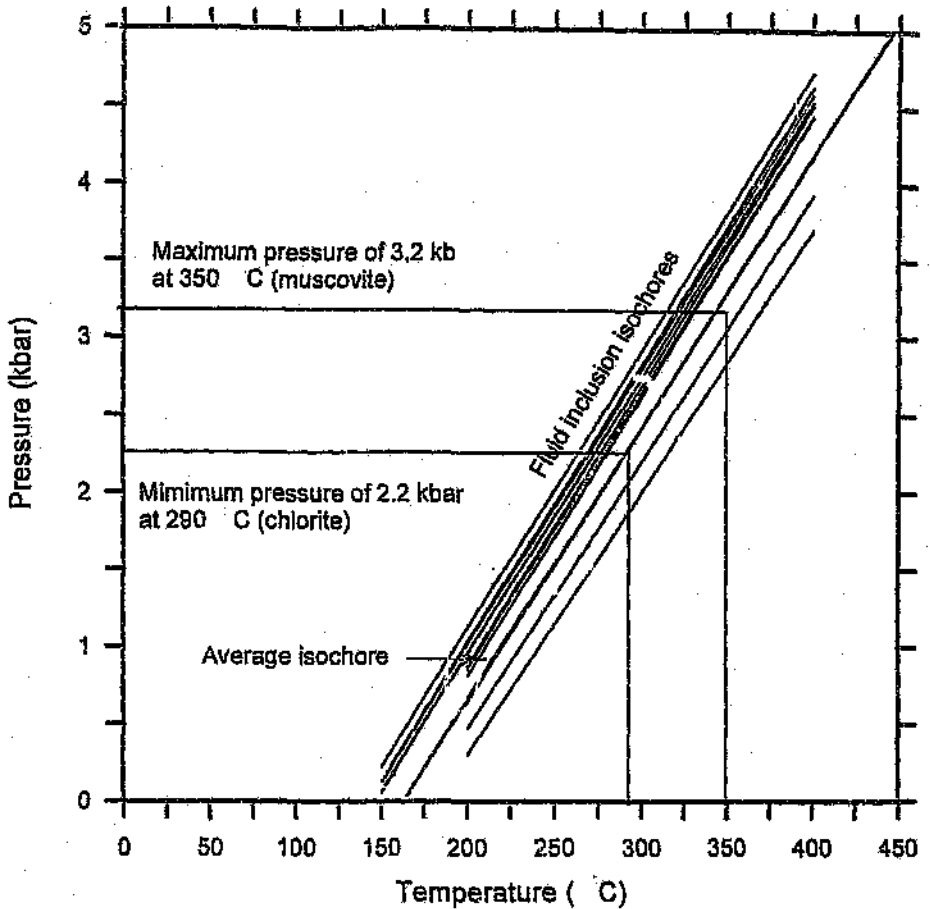


Fig. 7-4 P-T fields of hydrothermal fluids during alteration of the VCR. Fluid inclusion isochores are calculated from final ice melting and homogenization temperatures of fluid inclusions (Brown, 1989). The maximum temperature of 350°C is estimated from the muscovite geothermometer and the minimum temperature of 290°C is estimated from the chlorite geothermometer, corresponding to entrapment pressures of 2.2 and 3.2 kbar, respectively.

geothermal gradient is 39 °C/km, which is consistent with 38±5 °C (Frimmel et al., 1993) and 35 to 40 °C/km (De Yoreo et al., 1991; Gibson & Stevens, 1995).

7.5.3 Interpretation of the pressure data

The entrapment pressures of the fluids of the VCR during hydrothermal processes are constrained by the fluid inclusion isochores (Fig. 7-5). The minimum entrapment pressure, 2,2 kbar is consistent with the lithostatic pressure estimated from 9 km of overburden strata of the Ventersdorp and Transvaal Supergroups. The maximum pressure, 3,2 kbar is consistent with pressures of about 3 kbar for green schist facies metamorphism (Phillips and Law, 1994) and in agreement with a pressure of at least 2,5 kbar, determined from the fault related kyanite occurrence close to the Kimberly and Monarch reefs (Wallmach & Meyer, 1990).

7.6 f_{O_2} , f_{S_2} , $f_{H_2S(g)}$, $a_{H_2S(aq)}$ and pH values

7.6.1 Previous work

Using sulfur fugacities constrained by a combination of graphite-CO₂-CH₄ equilibrium and arsenopyrite-pyrite stability and pH defined by muscovite stability, Robb and Meyer (1991) estimated the Witwatersrand fluid conditions at the peak metamorphic temperature of 350 °C to be: (1) log f_{O_2} between -31 and -29; and (2) pH, around 5. Drennan (1997) determined oxygen fugacity for CO₂-rich inclusions in the Witwatersrand Basin based on the nickel-nickel oxide (Ni-NiO) buffer and the quartz-fayalite-magnetite buffer. Chlorite temperatures (300 to 400 °C) were used to constrain f_{O_2} to be between -35 and -27 for the Witwatersrand Basin.

Based on the thermodynamic modelling, Boer et al. (1995) suggested that the peak metamorphism and hydrothermal alteration for the VCR took place at (1) a temperature of 350 °C; (2) a minimum pressure of 2,5 kbar; (3) f_{O_2} , between 10⁻²⁹ and 10⁻²⁶; (4) log $f_{H_2S(g)}$, -0.22 and 0.04;

(5) $\log a_{\text{H}_2\text{S(aq)}}$ -1,5 and -2,6; (6) at acidic pH, 3 (neutral pH at 350 °C, 5,1); (7) a_{CO_2} from 2,4 to 0,3; and (8) a_{CH_4} from 0,2 to 0,5. The authors further conclude that the fluids are associated with the Bushveld or Vredefort events.

7.6.2 Principle of the methodology

Based on the six-component chlorite solid solution model of Walshe (1986), (1) oxygen fugacity can be calculated from a chemical reaction:



(2) $f_{\text{H}_2\text{S(g)}}$ and $a_{\text{H}_2\text{S(aq)}}$ content of the fluid can be calculated based on the coexistence of quartz and chlorite with an iron sulfide; (3) $\log a_{\text{Na}^+}/a_{\text{H}^+}$ and $\log a_{\text{K}^+}/a_{\text{H}^+}$ can be calculated based on stable albite and muscovite, respectively, and (4) $\log f_{\text{S}_2}$ can be calculated based on the coexistence of pyrrhotite with pyrite.

7.6.3 Results

$\log f_{\text{O}_2}$, $\log a_{\text{Na}^+}/a_{\text{H}^+}$, $\log a_{\text{K}^+}/a_{\text{H}^+}$, $\log a_{\text{H}_2\text{S(aq)}}$, $\log f_{\text{H}_2\text{S(g)}}$ and $\log f_{\text{S}_2}$ were calculated using the Ch-1 computer programme of Walshe (1987) and averages of the data with standard deviation (Std.) are tabulated in Table 7-4 in terms of host rocks, i.e. VCR conglomerate, quartzites, and average of the sediments (VCR conglomerate and quartzites), and lavas. Average values of $\log f_{\text{O}_2}$ of VCR is $-29,4 \pm 1,3$; quartzites $-29,9 \pm 4,1$; $-29,65$ for the average of the sediments; and $-35,5 \pm 7,6$ in the lavas.

$\log f_{\text{S}_2} \text{ (py/po)}$ is $-10,5 \pm 0,7$ in the VCR; $-11,6 \pm 1,6$ in quartzites; $-11,1 \pm 1,2$ in the lavas. $\log f_{\text{H}_2\text{S(g)}}$ is $0,9 \pm 0,2$ in VCR; $1,3 \pm 0,3$ in quartzites; $-1,1 \pm 0,2$ in average of the sediments; and $-1,3 \pm 0,5$. $\log a_{\text{H}_2\text{S(aq)}}$ is $-2,3 \pm 0,2$ in VCR; $-2,7 \pm 0,3$ in quartzites; $-2,5 \pm 0,3$ in average of the sediments; and $-2,7 \pm 0,6$. $\log a_{\text{Na}^+}/a_{\text{H}^+}$ is $5,0 \pm 0,1$ in VCR, $5,0 \pm 0,5$ in quartzites; $5,0$ in average of

Table 7-4 Summary of $\log f_{O_2}$, $\log f_{S_2}$ (py/po), $\log f_{H_2S(g)}$, $\log a_{H_2S}$, $\log a_{Na^+}/a_{H^+}$, $\log a_{K^+}/a_{H^+}$ values estimated from the chlorite solid solution model of Walshe (1986).

		VCR (9)	Quartzites (29)	Average (for VCR and quartzite)	Lava (3)
$\log f_{O_2}$	Average	-29.4	-29.9	-29.7	-35.5
	Std.	1.3	4.1	2.7	7.6
$\log f_{S_2(py/po)}$	Average	-10.5	-11.6	-11.1	-13.3
	Std.	0.7	1.6	1.2	3.7
$\log f_{H_2Sg}$	Average	-0.9	-1.3	-1.1	-1.3
	Std.	0.2	0.3	0.2	0.5
$\log a_{H_2Saq}$	Average	-2.3	-2.7	-2.5	-2.7
	Std.	0.2	0.3	0.3	0.6
$\log a_{Na^+}/a_{H^+}$	Average	5.0	5.0	5.0	5.3
	Std.	0.1	0.5	0.3	0.5
$\log a_{K^+}/a_{H^+}$	Average	3.9	3.9	3.9	4.4
	Std.	0.7	0.6	0.7	0.6

Note: The number in brackets indicates the number of analyses. Std. - standard deviation (1σ).

sediments; $5,3 \pm 0,5$ in the lavas. $\log a_{K^+}/a_{H^+}$ is $3,9 \pm 0,7$ in VCR; $3,9 \pm 0,6$ in the quartzites; $3,9 \pm 0,7$ in average of the sediments; and $4,4 \pm 0,6$ in the lavas.

7.6.4 Interpretation of the data

Chlorite chemical compositions from different lithologies in the VCR have been calculated using the thermodynamic model of Walshe (1986). Although this is the only method used in the study, it may provide better understanding of some characteristics of the fluids during peak metamorphism and hydrothermal alteration of the VCR. The thermodynamic data from both the VCR and the quartzites are undistinguishable, and are strongly different from those of the lavas. As discussed above, accurate chlorite chemical compositions were difficult to obtain due to the fine-grained character and possible interlayer structures of chlorites. Therefore, the thermodynamic data obtained from the lavas were not used for evaluation of the conditions of peak metamorphism and hydrothermal alteration in the VCR in this study. In this case, the average thermodynamic data of the sediments were used.

Average $\log f_{O_2}$ is -30 which is in a good agreement with the data ($\log f_{O_2}$, -31 to -29) of Robb and Meyer (1991), the data ($\log f_{O_2}$, -35 to -27) of Drennan (1997) for the Witwatersrand Basin and also consistent with the data ($\log f_{O_2}$, -29 to -26) of Boer et al. (1995).

Average $\log f_{S_2}$ (py/pyo) is -11,1 and this is based on the coexistence of pyrite and pyrrhotite at between 290 ° and 350 °C. Average $\log f_{H_2S(g)}$ is -2,5 and is compared with the maximum $\log f_{H_2S}$, 0,5 of Robb & Meyer (1991), but lower than the data ($\log f_{H_2S(R)}$, 0,6 to 1,1) of Boer et al. (1995) for the VCR.

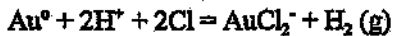
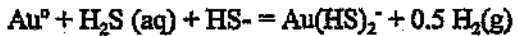
The lack of hydrothermal clay minerals (e.g. kaolinite) indicates that the pH value of the fluid was

not acidic and the absence of sulphates in the VCR suggests the fluids were not alkaline (e.g. Milkucki & Ridley, 1993). Thus, a neutral pH value for the fluids at peak hydrothermal alteration, of about 5 at temperature of between 290 ° and 350 °C is suggested, which is in a good agreement with the pH value of 5 of Robb and Meyer (1991). This is also consistent with the hydrothermal assemblages of albite - muscovite - chlorite - epidote - talc-carbonates - quartz - sulphides (see Chapter 5).

7.7 Mechanism of gold remobilization and precipitation in the VCR

7.7.1 Review

Based on experimental and thermodynamic data, the main gold species in hydrothermal fluids are bisulphide and dichloride gold complexes, whose formations are generally expressed as follows (Seward, 1984):



From these two reactions, the stability of Au depends on multiple factors, e.g. pressure, temperature, pH, fluid salinity, fugacities of oxygen and sulphur, and the activities of bisulphide and chloride.

Phillips and Myers (1989) assume that gold was transported as an unspecific gold-sulphur complex. Based on the calculation of Robb and Meyer (1991), the solubility of both thiosulphide complex and gold chloride complex can be as low as 1 ppb and solution pH values place an important constraint on gold transport as either thio- or chloro-complexes.

Starling et al. (1989) studied individual pyrite grains separated from four lode-type gold deposits using optical and scanning electron microscopy and identified the gold occurring as sub-spherical

to subhedral on pyrite surface through absorption-chemisorption processes. Similarly, Meyer et al. (1994) have investigated the micro-texture and chemistry of compact round pyrite and associated gold accumulations in the Witwatersrand reefs and establish that gold is preferentially deposited on chemically heterogeneous pyrite surfaces using an electrochemical approach. The principle is based on the attribution of Möller (1993), Möller and Kersten (1994) and Mironov et al. (1981), which the accumulation and reduction of gold on pyrite surfaces are mainly due to the semiconductive properties of minerals. Chemical zoning of pyrite with As, or Ni and Co, which can substitute for S and Fe respectively, results in mixed, n-p type semiconductors, and in the generation of self-driving galvanitic cells.

7.7.2 Fluid conditions and mineralization

Temperatures of hydrothermal fluids at peak metamorphism in the VCR are between 290 ° and 350 °C. The maximum $\text{Au}(\text{HS})_2^-$ solubility in these conditions is around 30 ppb (Robb & Meyer, 1991). With the pH buffered by the feldspar-muscovite-quartz assemblage and the redox state buffered by the $\text{CO}_2\text{-CH}_4$ reaction and muscovite stability, the AuCl_2^- solubility increases with temperature and is much less than 1 ppb at conditions of 290 - 350 °C (Seward, 1983). This suggests that the AuCl_2^- complex does not play a major role in the transportation of Au in Witwatersrand fluids. Therefore, the $\text{Au}(\text{HS})_2^-$ complex is probably the major gold species in the fluids.

Another possibility is that the gold transported locally around sulphides, specifically pyrite and the gold was deposited on chemically heterogeneous pyrite surfaces as suggested by Meyer et al. (1994). That is consistent with the fact that gold remobilization occurred at a maximum scale of centimeters (Frimmel, 1993) and little gold is present in post-depositional quartz veins in the Witwatersrand Basin as discussed in Chapter 4.

7.8 Summary

The environmental conditions of fluids at peak hydrothermal alteration in the VCR have been summarized and tabulated in Table 7-5. The data are presented as parameters, methods used, range and average of the data, notes, and data source.

All rocks of the Witwatersrand and Ventersdorp Supergroups were metamorphosed to greenschist facies including the VCR conglomerates, hanging wall Ventersdorp lavas and the footwall sediments of the Central Rand Group. At least two thermal events are recognized in this study. The major one is correspondent to the later thermal event (Stage 3) of the five major fluids of Frimmel (1997).

Both experimental muscovite and thermodynamic chlorite geothermometers were used to estimate the temperatures of fluids at the peak metamorphic conditions and to constrain the temperatures between 290 ° and 350 ° C in the VCR. These probably correspond to the major thermal events (Stage 5) of Bushveld magmatism and the Vredefort Dome. A lower temperature mineral assemblage of chlorite and muscovite is also revealed to be between 150 ° and 245 °C, which may represent post-Vredefort retrogression.

Fluid inclusions from vein quartz and lava amygdale quartz in the VCR are characterized by low densities of inclusions per area, small size and predominantly two-phase undersaturated liquid-rich aqueous types. Two populations of salinities from fluid inclusions have been identified in quartz veins and lava amygdalites (1) early high salinity (19 - 23 wt% eNaCl) with medium T_h of 152 - 164 °C and (2) the later moderate salinity (8,4 - 15 wt% e NaCl) with T_h of 143 to 183 °C.

Table 7-5 Summary of fluid characteristics during peak hydrothermal alteration of the VCR

Parameters	Method	Range (average)	Notes	Ref.
Th (°C)	F/Incl.	138 - 183	Aqueous-rich (L-V)	1
T (°C)	Ch, Mus	290 - 350 (320) 145 - 245 (200)	Higher temperature Lower temperature	1
P (kbar)	F/Incl. Lith.	2.2-3.2 (2.7)		1
Geotherm (°C/km)		39 27	Higher geotherm Lower geotherm	1
Salinity (wt% eNaCl)	F/Incl.	8.4 - 15 19 - 23	Lower salinity Higher salinity	1
pH	TC	3 5	Acidic Neutral	2 3
log f_{O_2}	TC	-33 - -27 (-29.7)		1
log f_{S_2}	TC	-9 - -12 (-11.1)		1
log $f_{H_2S(g)}$	TC	-0.9 - -1.3 (-1.1)		1
log $a_{H_2S(aq)}$	TC	-2.2 - 2.8 (-2.5)		1
Au(HS) ₂ ⁻ (ppb)	TC	1-30 ppb		3
AuCl ₂ ⁻ (ppb)	TC	1 ppb		3
Au Transportation	TC, others	Au(HS) ₂ ⁻ , electrochemical, rare AuCl ₂ ⁻		1, 4

Methods: Ch - chlorite geothermometer; Mus - muscovite geothermometer; F/Incl. - fluid inclusion; Lith. - lithostatic pressure; TC - calculation.

Reference (Ref.): 1 - this study; 2 - Boer et al. (1995); 3 Robb & Meyer (1991); 4 - Meyer et al. (1994).

The entrapment pressures of the fluids during the peak metamorphism and hydrothermal alteration in the VCR are constrained to be between 2,2 and 3,2 kbar with an average of 2,7 kbar, using the entrapment temperatures of the fluids between 290 and 350 °C and fluid inclusion isochores. The maximum geothermal gradient during the peak metamorphism in the VCR is constrained to be 39 °C/km at a temperature of 350 °C and overburden strata of the Ventersdorp and Transvaal Supergroups are estimated to give a maximum depth of 9 km.

f_{O_2} , f_{S_2} , $a_{H_2S(aq)}$, $f_{H_2S(g)}$ and pH values are estimated using the six chlorite solid solution model of Walshe (1986) based on the chlorite, pyrite-pyrrhotite buffers, stable muscovite and albite. They are summarized: $\log f_{O_2} = -29,7$; $\log f_{S_2} (py/po) = -11,1$; $\log f_{H_2S(g)} = -2,5$; $\log a_{H_2S(aq)} = -2,5$; and $pH = 5$ (neutral). Based on the fluid temperatures, f_{O_2} and pH values, transportation and remobilization of gold by hydrothermal fluids in the VCR during peak metamorphism were mainly in sulfur gold complex $(Au(H_2S)_2^-)$ in the fluids and possible physical absorption and movement over short distances on pyrite surfaces through electrochemical precipitation, as described by Meyer et al. (1994).

8 ISOTOPIC GEOCHEMISTRY (S, O, H, C)

8.1 Introduction

8.1.1 Genetic models of the Witwatersrand Basin

More than a century since the discovery of Witwatersrand gold by George Harrison in 1886, the origin of the gold and uranium is still debated between supporters of the two major genetic models: (1) modified placer model, described as original gold deposited in a placer but locally remobilised at centimetre scale after burial (Pretorius, 1964, 1976; Armstrong, 1966; Minter, 1978, 1979; Reimer & Mossman, 1990; Robb & Meyer, 1991; Frimmel et al., 1993; Frimmel, 1997) and (2) the hydrothermal model, described as dissolved gold introduced by hydrothermal fluids at a metre to kilometre scale in an epigenetic or metamorphic environment after sedimentation (cf., Phillips, 1987; Phillips & Myers, 1989; Parnell, 1996; Barnicoat et al., 1997; Phillips & Law, 1997). Stable isotope studies of ore minerals and quartz grains as well as other materials may help to solve the critical problem of the genetic processes of mineralisation for Witwatersrand reefs and to provide target areas for Witwatersrand type gold deposits during future gold exploration.

8.1.2 Previous work on sulphur isotopes

Mineralogical studies have revealed the existence and enrichment of detrital, mudball and authigenic pyrite and other sulphides as well as carbonaceous matter in the Witwatersrand Basin (e.g. Viljoen, 1963; Pretorius, 1974b; Robb & Meyer, 1987; Meyer et al., 1990b; Robb et al., 1994, 1997). They were derived separately from different source areas or origins and are representatives of different environments. For example, detrital pyrite represents the original sources of sulphides and possibly associated heavy metal minerals, such as gold. Mudball pyrite

is a syn-depositional product and possibly represents the syn-sedimentary environment. Authigenic pyrite and other sulphides are post-depositional products which probably represent post-depositional processes of metamorphism and hydrothermal alteration. Detrital, mudball and authigenic pyrite and pyrrhotite are enriched in the VCR, together with a variety of other sulphides, e.g. chalcopyrite, arsenopyrite, galena and sphalerite.

Sulphur isotope : Studies on different pyrite types and other sulphides as well as carbonaceous matter have been carried out by various workers, e.g. Jensen and Dechow (1964); Hoefs et al. (1968); Chukhrov et al. (1970); Hattori et al. (1983); Förster (1986); Drennan (1997). However, a systematic sulphur isotope study for the VCR horizon has not been conducted except for limited analysis on sulphides from quartz veins from the VCR (e.g. Drennan, 1997).

The available $\delta^{34}\text{S}$ values for detrital pyrite collected from the above authors fall within a narrow range of -1‰ to $+5,6\text{‰}$ which are far different from those of some sedimentary sulphides (between -35‰ and $+25\text{‰}$) (Hoefs et al., 1968). Based on the above results, for ore genesis most of the authors agree with the interpretation of an original magmatic source of the sulphur for detrital pyrite in the Witwatersrand reefs (e.g., Jensen and Dechow, 1964; Hoefs et al., 1968; Drennan, 1997). However, Förster (1986) suggests that original sulphur in detrital pyrite originated from subaerial volcanic smokers in the Witwatersrand Basin. For example, reported $\delta^{34}\text{S}$ values for detrital pyrite are between $+0,2\text{‰}$ and $+5,6\text{‰}$ from the Vaal reef of the Klerksdorp goldfield (Jensen and Dechow, 1964); between $+1,0\text{‰}$ and $+4,0\text{‰}$ from the Elsburg, Basal and "B" reefs in the Welkom gold field (Hoefs et al., 1968); between $+2,5\text{‰}$ and $+4,4\text{‰}$ for detrital porous pyrite and $-1,4\text{‰}$ and $8,2\text{‰}$ for compacted pyrite (Förster, 1986); and $-1,5\text{‰}$ and $+2,6\text{‰}$ for detrital pyrite from the Kimberley and Basal reefs in the Welkom goldfield and

VCR in West Wits Line (Drennan, 1997).

For mudball pyrite, Hattori et al. (1983) reported that the $\delta^{34}\text{S}$ values are between $-0,5\text{‰}$ and $+4,0\text{‰}$, which are not much different from the detrital pyrite (-1‰ to $+5,6\text{‰}$) based on an investigation of sulphur isotopes in the Carbon Leader, Carletonville goldfield, Witwatersrand Basin. Hattori et al. (1983) suggest that the $\delta^{34}\text{S}$ values of mudball pyrite are best attributable to global anaerobic conditions at that time, which inhibited oxidation of sulphur in the sedimentary cycle. This conclusion supports the models of low atmospheric oxygen during the Proterozoic time as suggested by Cloud (1968) and Garrels et al. (1968).

For authigenic pyrite, the available $\delta^{34}\text{S}$ values have a range of -2‰ and $+6,5\text{‰}$ (e.g. Hoefs et al., 1968; Förster, 1986; Drennan, 1997), which are very similar to those for detrital pyrite in a range of -1‰ and $+5,6\text{‰}$ (e.g. Hoefs et al., 1968; Hattori et al., 1983; Förster, 1986; Drennan, 1997). In addition, no obvious difference in $\delta^{34}\text{S}$ values has been found (1) between the authigenic pyrite and the pyrite associated with carbonaceous matter (Hoefs et al., 1968; Hattori et al., 1983) and (2) between pyrite and associated carbonaceous matter in the Witwatersrand reefs (Hattori et al., 1983).

The characteristics of the $\delta^{34}\text{S}$ values supports the argument that sulphur from the Witwatersrand reefs is representative of partial reconstitution of the allogenic sulphides (Drennan, 1997) rather than being introduced, together with Au, by hydrothermal fluids as suggested by some workers (e.g. Phillips et al., 1987; Barnicoat et al., 1997; Phillips & Law, 1997).

8.1.3 Previous work on oxygen and hydrogen isotopes

Quartz is enriched in the Witwatersrand reefs and sediments and some lavas, and includes quartz and chert pebbles, quartz sands, authigenic quartz, vein quartz, and lava amygdale quartz. Oxygen isotope studies on these materials, together with calcite, muscovite and chlorite can provide invaluable information for the source of the sediments and possible mineralization history during the basin evolution. Oxygen isotope studies of quartz pebbles, authigenic quartz and post-depositional vein quartz have been carried out in the Witwatersrand Basin by various workers (e.g., Savin & Epstein, 1970; Barton et al., 1992; Vennemann et al., 1992, 1995).

For example, oxygen isotope studies on quartz pebbles including white and grey quartz, and chert have been carried out in the Witwatersrand Basin by Barton, et al. (1992) and Vennemann et al. (1992, 1995). The samples of Barton et al. (1992) covered a large part of the Witwatersrand stratigraphy together with the Dominion Group and Transvaal Sequence, and a wide geographic area, while those of Vennemann et al. (1992, 1995) were from several distinct reefs in the Central Rand, West Rand, and Welkom gold fields. However, the results of both Barton et al. (1992), and Vennemann et al. (1992, 1995) are similar and report that the $\delta^{18}\text{O}$ values of quartz pebbles from Witwatersrand reefs are in a range of 8,8 ‰ to 14,5 ‰ (Vennemann et al., 1992) or 8,8 ‰ to 13,1 ‰ (Barton et al., 1992). Also there is an isotopically significant heterogeneity among the quartz clasts within individual hand specimen samples (Vennemann et al., 1992) or from centre to rim within some individual quartz clasts (Barton et al., 1992). Both studies argue that the quartz pebbles and chert clasts preserve their original isotopic compositions of the source area and were not significantly recrystallized with no oxygen isotopic reequilibration during post-depositional processes due to the absence of any textural evidence of emplacement by silica veining and overgrowth (Barton et al., 1992; Vennemann et al., 1992, 1995). $\delta^{18}\text{O}$ values of

eleven chert clasts from the Witwatersrand reefs have an identical, relatively narrow range of between 5 ‰ and 12,5‰, which are, however, similar to the matrix values of the quartz clasts (9,8‰ and 11,5‰) (Vennemann, 1992).

For quartz sands in the matrix of conglomerates, the only study has been carried out by Vennemann et al. (1995) on the Monarch Reef and the Main Reef in the Witwatersrand Basin. They reported the $\delta^{18}\text{O}$ values to range of between 7,8‰ and 11,8‰, which is lower than the range for quartz clasts and cherts (9,0‰ and 12,5‰). In this case, the quartz sand population in each of the conglomerate horizons in the Witwatersrand Basin does not have $\delta^{18}\text{O}$ values in excess of 11,5‰, which may suggest a different sediment source (Vennemann et al., 1995).

In order to find the possible source area for the Witwatersrand reefs, Barton et al. (1992) have investigated five potential source areas for the clasts and reported the results: (1) Beit Bridge Group in the Central Zone of the Limpopo Belt, near Messina (9,5‰ and 10,7‰) and near Alldays (7,8‰); (2) quartzite from the Promise Formation of the West Rand Group (8,4‰ and 8,8‰); (3) quartzite from Gembokfontein Member of the Westonia Formation in the Turffontein Subgroup, Central Rand Group (9,6‰ and 10,0‰); (3) barren, white hydrothermal quartz veins from the Roodepoort gold field, Pietersburg granite greenstone terrane (11,6‰ and 11,8‰); (4) gold-bearing white quartz vein, Roodepoort gold field, Pietersburg granite greenstone terrane (14,1‰ and 14,2‰); and (5) white quartz hydrothermal veins at the Barbrook Gold Mine from Barberton granite greenstone terrane (14,7‰ and 15,0‰). The $\delta^{18}\text{O}$ ‰ values of quartz in hydrothermal quartz veins and quartz clasts in quartzite exhibit a variety of overlapping in most of the samples, however, they appear to be isotopically homogeneous. In addition, Beattie (1991) has investigated the gold-bearing hydrothermal quartz veins in the northern Kaapvaal Craton and

Limpopo belt and reported two populations for the $\delta^{18}\text{O}\text{‰}$ values in a range of between 9,2‰ and 13,1‰, and between 14,0‰ and 14,4‰. The first group of $\delta^{18}\text{O}\text{‰}$ values almost completely overlaps those of the large clasts in the Witwatersrand Basin, and the second group is heavier than those of any clasts yet measured.

Vennemann et al (1995) have compared the $\delta^{18}\text{O}\text{‰}$ values of quartz pebbles and quartz sands in quartz pebble conglomerates with likely known rock types in the world including granitoids, pegmatites, paragneisses, metavolcanic rocks and metasandstones, and suggested that the compositionally homogeneous granites and related pegmatites are the dominant source of uranium, whereas hydrothermal lode gold veins are the dominant source for gold.

The oxygen isotope systematics of Ventersdorp-age dolerite intrusions have recently been investigated by Harris and Watkins (1990) who have studied several Ventersdorp-age dolerite intrusions which have metamorphosed up to lower greenschist facies. These include the thick Conera Sill and Lotgeval Dyke and some smaller dykes from Klerksdorp. The results show that the Ventersdorp-age dolerite intrusions have 'mantle' $\delta^{18}\text{O}$ values of between 5,5 ‰ and 6,7‰ which indicates no exchange in $^{18}\text{O}/^{16}\text{O}$ between the Witwatersrand quartzites ($\delta^{18}\text{O}\text{‰} = 8,6\text{‰}$ to 10,3‰), dolerite and fluids.

The oxygen isotope systematics from agates in Karoo volcanics have been investigated by Harris (1989). The author measured a profile through six textural-zoned agates from Sarusas, in the Skeleton Coast Park, Namibia and obtained $\delta^{18}\text{O}$ values of between 20,4‰ and 28,9‰. This suggests that the oxygen isotope values represent a prolonged boiling fluid system of meteoric water, accompanying loss of vapour at 120 °C.

8.1.4 Previous work on carbon isotopes

The majority of the carbon in the Witwatersrand reefs, including the VCR, occurs as carbonates (calcite and siderite) (Zhao et al., 1994), bitumen (Robb et al., 1994) and CO₂ in fluid inclusions (e.g. Frimmel et al., 1993; Boer et al., 1995; Drennan, 1997).

Klerks et al. (1994) has studied the carbon isotopes in carbon nodules from the Schweizer Reneke and Varkenskraal altered granitoids and the VCR in the Witwatersrand Basin. The results from carbon nodules of the Schweizer Reneke and the Varkenskraal altered granitoids (-25,7‰ and -36,0‰) and bitumen (fly-speck) from the VCR (-20,6‰ and -32,4‰) suggest an organic origin.

8.1.5 Aim of this chapter

The purpose of the analyses of sulphur, oxygen, hydrogen and carbon isotopes for different materials of the VCR conglomerates and related lithologies is to characterize the isotopic chemical signature of the fluids involved in post-depositional fluid circulation and the possible source of ore minerals for the VCR in the Witwatersrand Basin.

8.2 Review of stable isotopes (S, O, H, C)

8.2.1 Delta notation (δ)

Stable isotope ratios are measured relative to a standard and expressed in the δ notation (parts per mil) (e.g. Faure, 1986; Rollinson, 1993). Using oxygen isotopes as an example, the δ value is calculated as follows:

$$\delta^{18}\text{O}\text{‰} = \left[\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{sample}} - \left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{standard}} \right] / \left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{standard}} \times 1000 \dots \dots \dots (8-1)$$

The standard is the Standard Mean Ocean Water (SMOW). The standard notation is used to express the data where the value is the difference in isotopic ratio between the sample and a

standard.

8.2.2 Isotopic fractionation

As described by Rollinson (1993), the known isotopic fractionation in nature occurs in three different ways: (1) isotope exchange reactions; (2) kinetic processes; and (3) physicochemical processes such as evaporation, condensation, melting, crystallization and diffusion. The fractionation of an isotope between two substances A and B can be defined by the fraction factor α :

$$\alpha_{A-B} = \text{ratio in A} / \text{ratio in B} \dots\dots\dots (8-2)$$

Experimental studies have shown that $1000 \ln \alpha$ is a smooth and often linear function of $1/T^2$ for mineral-mineral and mineral-fluid pairs (cf., Faure, 1986; Rollinson, 1993). This gives rise to the general relationship for the fraction factor:

$$1000 \ln \alpha_{A-B} = A (10^6/T^2) + B \dots\dots\dots (8-3)$$

If δ values are less than 10, by approximation, the relationship between $1000 \ln \alpha_{A-B}$ and measured isotope ratios can be expressed as:

$$\Delta_{A-B} = \delta_A - \delta_B \approx 1000 \ln \alpha_{A-B} = A (10^6/T^2) + B \dots\dots\dots (8-4)$$

If δ values are larger than 10, formula 8-3 has to be used.

8.2.3 Isotopic compositions of geological materials

8.2.3.1 Sulphur

Naturally occurring sulphur-bearing species include (1) native sulphur, (2) sulphate; (3) sulphides; (4) gaseous H_2S and SO_2 ; and (5) a range of oxidized or reduced sulphur ions in solution. There are four types of stable isotopes of sulphur in nature which have the following abundances:

$^{32}S=95.02\%$, $^{33}S=0.75\%$, $^{34}S=4.21\%$ and $^{36}S=0.02\%$ (Faure, 1986).

Rollinson (1993) has summarized the critical values of three isotopically distinct reservoirs in $\delta^{34}\text{S}$: (1) mantle-derived sulphur with $\delta^{34}\text{S}$ values in the range $0\pm 3\%$ (Chaussidon and Lorand, 1990); (2) seawater sulphur with $\delta^{34}\text{S}$ values today of about $+20\%$ (Sakai et al., 1984); (3) strongly reduced (sedimentary) sulphur with large negative $\delta^{34}\text{S}$ values from -25% to $+35\%$ (Hoefs et al., 1968).

8.2.3.2 *Oxygen and hydrogen isotopes*

Oxygen

There are three stable isotopes of oxygen which have the following abundances:

$^{16}\text{O}=99,763\%$, $^{17}\text{O}=0,0375\%$ and $^{18}\text{O}=0,1995\%$ (cf., Rollinson, 1993).

$^{18}\text{O}/^{16}\text{O}$ (sample) refers to individual samples while $^{18}\text{O}/^{16}\text{O}$ (standard) is the concentration in Standard Mean Ocean Water (SMOW). The ratios of oxygen isotopes are calculated relative to SMOW.

Chondritic meteorites have a very restricted range of $\delta^{18}\text{O}$ values and the mantle has $\delta^{18}\text{O}$ values of $5,7\pm 0,3\%$, which seem to have been constant through time for the earth and the Moon (Taylor, 1980). Meteoric water has a large range of about -40% to $5,7\%$. Most granites, metamorphic rocks and sediments are enriched in $\delta^{18}\text{O}$ values relative to the mantle value, whereas seawater and meteoric waters are depleted, thus forming complementary $\delta^{18}\text{O}$ reservoirs.

Hydrogen

There are two hydrogen isotopes in nature: $^1\text{H}=99,9844\%$ and $^2\text{D}=0,0156\%$ (deuterium).

Hydrogen isotopes are measured in parts per thousand relative to the SMOW standard and are

calculated in an analogous manner to that for oxygen isotopes and expressed as $\delta D\text{‰}$.

8.2.3.3 Carbon

Carbon naturally occurs in its oxidized forms (CO_2 , carbonates and bicarbonates), and reduced carbon (methane and organic carbon, diamond, graphite). Carbon has two stable isotopes with the following abundances: $^{12}\text{C} = 98,89\%$; and $^{13}\text{C} = 1,11\%$. Carbon isotope composition systems in nature are (1) meteorites (a wide range); (2) mantle (-3‰ and to -8‰ with an accept mean value of about -6‰); (3) seawater (0‰); (4) marine carbonates (-1‰ and $+2\text{‰}$); (5) marine bicarbonate (-2 and $+1\text{‰}$); (6) non-marine organic carbon (-20‰ and -30‰).

8.3 Sulphur isotopes

8.3.1 Description of the samples

A total of 14 rock samples containing sulphides were collected from the hanging wall lavas of the Klipriviersberg Group ($n=2$), VCR conglomerates ($n=4$), and footwall quartzites in the Central Rand Group ($n=8$) (Table 8-1). Mineral assemblages of sulphides in these samples are pyrite-pyrrhotite-chalcopyrite-sphalerite-galena. In total, 28 single sulphides from the 14 rock samples have been analyzed, and include authigenic pyrite (10), pyrrhotite (10), sphalerite (3), chalcopyrite (2) and galena (3).

8.3.2 Methodology

8.3.2.1 Mineral separation

The mineral separation was carried out at BPI, University of the Witwatersrand, Johannesburg following the normal procedures employed in the laboratory. They include: (1) crushing the

Table 8-1 $\delta^{34}\text{S}$ data of sulphides from the VCR conglomerate, hanging wall lava, and footwall quartzite (total of 28 analyses)¹

Lithology	Sample No	$\delta^{34}\text{S}_{\text{‰}}$				
		Py	Po	Sph	Cpy	Ga
Lava	R-1	0.0	-0.7		-0.3	-1.3
	B0413a	-0.6				
VCR	X0427		0.6			
	XR1654		1.0			
	XR1645-1	0.8	0.3			
	XR1645-2	0.1	-0.4		-0.2	
DGG quartzite	B0384			0.9		-1.5
	B0376	1.8	0.3	0.9		
	B0372			0.4		-0.8
	X0439	0.1	-0.4			
	XR1646	1.0	-0.2			
	XR1643	-0.1	-0.5			
	XR1642					
	XR1609					

¹ Py - pyrite; Po - pyrrhotite; Sph - sphalerite; Cpy - chalcopyrite; Ga - galena.

samples to chips and further to fine grains of 125 to 1700 μm in diameter; (2) heavy fluid separation using bromoform; and (3) Franz Isodynamic Magnetic Separator to separate different sulfides following adaptation of the original method used by Hass (1959). The samples were finally purified with a vacuum hand-picker at the Council for Geoscience of South Africa, Pretoria. Separated minerals include authigenic pyrite, pyrrhotite, chalcopyrite, sphalerite and galena.

8.3.2.2 *Sulphur isotope analysis*

Sulphur isotope analyses were carried out at the Isotope Laboratory of the Council for Geoscience of South Africa, Pretoria, using conventional SO_2 extraction facilities and a Finnigan Mat 251 gas source mass spectrometer. The international reference materials, NBS123 and Soufre de Lacq, are used to calibrate the in-house SO_2 bottle standard. Errors are mainly produced from the sulphur extraction line and mass spectrometer measurement. In this study, the total error of $\delta^{34}\text{S}$ values is better than 0,4‰ including a total method reproducibility of 0,35‰ and an error of 0,05‰ from mass spectrometer measurement. All $\delta^{34}\text{S}$ values are reported in per mil relative to Canyon Diablo Troilite (CDT).

Sulphur was converted to SO_2 under vacuum following an adaptation of the original method of Robinson and Kusakabe (1975). The structure of the sulfur extraction line is presented in Fig. 8-1 and constituted by: (1) a high temperature furnace (up to 1120 $^{\circ}\text{C}$); (2) a rotary pump; (3) a diffusion pump; (4) main pump producing high vacuums; (5) an acetone-dry ice trap; (6) a liquid nitrogen-pentane trap (n-pentane trap) (trapping CO_2); (7) a liquid nitrogen trap (trapping SO_2); (8) glass sample bottles (collecting SO_2); and (9) gauges for pressure measurements (normal pressure $<10^{-7}$ bar).

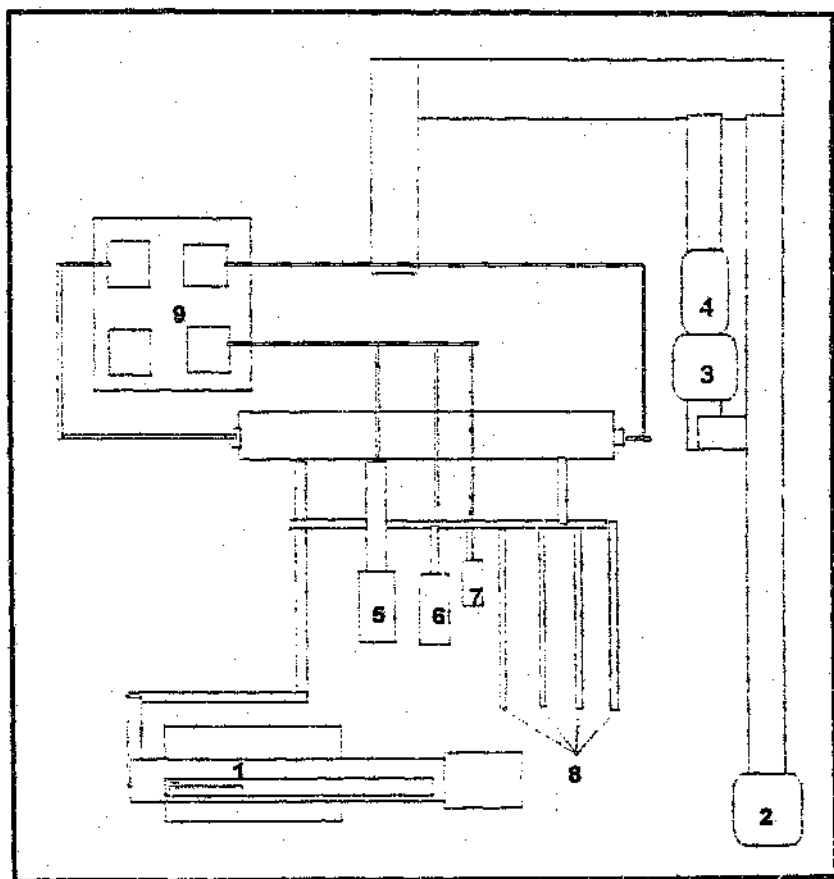
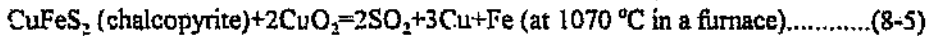
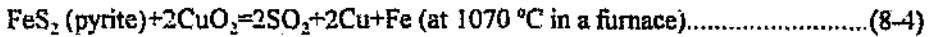


Fig. 8-1 Sulfur dioxide preparation line (after the Council for Geoscience, South Africa).
 1—Furnace producing high temperature up to 1120 °C, 2—Rotary pump, 3—back pump,
 4—main pump producing high vacuum, 5—acetone dry ice trap for water, 6—N-pentane
 trap with coil glass tube, 7—liquid nitrogen trap, 8—glass tubes, 9—pressure gauges.

The procedures for the extraction of sulfur are presented as follows:

(1) In order to produce SO_2 , powder sulphide samples are intimately mixed and reacted with Cu_2O at temperatures up to 1070°C , which was prepared by heating CuO at a temperature of 910°C under vacuum for approximately one hour. Reactions of pyrite and chalcopyrite with Cu_2O are presented as two examples:



(2) At first, SO_2 gas is purified by extraction of water vapour in an n-pentane trap by liquid nitrogen:

(3) Secondly, all incondensable gases are extracted in a vacuum system. The SiO_2 is trapped somewhere and then revolatilized into the mass spectrometer;

(4) Finally, sulphur isotopic ratio in sulfur dioxide is measured by a Finnigan Mat 251 gas source mass spectrometer. The mass spectrometer analysis is based on the procedures of Coleman and Moore (1980).

8.3.3 Results of $^{34}\text{S}/^{32}\text{S}$ analyses

8.3.3.1 Sulphur isotope data

A total of 28 analyses were obtained from authigenic pyrite ($n=10$), pyrrhotite ($n=10$), sphalerite ($n=3$), galena ($n=3$), and chalcopyrite ($n=2$) and are tabulated in Table 8-1. The $\delta^{34}\text{S}$ values of authigenic sulphides are between -1.5‰ and $+1.8\text{‰}$ with a cluster of around 0.0‰ . Individually, sulfur isotopic compositions of sulphides are: (1) -1.5‰ and -0.8‰ for galena; (2) -0.7‰ and $+1.0\text{‰}$ for pyrrhotite; (3) -0.3‰ and -0.2‰ for chalcopyrite; (4) $+0.4\text{‰}$ and $+0.9\text{‰}$ for sphalerite; and (5) -0.6‰ and 1.8‰ for pyrite. $\delta^{34}\text{S}$ values of single sulphide minerals are plotted in a histogram (Fig. 8-2) The results indicate that the $\delta^{34}\text{S}$ values for both pyrite and pyrrhotite have almost identical normal distribution patterns with two modes around -0.5‰ and $+0.5\text{‰}$.

respectively (Fig. 8-2a, b). No distinctive distribution patterns of $\delta^{34}\text{S}$ values for sphalerite, chalcopyrite and galena can be discerned as shown in Fig. 8-2c, d, e, due to limited analyses.

Fig 8-3 shows $\delta^{34}\text{S}$ values of single sulphide minerals from different host rocks. The $\delta^{34}\text{S}$ values of single sulphides from two completed profiles of hanging wall lavas, VCR conglomerates and footwall quartzites shows more or less similar distributions (Fig. 8-a, b, c, d, e, f), i.e., no obvious difference in the distribution of $\delta^{34}\text{S}$ values for different lithologies has been found. The $\delta^{34}\text{S}$ values of sulphides for the two uncompleted rock series show almost the same distribution as each other among lavas, VCR conglomerates and footwall quartzites (Fig. 8-3g, h, i, j). Fig. 8-3k shows the distribution of the $\delta^{34}\text{S}$ values for sphalerite only in footwall quartzites.

8.3.3.2 *Sulphide precipitation temperature*

Paragenetic sequences of sulphides

When sulphide minerals are precipitated from aqueous solutions or crystallize from sulphide liquids, small differences may occur in $\delta^{34}\text{S}$ values of cogenetic minerals due to isotopic equilibrium among the solids and between the solid and liquid (Sakai, 1957; Thode, 1970; Fauer, 1986). The differences in the isotopic composition of S in cogenetic sulphide minerals may reflect the temperature of isotope equilibrium. Theoretical considerations by Sakai (1968) and Bachinski (1969) based on bond strengths indicate that the ^{34}S enrichment of some common sulphide minerals should decrease in an order: pyrite > sphalerite > chalcopyrite > galena. This is consistent with the results of this study: sphalerite (+0.4‰ and +0.9‰) > chalcopyrite (-0.3‰ and -0.2‰) > Galena (-1.5‰ and -0.8‰) (Fig. 8-2). However, pyrite (-0.6‰ and 1.8‰) and pyrrhotite (-0.7‰ and +1.0‰) do not fit into the sequence. This is attributed to the two paragenetic sequences of early pyrite- pyrrhotite, and later sphalerite-chalcopyrite-galena (see Chapter 4).

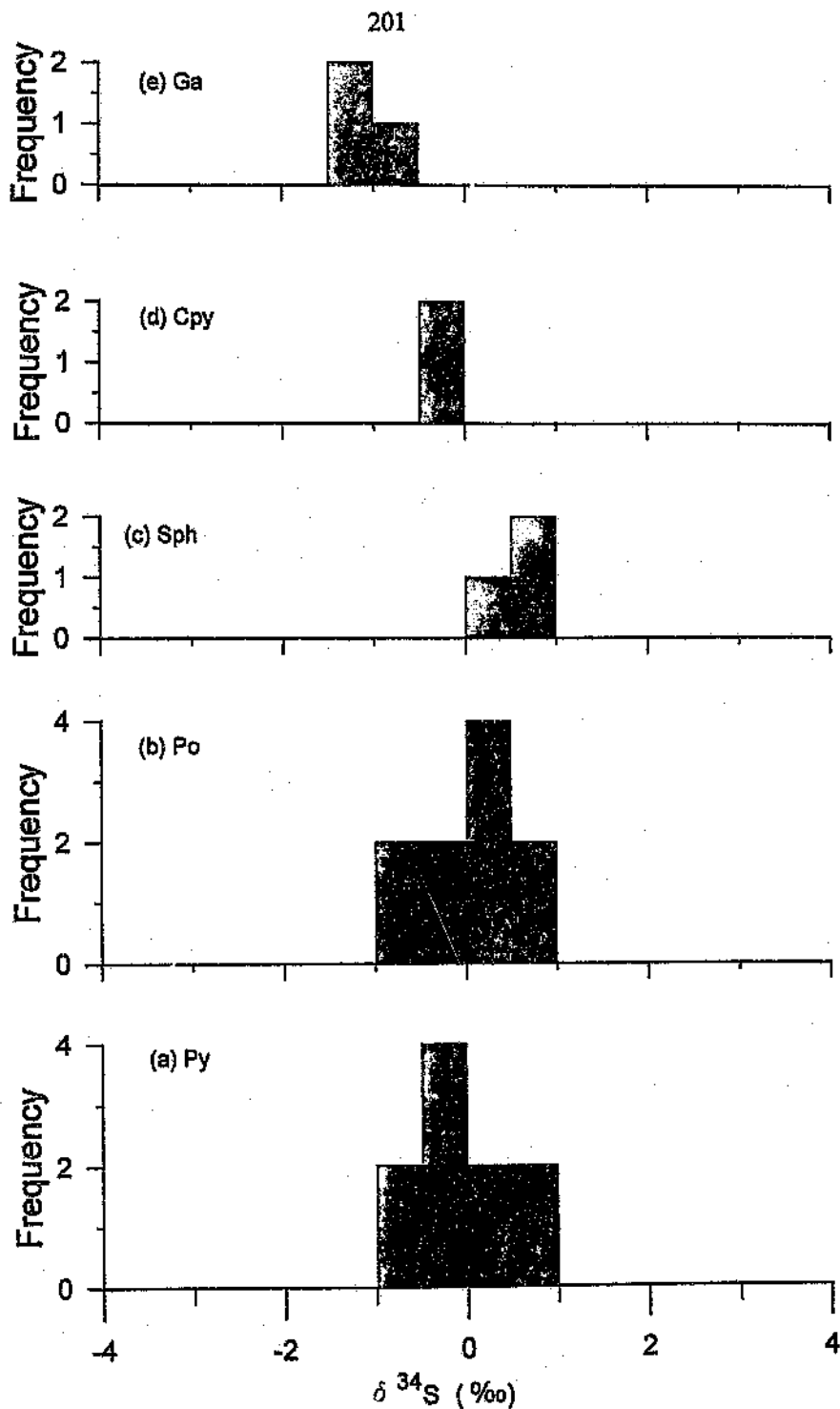


Fig. 8-2 Histogram of $\delta^{34}\text{S}$ values in single authigenic sulphide minerals from the VCR and its related rocks. Py-pyrite; Po-pyrrhotite; Sph-sphalerite; Cpy-chalcopyrite; Ga-galena.

Sulphur isotopic geothermometry

The precipitation temperatures of sulphide minerals are estimated from the $\delta^{34}\text{S}$ values of pyrite-pyrrhotite in the early paragenetic sequence, and sphalerite-galena and sphalerite-chalcopryrite in the later one. Those of pyrite and chalcopryrite and galena from two different paragenetic sequences are also estimated to test the equilibrium between those minerals. The temperatures are calculated based on the sulphur isotope geothermometers of Ohmoto & Rye (1979), which were obtained by solving equation 8-4. Uncertainties in the calculated temperatures are caused by the uncertainty of the equation at a temperature of 300 °C and the analytical error in $\Delta^{34}\text{S}$ of $\pm 0.2\%$.

The sulphur geothermometers, used for calculation of sulphide precipitation temperatures, are listed as follows:

$$T(^{\circ}\text{K}) = (0.55 \pm 0.04) \times 10^3 / \Delta^{1/2} (\pm 95^{\circ}\text{K}) \text{ (pyrite-pyrrhotite)} \dots\dots\dots (8-6);$$

$$T(^{\circ}\text{K}) = (0.67 \pm 0.04) \times 10^3 / \Delta^{1/2} (\pm 75^{\circ}\text{K}) \text{ (pyrite-chalcopryrite)} \dots\dots\dots (8-7);$$

$$T(^{\circ}\text{K}) = (1.01 \pm 0.04) \times 10^3 / \Delta^{1/2} (\pm 45^{\circ}\text{K}) \text{ (pyrite-galena)} \dots\dots\dots (8-8);$$

$$T(^{\circ}\text{K}) = (0.85 \pm 0.03) \times 10^3 / \Delta^{1/2} (\pm 45^{\circ}\text{K}) \text{ (sphalerite-galena)} \dots\dots\dots (8-9).$$

The results of sulphide precipitation temperatures are tabulated in Table 8-2. The uncertainty of the geothermometers is not applied to the data, but only the standard deviation is considered.

The sulphur isotopic equilibrium temperatures in the VCR have a wide range of 176 ° and 597 °C with an average of $393 \pm 149^{\circ}\text{C}$ using the early paragenetic sequence pyrite-pyrrhotite geothermometer. Similarly, the sulphur equilibrium temperatures are estimated to be between 276 ° and 503 °C with an average of $389 \pm 157^{\circ}\text{C}$ using the sphalerite-chalcopryrite and sphalerite-galena geothermometers. The pseudo-isotopic equilibrium temperatures of pyrite-chalcopryrite and pyrite-galena geothermometers in two different paragenetic sequences are between 503 and 950 °C with an average of $723 \pm 202^{\circ}\text{C}$ (see interpretation of the data).

Table 8-2 Temperatures calculated using fraction equations of sulphide mineral pairs from Ohmoto and Rye (1979) for the VCR, the Witwatersrand Basin

Sample no	Host rock	Sulphide-A	$\delta^{34}\text{S}$ (‰)	Sulphide-B	$\delta^{34}\text{S}$ (‰)	Δ_{A-B} (‰)	T (°C)
R-1	Lava	Py	0.0	Po	-0.7	0.7	384
XR1645-1	VCR		0.8		0.3	0.5	505
XR1645-2			0.1		-0.4	0.5	505
B0376	Quartzite		1.8		0.3	1.5	176
X0439			0.1		-0.4	0.5	505
XR1646			0.0		-0.2	1.2	229
XR1643			-0.1		-0.5	0.4	597
XR1642			1.0		-0.1	1.1	251
Average temperature for the early paragenetic sequence (Py-Po) = $394 \pm 157^\circ\text{C}$							
B0372	Quartzite	Sph	0.4	Ga	-0.5	1.2	503
B0384			0.9	Cpy	-1.5	2.4	276
Average temperature for the later paragenetic sequence (Sph-Ga-Cpy) = $389 \pm 157^\circ\text{C}$							
XR1645-2	VCR	Py	0.1	Cpy	-0.2	0.3	950
			0.4	Ga	-0.8	1.2	503
R-1	Lava	Py	0.0		-1.3	1.3	613
		Py	0.7		-1.3	0.6	824
Average meaningless temperature for the two different paragenetic sequences = $723 \pm 202^\circ\text{C}$							

Note 1: Temperatures calculated based following equilibrium:

pyrite-pyrrhotite: $(0.55 \pm 0.4)10^3/\Delta^{1/2}$,

pyrite-sphalerite: $(0.55 \pm 0.4)10^3/\Delta^{1/2}$,

pyrite-galena: $(1.01 \pm 0.4)10^3/\Delta^{1/2}$,

sphalerite-galena: $(0.85 \pm 0.03)10^3/\Delta^{1/2}$,

pyrrhotite-galena: $(0.85 \pm 0.03)10^3/\Delta^{1/2}$.

Note 2: Py - pyrite; Po - pyrrhotite; Sph - sphalerite; Cpy - chalcopyrite; Ga - galena.

8.3.4 Interpretation of the data

$\delta^{34}\text{S}$ values of authigenic sulphides in the VCR from this study are plotted together with the collected sulphur isotope data from various workers (Hoefs et al., 1968; Hattori et al., 1983; Jensen & Dechow, 1968; Drennan, 1997) in Fig. 8-4. These data are categorized after Drennan (1997) as follows: (1) detrital pyrite; (2) detrital pyrite associated with carbonaceous matter; (3) authigenic pyrite; (4) authigenic pyrite associated with carbonaceous matter; (5) other authigenic sulphides as a whole (pyrrhotite, sphalerite, chalcopyrite, galena); and (6) carbonaceous matter.

The $\delta^{34}\text{S}$ values of detrital pyrite from the Witwatersrand reefs define a spread in $\delta^{34}\text{S}$ values from 0‰ to +8‰ with a roughly normal distribution. In the normal distribution pattern, the mode of the $\delta^{34}\text{S}$ values is around +2,8‰ (Drennan, 1997) (Fig. 8-4a). Moreover, the $\delta^{34}\text{S}$ values of detrital pyrite associated with carbonaceous matter are in a range of -1‰ to +4‰ and show a slightly scattered distribution pattern (Fig. 8-4b). However, no significant difference between the two distributions of $\delta^{34}\text{S}$ values for pyrite associated with carbonaceous matter and pyrite can be described. The pattern of $\delta^{34}\text{S}$ values for detrital pyrite with bitumen related to detrital pyrite (Fig. 8-4a, b) probably indicates a single source which can be related to a magmatic source as suggested by various workers (Hoefs et al., 1968; Förster, 1986; Drennan, 1997).

For authigenic/recrystallized pyrite, $\delta^{34}\text{S}$ values in the VCR from this study coincide with the overall model of the collected sulphur isotope data except for a slightly narrower compositional range (Fig. 8-4c). It seems that there are two clusters for the distribution of $\delta^{34}\text{S}$ values for authigenic pyrite with one mode of +1,8‰ and another of +0,5‰ (Fig. 8-4c) as suggested by Drennan (1997). The former cluster of $\delta^{34}\text{S}$ values shifts the maximum about 3‰ in mode value to the left away from the distribution of the detrital pyrite along the X-axis, while the latter one

largely overlaps with the detrital pyrite (see later discussion).

Similarly, $\delta^{34}\text{S}$ values of other authigenic sulphides (pyrrhotite, sphalerite, chalcopyrite, galena) in the VCR from this study indicate no difference from the data of Drennan (1997). The other sulphides as a whole show a shift to the left along the X-axis in comparison with those of the authigenic pyrite and have a rough normal distribution in a pattern with a mode of -0,3‰ in $\delta^{34}\text{S}$ value. Slight fractionation of sulphides has been observed and proved by the decrease in $\delta^{34}\text{S}$ values from sphalerite, chalcopyrite and galena from the VCR as above-mentioned in this study.

For authigenic pyrite associated with carbonaceous matter, the four available analyses of $\delta^{34}\text{S}$ values are between +1,0‰ and +5,0‰ (Fig. 8-4e) and show no difference between those of the detrital pyrite (Fig. 8-4a), and detrital pyrite associated with carbonaceous matter (Fig. 8-4b). Moreover, the five available analyses of $\delta^{34}\text{S}$ values for carbonaceous matter are between +2,0‰ and +4,0‰ (Fig. 8-4f) that are also indistinguishable from those of the detrital pyrite (Fig. 8-4a), and detrital pyrite associated with carbonaceous matter (Fig. 8-4b).

Sulphide precipitation temperatures in the VCR have been estimated from the early paragenetic sequence of pyrite-pyrrhotite to be 394 ± 157 °C. These temperatures are in a relatively wide range and are about 100 °C higher than those estimated from the chlorite and muscovite geothermometers (290 ° and 350 °C). The differences in the temperatures can be due to the sulphur isotope geothermometers, disequilibrium of the mineral pairs or both. In terms of the errors (157 °C), the temperatures from the above estimates are not very conclusive. However, this is consistent with the paragenetic sequence of sulphides (Chapter 4), which precipitated at the early stage and possibly at relatively higher temperatures than the silicates, such as muscovite,

chlorite and quartz. The temperatures estimated using sphalerite-galena and sphalerite-chalcopyrite geothermometers in the VCR are similar to the estimation of sulphide precipitation temperature at 389 ± 157 °C, but they are not included due to limited data (two analyses). The pseudo-temperatures are 723 ± 202 °C from pyrite - chalcopyrite and pyrite - galena geothermometers, which are unreasonably high compared to the observed greenschist facies of metamorphism in the Witwatersrand Basin as described by Phillips et al. (1989; Wallmach & Meyer, 1990; Law, 1990; Phillips & Law, 1997). This clearly indicates a non-equilibrium sulphur system between authigenic pyrite and authigenic sphalerite, chalcopyrite and galena, and supports the observation of two paragenetic sequences of sulphides by optical observation as described in Chapter 4.

In terms of host rocks, there is a large range of overlap of sulphur isotopic compositions of sulphide from the three environments, i.e. hanging wall lavas, the VCR, footwall quartzites (Table 8-1, Fig. 8-3). There is no clear relationship for $\delta^{34}\text{S}$ values between sulphides and their host rocks. This probably suggests no reflection of the three environments, but only the original source, i.e. detrital pyrite and detrital sulphides in the Witwatersrand Basin.

Based on above discussion, it is clearly suggested that input of S by bacteria to the sulphur system in the Witwatersrand system is unlikely due to the limited fraction of sulphur isotopes between carbon materials, detrital pyrite and authigenic pyrite. Moreover, there is very little influence by different host rocks, which suggests a single source for the sulphur isotopes. However this fraction can be interpreted by the effects of pH, f_{O_2} and temperature in a hydrothermal system (Ohmoto, 1972). Here, $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ is taken as an example. The neutral pH is insignificant for oxygen fractionation (see Figure 5 of Ohmoto, 1972) in the VCR during peak hydrothermal alteration.

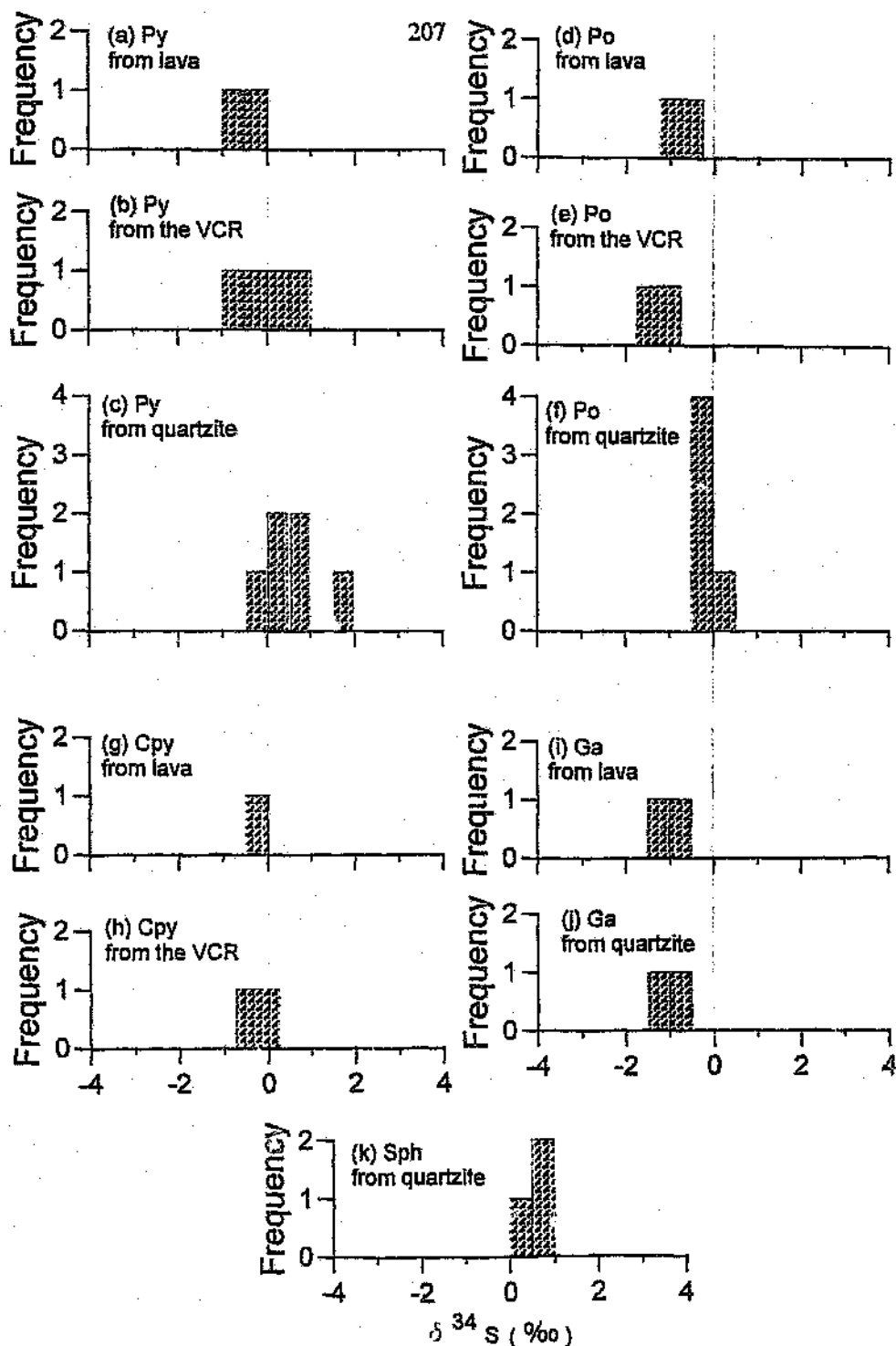


Fig. 8-3 Histogram of $\delta^{34}\text{S}$ values in single authigenic sulphide minerals and in different host rocks from the VCR and its related rocks. Py-pyrite; Po-pyrrhotite; Cpy-chalcopyrite; Ga-galenite; Sph-sphalerite.

At log $f_{O_2} = -30$ and the maximum temperature of 350 °C, $\delta^{34}S_{H_2S}$ decreases by about 1‰ (see Figure 7, 8 of Onmoto, 1972). If the initial $\delta^{34}S_{H_2S}$ values are assumed to be from detrital pyrite and equals 2,5‰ (mode value for detrital pyrite), the $\delta^{34}S_{H_2S}$ decreases by 1,0‰ and becomes to 1,5‰ due to the effect of oxygen fugacity ($f_{O_2} = -30$). This weak fractionation is consistent with the low oxygen levels of the atmosphere at the time of formation as proposed by various workers (Cloud, 1968; Garrels et al. 1973; Hattori et al., 1983).

Two clusters of $\delta^{34}S$ values for authigenic pyrite (Fig. 8-4c) can be interpreted to be due to partial resetting of the sulphur isotopes of authigenic pyrite by the newly formed chalcopyrite, galena and sphalerite. If a recalculation exercise of $\delta^{34}S$ values is done based on the equations 8-8, 9, $\delta^{34}S$ values for authigenic pyrite are recalculated to be from -0,7 to 1,1‰ at temperature of 350 °C. They match well with the actual $\delta^{34}S$ values for authigenic pyrite. The above discussion can be summarized as a two stage model: (1) fractionation of detrital sulphur isotopes at a very low oxygen level, related to global anaerobic conditions; (2) preferential partial resetting of sulphur isotopes of the authigenic pyrite and related mineralisation of chalcopyrite, sphalerite and galena on a regional scale.

The $\delta^{34}S$ values for sulphides in the Witwatersrand Basin, together with two magmatic reservoirs, several distinctive types of deposits are plotted in Fig 8-5. For detrital pyrite in the Witwatersrand Basin, the $\delta^{34}S$ values are far different from the Mississippi Valley-type massive Pb-Zn deposit (-35 ‰ and +25‰) and sediment-hosted massive sulphides with three clusters (-20‰ and +15‰). The $\delta^{34}S$ values for sulphides in the Witwatersrand Basin are also different from the red-bed copper mineralization in the Cheshire basin of north-west England, which is associated with evaporite deposits with a wide range of $\delta^{34}S$ values (-1,8‰ and +16,2‰) (Rollinson, 1993).

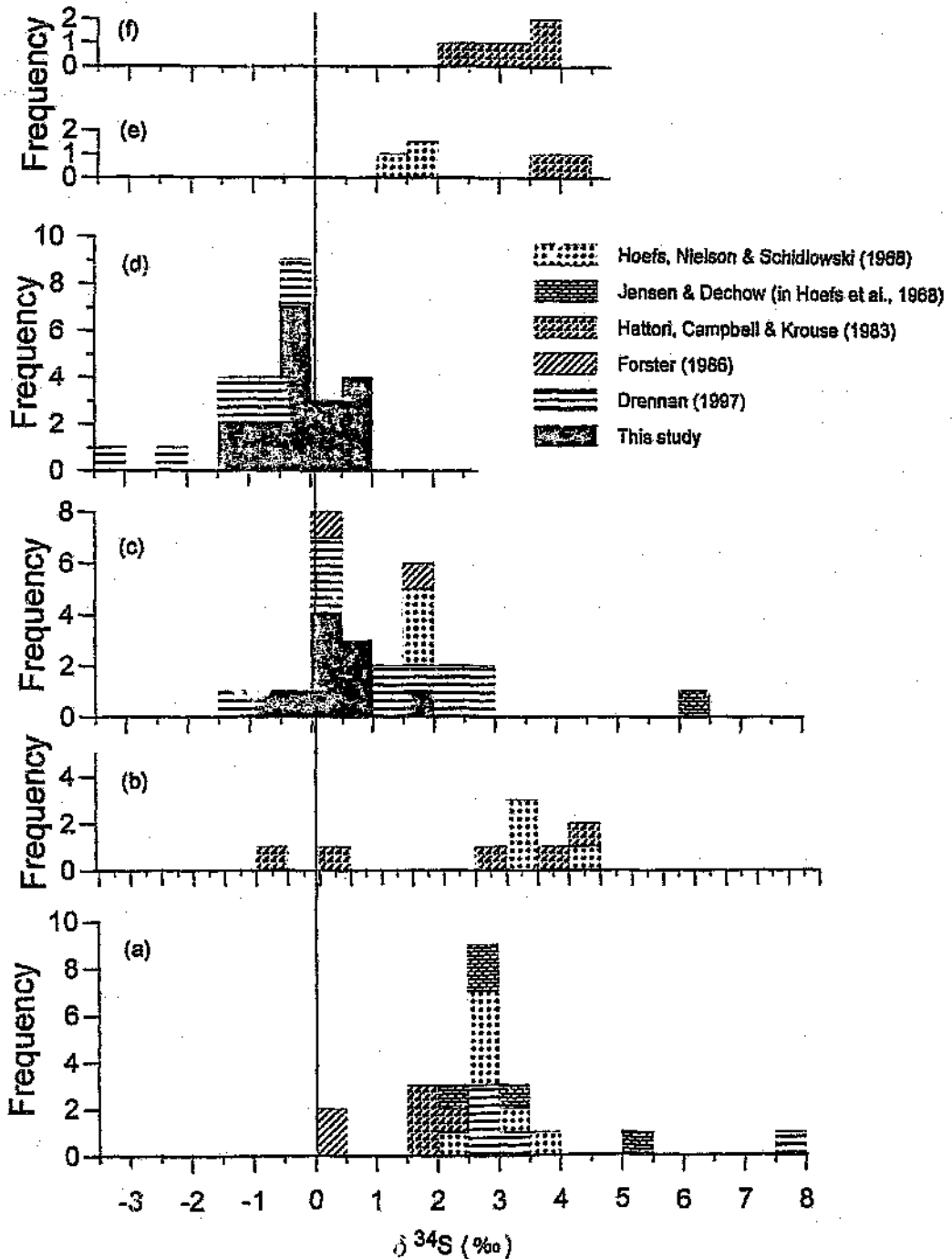


Fig. 8-4 $\delta^{34}\text{S}$ values for sulphides from the VCR in this study, together with collected sulphur isotope data for sulphides and bitumen (carbonaceous matter) from the Witwatersrand reefs and quartz veins (after Drennan, 1997). (a) detrital pyrite; (b) detrital pyrite associated with bitumen; (c) authigenic pyrite; (d) authigenic chalcopyrite, galena, sphalerite, and pyrrhotite; (e) authigenic pyrite associated with bitumen; and (f) bitumen.

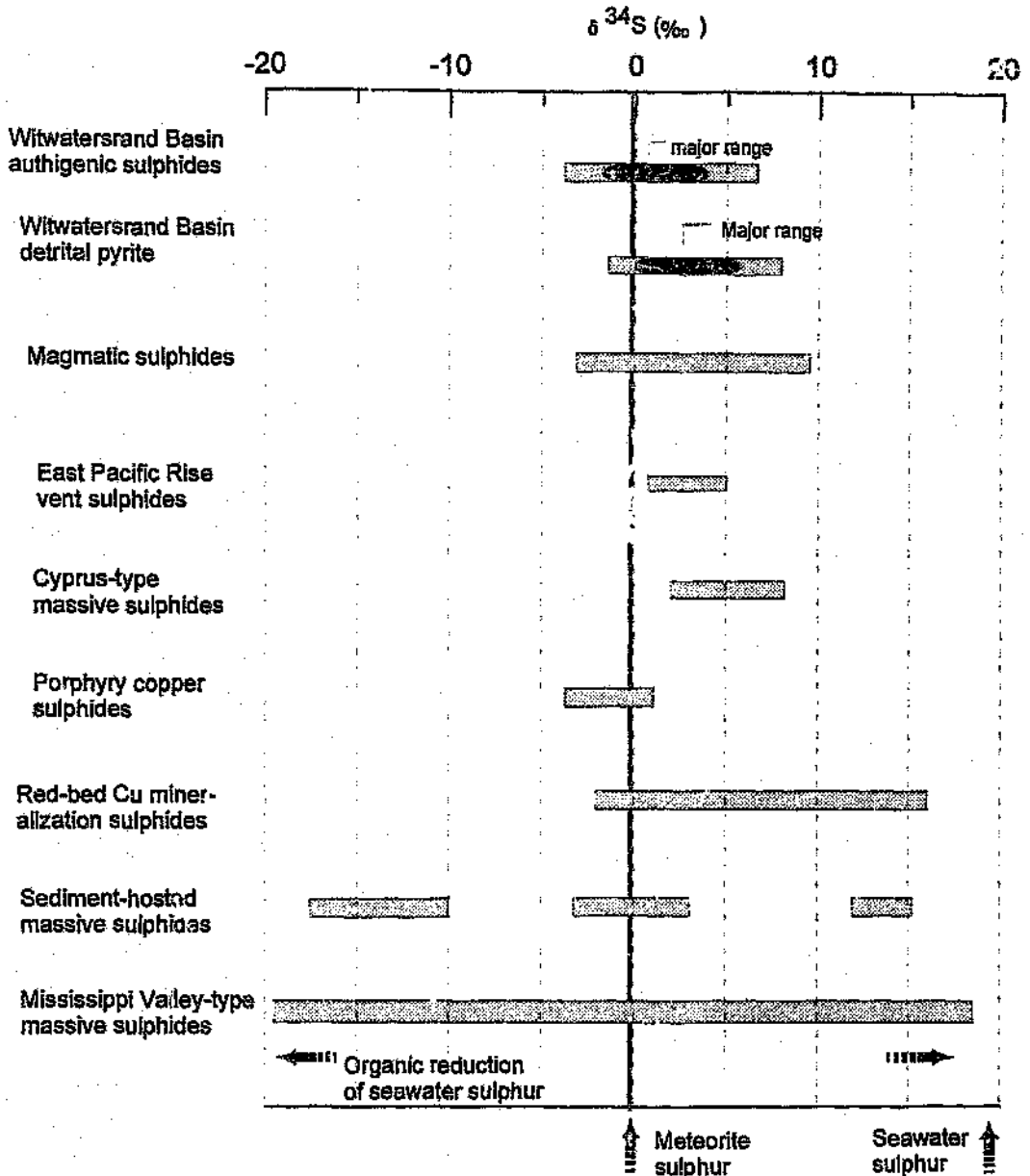


Fig. 8-5 The $\delta^{34}\text{S}$ values for sulphides in the Witwatersrand Basin, together with typical hydrothermal deposits and magmatic origin (after Rollinson, 1993). Data from Kerridge et al. (1988), Ohmoto and Rye (1979), Halbach et al. (1989), Naylor et al. (1989), Eldridge et al. (1988), and the Witwatersrand data from this study and other authors indicated in the text

In this case, the narrow range of $\delta^{34}\text{S}$ values for detrital pyrite in the Witwatersrand Basin is consistent with a single source, while a wide range of $\delta^{34}\text{S}$ values are normally thought to be from multiple sources (Rollinson, 1993).

Except for magmatic sulphides (-4,0‰ and +9,0‰) and the East Pacific Rise vent sulphides (-0,5‰ and 5‰), porphyry copper sulphides (-3‰ and +1‰) and Cyprus-type sulphides (-1,5‰ and +8‰) are close to mantle range and are the most likely candidate for a magmatic, igneous source of sulphur (Rollinson, 1993). The results support the concept that detrital pyrite and other sulphides are originally from a single source of magmatic activity. However, the direct source of detrital pyrite can be from erosion of the altered granites, mesothermal quartz veins, veinlets in the granitic hinterland of the Witwatersrand Basin as suggested by Klemd & Hallbauer (1987), Robb & Meyer (1991) or subaerial volcanic smoker by Förster (1986), or exhalites along the tectonically active northwestern margin of the Basin by shallow marine hydrothermal discharge by Hutchinson & Viljoen (1988).

The $\delta^{34}\text{S}$ values for authigenic sulphides in the Witwatersrand Basin have a slightly wider range than the detrital pyrite but no obvious differences can be described in this study. These characteristics indicate a single source of the authigenic sulphides and weak fractionation at the time of their formation and during post-depositional events, which is consistent with the interpretation of the two stage model.

8.4 Oxygen and hydrogen isotopes

8.4.1 Descriptions of the samples

Samples were collected from the VCR and related lithologies and include three types of sample:

(1) single minerals (quartz, calcite); (2) muscovite-rich mineral separates; and (3) bulk rocks.

The samples of individual minerals

(a) vein quartz from calcite-quartz veins, which normally cut through the VCR conglomerates, and related lithologies, e.g. hanging wall lava of the Westonaria Formation in the Kliprivierberg Group, Ventersdorp Supergroup, and footwall quartzites in the Central Rand Group and proved to be the product of the post-depositional events.

(b) amygdale quartz from amygdaloidal lavas in the VCR hanging wall. The lavas belong to the Westonaria Formation, Klipriviersberg Group, Ventersdorp Supergroup. The amygdales are up to 300 mm in diameter and consist of coarse-grained white quartz and calcite with minor amounts of chlorite, and sulphides. Fluid inclusion study indicates moderate temperatures (290° and 350 °C) and moderate pressures (2,7 kbar), which support the formation of the amygdales during post-depositional events instead of in a subaerial environment. No zonation of the quartz amygdales has been identified and they are obviously distinctive from the zoned agates in the Karoo lava amygdales which formed at low temperatures of 120 °C in a subaerial environment (Harris, 1989);

(c) vein calcite from quartz veins and is coarse-grained in size. Similar to vein quartz, it formed at moderate temperatures of 290° and 350 °C and at a moderate pressure of 2,7 kbar.

Mineral separates

Powdered samples were separated into different size fractions by use of natural settling techniques in Strasbourg, France for K-Ar dating purposes. Some accessory samples of muscovite-rich with

minor chlorite-rich samples have been analysed for oxygen and hydrogen isotopes. The nine muscovite-rich mineral separates contain from 95 to 100% of muscovite with less than 5% chlorite. The chlorite-rich mineral separate has 85% chlorite with less than 15% muscovite. The mineral separates contain a few quartz grains. These samples have been analysed for both oxygen and hydrogen isotope compositions.

Bulk rocks

In order to analyse variation of the oxygen isotope in different alteration zones and rock types, a total of fourteen bulk rocks have been analysed. They include: five samples from the Ventersdorp lava in the multicolour zone (MC) (2) and the dark grey zone (DG) (3); three VCR conglomerate samples (RA); and six quartzite samples from the dark grey zone (DGA) (3) and the grey zone (GG) (3).

8.4.2 Methodology

Analyses of oxygen and hydrogen isotope ratios were completed by Dr. C. Harris at the Department of Geoscience, University of Cape Town.

Oxygen analysis

The extraction of oxygen from quartz and silicates followed the analytical procedures described by Harris (1989) and Vennemann and Smith (1990). The silicates, including quartz grains, bulk rocks and mineral separates are ground in an agate mortar to a powder of less than 90 mesh. Samples were dried at 50 °C for a minimum of 48 hours, before loading into nickel reaction vessels (outside diameter 19 mm, inside diameter about 12 mm), which are overpressurized above atmospheric by dry nitrogen. All samples were degassed at 200 °C and at about 10^{-5} mbar for a

minimum of two hours in order to remove absorbed moisture. The reaction vessels are then charged with about seven times the stoichiometrically required amount of ClF_3 and, after further short evacuation at liquid nitrogen temperatures, are isolated and heated to between 550° and 650°C for overnight. Reaction temperatures are considered to be correct to within $10 - 15^\circ\text{C}$. It takes 15-20 minutes to do the temperature calibrations of the Lindberg[®] electronic heating elements (type 73-KS). The extracted oxygen was converted to CO_2 by passing over a hot platinized carbon rod. The procedures of extraction of oxygen were completed after final dumping of the residual gases by passing over heated KBr crystals and residue powders (AlF_3 , CaF_2 , FeF_2 , MgF_2 , NaF , etc.) from the reaction vessels.

The extracted pure CO_2 gas was analysed for its $^{18}\text{O}/^{16}\text{O}$ using a Micromass[®] VG602E, double-collector ratio mass spectrometer in the Department of Archaeology, University of Cape Town.

In each run, eight samples were loaded together with two NBS-28 standards for calibration of the samples. Some samples were run in duplicate to estimate the errors for the extraction line. The results are expressed in δ notation in per mil units relative to the V-SMOW standard. The $\delta^{18}\text{O}$ values were normalized based on the standards ($\text{NBS-28} = 9.64\text{‰}$), and then transferred from V-SMOW standard to the SMOW standard. A duplication of a vein quartz (X0451) produced two $\delta^{18}\text{O}$ values of 11.23‰ and 11.36‰ , and resulted in a reproducibility error of 0.13‰ . Therefore the total error of $\delta^{18}\text{O}\text{‰}$ values is better than 0.2‰ in this study.

For oxygen isotopic analyses of calcite, each sample was reacted with 100% phosphoric acid in a glass tube in vacuum at 50°C for overnight, and the carbon oxide of calcite was extracted for carbon isotopic analysis. The Namaqualand Marble (NM) standard was used for calibration. The

analytic reproducibility is better than 0.2‰ (Vennemann and Smith, 1990) (see detailed description in carbon isotopes).

Hydrogen analysis

With respect to chlorite- and muscovite-rich mineral separates, the analytical method for hydrogen isotopes is based on Zn reagent for the qualitative conversion of H_2O to H_2 , which is adapted from Vennemann and O'Neil (1993). Standard NBS-30 was run twice with the separated chlorite- or muscovite-rich samples. Duplication of NBS-30 and some samples was within 1.5‰ and the probable error is about $\pm 2\%$. Water measurements were not calibrated in this study due to technical problem.

The major procedures of the analyses are as follows: (1) Sample loading. Sufficient amount of chlorite- or muscovite-rich mineral separates to produce more than 1 mg H_2O are loaded into 12 cm long quartz tubes, pre-roasted at 800 °C and stored at 110 °C prior to use. About 100-200 mg of coarse-grained ($\sim 800 \mu m$) quartz are added into the tubes to prevent collapse of the tube on heating and to retain powders in the bottom of the tube during initial stages of degassing and lowering the temperature of water, released by chemical reaction with sample;

(2) Oxidation of H_2 gas into H_2O by adding CuO. Some H_2 is occasionally released from the reaction and oxidized into H_2O by adding CuO which was held in place by quartz-wool plugs and heated to 700 °C by a high-temperature heating tap. During the reaction, the line is closed off from pumping system, the bypass is isolated and liquid nitrogen is added to the bottom 1/3 of the two traps.

(3) Releasing H_2O from hydrous minerals. The water is released by heating hydrous minerals using a fuel-gas-oxygen torch;

(4) Producing a yield of H_2 by the reaction of H_2O with Zn. The released H_2O is subsequently transferred into a labelled Pyrex tube containing Zn, which is then inserted into a muffle furnace at $480^\circ C$ for ten minutes for a reaction between Zn and H_2O . The reaction of H_2O with Zn produces ZnO and a quantitative yield of H_2 . AnalaR® Zn shot (0,5 - 2 mm) and Zn laths are supplied by the biogeochemical laboratory of the University of Indiana.

(5) Isotopes of H_2 are measured by using Micromass® VG602E, double-collector ratio mass spectrometer in the Department of Archaeology, University of Cape Town.

8.4.3 Results

A total of thirty six $\delta^{18}O$ values and ten δD values for bulk rocks, mineral separates and quartz and calcite were obtained and are tabulated in Table 8-3.

Oxygen

For the entire bulk rocks, the $\delta^{18}O$ values are in a range of from 6,1 to 10,4‰ (Table 8-3). For different rock types, the $\delta^{18}O$ values are (1) between 6,1‰ and 8,3‰ for lava samples; (2) between 9,1‰ and 10,6‰ for conglomerates; and (3) between 9,4‰ and 10,4‰ for quartzites (Table 8-3).

A histogram of $\delta^{18}O$ values for bulk rocks in terms of alteration types has been plotted, together with the $\delta^{18}O$ values for the Ventersdorp-age dolerite and the world gabbros/basalts for

Table 8-3 Oxygen isotope compositions for bulk rocks, mineral separates, vein and amygdale quartz and vein calcite in the VCR

Sample	Type	Lithology	Zones	Description	$\delta^{18}O_{\text{‰}}$ (SMOW)
BH020	Rock	Lava	MC	Strongly altered amygdaloidal lava	8,3
GBE-2	Rock	Lava	MC	Strongly altered amygdaloidal lava	7,4
1145A	Rock	Lava	DG	Least altered phenoclastic lava	6,1
1145B	Rock	Lava	DG	Least altered amygdaloidal lava	6,5
BHE-1	Rock	lava	DG	Least altered massive lava	6,9
B0364	Rock	VCR	RA	Ms-rich conglomerate	10,6
XR1614	Rock	VCR	RA	Light green conglomerate	9,1
XR1618	Rock	VCR	RA	Dark grey conglomerate	10,2
I0705	Rock	Qtz	DGA	Qz-Ch-Ms-sulfides	9,6
B0366	Rock	Qtz	DGA	Qz-Ms-Ch	9,8
B0415	Rock	Qtz	DGA	Qz-Ms-Ch	10,4
BH021	Rock	Qtz	GG	Qz-Ms	9,4
BH1-10	Rock	Qtz	GG	Qz-Ms	9,8
BGH14	Rock	Qtz	GG	Qz-Ms	10,0
133019	M-sep	Lava	MC	85%Ch, 15% Ms with Qz	6,1
133729	M-sep	VCR	RA	100% Ms with Qz	7,8
133730	M-sep	VCR	RA	100% Ms with minor Qz	7,2
133017	M-sep	qtz	DGA	95%Ms, 5%Ch with Qz	8,4
133731	M-sep	qtz	DGA	95%Ms, 5%Ch with Qz	8,4
133732	M-sep	qtz	DGA	100%Ms with Qz	8,5
133020	M-sep	qtz	GG	100%Ms with Qz	7,4
133734	M-sep	qtz	GG	100%Ms with Qz	7,9
133736	M-sep	qtz	GG	95%Ms, 5%ch with Qz	8,0
133737	M-sep	qtz	AGNQ	95% Ms, 5% Ch with minor Qz	8,1
R-1	Qz-A	Lava	-	From amygdaloidal lava	10,7
XR1662	Qz-A	Lava	-	From amygdaloidal lava	10,3
XR1640	Qz-A	Lava	-	From amygdaloidal lava	10,4
BHE-6	Qz-A	Lava	-	From amygdaloidal lava	9,5
B0397	Qz-A	Lava	-	From amygdaloidal lava	10,7
X0436	Qz-V	Cc-Qz-V	-	From Qz vein with some Ms	10,3
X0451	Qz-V	Cc-Qz-V	-	from zoned Qz calcite vein	11,3
XR1669	Qz-V	Cc-Qz-V	-	From calcite Qz vein in shale	10,3
No4	Qz-V	Cc-Qz-V	-	From calcite Qz vein	9,6
B0397	Cc-V	Cc-Qz-V	-	From calcite Qz vein	9,7
X0451	Cc-V	Cc-Qz-V	-	From calcite Qz vein	9,0
XR1699	Cc-V	Cc-Qz-V	-	From calcite Qz vein	8,9

Note: M-sep - mineral separate; Qz - quartz; Cc - calcite; Qtz - quartzite; A - lava amygdale; V - vein; Ms - muscovite

comparison in Fig. 8-6. The results show that they plot in centralised clusters and there exists isotopic shifting between different alteration zones, although no clear distribution patterns, e.g. normal pattern etc., can be identified due to the limited data sets. For the lava samples, the least altered lavas are more or less similar to those (5,5‰ and 6,7‰) of the Ventersdorp-age dolerite from the Witwatersrand Basin, which cut through some quartzites of the Witwatersrand Supergroup (Harris & Watkins, 1990) and are in the range of the world gabbros/basalts (cf., Faure, 1986). The dolerite has been thought to have had no exchange with the hosting quartzite at the conditions of lower greenschist facies (Harris & Watkins, 1990). The VCR seems to have the heaviest $\delta^{18}\text{O}$ values. The GG zone quartzite, being thought least altered in the profile through the VCR hanging wall lavas, VCR conglomerates and footwall quartzite, seems to be skewed to lighter $\delta^{18}\text{O}$ values and the DGG zone quartzite seems to be closer to these of the VCR conglomerates. The $\delta^{18}\text{O}$ values of quartzite (Harris & Watkins, 1990) almost overlap with the GG zone quartzite. These quartzites are not related to any reefs and are away from the dolerite dykes (Harris & Watkins, 1990).

The $\delta^{18}\text{O}$ values of muscovite/chlorite mineral separates from the VCR and related lithologies are plotted in Fig. 8-7, together with the bulk rocks and world gabbros/basalts for comparison. It clearly indicates a very similar distribution trend for the mineral separates to those of the bulk rocks as shown in Fig. 8-6. All the mineral separates are lighter than the correspondent bulk rocks.

For single minerals, all $\delta^{18}\text{O}$ values of the studied samples are (1) between 9,5‰ and 10,7‰ for the amygdale quartz; (2) between 9,6‰ and 11,3‰ for the vein quartz; (3) between 8,9‰ and 9,7‰ for vein calcite. The $\delta^{18}\text{O}$ values are plotted together with those from lava agates from the Karoo for comparison in Fig. 8-8. The results show that the $\delta^{18}\text{O}$ values from amygdale quartz

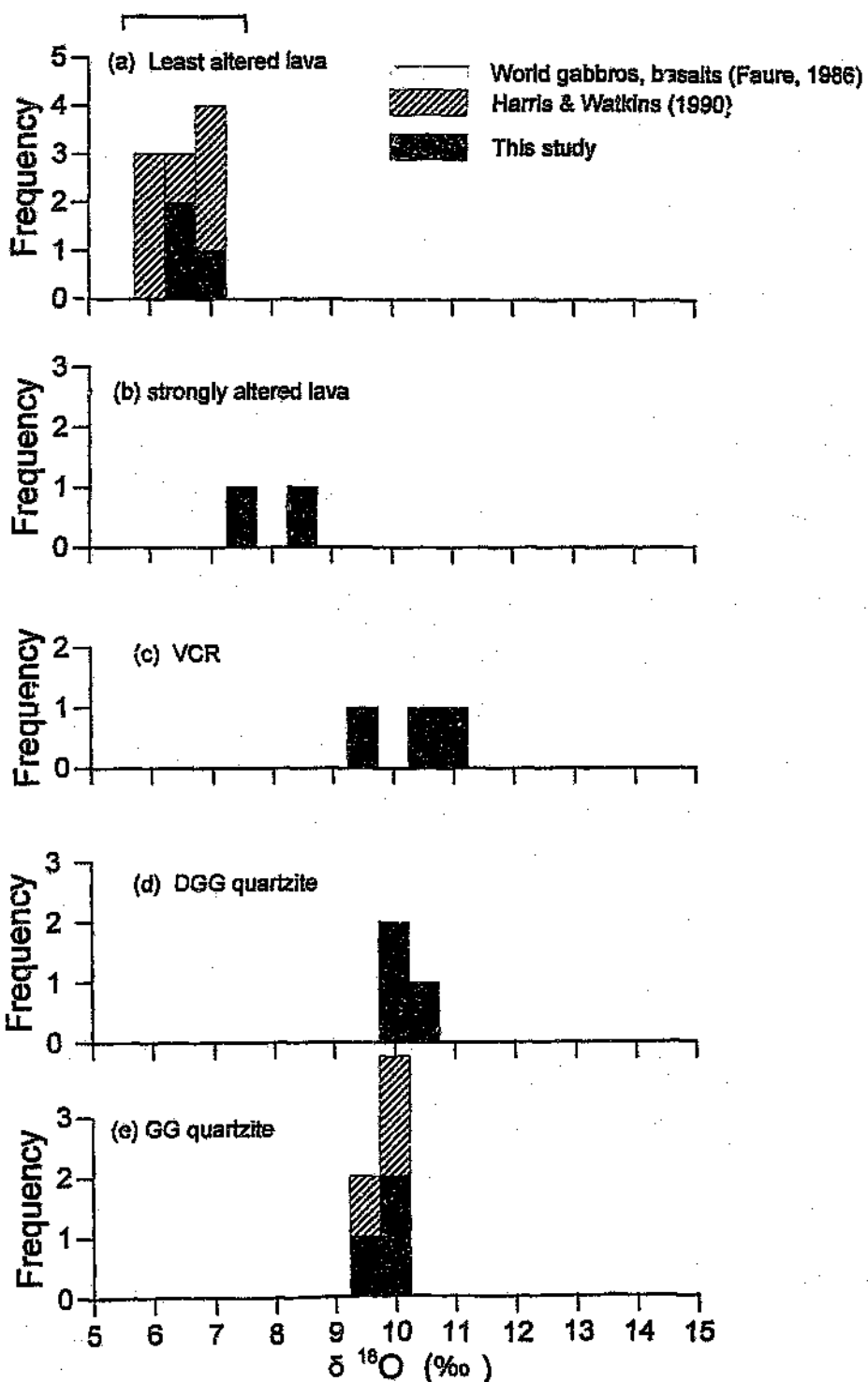


Fig. 8-6 Histogram of $\delta^{18}\text{O}$ (‰) for bulk rocks in the VCR, together with collected data from Harris & Watkins (1990). (a) Least altered lava; (b) Strongly altered lava; (c) VCR conglomerate; (d) Strongly altered quartzite (DGG); (e) Least altered quartzite (GG).

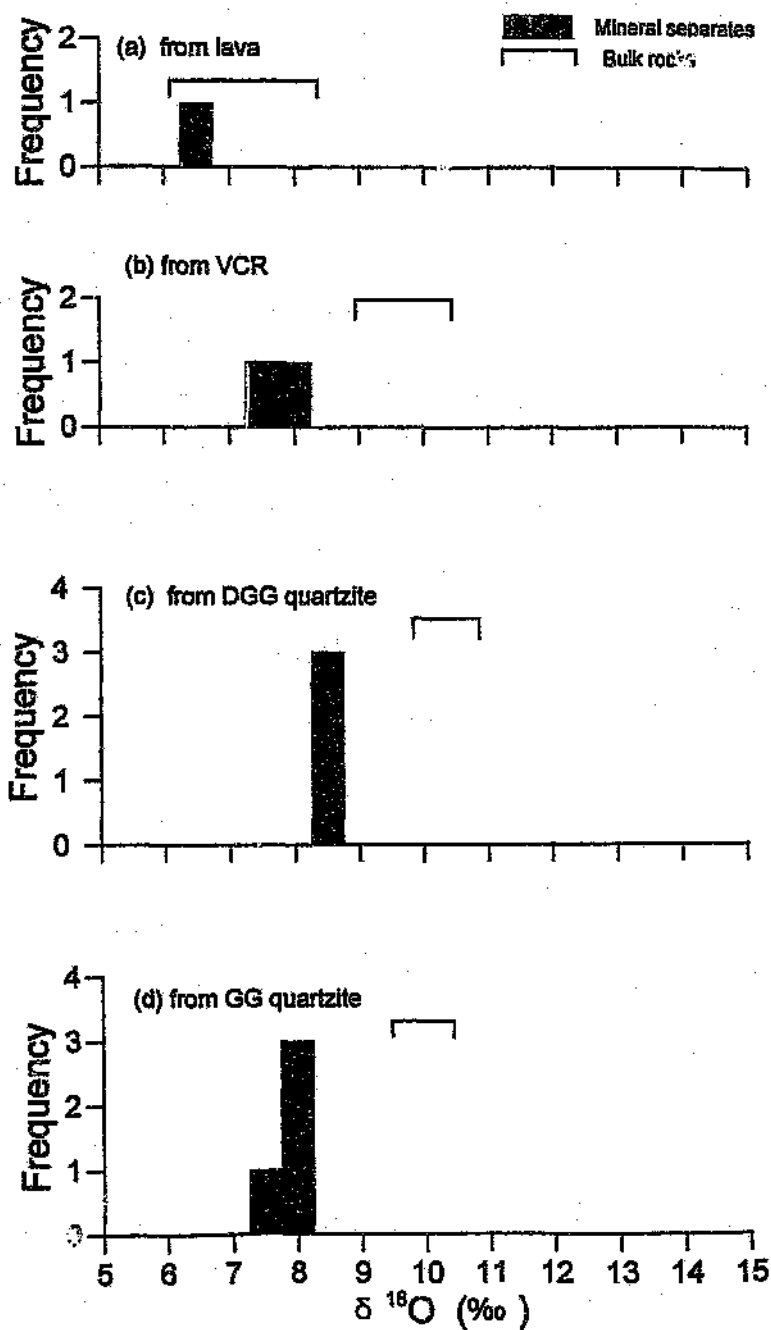


Fig. 8-7 Histogram of $\delta^{18}\text{O}$ (‰) values for muscovite and chlorite mineral separates in the VCR, together with the correspondent bulk rocks.

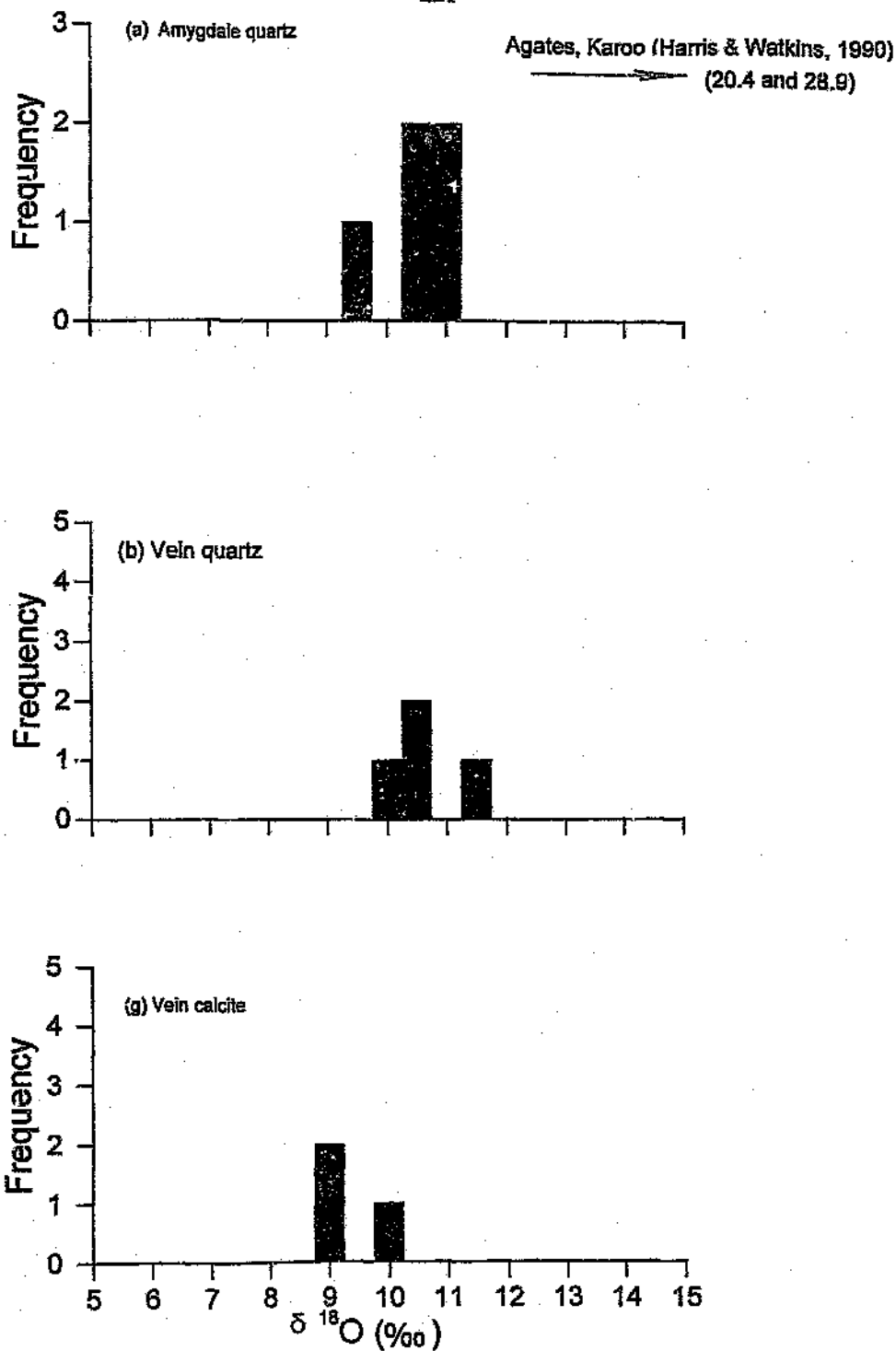


Fig. 8-8 Histogram of $\delta^{18}\text{O}$ (‰) for amygdale quartz, vein quartz, vein calcite in the VCR., together with values for the agates from the Karoo (Harris & Watkins, 1990).

almost totally overlap with those of vein quartz, while the $\delta^{18}\text{O}$ values for vein calcite are obviously lighter than these of both amygdale and vein quartz with some overlap. Moreover, $\delta^{18}\text{O}$ values are much lighter than those from lava agates in Karoo volcanics, which are representative of enrichment of meteoric fluid by boiling at low temperature (Harris & Watkins, 1990).

Oxygen and hydrogen in fluids

A total of ten δD values for minerals were obtained from the separated chlorite-rich (1) and muscovite-rich (9) samples in hanging wall lava, VCR conglomerates (RA zone and AGNQ quartzite) and footwall quartzite (DGG zone, GG zone). Most of the data are between -52‰ and -62‰ with one extreme of -31‰ (Table 8-1).

(a) calculation of oxygen and hydrogen isotopes for hydrothermal fluids

The isotopic composition of 'fossil' waters can be measured in fluid inclusions (Ohmoto & Rye, 1974; Richardson et al., 1988) and estimated based on the laboratory calibrations of equilibria between rock-forming minerals and water (cf., Rollinson, 1993). The latter method is used in this exercise to calculate the δD and $\delta^{18}\text{O}$ values in the fluids.

An equation of the equilibrium O-isotope fractions for illite based on experimental, empirical and /or theoretical data has obtained by Sheppard and Gilg (1996):

$$1000\log \alpha_{\text{illite-water}} = 2.39 \times 10^6 \times T^{-2} - 3.76$$

The equation is suitable for the temperature condition of 400 ° - 200 °C. If we assume that muscovite is the illite type the equation is suitable for the purpose of calculation of $^{18}\text{O}/^{16}\text{O}$ in this study.

Based on equilibrium of muscovite-water, most of the empirical and experimental data for hydrogen suggest the fraction is not very sensitive to temperature variation in the range of between 400 ° and 120 °C and can be approximate as $1000 \ln \alpha = -25 \pm 5\text{‰}$ (Sheppard & Gilg, 1996).

The mineral separates contain muscovite, chlorite and quartz. Nine of the 10 mineral separates are muscovite predominant (>95 wt%). Quartz in the samples is negligible for hydrogen isotopes and currently no proper oxygen and hydrogen fractionation factors for chlorite-water equilibrium are presented at temperatures between 290 ° and 350 °C. Therefore the nine muscovite-rich samples are used for the calculation of $^{18}\text{O}/^{16}\text{O}$ and $\text{D}/^1\text{H}$ for hydrothermal fluids in the VCR using the two equations of Sheppard and Gilg (1996) based on muscovite-water equilibrium. The maximum temperature condition at 350 °C is used for the calculation. The results show that all the δD values for the hydrothermal fluids are between -27‰ and -39‰ with one extreme of -6‰ which comes from apple green quartzite (AGNQ) and all the $\delta^{18}\text{O}$ values are between 4,8‰ and 6,1‰ (Table 8-4). Moreover, the apple green quartzite is also different from the other sediments in terms of geochemistry in the VCR as described in Chapter 5.

A diagram of oxygen and hydrogen isotopic compositions of the hydrothermal fluids in terms of alteration zones is plotted in Fig 8-10. Fields of magmatic water (Taylor, 1974) and metamorphic water (Taylor & Sheppard, 1981), together with the meteoric water line (Epstein et al., 1965; Epstein, 1970) are also plotted for comparison. Fig. 8-9 demonstrates that all the data in this study plots in the field of metamorphic water except for the extreme point which does not plot in any of the fields of magmatic and metamorphic waters. The $\delta^{18}\text{O}$ and δD values of modern waters from several major gold mines in the Witwatersrand Basin (Duane et al., 1997) are also

Table 8-4 Oxygen and hydrogen isotope data from mineral separates and for hydrothermal fluids estimated from mineral-water equilibria in the VCR

Sample	Lithology	Zones	Description	$\delta D\text{‰}$ (SMOW)		$\delta^{18}O\text{‰}$ (SMOW)		Water wt.%
				M/separates	Water	M/separates	Water	
133019	Lava	MC	85%Ch, 15%Ms with Qz	-61	-	7.8	-	8.49
133729	VCR	RA	100% Ms with Qz	-61	-36	7.8	5.4	1.89
133730	VCR	RA	100% Ms with minor Qz	-52	-27	7.2	4.8	4.00
133017	qtz	DGG	95%Ms, 5%Ch with Qz	-58	-33	8.4	6.0	4.39
133731	qtz	DGG	95%Ms, 5%Ch with Qz	-62	-37	8.4	6.0	4.01
133732	qtz	DGG	100%Ms with Qz	-64	-39	8.5	6.1	2.95
133020	qtz	GG	100%Ms with Qz	-52	-27	7.4	5.0	4.05
133734	qtz	GG	100%Ms with Qz	-59	-34	7.9	5.5	4.26
133736	qtz	GG	95%Ms, 5%Ch with Qz	-62	-37	8.0	5.6	3.71
133737	qtz	AGNQ	95% Ms, 5% Ch with minor Qz	-31	-6	8.1	5.7	3.46

Note: M/separates - mineral separates; Ms - muscovite; Qz - quartz; Ch - chlorite; qtz - quartzite; MC, RA, DGG, GG, AGNQ see Chapter 4.

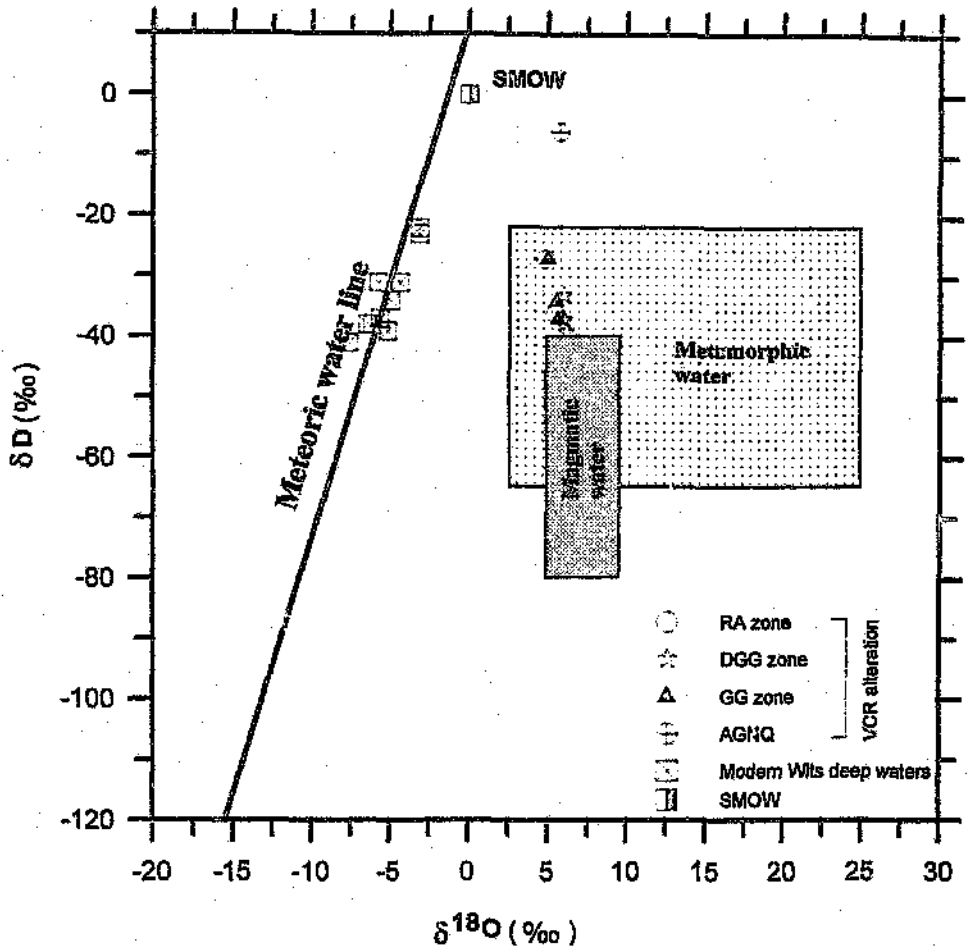


Fig. 8-9 Diagram of oxygen and hydrogen isotopic compositions of hydrothermal fluids calculated from muscovite in alteration zones of the VCR at WDLMS. The calculated fraction factors of oxygen and hydrogen for muscovite-water are from Sheppard and Gilg (1996). The data of the modern Witwatersrand gold mine deep waters (Duane et al., 1997), fields of magmatic water (Taylor, 1974), metamorphic water (Taylor, 1974; Sheppard, 1981) and meteoric water line (Epstein et al., 1965; Epstein, 1970) are also plotted.

added in the diagram for comparison and for interest (Fig. 8-9). All the samples plot along the meteoric water line except for two eliminated points, which have been interpreted to be of meteoric water origin with modifications (Duane, et al., 1997). If no oxygen and hydrogen isotopic composition variation through geological time is assumed, it seems that none of the δD and $\delta^{18}O$ values for the hydrothermal water correspond to a meteoric component.

8.4.4 Interpretation of the data

$\delta^{18}O$ values of authigenic quartz including both amygdale and vein quartz in VCR, together with those of quartz pebbles from VCR conglomerates (Barton et al., 1992), from the Witwatersrand reefs excluding the VCR (Barton et al., 1992; Vennemann et al., 1992, 1995), and quartz sands from Monarch and Main Reefs in the Witwatersrand Basin, are plotted in a histogram (Fig. 8-10). The results demonstrate that $\delta^{18}O$ values of authigenic quartz (amygdale and vein) form a cluster with a modal value of 10,5‰ (Fig. 8-10a). The $\delta^{18}O$ values for quartz pebbles of the VCR form a cluster with a modal value of 11,5‰, which shows no clear distribution patterns. This probably suggests more than one source for the quartz pebbles if the oxygen isotopes preserve the original characteristics of the source as suggested by Vennemann (1992, 1995) and Barton et al. (1992). $\delta^{18}O$ values for quartz pebbles of the Witwatersrand reefs, excluding the VCR, form a cluster with a modal value of 11,0‰. $\delta^{18}O$ values of quartz sands in the Witwatersrand Basin have a single skewed cluster less than 11,5‰ for the quartz pebbles, which suggests a different source from that of the quartz pebbles (Vennemann, 1995).

In comparison with the $\delta^{18}O$ values of quartz pebbles in the VCR, quartz pebbles and quartz sands in other reefs of the Witwatersrand basin (Barton et al., 1992; Vennemann et al., 1992, 1995), the $\delta^{18}O$ values for authigenic quartz in this study are right in the range of the other $\delta^{18}O$ values. The

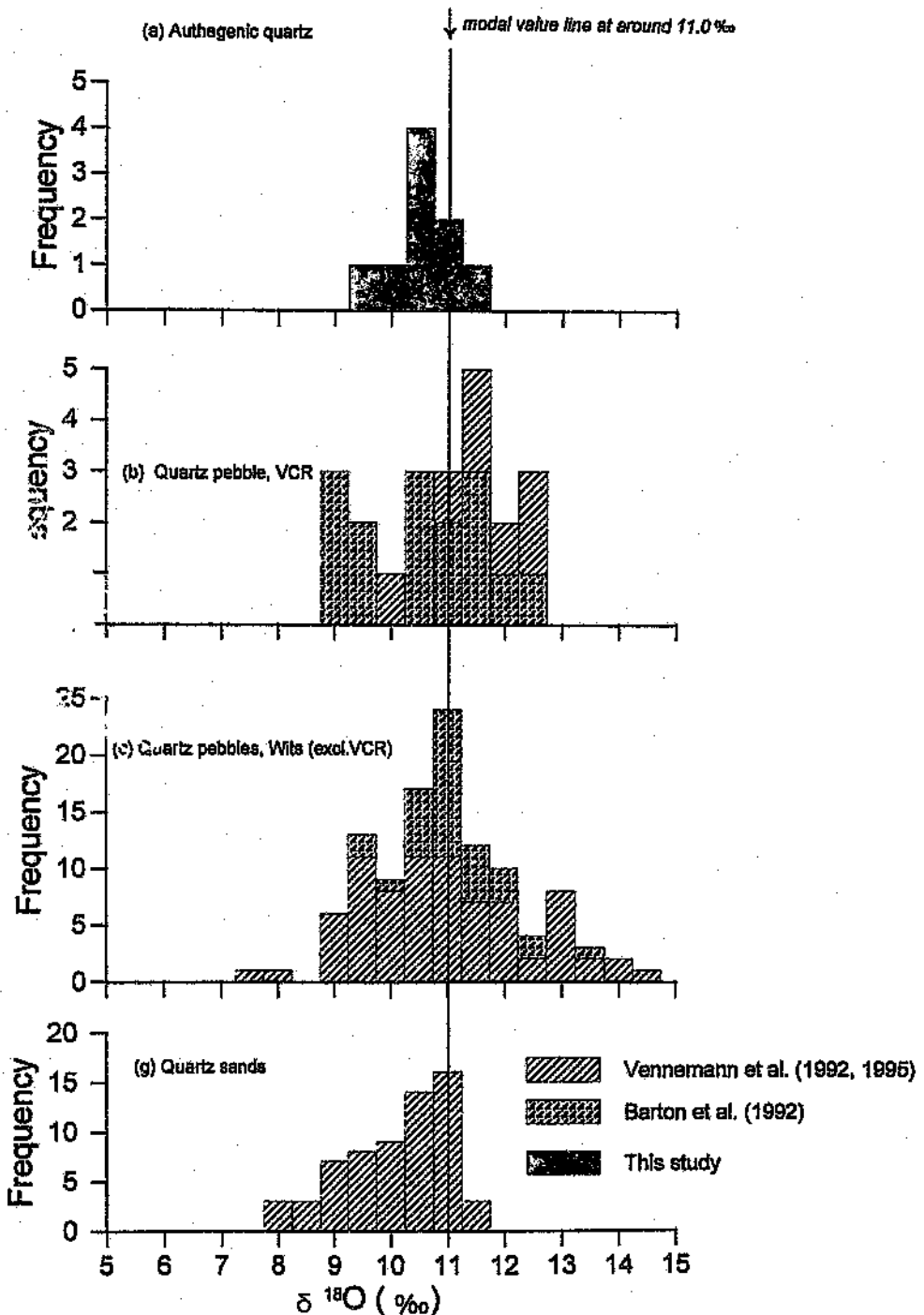


Fig. 8-10 Histogram of $\delta^{18}\text{O}$ (‰) values for authigenic quartz including both vein and amygdale quartz in the VCR, together with those for quartz pebbles from the VCR (Barton et al., 1992; Vennemann et al., 1995), and from Witwatersrand reefs (excluding the VCR) (Barton et al., 1992; Vennemann et al., 1992, 1995), and for quartz sands from the Monarch and Main reefs (Vennemann et al., 1995).

diagram of oxygen and hydrogen clearly indicates a metamorphic origin for the hydrothermal waters, which were produced by processes of degassing, partially or fully dewatering of hydrous minerals and releasing of pore water from the sediments during metamorphism in the Witwatersrand Basin (Stevens et al., 1996; Drennan, 1997). Furthermore, buffering of oxygen isotopes for the hydrothermal fluids mainly by detrital quartz materials (quartz pebbles and quartz sands) is clearly supported by the results of oxygen and hydrogen isotopes.

8.5 Carbon isotopes

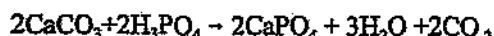
Three calcite samples from quartz-calcite veins have been described in the oxygen isotopes.

8.5.1 Methodology

Carbonate samples were reacted with 100% phosphoric acid at 25 °C and carbon was analysed as CO₂ gas using mass spectrometers equipped with double collectors. Measurements were made relative to the PDB standard of the University of Chicago (*Belemnitella americana* from the Cretaceous Peedee formation, South Carolina) which has $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are close to those of average marine limestone. A summary of the sample preparation and analytical procedures is as follows:

- (1) Sample preparation. Vein samples containing calcite and quartz were crushed into small chips, from which the calcite grains were collected in a reasonable purity by hand due to the coarse-grained texture.
- (2) Sample loading. 10-20 mg ground powder sample (not too fine) was loaded into the sample chamber in the carbonate line;
- (3) CO₂ was produced by the reaction of CaCO₃ with acid. 5 ml of 100% H₃PO₄ was added (density between 1,9 and 1,92) to the reaction chamber for the reaction of CaCO₃ at 25,2 °C

constantly for about one hour. The reaction is as follows:



(4) Isotopes of CO_2 were measured using Micromass[®] VG602E, double-collector ratio mass spectrometer in the Department of Archaeology, University of Cape Town.

NM (Namaqualand Marble) standard was run with each batch of samples. The difference between the NM result and the actual value is then subtracted from each sample. The observed reproducibility of the internal laboratory standards is about $\pm 0.2\%$.

8.5.2 Results and interpretation of the data

Three $\delta^{13}\text{C}$ values of calcite from quartz-calcite veins in VCR were analysed and show a range of from -8.4% to -10.0% (Table 8-5). In order to compare the carbon isotope data with those of Kiemd et al. (1994) from bitumen in the VCR, the $\delta^{13}\text{C}$ values of graphite have been calculated based on the calculated isotope fraction factors for carbon from Bottinga (1969) (Table 8-5). The $\delta^{13}\text{C}$ values of graphite estimated are in a range of between -20.0% and -18.4% and are in the lower limit of the $\delta^{13}\text{C}$ values (-20.6 and -32.4%) of Kiemd et al. (1994).

Table 8-5 Carbon isotope data for calcite from quartz veins and for graphite estimated from calcite-graphite equilibrium (Bottinga, 1969) in the VCR

Sample	$\delta^{13}\text{C}\%$ (PDB)	
	Calcite	Graphite
B0397	-8.4	-18.4
X0451	-8.9	-18.9
XR1699	-10.0	-20.0

The $\delta^{13}\text{C}$ values of carbon, calculated from calcite-graphite equilibrium are plotted together with those of bitumen from VCR conglomerates of Klemd et al. (1994) in the diagram of Rollinson (1993) for natural carbon reservoirs (Fig. 8-11). The results show that the $\delta^{13}\text{C}$ values of the VCR bitumen are in the range of biomass and largely overlap with the sedimentary organic carbon. This supports an organic origin for the VCR bitumen as suggested by Klemd et al. (1994). Furthermore the calculated $\delta^{13}\text{C}$ values of carbon in calcite do not correspond to the ranges of the VCR bitumen, but there is some overlap of the upper limits of natural biomass reservoir and the VCR bitumen. In addition, the carbon in calcite in the VCR is different from the other natural reservoirs. There is no evidence of the existence of chondritic meteorites, therefore an origin due to chondritic meteorites can be excluded from the source of carbon for the VCR. This suggests that C in both calcite and bitumen in the VCR is organic in origin.

8.6 Summary

A large data set of sulphur, oxygen, hydrogen and carbon isotopes in the VCR has been obtained in this study (Table 8-1, 2, 3, 4, 5), and also has been compared with the previous data for the Witwatersrand Basin (Fig. 8-4, 9), which have provided invaluable information about the history of mineralisation, sources of major detrital minerals and authigenic minerals and some physicochemical conditions for the VCR and the Witwatersrand Basin as a whole. $\delta^{34}\text{S}$ values for authigenic sulphides in the VCR have a narrow range of between -1,5‰ and +1,3‰. $\delta^{18}\text{O}$ values are in a range of between 6,1‰ and 10,4‰ for bulk rocks and between -8,4‰ and 11,3‰ for authigenic quartz and calcite. $\delta^{18}\text{O}$ values and δD values for hydrothermal fluids in the VCR are between 1,9‰ and 4,4‰, and between -27‰ and -39‰ with one extreme value of -6‰,

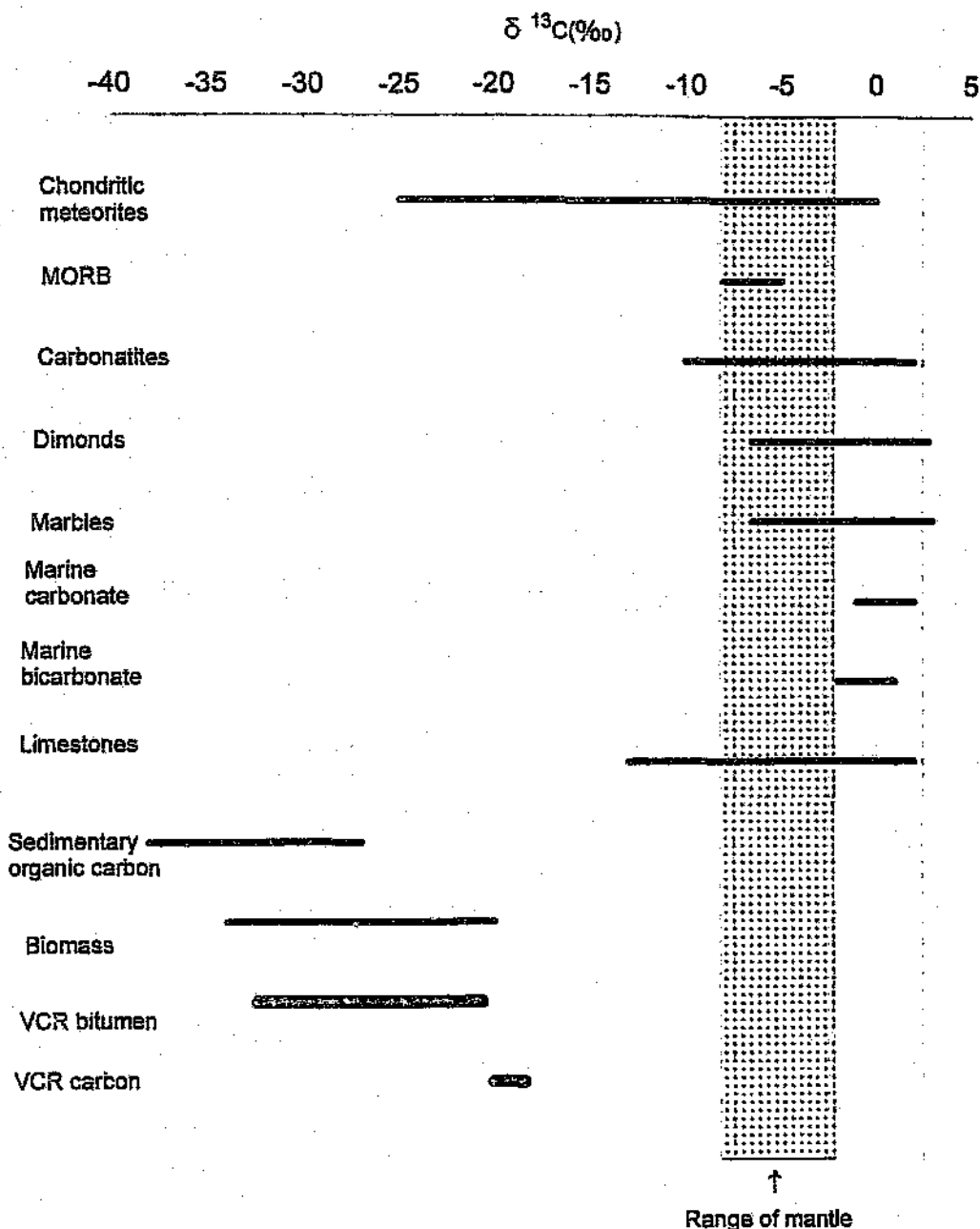


Fig. 8-11 Plot of $\delta^{13}\text{C}$ values of graphite calculated from calcite-graphite equilibrium, together with the VCR bitumen in the diagram of natural carbon reservoirs (after Rollinson, 1993). Data of natural reservoirs from Kenridge (1985), Exley et al. (1986), Field and Fifarek (1986), Hoefs (1987) and Schidlowski (1987).

respectively. $\delta^{13}\text{C}$ values in the VCR are between -8,4‰ and -10,0‰ for vein calcite and -20,0‰ and -18,4‰ for estimated carbon material (graphite).

Two sulphide paragenetic sequences have been suggested by the sulphur isotope data which is consistent with the results of mineralogical study in Chapter 4. The sulphide precipitation temperatures from the earlier paragenetic sequence of pyrite and pyrrhotite are $394 \pm 157^\circ\text{C}$. The effect of alteration on oxygen isotopes is suggested by the increase of $\delta^{18}\text{O}$ values with alteration scale in the bulk rock samples and muscovite- and chlorite mineral separates (Fig. 8-6, 7). $\delta^{18}\text{O}$ values in the quartz veins are similar to those of amygdale quartz (Fig. 8-8), suggesting an origin in the same fluid system during the post-depositional events.

Isotopic data for sulphur, oxygen and carbon suggest a sedimentary system, altered by post-depositional hydrothermal fluids. The major detrital materials (sulphides, quartz pebbles and sands) were provided by sedimentary processes for the VCR and the Witwatersrand Basin as a whole, while major carbon materials (bitumen and calcite) are organic in origin. Circulation of hydrothermal fluids in the VCR and the Witwatersrand Basin reconstituted the detrital materials and organic carbon, resulting in resetting of the sulphur, oxygen, hydrogen and carbon isotope systems. Hydrothermal fluids in the VCR were derived from metamorphism (Fig. 8-10) with the multiple processes of dewatering, degassing and pore-water releasing of clay minerals during the peak metamorphism and circulation in the Witwatersrand Basin.

9 K-Ar DATING

9.1 Introduction

9.1.1 Previous isotopic age determinations relevant to the present study

The Witwatersrand strata were deposited by 2714 Ma, the presently accepted age for the base of the Ventersdorp Supergroup (Armstrong et al., 1991). Very little systematic thermochronology has, however, been published for the auriferous reefs of the Witwatersrand Basin and most of the post-depositional events considered applicable to the basin are inferred either from the age of superjacent strata or obtained from imprecise reset, whole-rock "ages" of rock suites in and around the depository. Robb et al. (1997) have presented a framework for the major post-depositional events of the Witwatersrand Basin and they inferred that these events are related to periods of enhanced fluid flow and alteration with which the development of a distinct paragenetic sequence of mineralization can be related. They recognized three main "events" which are; (i) ca. 2550 Ma which is an event associated with onset of deposition of the lower portion of the Transvaal Basin and further burial of the Witwatersrand Basin ; (ii) ca. 2300 Ma which is associated with deposition of the upper portion of the Transvaal Basin and further burial of the basin; and (iii) 2060-2020 Ma which is an interval contemporaneous with the intrusion of the Bushveld Complex and the catastrophic impact of the Vredefort meteorite into the basin (Reimold & Gibson, 1996, Gibson et al., 1997).

A significant proportion of the rocks in and around the Witwatersrand Basin is characterized by isotope systems that were initiated or re-set in the interval 2060 to 2020 Ma. This time period is characterized by two significant events on the Kaapvaal Craton,

namely the emplacement of the Bushveld Complex and its satellites at 2060-2054 Ma and the Vredefort impact structure at 2020 Ma (Walraven et al. 1990; Kamo et al., 1996; Gibson et al., 1997). Both these events impinged geographically on the Witwatersrand basin, and a feature which supports the now general view that the peak of metamorphism and the most extensively developed hydrothermal alteration in the basin also occurred in the interval 2060 to 2020 Ma (Gibson & Wallmach, 1995; Stevens et al., 1997). Direct evidence for thermal and isotopic perturbation in the basin at this time is provided by detrital uraninite in the conglomerate layers which has been re-set at 2040 ± 100 Ma (Rundle & Snelling, 1997). Witwatersrand shales yield a K-Ar age of 1946 ± 40 Ma for the <2 mm clay fractions, that was interpreted as resulting from a recrystallization process (Layer et al., 1988), while pseudotachyllite from the Ventersdorp Contact Reef yields well-defined and consistent $^{40}\text{Ar}/^{39}\text{Ar}$ plateau ages which average 2006 ± 17 Ma (Trieloff et al., 1994). Mylonite from the Joel Gold Mine in the Free State yields an $^{40}\text{Ar}/^{39}\text{Ar}$ plateau age of 2038 ± 5 Ma, and pseudotachyllite breccia from Witwatersrand quartzites in the collar rocks of the Vredefort Dome provide ages of 2023 ± 6 Ma (Reimold et al., 1996). Muscovite from the same area also yields $^{40}\text{Ar}/^{39}\text{Ar}$ plateau ages of 2029 ± 5 Ma. Biotite from the central, granulite grade, gneissic core to the Vredefort structure yields similar ages of 2026 ± 4 Ma (Reimold et al., 1995).

Intrusion of the Bushveld Complex between 2060 and 2054 Ma is now believed to have been associated with the development of a major high-level crustal plume and magmatic underplate which caused regional metamorphism over much of the Kaapvaal Craton (Gibson & Stevens, 1997). This event was followed by a massive bolide impact into the Witwatersrand Basin some 30 million years after emplacement of the Bushveld Complex.

Unequivocal evidence for this is provided by the recognition of planar deformation features in quartz which are related to shock deformation, and similar features in zircons and in an impact melt, which yield U-Pb concordia ages of 2023 ± 4 Ma and 2017 ± 5 Ma respectively (Kamo et al., 1996; Gibson et al., 1997).

These events are clearly related to the peak of metamorphism in the Witwatersrand Basin, as well as widespread retrogression and hydrothermal fluid circulation that must have accompanied thermal relaxation and crustal rebound after the impact event. What is less well documented is the influence of Eburnian (or Kheisian in local parlance) orogenesis along the western edge of the Kaapvaal Craton during the Palaeoproterozoic. Although age data are less well constrained, it is clear from a compilation of whole rock Rb-Sr, U-Pb, Pb-Pb and K-Ar data for Archaean rocks of the Kaapvaal Craton that widespread re-setting of isotope systems took place between 2.0 and 1.9 Ga (Duane & Kruger, 1991). The lower end of this range coincides with development of the Eburnian orogeny to the West of the craton. Furthermore, carbonate-hosted Mississippi-Valley type Pb-Zn deposits in the dolostones of the Transvaal Supergroup in the western portion of the latter basin are now believed to be related to tectonically driven, district-scale brine migration also induced by easterly verging compression associated with the Kheis orogeny (Duane & Kruger, 1991; Duane et al., 1991). The existence of at least one K-Ar age at ca. 1950 Ma from shale from the Witwatersrand Basin (Leyer et al., 1988) suggests that Eburnian-aged re-setting and/or fluid circulation might also have affected the latter basin in the central portion of the craton.

9.1.2 Aims of this chapter

The object of this chapter is to undertake a detailed petrographical, mineralogical and morphological study of the phyllosilicates present in the major lithologies of the VCR and to compliment this study by detailed K-Ar isotopic dating in order to be able to date the paragenetic sequences of alteration and gold mineralization in the reef.

9.2 Sample description

Four types of mica were recognized optically in the present study, on the basis of paragenetic sequence and grain size. Coarse-grained ($>200\text{ }\mu\text{m}$) detrital muscovite is often kinked, banded and replaced by chlorite. Medium-grained ($100\text{--}200\text{ }\mu\text{m}$) muscovite has a tabular texture and overgrows quartz grains, or it occurs as interstitial filling replacing albite and chlorite. Fine-grained ($40\text{--}50\text{ }\mu\text{m}$) muscovite typically replaces feldspar detritus along crystallographic axes. Extremely fine-grained mica ($<10\text{ }\mu\text{m}$) comprises the matrix of the sediments and alteration products of lava. Electron microscopy has revealed that fine grained muscovite exhibits a typical authigenic morphology (See later). Ore mineralogy in the VCR is also characterized by a predominance of authigenic phases by comparison with less altered conglomerate horizons and there are very few obvious detrital heavy minerals other than zircon. Round pyrite grains of possible detrital origin are rarely observed overgrown by abundant pyrrhotite, which is also associated with minor arsenopyrite, sphalerite, chalcopyrite and galena (see Chapter 4). Gold in the VCR is invariably associated with the alteration mineral assemblage with little or no textural evidence for any remnants of detrital grains.

Samples were selected from a variety of lithologies in and around the Venterspost

Conglomerate Formation, including the hanging-wall lava, the conglomerate itself, and quartzite from the footwall succession. Samples were also selected to be representative of the various alteration zones (Table 9-1). In total fourteen samples for K-Ar dating were collected: three from the Ventersdorp lavas; three from the Reef Alteration (RA) zone of the VCR itself; four from the Dark Grey (DGG) zone of the footwall quartzites; three from the Greenish-Grey (GG) zone of quartzites; and one from the Apple-Green Quartzites (AGNQ) (Zhao et al., 1994). Samples from the lavas are characterized by enrichment of chlorite and quartz with minor amounts of muscovite. Chlorite is enriched in the dark-coloured samples, whereas muscovite is concentrated in light coloured samples from the RA zone. Samples from the DGG zone of the quartzites are mainly composed of muscovite and quartz, with minor chlorite and sulphides. Fine-grained muscovite is enriched in the samples from both the GG and AGNQ zone quartzites.

9.3 Analytical techniques

Fig. 9-1 is a flow chart showing analysis techniques and procedures employed in this study. Some quartzite samples were processed in distilled water after gentle disaggregation using repetitive cycles of freezing and thawing, that was designed to avoid artificial reduction of the framework components of the rocks (See Appendix B). The indurated conglomerate and quartzite samples were crushed in a jaw and an agate-bowl crusher. Separation of <2 , 2-6 and 6-10 μm size fractions was performed by sedimentation in distilled water (see Appendix C). Each separated size fraction was examined by X-ray diffraction (XRD) analysis made on an untreated, an ethylene-glycolated, and a heated aliquot. Some of the <2 μm size fractions were separated into further sub-fractions ($<0,4$ or $<0,6$, 0,4-1 or 0,6-1, 1-2 μm) by continuous-flow

Table 9-1 Concentration of K₂O, K-Ar isotopic data from separated clay fractions at WDLSP

[illegible]

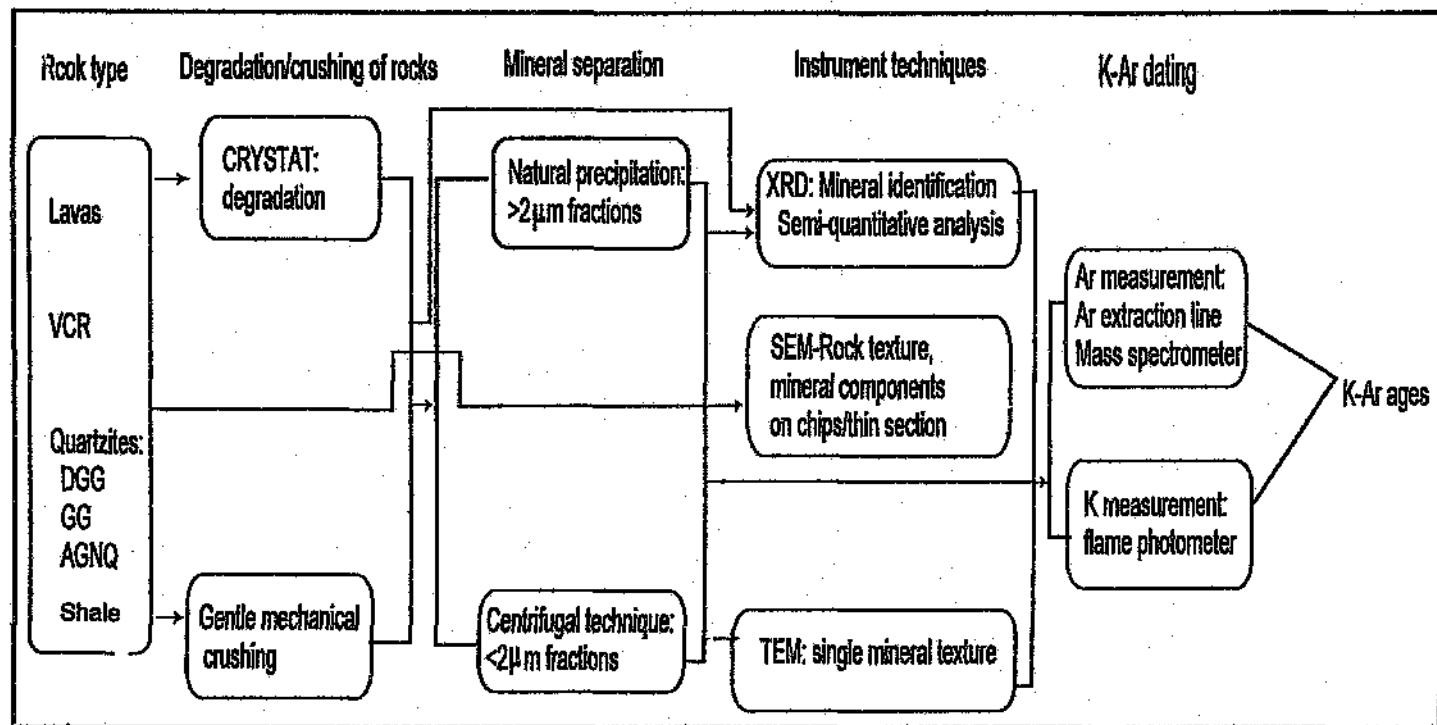


Fig. 9-1 Flow chart showing analytical techniques employed for K-Ar dating in this study.

The separated fractions were dated by the K-Ar method following a procedure close to that described by Bonhomme et al. (1975) and also similar to the description of Dallmeyer et al. (1989). Fig. 9-2 is a schematic diagram of an argon extraction system. The samples were stored under vacuum for about 24h and heated at 100 °C before Ar analysis to remove Ar of atmospheric origin. Potassium analyses were carried out by flame spectrophotometry with an accuracy better than $\pm 2\%$. The spike used for calibration was enriched ^{39}Ar at 99,99% purity. The spike was calibrated in comparison with the GLO-glaucinite standard with a value of $24,80 \times 10^{-6} \text{ cm}^3$ (STP) radiogenic ^{40}Ar . The $^{40}\text{Ar}/^{39}\text{Ar}$ ratio of the residual atmospheric Ar of the mass spectrometer and the extraction line was also controlled during the course of the study. The decay constants used for age calculation are those recommended by Steiger & Jäger (1977).

9.4 Results

9.4.1 Petrographical and mineralogical characteristics of the samples

The euhedral morphological characteristics of mica-type alteration minerals interstitial to detrital quartz grains in the footwall quartzites are shown in SEM photomicrographs (Fig. 9-3a, b and c). The TEM photomicrography also reveals the distinctive pseudohexagonal hypidiomorphic character of single muscovite grains with sharp edges (Fig. 9-3d) which are assumed to represent typical features for authigenesis.

Mineral compositions were also subjected to semi-quantitative XRD analysis. Diffractograms of some illite (used as a genetic term for micaceous material here)-rich clay fractions of untreated samples showing the first basal reflections in different lithologies (Fig. 9-4). The results of the XRD study indicate a monotonous phyllosilicate

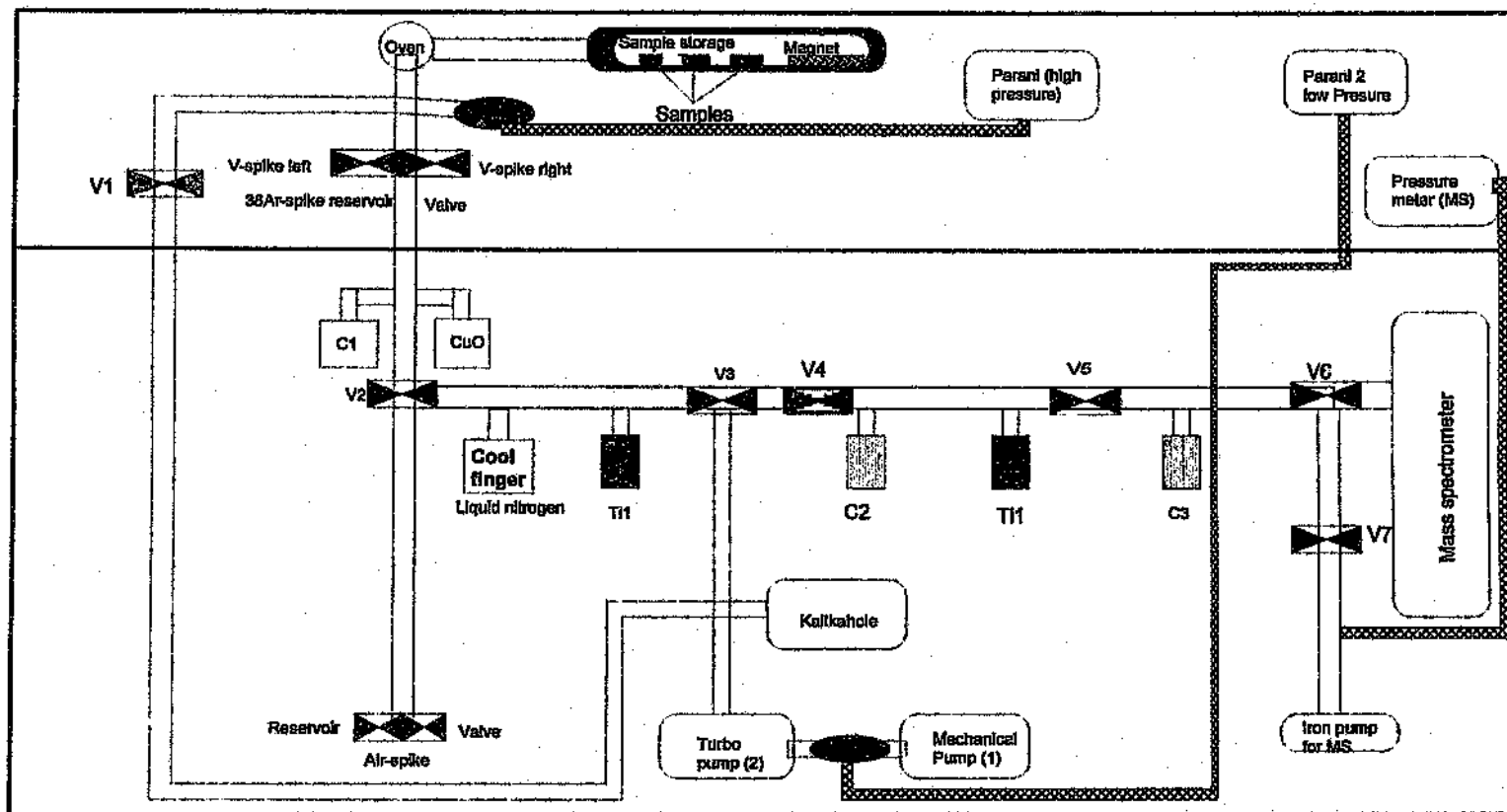


Fig9-2 Diagram of Ar extraction line with mass spectrometer at the Centre de Gechimie de la Surface, Strasbourg, France

C-Activated charcoal finger absorbing all gases, Ti- titanium removing all the reactive gases (O_2 , N_2 , CO_2 , H_2), CuO-Oxidize H_2 and Hydrocarbone to H_2O and others respectively, V1-numbered valve. See text for more details.

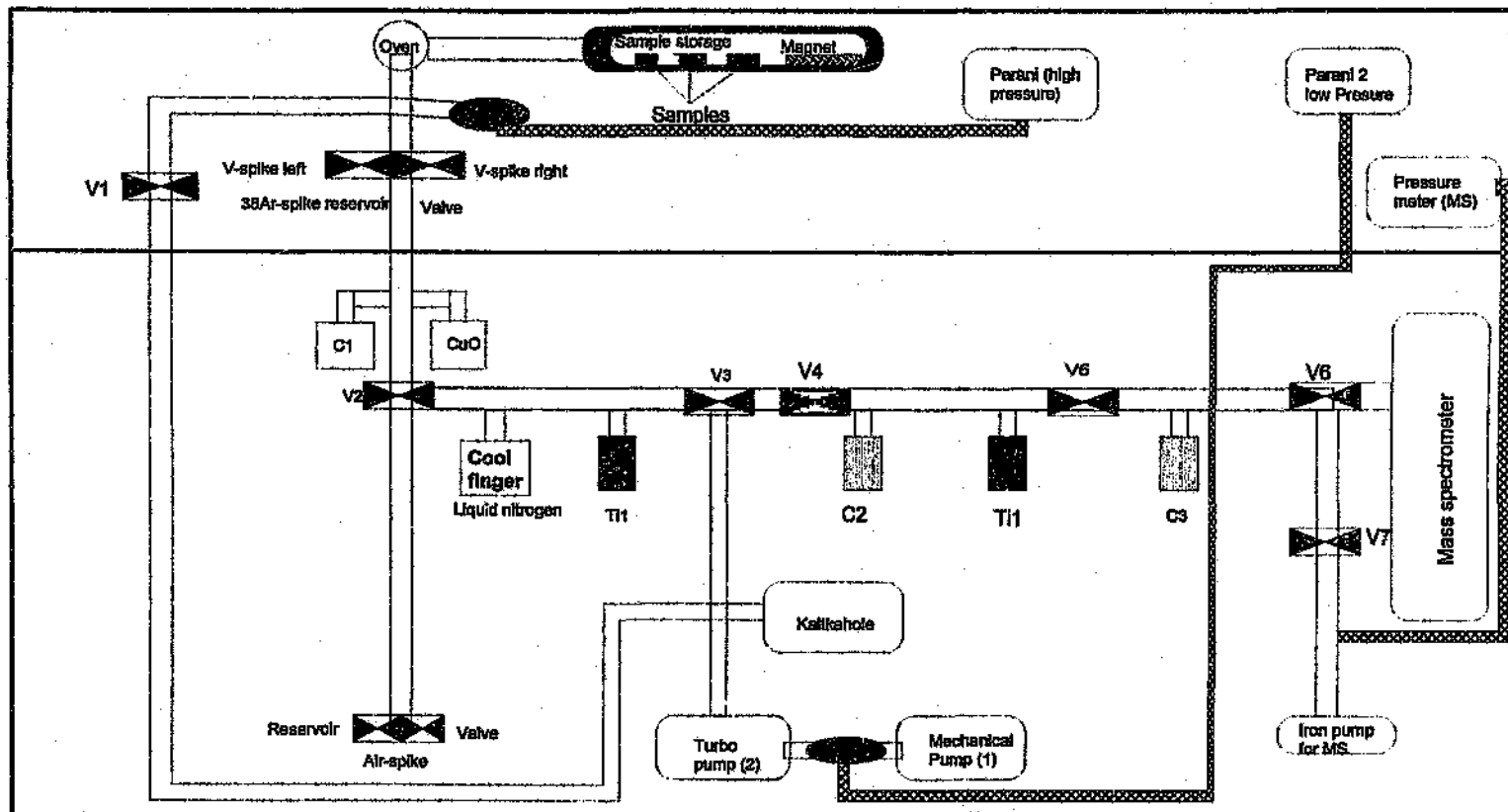


Fig9-2 Diagram of Ar extraction line with mass spectrometer at the Centre de Géchimie de la Surface, Strasbourg, France

C-Activated charcoal finger absorbing all gases, Ti- titanium removing all the reactive gases (O_2 , N_2 , CO_2 , H_2), CuO-Oxidize H_2 and Hydrocarbone to H_2O and others respectively, V1-numbered valve. See text for more details.

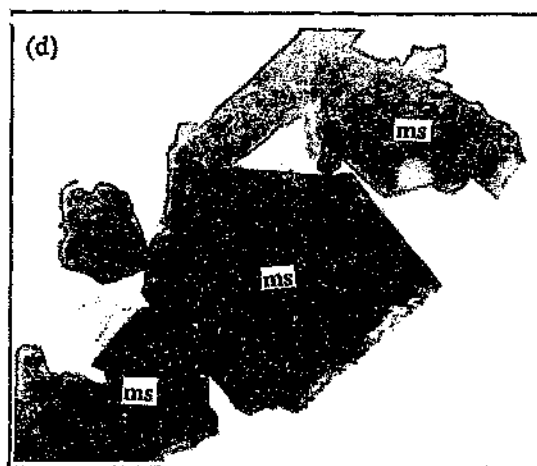
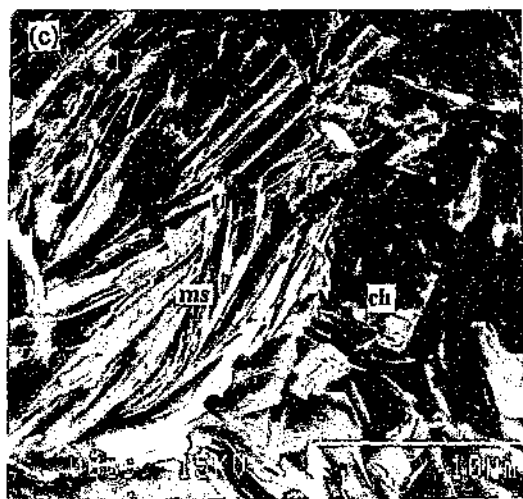


Fig. 9-3 SEM and TEM photomicrographs showing the authigenic nature of mica-type mineral in the VCR. a) co-existence of secondary chlorite, quartz and muscovite in between larger detrital quartzite pebbles; b) euhedral quartz grain intergrown with authigenic muscovite in footwall quartzite; c) intergrown, euhedral muscovite and chlorite in apple-green quartzite; and d) separated, pseudo-hexagonal, hypidiomorphic muscovite grains from the VCR. q (I)—detrital quartz; q (II) authigenic quartz; ms—muscovite; ch—chlorite.

assemblage of illite and chlorite ranging from almost pure fraction to trace amounts depending on the samples and size fractions (Fig. 9-4). The separation and fractionation procedure has not significantly "contaminated" the size fractions in feldspar grains (Fig. 9-4). Quartz is generally present in larger amounts (Fig. 9-4), but it is not affecting the K-Ar dates of the phyllosilicates. Each sample was examined by X-ray diffraction (XRD) analysis on untreated, ethylene-glycolated, and heated aliquots, and shows an absence of pyrophyllite, kaolinite and interlayered clays.

The illite crystallinity index (ICI) is measured as the width of the (001) XRD peak of the illite component in the size fractions following a technique advocated by Kübler (1968). Basically the sharper the XRD peak, which means in turn the smaller the ICI, the better is the mineral crystallized and the higher were the temperature conditions of its crystallization. The ICI is here sharp (Fig. 9-4) and is very consistently between 2,0 and 2,5 which corresponds to formation temperatures probably as high as 300 °C. The determined polymorphic type is systematically 2M1, confirming high crystallization conditions (see Chapter 4).

9.4.2 K-Ar dates

The K-Ar dates of the different size fractions extracted from different lithologies are scattered between 1830 and 2054 Ma (Table 9-1). However, most of the results range from 1863 to 2054 Ma. Plots of all K-Ar dates and selected data for more than one analysis in the single samples versus size fractions show that the K-Ar dates are not distinguishable from each other in terms of rock types and alteration zones (Fig. 9-5a) and that the range in the K-Ar data seems to be size dependant for all fractions, in particular, the <2 µm size fractions (Fig. 9-5a, b).

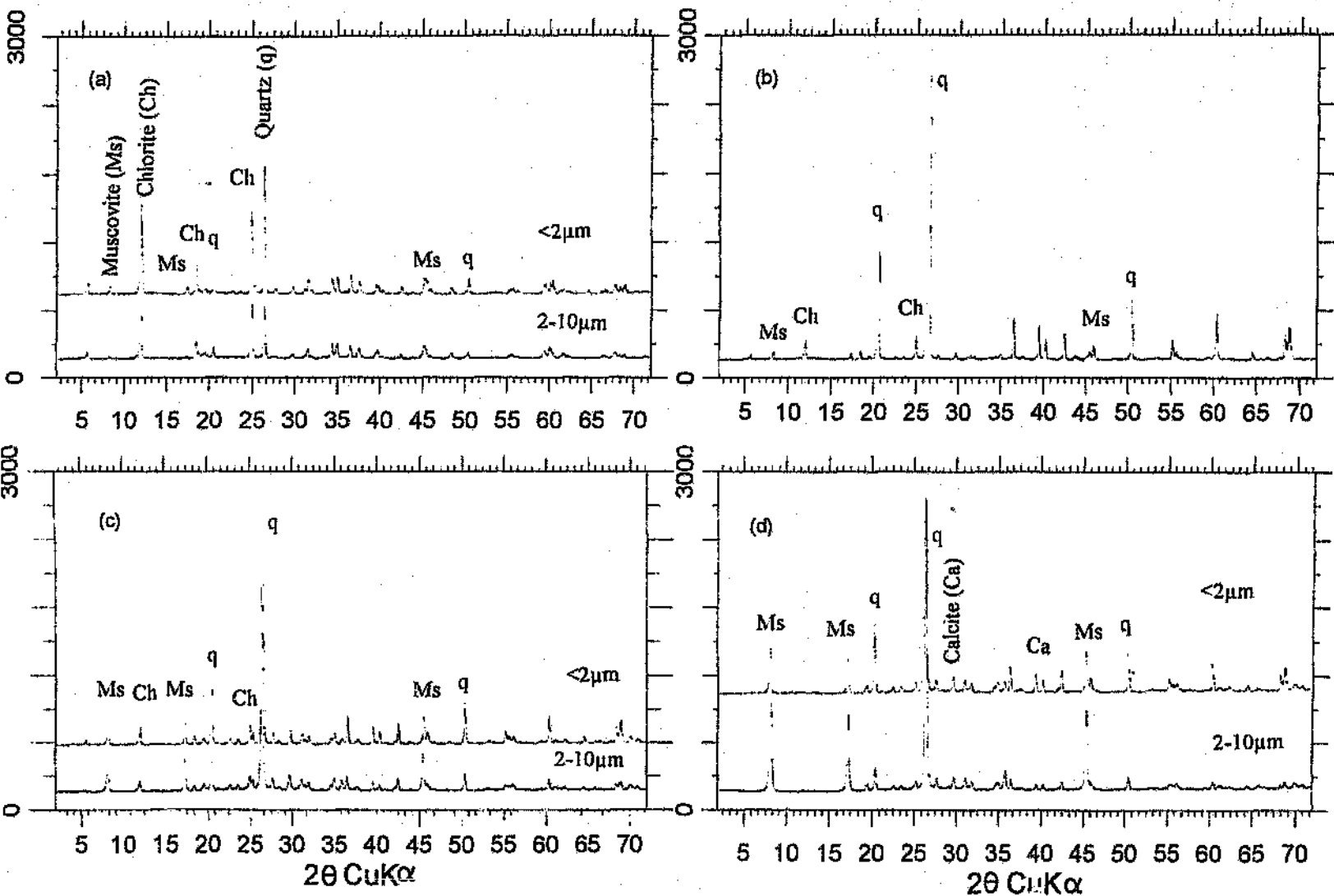


Fig. 9-4 Diffractograms of some illite-ch clay fractions showing the first basal reflections in different lithologies. (a) lava (019); (b) VCR (016); (c) DGG quartzite (017); and (d) GG zone quartzite (020).

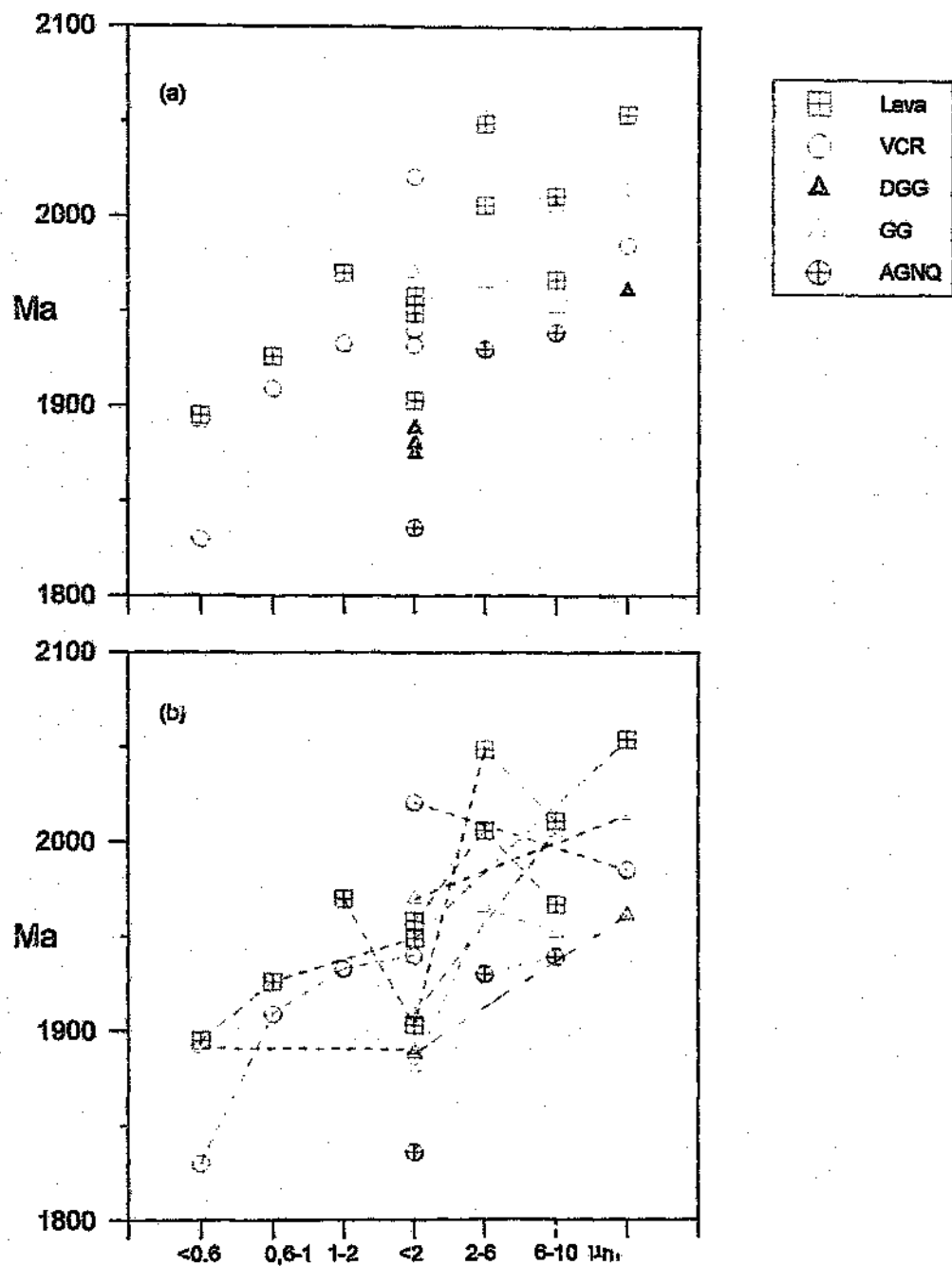


Fig. 9-5 Plots of K-Ar dates vs size fractions in the VCR. (a) all data; (b) the selected data (>1 analysis in single samples).

The K-Ar dates are further subgrouped into $<2\ \mu\text{m}$ and $2\text{--}10\ \mu\text{m}$ size fractions and plotted in a frequency histogram, showing distribution of K-Ar ages as a function of size fraction (Fig. 9-6). It seems that there are two distributions separately for the $<2\ \mu\text{m}$ and $2\text{--}10\ \mu\text{m}$ size fractions although the dates of the $<2\ \mu\text{m}$ size fraction largely overlap those of the $2\text{--}10\ \mu\text{m}$ size fractions. The K-Ar dates of the $<2\ \mu\text{m}$ fractions scatter mainly in the range of 1890 to 1965 with an average of 1914 Ma, while those of the $2\text{--}10\ \mu\text{m}$ are in a range of 1931 to 2054 Ma with an average of 1982 Ma (Fig. 9-6, Table 9-1). There is a significant difference of 74 Ma in the averages between the two fractions.

9.5 Discussion

The results of detailed mineralogical studies of the alteration mineral assemblage in the VCR suggest that the sequence underwent pervasive recrystallization and/or neoformation of minerals at about 300 °C. This temperature based on illite crystallinity indices and fluid inclusion microthermometry (Zhao et al., 1994) indicates that the K-Ar isotopic signatures of the precursor phyllosilicates have effectively been re-set, at least in the small grain sizes. If it is assumed that little or no radiogenic ^{40}Ar has diffused out of the clay- and mica-type fractions extracted from the low-grade VCR metasediments, and if the K-Ar dates of size subfractions in the $<2\ \mu\text{m}$ range provide very similar ages within analytical uncertainty, it can be taken that the dates provide an indication of the mineral paragenesis (e.g. review by Clauer & Chaudhuri, 1995; Clauer et al, in press). Alternatively, if the K-Ar dates increase as a function of the size fractions, then one might be dealing with two or more generations of minerals (and/or geological events), or with some preferential loss of Ar from smaller grains.

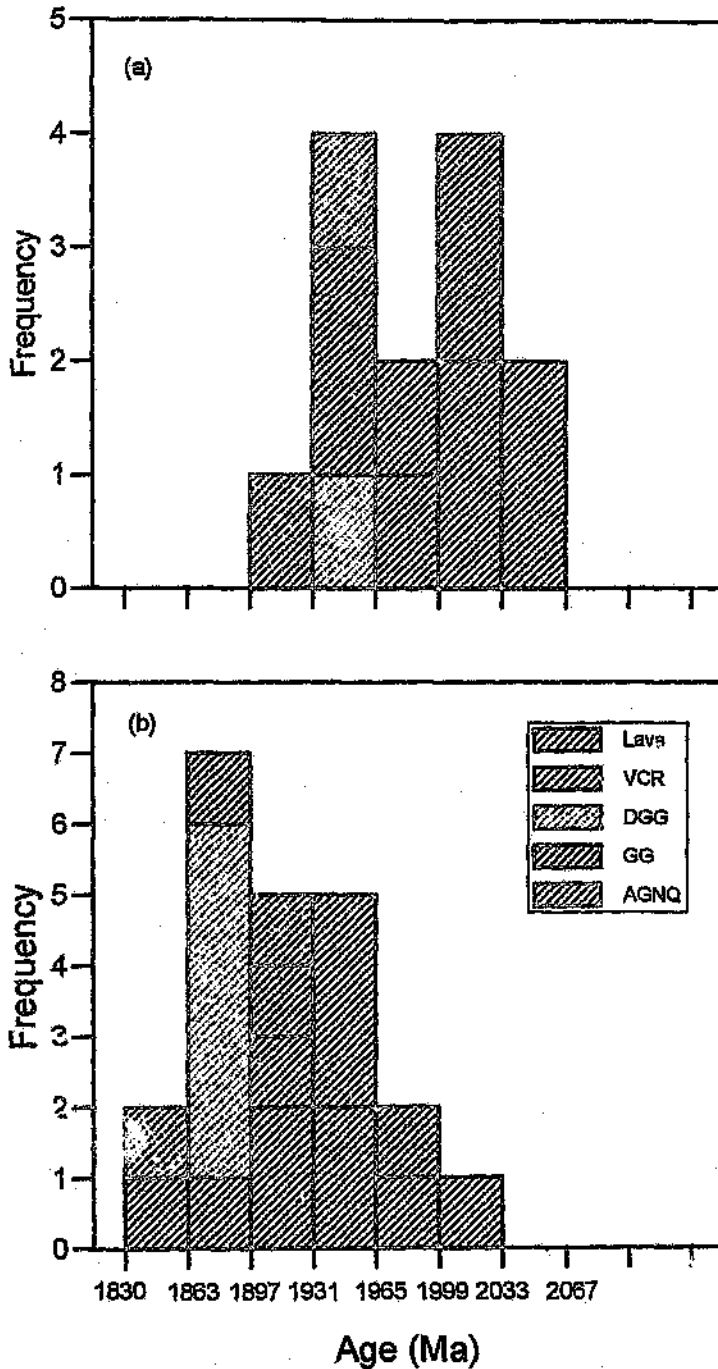


Fig. 9-6 Frequency histogram showing distribution of K-Ar ages as a function of size fraction. (a) >2 μ m; (b) <2 μ m. DGG—dark grey quartzite; GG—light grey quartzite; and AGNQ—apple green quartzite.

Most of the K-Ar ages reported for the $>2\mu\text{m}$ fractions of the VCR fall in the range 1930-2056 Ma. Any thermally sensitive radiometric age determination in the range 2054-2017 Ma in the Witwatersrand Basin can logically be ascribed to re-setting of isotope systems or neoformation of minerals during the regional climax of Witwatersrand metamorphism attributable to Bushveld magmatism, as well as the catastrophic bolide impact, crustal fracturing and fluid flow that accompanied formation of the Vredefort structure. Alternatively, metamorphic retrogression and waning of fluid flow subsequent to these events could also explain crystallization of minerals with ages somewhat younger than ca. 2020 Ma. It is also conceivable that at least two generations of micas are mixed in the size fractions, one having a probable age of about 1914 Ma or less and the other having an age of 1988 or more in average. This is supported by the fact that the K-Ar dates of the $<2\mu\text{m}$ fractions from different lithologies in the VCR package, scatter mainly in the range 1890 to 1970 Ma ages which extend for up to 130 million years after the Vredefort cataclysm. It is highly unlikely that these ages would reflect continuous retrogression and isotope re-setting of the Witwatersrand rocks and a more likely interpretation of these data should be found in another, unrelated geological event. Such an event does exist in the form of the Eburnian orogeny to the West of the craton, which although not yet dated with precision, is known to have lasted between 1800 and 2000 Ma. As mentioned previously, this orogeny is also believed to be related to sub-crustal scale, tectonically driven fluid migrations which could have affected selected fluid channelways within the Witwatersrand Basin (Friese et al., 1995). This event may re-set existing mica-types and may have been responsible for the newly formation of very fine-grained authigenic minerals along particularly permeable channelways such as the VCR. Many of the $<0,2\mu\text{m}$ subfractions and even some of the $<2\mu\text{m}$ fractions of the volcanics, the

conglomerates, and the quartzites yield a mean K-Ar age of 1900 ± 10 Ma. Such an age for mica-type minerals occurring in VCR lithologies has not yet been reported in the literature to the best of our knowledge. Only the whole-rock K-Ar dates by Layer et al. (1998) approach this value.

The VCR is recognized as one of the most severely altered and metamorphosed of the conglomerate reef packages in the Witwatersrand Basin. It records evidence, in terms of K-Ar ages of micaceous minerals, of extensive isotope re-setting and neoformation of authigenic minerals in the interval 2050-1850 Ma. This broad interval is suggested to reflect at least two unrelated geological events, initially coincident with the peak of Witwatersrand Basin metamorphism, which include intrusion of the Bushveld Complex and its satellites, the Vredefort meteorite impact and the palaeoproterozoic Eburnian (or Kheisian) orogeny. These events are likely to have had a pronounced effect, not only on the VCR, but on strata throughout the basin, and impinge on the important consideration of when gold was remobilized and authigenically concentrated. The absence of earlier post-depositional events, recorded elsewhere at ca. 2550 Ma and 2300 Ma (Robb et al., 1997) suggests that, at least in the VCR, the period between 2050 and 1850 Ma was the most important as far as alteration and gold mineralization are concerned.

9.6 Summary

The minerals were separated into various grain sizes (between 0.4-10 μm) either by freezing/thawing disaggregation or normal crushing, with subsequent sedimentation and centrifuging. XRD, SEM, and TEM were employed to characterize the mineral separates in terms of composition, paragenetic sequence and texture (Fig. 9-1). The information

obtained from these techniques was used to interpret the ages obtained from the size fractions.

The K-Ar dates define a continuum of ages between ca 1830 Ma and 2050 Ma; this is a tendency for smaller size fractions to yield younger ages in the range (Table 9-1, Fig. 9-5, 6). The older ages range of 1931 to 2054 Ma (1988 Ma in average) overlap with the intrusion of the Bushveld Complex at 2061-2054 Ma, as well as the 2020 Ma event represented by the Vredefort catastrophism. Both of these events had a pronounced effect on the isotopic systematics over widespread areas of the Witwatersrand Basin. The younger age range of 1890 to 1965 Ma (1914 Ma in average) is less well constrained and may be related to Eburnian orogenesis along the western edge of the Kaapvaal Craton (Duane et al., 1991; Duane & Kruger, 1991), which resulted in continental scale fluid migration and hydrothermal activity that extended throughout the Griqualand Basin and even into the Witwatersrand Basin.

10 SUMMARY AND CONCLUSIONS

10.1 Nature of alteration associated with the VCR at WDLMS

The alteration at WDLMS is characterized by bleaching of the hanging wall lavas and colouration of the VCR and footwall quartzites. The alteration zone is about 1 to 10 m wide. In detail, at least seven alteration zones are recognized by the alteration mineralogy and geochemistry; they are the DG, WG and MC zones in the hanging wall lavas of the Klipriviersberg Group; the RA zone in the VCR itself, and the DGG, LDG and GG zones in the footwall quartzites of the Central Rand Group. The alteration mainly comprises the formation of chlorite, quartz, muscovite, albite, sulphide and carbonate with minor amounts of epidote, rutile, sphene and talc. The DG zone is characterized by enrichment of chlorite; the WG is enriched in carbonates; the MC is predominantly composed of sphene; the RA is marked by chlorite, muscovite, and sulphides (pyrite, pyrrhotite); the DGG is enriched in chlorite, muscovite and sulphides (sphalerite, galena, and pyrrhotite>pyrite); the LDG mainly consists of muscovite, chlorite, and sulphides (pyrite>pyrrhotite); and the GG is mainly composed of muscovite. The AGNQ internal quartzite, which is interbedded with the VCR, is characterized by enrichment of sphene and muscovite. These characteristics suggest that the alteration is produced by interaction of hydrothermal fluids with the diverse wall rocks including lavas, conglomerates and quartzites.

The major mineral paragenetic assemblage of the VCR-related alteration zones is chlorite-muscovite-quartz - albite - sulphide - carbonate $\pm$ rutile $\pm$ sphene $\pm$ epidote $\pm$ talc. Higher temperature mineral

assemblages, such as K-feldspar, amphibolite, pyroxene and garnet, are not observed at WDSLML. This indicates overall mesothermal physicochemical conditions for the alteration, which is consistent with regional metamorphic conditions of greenstone facies metamorphism as described by Phillips et al. (1989).

Albite is commonly observed in the strongly altered DG, RA, DGG and LDG zones, where it replaces sulphides or occurs as albite-quartz-calcite veins. These characteristics indicate that albite postdates sulphidization. Intensive chloritization in strongly altered zones, together with the local development of talc in the GG and MC zones indicates that the hydrothermal solutions were rich in Mg^{+2} . The widespread occurrence of muscovite in all the alteration zones suggests that the solutions were also enriched in K^{+} . Enrichment of carbonate in the WA in the hanging wall lava and occurrences in the RA zones and DGG zone footwall quartzite indicate enrichment of Ca^{+2} in the solutions. Sulphidization (pyrite, pyrrhotite, chalcopyrite, galena, and sphalerite) indicates that the solutions were enriched in Fe^{+2} , Cu^{+2} , Pb^{+2} , Zn^{+2} , and S^{+2} .

10.2 Geochemistry of whole rocks

Samples of hanging wall lava from WDSLML have been classified as subalkaline basalt-andesite, but some samples deviate from the standard compositions. This may be a result of hydrothermal alteration. The quartzites from the DGG, GG zones and AGNQ are grouped into Fe-sandstone, arkose-subarkose, and litharenites (Fig. 6-8). The division of the quartzites is based on their original rock characteristics, and an allowance is made for hydrothermal alteration.

The hanging wall lavas at WDLMS are characterized by enrichment of Fe_2O_3 , and K_2O but depletion of MgO , CaO and Na_2O relative to the Klipriviersberg Group lavas which represent the least altered rocks. The VCR (RA zone) is characterized by enrichment of MgO , CaO , and K_2O , but no obvious depletion of other elements in comparison with other Witwatersrand conglomerates. Major oxides of the quartzites from both DGG and GG zones are similar, but the DGG zone is relatively enriched in Fe_2O_3 , MgO , and Na_2O and depleted in CaO and K_2O . The AGNQ internal quartzite, however, is different from the DGG and GG zones, and is enriched in Al_2O_3 , CaO , and K_2O relative to the strongly altered footwall quartzite (DGG). The bulk compositions of the major rock types and alteration zones (lavas, RA, DGG, GG, AGNQ) in the study area clearly controlled the nature of the various alteration assemblages present.

For trace elements, the hanging wall lavas at WDLMS are characterized by enrichment of Ba, Cu, and Zn, and by depletion of Rb and Sr, in comparison with the Klipriviersberg Group (Fig. 5-23). The RA zone (VCR conglomerates) is enriched in Zn, and depleted in Cr relative to the VCR data from Elandsrand Gold Mine (Fig. 5-13). The difference in trace element pattern between the Upper Unit and Lower Unit conglomerates of the VCR at Elandsrand Gold Mine (Fig. 5-13), together with the similarity of the VCR in terms of the trace elements to the hanging wall lavas support the concept of incorporation of lava materials into the VCR (Chapter 5), rather than presence of different source areas as suggested by Henckel and Schweitzer (1994). Trace elements in the DGG are similar to those of the GG zones, however concentrations of Cu and Zn in the DGG zone are much higher than in the GG zone.

Mobile trace elements, in particular, Sr, Rb, Ba, Cu, Zn are most likely to be affected by hydrothermal fluids while immobile trace elements (Nb, Zr, Ti, V, Cr, Co, Ni) rather represent the primary signature of the original rocks. The fine-grained AGNQ internal quartzite, for example, has a similar pattern in terms of immobile trace elements as the footwall shale in the Booyens Shale Formation (Kimberley Shale). This suggests that it may be affected by its original textures, but it is also likely to be influenced by incorporation of volcanic ash which is also supported by existence of internal lavas in the VCR.

Chemical profiles of the boreholes BH1169 and a underground section (Fig. 5-24, 25, 26, 27) show a systematic relative change in ratios of SiO_2 , Fe_2O_3 , CaO and Na_2O versus Al_2O_3 and those of Cu, Zn, Rb, Sr, Ba versus V. These are probably related to hydrothermal alteration. However, enrichment of immobile elements (Cr, Ni, Zr, Y, Nb) in the DGG zone may indicate presence of a paleoweathering zone on VCR unconformity as suggested by Palmer et al (1989) and Ritger (1990).

Relative gains of mobile elements (MgO , CaO, K_2O) in the VCR (RA zone) conglomerates are evident, and there are matched with depletions of the same elements in the other alteration zones. For example, MgO and CaO in the hanging wall lavas, and K_2O in the DGG zone are depleted. In addition, relative losses of Fe_2O_3 and Na_2O in the VCR are matched by enrichments in the other zones. For example, Fe_2O_3 and Na_2O are enriched in the hanging wall lavas, and DGG zone quartzites. This indicates that a local chemical exchange of mobile components took place within and around the VCR conglomerates due to hydrothermal alteration. Enrichments of Cu and Zn in the hanging wall lavas and the DGG zone footwall quartzite are probably related to circulation of these elements from the VCR conglomerates. On the basis of the geochemistry of different alteration zones,

it is suggested that the fluids responsible for the alteration assemblages in and around the VCR have remobilised some major and trace elements in such a way that this system appears to have remained relatively closed; depletion in certain elements of one alteration zone is matched by concomitant enrichments in adjacent alteration zones, and vice versa.

10.3 Mineral geochemistry

Chlorite-group minerals in the VCR and the Witwatersrand Basin are identified as sudoite, stilpnomelane and ripidolite. They represent different environments and were possibly formed at different stages during metamorphism and hydrothermal alteration. Detrital pyrite is distinguishable from authigenic pyrite in terms of the Co/Ni ratios, indicating that both types of pyrite were generated in different environments. The detrital pyrite represents the original sulphide source for the VCR, whereas the authigenic pyrite formed during post-depositional hydrothermal activity. The source of detrital sulphides and heavy minerals was probably mainly from veins in granitoids with minor amounts from other sources as evidenced by the characteristics of the above mentioned detrital pyrite geochemistry (Fig. 6-8). The chemical compositions of banded sp^{Fe} are inferred to be produced by fluid infiltration during hydrothermal alteration. Some authigenic chalcopyrite show enrichment in Ag. This is indicative of remobilisation of precious metals (Ag, Au?) during mineralization.

The mineral geochemistry of almost all the analysed minerals, such as chlorite, muscovite, albite, pyrite, chalcopyrite, sphalerite and galena, from the different rock types and alteration zones indicate that variations of some elements in these minerals are controlled by their host rocks which buffered fluid and authigenic mineral compositions. This suggests that the authigenic minerals were formed

in a rock-dominated system during peak hydrothermal mineralisation and alteration.

10.4 The nature of the fluids associated with the alteration of the VCR

The microthermometry of fluid inclusions from vein quartz and amygdaloids in the research area indicates that the hydrothermal fluids were H_2O -NaCl solutions, with moderate to high salinities of 8 to 23 wt% NaCl equivalent (eNaCl). The final homogenization temperatures of the inclusions from vein quartz range from 140 to 170 °C, with an average of about 156 °C, and final ice melting temperatures are between -11 to -5 °C, corresponding to salinities of 8 to 12 wt% eNaCl. Fluid inclusions from quartz amygdaloids indicate final homogenization temperatures of 140 to 180 °C, with an average of about 159 °C and salinities of 10 to 23 wt% eNaCl. The plot of the salinity versus homogenization temperatures shows two populations: (1) low salinity, ranging from 10 to 15 wt% eNaCl; and (2) high salinity, from 19 to 23 wt% eNaCl. These salinities may indicate two types of saline fluids during the hydrothermal processes, but this proposition requires additional studies of fluid inclusions.

Recently a summary and study of fluid inclusions from vein quartz in the Witwatersrand Basin by Drennan (1997) and references therein, indicates four types of fluid inclusions: (1) H_2O -NaCl (2 to 15 wt% eNaCl), with total homogenization temperatures (T_h) of 120 to 170 °C; (2) H_2O - CO_2 -NaCl (5 to 30 wt% NaCl equiv.), with T_h of 230 °C; (3) H_2O - CO_2 - CH_4 - N_2 -NaCl (8 to 10 wt% eNaCl), with T_h of 230 to 280 °C; (4) CH_4 - N_2 -rich vapours, with T_h of -40 to -80 °C. The results of limited study of fluid inclusions during this study indicate fluids similar to the Type 1 of Drennan (1997) and the results of ... et al. (1995).

Chlorite and muscovite geothermometers were applied in this study to determine the temperature of mineral formation. The low Si and intermediate Fe contents of authigenic chlorite in the present study are suitable for the chlorite geothermometer (Walshe, 1986), and give estimated temperatures from 290 to 313 °C, which are in good agreement with the chlorite temperature data (305-310 °C) from Meyer et al. (1990). A higher temperature range of 350 ± 57 °C is also estimated from the muscovite geothermometer. This is consistent with the peak metamorphic temperatures of 350 °C for the Witwatersrand Basin (Wallmach and Meyer, 1990). However, low temperature and pressure minerals such as chlorite and 1M muscovite are also observed at WDL SM. Kaolinite was also reported in the Witwatersrand Basin (Zhou et al., 1994). The 1M muscovite and chlorite (Ch2) yield temperatures of 155-245 °C (Table 7-1, 2), which indicates the presence of a low temperature authigenic mineral assemblage, relative to the higher temperature chlorite and muscovite in the VCR. This may imply two periods of thermal activity and hydrothermal fluids in the VCR during hydrothermal alteration.

In combination with the T-P isochores from the fluid inclusions, the trapping temperatures, determined by independent geothermometry of chlorite and muscovite, are at 290 to 350 °C, and these temperatures give the trapping pressures for the fluids of 2,2 to 3,2 kbar, with an average of 2,7 kbar. These pressures are close to the lithostatic pressures of 2,2 to 2,4 kbar, calculated from the maximum stratigraphic thickness of 8 to 9 km for the hanging wall overburden (the Ventersdorp and Transvaal Supergroups). These T-P conditions are consistent with regional metamorphism of greenschist facies at 350 ± 50 °C and 3 kbar (Phillips et al., 1989; Phillips and Law, 1994). Therefore the maximum T-P values for the alteration in the VCR are 350 °C and 3,2 kbar. Based on the maximum temperatures of 350 °C and the maximum stratigraphic thickness of 9 km, a lithostatic

thermal gradient of 39 °C/km for the VCR is estimated, which is close to the geothermal gradient of 40-50 °C/km (Wallmach and Meyer, 1990; Gibson and Stevens, 1997).

The estimated f_{O_2} , f_{S_2} , $a_{H_2S(aq)}$, $f_{H_2S(g)}$ and pH values are: $\log f_{O_2} = -29,7$; $\log f_{S_2} (py/po) = -11,1$; $\log f_{H_2S(g)} = -2,5$; $\log a_{H_2S(aq)} = -2,5$; and pH = 5 (neutral). These values indicate that the fluids responsible for mineralization and alteration were in a reduced, near neutral pH environment during peak metamorphism in the VCR.

10.5 Sources of the fluids inferred from stable isotope geochemistry

The $\delta^{34}S$ values for authigenic pyrite and other sulphides (pyrrhotite, sphalerite, galena, chalcopyrite) in the VCR span a narrow range from between -0,6‰ and -1,8‰ and between -1,5 and 1,0‰, respectively, which is similar to those determined for the detrital pyrite (-1 to 5,6‰). As described in Chapter 8, the sulphur isotope signature for detrital pyrite suggests a derivation from a magmatic source (Jensen & Dechow, 1964; Hoefs et al., 1968; Chukrov et al., 1970; Hattori et al., 1983; Förster, 1986; Drennan, 1997). Under reduced and neutral pH physicochemical conditions, the sulphur isotope compositions of the fluids were little fractionated ($\delta^{34}S$ values $< \pm 2\%$) so that the $\delta^{34}S$ values of authigenic pyrite and pyrrhotite, sphalerite, galena, chalcopyrite are representative of the total sulphur isotope compositions of the fluids. In this case, it is suggested that the restricted $\delta^{34}S$ values for the authigenic pyrite, pyrrhotite, sphalerite, galena, and chalcopyrite reflect a mainly homogeneous origin for the sulphur, which may be produced from the remobilization of sulphur derived from the detrital pyrite. Detrital pyrite and other heavy minerals are largely from a single source which is related to magmatic lithologies including the hydrothermally altered granitoids (HAGS) (Hallbauer, 1982; 1984; Robb & Meyer, 1985; Hallbauer, 1986), extinct volcanic smokers

(EVS) (Hoefs, et al., 1968) or shallow marine hydrothermal discharges (Hutchinson & Viljoen, 1988).

The hanging wall lavas have $\delta^{18}\text{O}$ values between 6,1 and 8,3 ‰ and the VCR shows $\delta^{18}\text{O}$ values ranging from 9,1 to 10,6‰. The $\delta^{18}\text{O}$ values of quartzites range from 9,4 to 10,4‰. The $\delta^{18}\text{O}$ values of vein and amygdale quartz in the VCR are between 9,6 and 11,3‰. Authigenic calcite shows $\delta^{18}\text{O}$ values in a range from 8,9 to 9,7‰. Muscovite in the VCR and quartzite has $\delta^{18}\text{O}$ values ranging from 7,2 to 7,8‰ and from 7,4 to 8,5‰. The δD values for muscovite in the VCR range from -31 to -64‰. The estimated $\delta^{18}\text{O}$ and δD values for hydrothermal fluids in equilibrium with muscovite at 350 °C are between 1,9 and 4,4‰, and between -27 and -39‰, respectively. This suggests that the hydrothermal fluids in the VCR were derived from metamorphic fluids (Fig. 8-6), possibly related to multiple processes of degassing, pore-water release and dewatering of fine-grained sediments (DFGS) during the peak of metamorphism in the Witwatersrand Basin, as suggested by Stevens et al (1996) and Drennan (1997).

The $\delta^{13}\text{C}$ values of late-stage vein calcite in the VCR are between -8,4 and -10,0‰. The estimated $\delta^{13}\text{C}$ values of calcite equilibrated with graphite at 350 °C range from -20,0 to -18,4‰. This suggests that the carbon in the fluids in the VCR is organic in origin. This is consistent with the results of Klemd et al. (1994), Robb et al. (1994, 1997) and Drennan (1997).

10.6 Age of alteration in the VCR

The age of alteration in the VCR has been discussed in detail in Chapter 9 (K-Ar dating). The K-Ar dates define a continuum of ages between 1830 Ma and 2054 Ma; there is a tendency for smaller size

fractions to yield younger ages within this range. The older age range of 1931 to 2054 Ma (average 1988 Ma) overlaps the 2020 Ma event represented by the Vredefort catastrophe and is close to the age range of 2061–2054 Ma for the intrusion of the Bushveld Complex and its satellites. Both of these events had a pronounced effect on the isotopic systematics over widespread areas of the Witwatersrand Basin. The younger age range of 1890 to 1965 Ma (1914 Ma in average) is less well constrained and may be related to Eburnian orogenesis between 1800 to 2000 Ma (Friese et al, 1995) along the western edge of the Kaapvaal Craton. This event resulted in continental scale fluid migration and hydrothermal activity that extended throughout the Griqualand Basin and into the Witwatersrand Basin (Duane, 1991; Duane et al., 1991).

10.7 Implications for Cu, Pb, Zn, Ag and Au mineralization in the VCR

Authigenic pyrite, pyrrhotite, galena, sphalerite, and chalcopyrite formed in the various alteration zones as described previously, and these are replaced by albite, muscovite and chlorite. The ore-forming fluids possessed moderate to high salinities of 8 to 23 wt% eNaCl. Mole fractions of H_2S in the inclusion fluids are between 0 to 0.014, with an average of 0.0047 (Drennan, 1995). This suggests that base metals (Cu, Pb and Zn) were transported as chloride complexes in the fluids, such as: $[CuCl_2]^{2-}$; $[CuCl_3]^{-}$; $[PbCl_2]$, $[ZnCl_2]$ (Barnes, 1979; Seward, 1984a).

Gold occurs as detrital grains, authigenic grains associated with pyrite, arsenopyrite, chalcopyrite, galena, sphalerite, quartz and carbonates, and in aggregates of chlorite flakes in the VCR (Henckel and Schweitzer, 1994; Smits, 1994; Robb and Meyer, 1995). This indicates that gold is closely related to sulphides. Based on experimental results, the bisulphide and dichloride gold complexes such as $Au(HS)^{-}$ and $AuCl_2^{-}$ (Seward, 1984b) are considered to be the principal gold complexes trans-

ported in the hydrothermal fluids. Under moderate P-T conditions, the bisulphide gold complex is the predominant gold species (Seward, 1984b; Shenberger and Barnes, 1989; Hayashi and Ohmoto, 1991). Based on the physicochemical conditions described in the present study, it is also suggested that the gold in the VCR was transported mainly as the bisulphide gold complex in the fluids. This is consistent with the gold occurrences and estimated P-T conditions of the fluids. Meyer et al. (1994), and Robb and Meyer (1995) discussed an association of gold with pyrite in the Witwatersrand Basin, using a model of electrochemical reduction of the $\text{Au}(\text{HS})_2^-$ complex at a surface of a mixed np-type pyrite modified from Möller and Kirsten (1994); the transport of gold as a thio-gold complex in the Wits Basin was also proposed by Drennan (1997), based on fluid inclusion data. The suggestions of a bisulphide gold complex are suitable for the VCR due to its similar geological setting and geochemical characteristics to Witwatersrand reefs.

Based on a study of the micro-texture and chemistry of compact round pyrite and associated gold accumulations in the Witwatersrand reefs, Meyer et al. (1994) proposed that gold was preferentially deposited on chemically heterogeneous pyrite surfaces by an electrochemical mechanism. Due to the semiconductive properties of sulphide minerals, gold is mainly accumulated and reduced by possible absorption and movement over short distances on pyrite surfaces. This study favors the suggestion of Meyer et al. (1994) that remobilization of Au occurred over short distances in a rock-dominated system, as previously discussed in this chapter and Chapter 6, 7.

10.8 Models for the alteration in the VCR

Based on detailed studies of the geology, mineralogy, geochemistry, physicochemical conditions, stable isotope geochemistry and dating, a schematic diagram is constructed to illustrate the post-

stable isotope geochemistry and dating, a schematic diagram is constructed to illustrate the post-depositional evolution and paragenetic sequence of mineralization for the VCR (Fig. 10-1). In this diagram, a possible paleoweathering stage is excluded in the model because it is not well-defined. Therefore, the metamorphism and hydrothermal alteration associated with the VCR are generalized into three stages described as follows:

(1) Burial Metamorphism (BMT) at ca 2550 to 2300 Ma (Fig. 10-1a).

The model is constructed such that either hydrothermally altered granitoids (HAGS) (Hallbauer, 1982; 1984; Robb & Meyer, 1985; Hallbauer, 1986), extinct volcanic smokers (EVS) (Hoefs, et al., 1968) or shallow marine hydrothermal discharges (Hutchinson & Viljeon, 1988) could have been the dominant sources to supply detrital particles of Au, Ag and other heavy minerals.

The BMT mainly covers the whole period of deposition of the Transvaal Sequence. Existence of BMT has been discussed in Chapter 7. This is supported by petrographic and fluid inclusion study (e.g. Frimmel, 1994, 1997; Stevens et al., 1996; Drennan, 1997) and age dates (Robb et al., 1990, 1996). The processes included recrystallization of authigenic and porous pyrite, and clay minerals, such as chlorite, muscovite and pyrophyllite. The dewatering of the fine-grained sediments (DFGS) was possibly a major process. The resultant fluids moved upwards and towards the basin margin along major faults, microfractures, foresets, bedding plane, and pores of the sediments. The peak P-T conditions were about 300 °C and 3 kbar with a geothermal gradient of about 28 °C/km (Frimmel, 1997).

Catagenetic maturation of primitive algal materials took place at diagenesis section and released

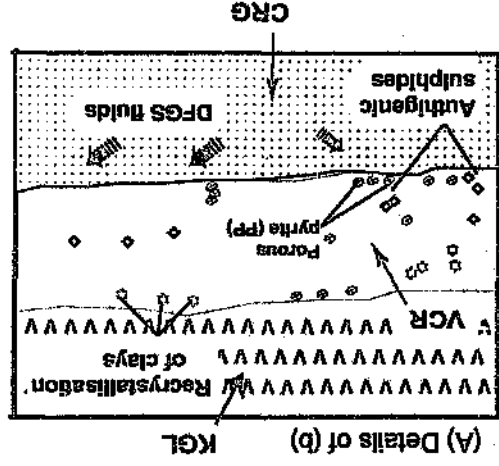
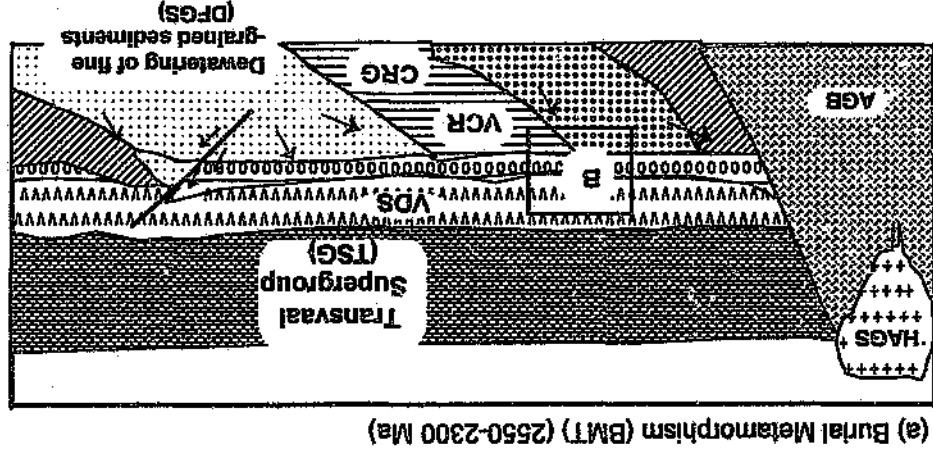
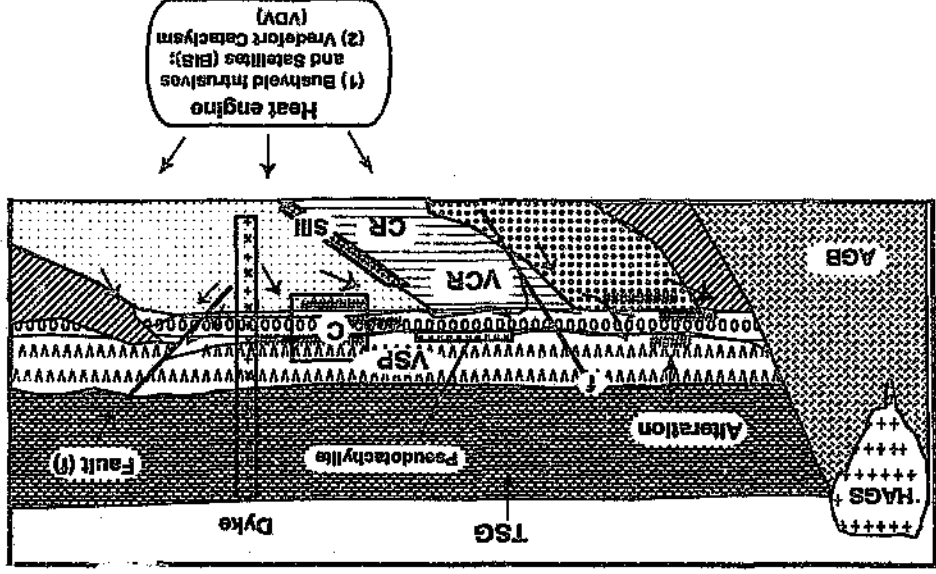


Fig. 10-1 Schematic diagram illustrating the post-depositional evolution and paragenetic sequences of mineralization of the VCR. (a) Burial Metamorphism (BMT) (ca 2550 to 2300 Ma); (b) Peak Hydrothermal Alteration (PHA) (2054 to 2020 Ma); and (c) Eburnian Orogeny (EBO) (1890-1965 Ma).

(b) Peak Hydrothermal Alteration (PHA) (2054-2020 Ma)



(B) Details of (b)

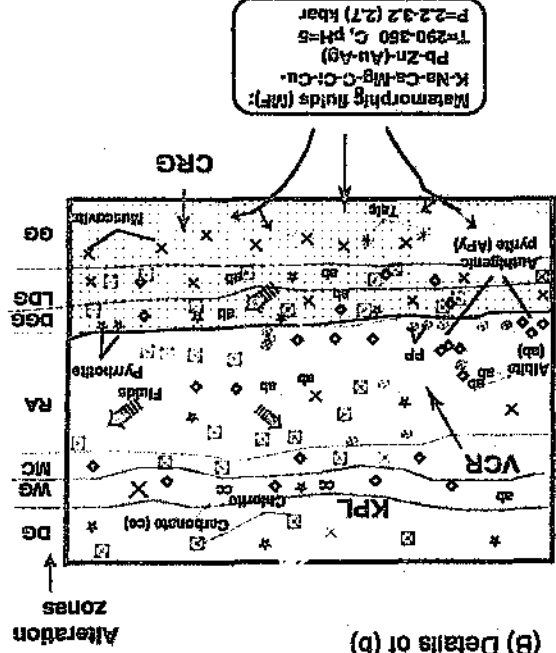
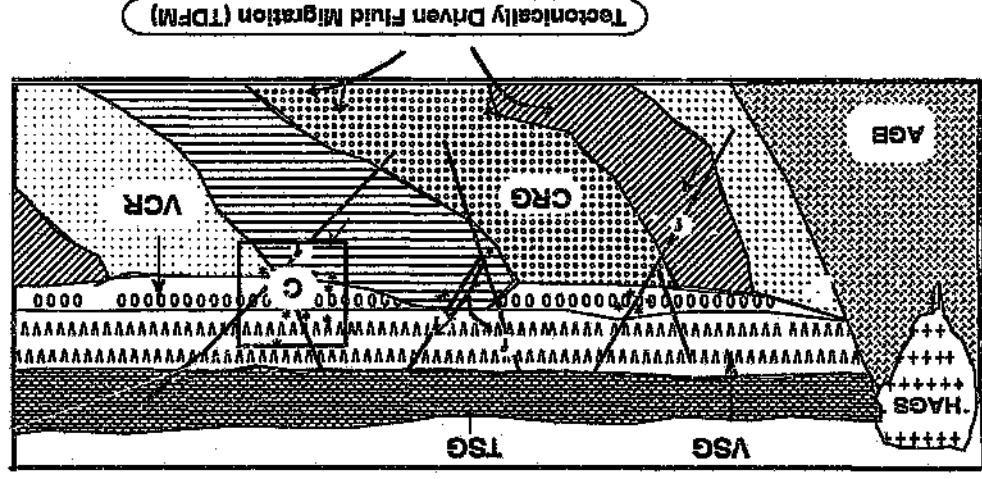


Fig. 10-1 Schematic diagram illustrating the post-depositional evolution and paragenetic sequence of mineralization of the VCR (continued).

(c) Eburnian Orogeny (EBO) (1890-1985 Ma)



(C) Details of (c)

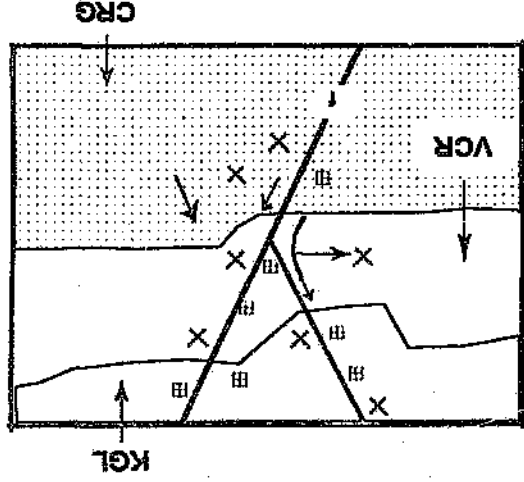


Fig. 10-1 Schematic diagram illustrating the post-depositional evolution and paragenetic sequence of mineralization of the VCR (continued).

occurred at about 2300 Ma (Robb et al., 1994; Drennan et al., 1997; Drennan, 1997). Hydrocarbons migrated through the sediments and into underlying/adjacent granitic rocks and underwent polymerization and condensation due to the effect of ionizing radiation in the proximity of detrital uraninite.

(2) Peak Hydrothermal Alteration (PHA) (Fig. 10-1b). The PHA took place between 2054 - 2020 Ma. The heat engine was driven by either Bushveld intrusives and its satellites (BIS) or the Vredefort Cataclysm (VDC) or both. Pseudotachylite, sills and dykes were possibly also part of the heat engine. Faults, dykes and fractures comprised the fluid channels. The metamorphic fluids moved along faults, fractures, dykes and sills and gave rise to hydrothermal alteration. The metamorphic fluids were characterized by enrichment of K, Na, Ca, Mg, C, Cl, Cu, Pb, Zn, and possibly some Au and Ag (Chapter 5, 6). Alteration took place in all lithologies of the VCR and along discontinuities, such as faults, dykes, and even pseudotachylites. Seven alteration zones were recognized within and around the VCR, namely the DG, WC, MC, RA (VCR), DGG, and GG zones.

Mineral assemblages of all alteration zones mainly comprise muscovite - chlorite - quartz - albite - epidote - calcite - talc - pyrite - pyrrhotite - galena - chalcopyrite - sphalerite. Chemical exchanges between different alteration zones were common. In the DG, WC and MC zones of lavas, Si, K, Fe, Cu, Zn, and (Au) were gained, but Mg, Ca and Na were lost; the RA zone shows gains of Mg, Ca and K, and losses of Fe and Na; the DGG zone shows gains of Mg, Fe, Na, Cu, Zn, (Pb), and (Au), and losses of Ca, and K.

The hydrothermal alteration took place in a rock-dominated system, as indicated by the underground

geology, alteration mineralogy and geochemistry, and sulphur and oxygen stable isotopes of minerals and bulk rocks. The fluids were metamorphic solutions derived from basin-wide dewatering of rocks during regional metamorphism of green schist facies. The fluids ascended along faults, joints, and dykes, micro-sedimentary structures, and brought Cu, Pb and Zn ore-forming elements, and Na-K-Ca-Mg-C-Cl components into the alteration zones. These fluids were active at 290 to 350 °C, and 2.2 to 3.2 kbar, with $\log f_{O_2}$ less than 10^{-30} , and $\log f_{S_2}$ of 10^{-20} , and neutral pH values of about 5.

(3) Eburnian Orogeny Retrograde (EOR) stage (Fig. 10-1c). It is defined as a long-lived thermal event which related to sub-crustal scale, tectonically driven fluid migrations (Friese et al., 1995). The existence of this event in this study is recorded by the younger range of the K-Ar dates (1890 -1960 Ma) and the low temperature mineral assemblage of muscovite (1M), and chlorite (replacement of detrital muscovite) (150-245 °C). The alteration is locally around or nearby the discontinuities.

APPENDICES

APPENDIX A Chemical compositions of chalcopyrite, pyrrhotite, sphalerite, galena and pentlandite.

APPENDIX B CRYOSTAT technique for disaggregation of rock samples.

APPENDIX C Natural precipitation technique for extraction of $> 2 \mu\text{m}$ fractions of clays.

APPENDIX D Ultracentrifugation technique for extraction of $< 2 \mu\text{m}$ fractions of clays.

[illegible]