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STABLE ISOTOPE EVIDENCE FOR CRUSTAL CONTAMINATION AND DESULPHIDATION OF THE CUPRIFEROUS KOPERBERG SUITE, NAMAQUALAND, SOUTH AFRICA

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by

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ABSTRACT

The middle Proterozoic Koperberg Suite occurs as a swarm of differentiated mafic dykes in a granulite facies terrane in the north-western Cape Province of South Africa. Rock types include pyroxenite, norite, anorthosite, diorite and glimmerite. The Koperberg Suite constitutes an important repository of copper ore and, therefore, for more than a century has been a major focus of geological research. This paper reports petrographic and stable isotope data that place new constraints on the magmatic and metamorphic evolution of the Koperberg Suite and associated copper mineralization. Oxygen isotope ratios of the basic bodies are significantly enriched in 18 O (δ^{18} O_{plag}=6.6 to 9.6%; δ^{18} O_{opx}=6.2 to 7.4%; and δ^{18} O_{rock}=6.5 to 8.1%) relative to mantle-derived basic rocks. This enrichment resulted from contamination of the magmas with crustal rocks. Granite-gneiss country rocks exhibit $\delta^{18}O$ values in the range from 7.8 to 8.7%. Mixing calculations based on a two end-member model show that an ¹⁸O enrichment of the Koperberg Suite by 1.7‰ requires approximately 40% contamination by crustal material with a δ^{18} O value of 10%. The systematics of oxygen isotope data between individual minerals suggests that in addition to crustal contamination further modification took place due to subsolidus exchange with an isotopically heavy fluid of metamorphic origin. This is indicated by the lack of temperature concordancy and the isotope heterogeneity emphasized by the range in $\delta^{18}O_{plag}$ values from 6.2 to 9.6% and in $\delta^{18}O_{rock}$ values from 5.9 to 8.3%.

Sulphur isotope ratios are light relative to mantle values and co-genetic mineral pairs show a lack of temperature concordancy. The ranges in $\delta^{34}S$ values for the sulphides are: $\delta^{34}S_{cpy}$, -1.5 to -3.8%, $\delta^{34}S_{bo}$, -1.9 to -4.1%; and $\delta^{34}S_{po}$, -1.9 to -2.5%. Bulk ore samples show a systematic decrease in $\delta^{34}S$ values with increasing Cu/S ratios. This is seen as being diagnostic for an oxidation process and the degassing of a SO_2 -rich vapour phase. Petrographic observations and mineral chemistry data support this conclusion and indicate that the devolatilization event was caused by granulite facies metamorphism.

A genetic model is presented which envisages an ultimate mantle origin for the Koperberg Suite. The original magma was modified in the deep lower crust through assimilation and fractional crystallization processes. Later modification occurred at the level of emplacement through differentiation and metamorphism. Crustal contamination can explain the origin of the enriched O-isotope values, the high levels of incompatible trace elements as well as the high initial ⁸⁷Sr/⁸⁶Sr ratios in the basic bodies.

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INTRODUCTION

The Koperberg Suite occurs in the northern Cape Province of South Africa and covers an area of ca. 3000 km². The intrusives are easterly trending, steep north-dipping bodies, usually 60 to 100 m wide and seldom exceeding 1 km in strike (Lombaard and Schreuder, 1978). Compositionally, the Koperberg Suite ranges from pyroxenite to anorthosite to diorite and glimmerite and is collectively referred to as basic bodies or noritoids. The Koperberg Suite intrudes into the gneissic terrane of the ca. 1200 Ma old Namaqualand Metamorphic Complex and has been dated at 1042 ± 40 Ma by Nicolaysen and Burger (1965) and at 1072±20 Ma by Clifford et al. (1975). Copper mineralization is contained in the more mafic rock types and the general perception is that the ore is of syngenetic magmatic origin. All studies into the genesis of the mineralization, therefore, invariably have also addressed questions related to the origin of the host rocks and various workers have expressed contrasting views on the genesis of the Koperberg Suite as well as the associated Cu ore. A metasomatic origin was suggested by Benedict et al. (1964), according to which the rocks were formed from metasedimentary schists by metamorphic differentiation and the Koperberg Suite was thus seen as a by-product of a postulated regional granitization. Clifford et al. (1975) proposed a source-bed model involving the generation of the noritoid magma from Cu-bearing basic and intermediate metasedimentary rocks. This theory was based on high initial ⁸⁷Sr/⁸⁶Sr ratios and chemical data and was also supported by Stumpfl et al. (1976). Van Zyl (1967) reiterated the intrusive nature of the Koperberg Suite and suggested that the basic bodies were the product of magmatic differentiation in a deep-seated magma chamber whereby emplacement of the magma took place in form of successive surges of different composition. The above models were criticized by McIver et al. (1983) who envisaged the formation of the noritoids from a series of mantle-derived magmas that intruded into an amphibolite facies environment, assimilated peraluminous anatects in transit, and was emplaced into dilation zones in the gneisses. Similarities between the Koperberg Suite and massif-type anorthosite complexes were emphasized by Clifford et al. (1981), and Conradie and Schoch (1986, 1988). The latter authors suggested that the Koperberg Suite represents the deeper levels of such an anorthosite complex. Andreoli and Hart (1987) suggested that the Koperberg Suite formed part of an aborted cryptoexplosion with a kinship to the KREEP basalts of the Sudbury eruptive.

Most of the above studies accept a pristine primary magmatic origin for the copper ore. McIver et al. (1983) and Cawthorn and Meyer (1992), however, questioned this perception and proposed major metamorphic reconstitution of both host rock and mineralization. They found that the ore mineralogy as well as S/Se and Cu/Ni ratios are atypical for magmatic sulfides, that the style of mineralization is unique and that the deposits cannot be simply classified in terms of well-known ore-deposit types. The objective of this paper is to present mineralogical and stable isotope data which place new constraints on the magmatic and metamorphic evolution of the Koperberg Suite and associated Cu mineralization.

GEOLOGICAL SETTING

The Koperberg Suite is situated in the gneissic terrane of the Proterozoic Namaqualand Metamorphic Complex (Fig. 1) which forms part of the southern extension of the 1200 Ma Kibaran orogenic belt. The lithostratigraphic column shown in Table 1 is subdivided into a metavolcano-sedimentary succession, the Okiep Group, and three polyphase suites of granite-gneisses, namely the 1213±22 Ma old Gladkop and Klein Namaqualand Suites and the younger, 1166±26 Ma old Spektakel Suite (Clifford et al., 1975). The

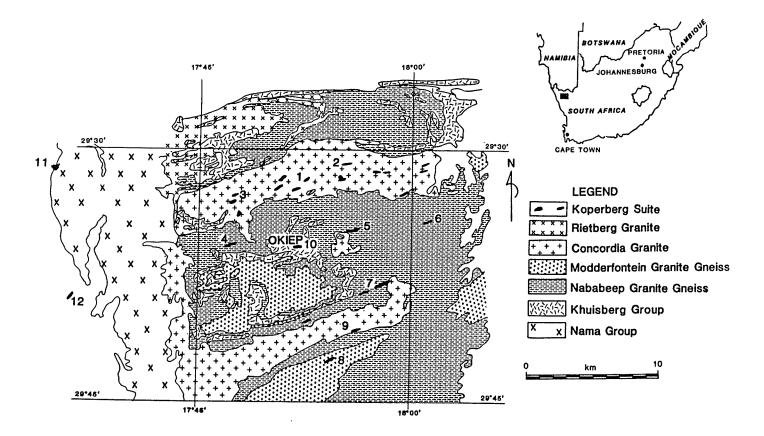


Figure 1: Simplified geological map of the Okiep Copper District. The mine localities indicated are as follows: 1 - Kliphoog North Mine (KHN), 2 - Tweefontein Mine (TFM), 3 - Flat Mine North (FMN), 4 - Nababeep West Mine (NAB), 5 - Narrap East Mine (NE), 6 - Hoits Mine (HT), 7 - Carolusberg West Mine (CW), 8 - Koperberg Central Mine (KC), 9 - Fonteinjie West Mine (FTW), 10 - East O'okiep Mine (EOK).

granite-gneisses form large, locally transgressive, sheet-like bodies and their emplacement occurred at different stages relative to the main structural and metamorphic events (Joubert, 1971; 1986). The inferred maximum P-T conditions are 5 kbar and $\geq 800^{\circ}$ C (Clifford *et al.*, 1975). As in most granulite terranes, the dominant regional-scale deformation style is sub-horizontal, with large recumbent folds and flat-lying foliation. The Koperberg Suite

Table 1. Lithostratigraphy of the Okiep Copper District

	Nama Group	
	Koperberg Suite	
	Spektakel Suite	Kweekfontein Granite
		Rietberg Granite
INTRUSIVE ROCKS		Concordia Granite
	Klein Namaqualand Suite	Modderfontein Granite-gneiss
		Nababeep Granite-gneiss
	Gladkop Suite	Noenoemaasberg Granite- gneiss
		Brandewynsbank Granite- gneiss
META VOLCANO-SEDIMENTARY	Okiep Group	. Lammerhoek Subgroup
ROCKS		Khurisberg Subgroup

represents the last major intrusive event in the region. The noritoid bodies occur in an east-west-trending dyke swarm and with an uniform attitude. They are localized along discontinuous zones characterized by steeply dipping foliations and associated folding, locally referred to as 'steep structures' (e.g. Benedict *et al.*, 1964). The lack of chilled margins, the coarse granular texture of the rocks, and the fact that the basic bodies are deformed indicates that they intruded during prograde metamorphism into country rocks of probably upper amphibolite grade (McIver *et al.*, 1983).

PETROGRAPHY

Comprehensive petrographic descriptions of silicate phases (Stumpfl et al., 1976; McIver et al., 1983; Conradie and Schoch, 1986), oxide minerals (Conradie and Schoch, 1986; Cawthorn and Meyer, 1992) and sulphides (Latsky, 1942; Van Zyl, 1967, 1978; Stumpfl et al., 1976; Cawthorn and Meyer, 1992) of the Koperberg Suite have been documented. Rock textures have been generally interpreted as being typically igneous (Van Zyl, 1978; Conradie and Schoch, 1986, 1988), but McIver et al. (1983) argued that the textures are granoblastic and, therefore, of metamorphic origin. The mineralogy of the Koperberg Suite is dominated by variations in the modal proportion of plagioclase, orthopyroxene and biotite. Accessory minerals occur in variable amounts and include apatite, K-feldspar, zircon, quartz, anhydrite, various sulphides and Fe-Ti oxides. Amphibole and clinopyroxene are rare, while olivine is conspicuous by its absence. Exsolution features are common and include antiperthitic K-feldspar in plagioclase, sagenitic textures in biotite and ilmenite lamellae in one generation of magnetite, but they are absent in pyroxene. Magnetite is the dominant opaque phase in the leucocratic rocks. Sulphides predominate in the more mafic rock types and may occur interstitial between silicates, along cleavage planes in biotite, in granoblastic-textured rocks with polygonal and straight grain boundaries against

orthopyroxene and oxides and as massive ore. Cawthorn and Meyer (1992) recognized three distinct sulphide assemblages in the various ore bodies. They distinguished a typical igneous Fe- and S-rich paragenesis comprising chalcopyrite, pyrrhotite and minor pentlandite (e.g. in the East O'okiep ore body), an intermediate assemblage comprising chalcopyrite and bornite (e.g. in the West O'okiep ore body), and a Fe- and S-poor, Cu-rich end-member paragenesis consisting of bornite and chalcocite (e.g. in the Carolusberg West ore body). They further found that iron-titanium oxides also comprise three distinct assemblages indicating increasing degrees of oxidation. Magnetite with ilmenite oxyexsolution lamellae is present at East O'okiep; magnetite together with discrete ilmenite grains forms part of the intermediate assemblage; and Ti-free magnetite together with grains of titanohematite-ilmenite intergrowths constitute the dominant oxides at Carolusberg West. The textural features described above refer to fresh, unaltered basic bodies which are generally less common than those where silicates show alteration and the sulphide textures indicate remobilization due to later low-temperature hydrothermal overprinting (the Hoits-type ore of Stumpfl *et al.*, 1976).

SAMPLES AND ANALYTICAL PROCEDURE

Borehole core was collected from several mineralized and barren basic bodies (Fig. 1) and includes the majority of rock types of the Koperberg Suite. Most samples show an unaltered mineralogy while others were taken from hydrothermally overprinted basic bodies. Major and trace elements were determined by X-ray fluorescence techniques with a Philips PW1404 spectrometer, following the method of Norrish and Hutton (1969). Mineral compositions were analyzed with a wavelength dispersive Cameca electron microprobe. Natural standards were used for calibration. Matrix corrections were made using the ZAF procedure. Between 8 and 14 point analyses were performed per mineral grain.

Mineral fractions used for oxygen isotope analysis were more than 95% pure and the minerals showed no visible indication of alteration. Oxygen extraction was performed in the Department of Geochemistry, University of Cape Town, following the technique described by Borthwick and Harmon (1982). CO_2 -gas was analyzed with a VG Micromass 602E double collector ratio mass spectrometer in the Department of Archeology, University of Cape Town. NBS-28 and NBS-30 were used as reference standards and yielded values of 9.64% and 5.06% V-SMOW, respectively. The δ^{18} O-values of duplicated samples were generally within 0.2%. Oxygen isotope values are reported in δ -notation in per mil units relative to V-SMOW.

Bornite, chalcopyrite and pyrrhotite was hand-picked from crushed samples. The sulphur was converted to SO_2 , using the Cu_2O oxidation method of Coleman and Moore (1978). Sulphur isotope ratios of the purified SO_2 -gas were measured with a Micromass MM602, dual inlet mass spectrometer, at the Schonland Research Centre for Nuclear Sciences, University of the Witwatersrand, Johannesburg. The precision of the method is 0.2%, and the accuracy is approximately 0.3% (1σ). The values obtained for DSW and OGS references were +20.1% and +20.5%, respectively. Sulphur isotope values are reported in δ -notation in per mil units relative to Canyon Diablo troilite (CDT).

RESULTS

Mineral Chemistry

Orthopyroxene, mica and plagioclase reveal considerable compositional variations amongst the different rock types analyzed (Table 2). Plagioclase ranges from andesine (An_{31}) in anorthosite to labradorite (An_{72}) in norite. Orthopyroxene compositions vary between En_{38} and En_{69} and also display higher Mg/Fe ratios in the more mafic rocks such as glimmerite and pyroxenite. In Figure 2 it is shown that no correlation exists between plagioclase and orthopyroxene compositions typically found in basic rocks.

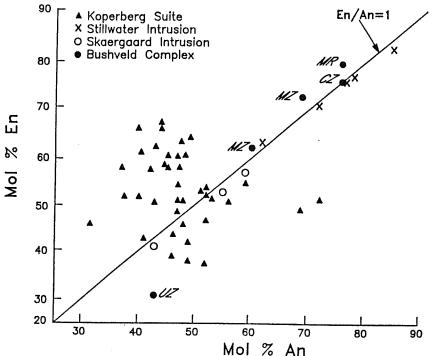


Figure 2: Mol% En vs. Mol% An for mafic rocks of the Okiep Copper District compared to a few typical layered igneous intrusions. MR - Merensky Reef, CZ - Critical Zone, MZ - Main Zone and UZ - Upper Zone. Bushveld data from Wager and Brown (1968). Data for the Okiep District from this study and Conradie and Schoch (1986).

Oxygen Isotopes

Oxygen isotope ratios were determined for 16 whole rock samples as well as for a number of mineral separates including magnetite, plagioclase, orthopyroxene, mica, apatite and zircon. The δ^{18} O values of the Koperberg Suite samples (Tables 3 and 4) are significantly heavier (plagioclase = 6.6 to 9.6%; orthopyroxene = 6.2 to 7.4%; and whole rock = 6.5 to 8.1%) than the values of uncontaminated, mantle-derived basic rocks (plag = 6.0%; opx = 5.5%; whole rock = 5.7%; Taylor, 1968). The δ^{18} O values of the granitegneiss country rocks are enriched in δ^{18} O (Rietberg Granite = 7.8%; Concordia Granitegneiss = 8.2% and Nababeep Granite-gneiss = 8.7%) relative to whole rock values of the Koperberg Suite (Fonteintjie West = 6.7% and Klein Nigramoep = 7.5%).

Table 2. Selected electron microprobe analysis of Koperberg Suite orthopyroxene and plagioclase. Data are from Boer (1989), McIver *et al.* (1983), Conradie and Schoch (1986) and Stumpfl *et al.* (1976). CW - Carolusberg West Mine, NG - Nababeep Gneiss, KHN - Kliphoog North, NE - Narrap East, JB - Jubilee, HW - Homeep West, FMN - Flat Mine North, EOK - East O'okiep, KC - Koperberg Central. nd - not determined

	Orthopyroxene							
Locality	CW	CW	CW	CW	NG	KHN		
Rock Type	leuconorite	leuconorite	leuconorite	hypersthenite	Nababeep Gneiss	leuconorite		
SiO_2	54.20	54.00	53.44	52.91	51.28	53.00		
TiO_2	0.07	0.08	0.07	0.09	0.06	0.10		
Al_2O_3	1.10	1.57	1.26	1.87	0.82	1.82		
Cr_2O_3	-	0.04	0.10	0.10	0.02	0.01		
FeO	21.85	20.21	21.68	22.21	26.28	21.32		
MnO	0.59	0.55	0.46	0.40	0.98	0.94		
MgO	22.42	23.00	22.80	20.96	18.99	22.04		
CaO	0.40	0.45	0.42	0.56	0.84	0.55		
Na ₂ O	0.02	0.01	0.01	0.02	0.04	0.02		
K_2O	0.01	0.01	-	-	0.01	-		
Total	100.66	99.92	100.24	99.12	99.32	99.80		
En	50.6	53.2	51.3	48.6	41.9	50.8		
Locality	NE	JB	HW	FMN	EOK	EOK		
Rock Type	leuconorite	norite	norite	norite	diorite	diorite		
SiO_2	54.04	51.22	48.82	52.57	50.3	49.1		
TiO ₂	-	0.25	0.28	0.12	-	-		
Al_2O_3	1.98	2.61	2.75	1.44	1.3	5.1		
Cr_2O_3	nd	0.20	0.17	-	nd	nd		
FeO	21.56	20.83	23.54	21.19	28.4	25.3		
MnO	nd	0.74	1.95	0.89	0.9	0.6		
MgO	21.63	22.68	21.17	23.28	17.6	19.0		
CaO	0.68	0.53	0.56	0.65	0.6	_		
Na ₂ O	nd	0.13	0.30	0.02	_	-		
K ₂ O	nd	0.08	0.06	0.00	-			
Total	99.89	99.49	99.6	100.88	99.1	99.1		
En	50.1	52.1	47.3	38.3	42.9	51.5		

Table 2 (continued)

		Plagioclase		
Locality	CW	CW	CW	CW
Rock type	anorthosite	leuconorite	diorite	norite
SiO ₂	58.60	61.57	52.56	55.95
TiO_2	0.01	0.01	0.01	-
Al_2O_3	26.29	24.48	30.40	27.01
FeO	0.12	0.21	0.15	0.21
MnO	-	0.01	0.01	0.01
MgO	-	0.08	_	_
CaO	9.99	7.88	14.79	11.84
Na ₂ O	4.51	6.51	3.08	4.46
K_2O	0.32	0.19	0.09	0.17
Total	99.84	100.94	101.09	99.65
X_{An}	0.54	0.40	0.72	0.59
X_{Or}	0.02	0.01	0.01	0.01
X_{Ab}	0.44	0.59	0.27	0.40

Table 3. Trace element and $\delta^{18}O$ analyses of rocks from Fonteintjie West (FTW), Klein Nigramoep (KN) and Waaihoek (WAK). Trace elements are presented in ppm and $\delta^{18}O$ values relative to V-SMOW

	FTW2/ 100	FTW2/ 205	FTW3/ 255	KN17/ 1210	KN17/ 1405	KN26/ 1360	KN27/ 203	KN27/ 330
Rb	115.54	188.82	48.99	28.20	76.37	17.17	13.34	28.19
K/Rb	148.0	72.1	84.7	214.9	112.0	227.2	360.9	147.2
$\delta^{18}O$	6.7	7.5	5.9	7.9	7.5	8.3	6.5	7.9

	KN29/ 133M	KN31/ 10M	KN31/ 60M	KN59/ 138	KN68/ 62M	WAK1/ 170	WAK10/ 610	WAK2/ 310
Rb	31.98	14.01	29.22	37.19	28.42	79.41	21.44	49.26
K/Rb	241.4	402.9	170.5	127.2	137.3	149.5	321.3	188.8
$\delta^{18}O$	7.5	7.2	7.6	6.9	7.3	7.5	8.2	8.1

Table 4. Oxygen isotope values of Koperberg Suite mineral separates. Values are expressed in per mil V-SMOW. NE - Narrap East, HE - Homeep East, NAB - Nababeep West Mine, EOK - East O'okiep Mine, KN - Klein Nigramoep, HT - Hoits Mine, KA - Kaip, CW - Carolusberg West Mine, WOK - West O'okiep Mine, G - Gougab, FMN - Flat Mine North, SPK - Spektakel Mine

Sample Number	Plagioclase	Pyroxene	Zircon	Apatite	Mica	Magnetite
NE47	7.8	7.2			5.1	3.9
HE215	7.5	7.2				3.4
NAB432	9.6	7.4				
EOK587	7.8	6.3			5.6	5.2
KN15	6.2					3.6
KN655	7.2			•	5.2	
HT713	7.4				5.7	4.3
KA1			5.9	5.5		
HT54			6.6			
CW19.05	8.4	7.0				3.0
CW29.3	7.7	6.7				2.4
CW58.2	6.8	6.9				4.6
CW50.8	7.4					8.5
WOK1			6.5		5.4	0.0
G1			7.1			
KA2		6.2		5.8		
FMN1				6.6		
HT716A	7.8	6.6				4.5
HT716B	7.6	6.6				4.6
HT 9Stope	8.2	6.6				3.6
SPK669	6.6	6.7				3.2

Oxygen isotopic values for individual minerals are given in Table 4. They are presented in order of decreasing exchange susceptibility. Mica is the only mineral with uniform δ^{18} O values (5.1 to 5.7%). All other minerals show substantial variations with plagioclase and orthopyroxene having the heaviest isotopic ratios. When the data are plotted in a δ - δ diagram (Fig. 3), it is obvious that no isotopic equilibrium exists between the mineral pairs. Under isotopic equilibrium conditions the data would plot along a 45° line (isotherm) which intersects the ordinate at the equilibrium isotopic fractionation factor. Obviously, this is not the case for these samples. The data patterns exhibited in Figure 3 are diagnostic for disequilibrium conditions. Open-system exchange is even more apparent when comparing δ^{18} O values between a fast-exchanging mineral such as plagioclase and a slow exchanging mineral such as orthopyroxene. The data shown in Figure 4 plot at values

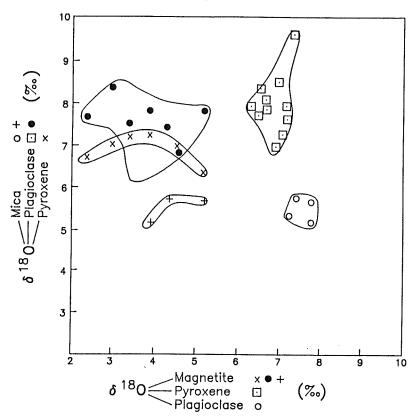


Figure 3: δ-δ Plot of disequilibrium arrays for Koperberg Suite mineral separates.

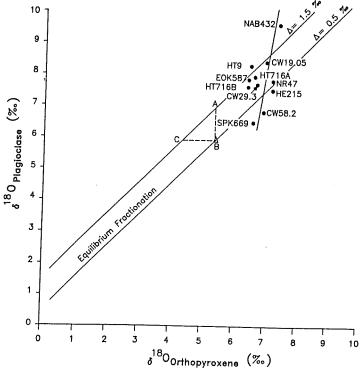


Figure 4: Plot of $\delta^{18}O_{Opx}$ vs $\delta^{18}O_{Plag}$. Point B indicates the "normal" mantle-derived magma composition. If pyroxene and plagioclase are the dominant minerals in the rock, then closed-system, equilibrium cooling will result in compositions that lie in triangle ABC. The equilibrium lines defined by $\Delta^{18}O = 1.5$ and $\Delta^{18}O = 0.5$ correspond to temperatures of approximately 960°C and 1100°C, respectively.

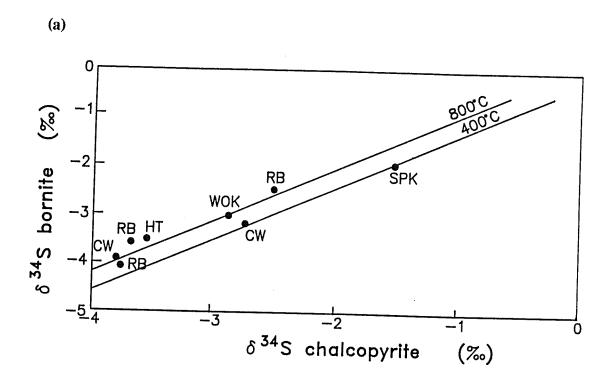
distinctly heavier than those characteristic of 'normal' mantle-derived mafic magmas (i.e. point B in Figure 4) and scatter around a steeply sloping trend.

Sulphur Isotopes

Sulphur isotope ratios were determined for chalcopyrite, bornite and pyrrhotite (Table 5). The δ^{34} S values obtained range from -1.9 to -2.5% for pyrrhotite, from -1.5 to -3.8% for chalcopyrite and from -1.9 to -4.1% for bornite. Pyrrhotite and chalcopyrite ratios clearly extend outside the range of -3 to 2% which is considered typical for mantle-derived rocks (Ohmoto, 1986). On examination of co-existing mineral pairs (Figures 5a, b) it becomes evident that there is a lack of temperature concordancy. This feature together with reversed chalcopyrite-bornite fractionation is suggestive of open-system, disequilibrium behaviour.

Table 5. Sulphur isotope values (δ^{34} S per mil TCD) for mineral separates

Locality	Pyrrhotite	Chalcopyrite	Bornite
Carolusberg West		-3.8 -3.7	-3.0 -3.0 -3.0 -3.9 -3.7 -3.1 -3.0 -3.0 -2.8
Rietberg		-3.8 -3.8 -3.7 -3.5 -3.8	-2.8 -3.4 -4.1
Homeep East Hoits West O'okiep		-3.7 -3.6 -3.6 -2.9	-3.7 -3.6 -3.0
Spektakel		-2.7 -1.5	-1.9
Narrap East	-2.5	-2.5	-2.0
East O'okiep	-1.9	-2.5 -2.0	
	-1.9	-1.7 -1.7	



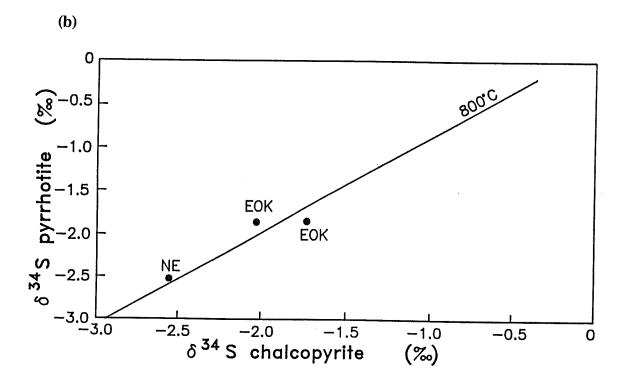


Figure 5: δ - δ Ratios of (a) bornite and chalcopyrite, as well as (b) chalcopyrite and pyrrhotite mineral-pairs plotted in δ - δ space.

DISCUSSION

Oxygen Isotopes

The δ^{18} O range for terrestrial igneous rocks is at least from -2 to 16% while ultramafic mantle rocks have an uniform O-isotope composition of approximately 5.7 \pm 0.3% (Kyser *et al.*, 1981). Fractional crystallization of a parental mantle-derived magma will result in more differentiated products enriched in ¹⁸O by no more than about 1% (Taylor and Sheppard, 1986). Thus, igneous rocks with O-isotope ratios outside the range of 5 to 7% cannot have been derived from the mantle through simple partial melting and/or differentiation processes. Plagioclase and orthopyroxene from the Koperberg Suite are clearly heavier than typical mantle values and the average δ^{18} O value for 16 whole rock samples is 7.4% (Table 3). Elevated δ^{18} O ratios in igneous and meta-igneous rocks can be generated by one or more of the following processes:

- (1) crustal contamination of the magma.
- (2) partial melting of a portion of the mantle enriched in ¹⁸O, and
- (3) exchange with an external, isotopically heavy fluid reservoir.

The systematics of δ - δ diagrams (Figure 4) provide a sensitive tool for monitoring effects of isotopic exchange between mineral pairs (e.g. Gregory and Criss, 1986). Point B in Figure 4 represents $\delta^{18}O$ values for plagioclase and pyroxene crystallized from a 'normal' mantle-derived mafic magma. In a simple two-phase system, with pyroxene and plagioclase as the dominant minerals, closed-system equilibrium exchange would result in δ^{18} O values confined to triangle ABC (Figure 4). In high temperature environments, samples plotting outside this field are diagnostic of open system, non-equilibrium exchange. Mafic rocks affected by fluid-rock interaction generally plot on steeply sloping trends because the isotopic exchange rate between plagioclase and fluid is much faster than between pyroxene and fluid. This disequilibrium trend will extend upwards from point B to higher δ^{18} O values in cases where the exchange takes place with an isotopically heavy fluid and will extend downwards from point B if the exchange takes place with an isotopically light fluid. In this study the pattern exhibited by samples in Figure 4 is considered to be diagnostic of this process. However, the distinct shift of the data along the equilibrium fractionation curve to ¹⁸O/¹⁶O ratios higher than mantle values (i.e. higher than point B in Figure 4) cannot simply be explained by fluid-rock exchange. The writers' interpretation is that this shift is caused by contamination of the magma with crustal material (process 1, above). heterogeneity (process 2, above) is difficult to evaluate, but at present there is no evidence to suggest that the sub-Namaqualand mantle is anomalous with respect to $\delta^{18}O$ values as mantle-derived igneous rocks from the adjacent Kaapvaal craton have 'normal' δ¹⁸O_{melt} values (Smith et al., 1984; Schiffries and Rye, 1989). There are many lines of evidence, however, which argue in favour of crustal contamination as the main process responsible for the observed shift in isotope ratios. Firstly, numerous granite-gneiss xenoliths occur in the Koperberg Suite at a number of localities and provide strong field evidence for magmatic assimilation of country rock (Lombaard and Schreuder, 1978). Furthermore, Rb-Sr isotope data for the Koperberg Suite (Clifford et al., 1990) yield high initial 87Sr/86Sr ratios of 0.705 to 0.725 when calculated for an age of 1100 Ma. The R_o values are far too high for pristine mantle material and clearly point to crustal contamination. For comparison, the granitegneiss host rocks to the Koperberg Suite are also characterized by high R_o values ranging from 0.705 for the Concordia granite-gneiss to 0.725 for the Nababeep gneiss (Barton, 1983; Clifford *et al.*, 1975). More evidence for crustal assimilation is provided by the Rb content of Koperberg Suite rocks. Given the low Rb concentrations in mantle-derived gabbroic rocks in the range 0-10 ppm (Reynolds *et al.*, 1969) it is obvious that the high Rb contents (13 to 189 ppm, Table 3) of the basic bodies is atypical for mantle rocks. Also, mantle derived basalts are characterized by K/Rb ratios ranging from 475 to 1830 (Gast, 1965), while crustal rocks have an average value of 230 (Heier and Adams, 1964). Obviously, the low K/Rb ratios for the Koperberg Suite (mean value = 194, Table 3) is consistent with the other evidence for crustal contamination discussed above.

In Figure 6 an attempt is made to correlate the normative An content in plagioclase with whole rock δ^{18} O values. The Nababeep granite-gneiss, a potential crustal contaminant, plots at the highest $\delta^{18}O$ values and the lowest normative anorthite values. The samples from the Koperberg Suite follow a rough trend which is directed towards the data point for the country rock. The observed deviations of the data from a regression curve can be explained by the fact that cumulus rocks are not representative of melt compositions and hence variations in modal mineralogy affect bulk rock isotope compositions (see Figure 3). Plagioclase-rich rocks ought to be enriched in ¹⁸O relative to magnetite-rich samples, as is generally observed in Figure 6 and this is also interpreted as evidence for crustal contamination. Mixing calculations, based on a simple two end-member model, show that an ¹⁸O enrichment of the Koperberg Suite by 1.7% requires approximately 40% contamination by crustal material with a δ^{18} O value of 10%. This large degree of contamination is not inconsistent with the chemical composition of the basic bodies (i.e. high Rb and low K/Rb ratios) and is also within the expected range if the magmas experienced turbulent flow during their ascent through the crust (e.g. Huppert and Sparks, 1985).

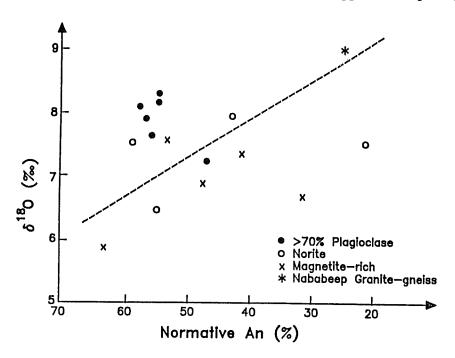


Figure 6: Whole rock $\delta^{18}O$ values vs. normative An content in plagioclase for the Okiep Copper District.

As discussed above, the steeply sloping disequilibrium trend for ¹⁸O occupied by the data in Figure 4 is most probably caused by fluid-rock interaction and exchange with an external, isotopically heavy fluid reservoir (process 3, above). There is one line of evidence suggesting that high-grade metamorphic fluids are enriched in ¹⁸O. Adirondack anorthosites are on average 2.4‰ heavier than 'normal' anorthosites and this enrichment has been proposed to result from exchange with granulite-facies H₂O and CO₂ (Valley and O'Neil, 1984). It has also been argued, however, that processes other than exchange with an isotopically heavy fluid could have been responsible for the enrichment in ¹⁸O (e.g. Morrison and Valley, 1988). McNaughton and Withnall (1990) recognized a systematic heavy isotope depletion in metamorphic rocks with increasing metamorphic grade. They concluded that this depletion was due to CO₂ distillation during decarbonation reactions. Obviously, such a process results in an enrichment of ¹⁸O in granulite-facies fluids. Considering all aspects discussed above there is little doubt that oxygen isotope data from the Koperberg Suite provide evidence for hybridization of the magmas with crustal material and for fluid-rock interaction during metamorphism.

Sulphur Isotopes

Sulphur isotope data for mineral pairs show a lack of temperature concordance and do not follow the theoretical order of $\delta^{34}S$ enrichment under equilibrium conditions with pyrrhotite > chalcopyrite > bornite (Figures 5a, b, Table 5). Because the fractionation factors among sulphide species at magmatic temperatures are less than 0.5% (Ohmoto and Rye, 1979), magmas formed by partial melting of the mantle should have $\delta^{34}S$ values around zero. The distinctly negative $\delta^{34}S$ values of our samples may be explained by a heterogeneous, ^{34}S -depleted mantle or may be the result of secondary fractionation processes such as assimilation, oxidation and sulphur devolatilization (e.g. Ohmoto, 1986). A plot of mean $\delta^{34}S$ values versus mean Cu/S ratios for sulphides from the various mineralized basic bodies (Figure 7, Table 6), illustrates that the two parameters are reversely correlated, i.e. $\delta^{34}S$ values decrease with increasing Cu/S ratios. Similar trends between $\delta^{34}S$ values and

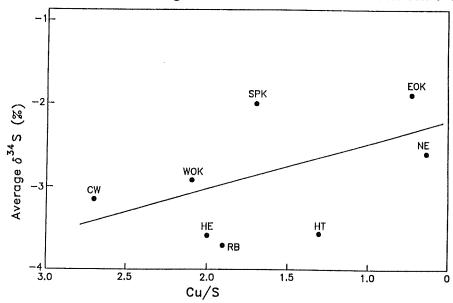


Figure 7: Binary plot of mean sulphur isotope ratios (δ^{34} S) versus Cu/S ratios for the major mining centres.

Table 6. Mean $\delta^{34}S$ values and Cu/S ratios for the ore bodies studied

Locality	Cu/S	δ^{34} S
East O'okiep	0.7	-1.9
Narrap	0.6	-2.5
Hoits	1.3	-3.6
Spektakel	1.7	-2.0
Homeep East	2.0	-3.6
Rietberg	1.9	-3.7
West O'okiep	2.1	-2.9
Carolusberg West	2.7	-3.2

whole rock sulphur contents have previously been interpreted as indications for sulphur devolatilization (Taylor, 1986). The different Cu/S ratios for the various ore bodies are a direct reflection of the differences in their sulphide assemblages. The East O'okiep ore, for example, representing a typical igneous, Fe- and S-rich paragenesis with mainly chalcopyrite and pyrrhotite is characterized by a low Cu/S ratio and the least negative δ^{34} S value. In contrast, the Carolusberg West ore comprising a Fe- and S-poor, Cu-rich paragenesis with bornite and chalcocite is characterized by a high Cu/S ratio and a light δ^{34} S value. observed variations in Cu/S ratios and δ^{34} S values are consistent with the above-mentioned mechanism of sulphur degassing and it is suggested that this process occurred during metamorphism. Cawthorn and Meyer (1992) derived a similar conclusion from the study of S/Se ratios and suggested that probably up to 90% of the original S was lost in the case of Carolusberg West. For metamorphic temperatures of around 800°C, ΔSO_2 -H₂S equals 2.94 (Ohmoto and Rye, 1979) and degassing of H_2S will result in an increase in the $\delta^{34}S$ value in the remaining sulphides. In the present case, however, the sulphides are depleted in 34S which suggests devolatilization of SO₂. The relevant redox reaction whereby chalcopyrite and pyrrhotite react to form bornite and Ti-free magnetite may be expressed in the form:

$$5\text{CuFeS}_2 + 5\text{FeS} + 6\text{H}_2\text{O} + 8\text{O}_2 \rightleftharpoons \text{Cu}_5\text{FeS}_4 + 3\text{Fe}_3\text{O}_4 + 6\text{H}_2\text{S}\uparrow + 5\text{SO}_2\uparrow$$

where the H_2S/SO_2 ratio in the vapour is controlled by the partial pressures of H_2O and O_2 . For example, an increase in pH_2O by 1 log unit will shift fO_2 at which $H_2S/SO_2=1$ by about 0.7 log units (Ohmoto and Rye, 1979). Clearly, an external source of oxygen is needed for the above reaction to proceed. The generation of H_2O-CO_2 fluids by the dehydration of rocks during prograde metamorphism from amphibolite to granulite facies was proposed by Newton et al. (1980), and Lamb and Valley (1985) concluded that streaming of CO_2 vapour at lower-crustal pressures and temperatures requires oxygen fugacities above that of the QFM buffer. The presence of anhydrite as a stable phenocryst phase (McIver et al., 1983) in these rocks suggests that oxygen fugacities were at least 1.0 to 1.5 log fO_2 units above the Ni-NiO buffer (Carroll and Rutherford, 1987). Oxidation at high-grade metamorphic conditions has been reported previously from other granulite facies terranes, such as the Bamble Belt of southern Norway (Cameron, 1989), and it is suggested that oxidizing conditions also prevailed during metamorphism of the Koperberg Suite.

Mineral Chemistry

Orthopyroxene and plagioclase compositions are presented in Table 2 and the mole fraction of enstatite in orthopyroxene versus the anorthite content of plagioclase is shown in Figure 2. Cumulus orthopyroxene and plagioclase from layered mafic intrusions, are, in general, characterized by constant enstatite/anorthite ratios and define a regression curve with a slope of 1 in Figure 2. In contrast, co-existing orthopyroxene and plagioclase from the Koperberg Suite is not confined to this trend and the data occupy a large field. Intercumulus phases and minerals of only minor abundance do not always reflect cumulus compositions due to reactions with interstitial liquid and thus, may not show concomitant chemical compositions (e.g. Barnes, 1986). However, this effect can be ruled out for the present data set since samples with abundant orthopyroxene and plagioclase samples are plotted in Figure 2. The deviation of the data from the regression line is probably caused by Na addition to plagioclase not matched by a corresponding Fe increase in orthopyroxene, or visa versa. Na enrichment of plagioclase may be indicative of crustal contamination, while increased Mg contents of orthopyroxene suggest equilibration under high fO_2 conditions, due to the formation of magnetite.

Experimental work has shown that the Fe-Mg site distribution in orthopyroxene is temperature dependent at fixed fO_2 conditions and that at constant temperature, and in equilibrium with magnetite and quartz, the Fe-Mg ratio of orthopyroxene is a function of the prevailing oxygen fugacity (e.g. Fonarev and Grafchikov, 1984). This relationship is utilized here to calculate fO_2 conditions at metamorphic temperatures for a number of basic bodies. The calculations are presented in Table 7 and inspection of the data makes it obvious that fO_2

Table 7. fO_2 conditions calculated from orthopyroxene compositions (assuming a temperature of 800°C)

Locality	En	$-\log f O_2$
Carolusberg West Mine	69.0	11.8
New Mine	70.1	11.8
Jan Coetzee Mine	68.1	12.0
Wheal Julia	67.2	12.0
Jubilee	66.8	12.1
Kliphoog North	65.8	12.1
Koperberg Central	64.5	12.2
Nababeep Mine	64.7	12.2
Sugar Loaf	64.3	12.2
Tweefontein Mine	59.0	12.6
Noribees	54.3	12.9
East O'okiep Mine	53.8	12.9

values are highest for Carolusberg West which also contains the most oxidized ore and lowest for the East O'okiep ore body which contains the least oxidized sulphide assemblage. Also, the calculated oxygen fugacities for most of the basic bodies studied fall within the stability range of anhydrite (Carroll and Rutherford, 1987). The above findings are consistent with the conclusions drawn from stable isotope analyses and it is obvious that the chemistry of coexisting plagioclase and orthopyroxene also suggests crustal assimilation and/or metamorphic oxidation.

Towards a Genetic Model

The Koperberg Suite is conspicuous by its wide range of rock types. The occurrence of orthopyroxene and the absence of clinopyroxene indicates that the basic bodies cannot represent melt compositions and the presence of layering suggests that these are cumulate rocks. Although there is no unequivocal proof of the origin of the Koperberg Suite the authors favour a derivation from the mantle. The oxygen isotope results, however, require a substantial amount of crustal assimilation to account for the non-mantle $\delta^{18}O$ values. It is imagined, therefore, that there existed a mechanism similar to the MASH process proposed by Hildreth and Moorbath (1988), whereby basaltic magmas ascend from the mantle, stall at the crust-mantle transition, and mix with each other as well as with an array of melts derived from the induced partial fusion of older deep-crustal rocks. Emplacement of the Koperberg Suite took place over a protracted period of time. The earliest basic bodies contain the S2 foliation and, therefore, intruded during a period of recumbent folding (D2) and prograde metamorphism which attained upper amphibolite to granulite grade. period was followed by the D3 event which is reflected by large, open, upright folds while metamorphic conditions prevailed at upper amphibolite to granulite grade. Most of the basic bodies intruded during and possibly post D3. The continuous intrusion of basic bodies from prograde through to retrograde stages of metamorphism explains why some of the ore bodies, such as Carolusberg West, show metamorphic oxidation, while others, such as East O'okiep, have preserved their igneous mineralogy.

CONCLUSIONS

This study reports the results of petrographic, chemical and stable isotope analyses of whole rock samples and mineral separates from the Koperberg Suite. These data offer new insight into petrological processes that were responsible for the magmatic and metamorphic evolution of the Koperberg Suite and associated copper mineralization. O-isotope ratios of rocks and mineral separates are significantly enriched in ¹⁸O relative to 'normal' mantle values. This enrichment is seen as a product of large-scale hybridization of mantle-derived magmas by crustal material. Mixing calculations indicate that at least 40% of high- δ^{18} O crust is needed to explain the observed increase in ¹⁸O. The overall range in δ^{18} O values from 6.2 to 9.6 for plagioclase and from 5.9 to 8.3 for whole rock samples and the lack of isotopic equilibrium indicates open-system behaviour. This is interpreted as being diagnostic for subsolidus exchange with an isotopically heavy metamorphic fluid. There is also evidence that metamorphism was accompanied by oxidation which resulted in the reconstitution of ore minerals (chalcopyrite-pyrrhotite to bornite-magnetite) and the degassing of SO₂. The oxidation and devolatilization event consequently led to a systematic decrease

in S-isotope values and an increase in Cu/S ratios in the ore. Finally, it is envisaged that the Koperberg Suite originated from mantle-derived basaltic magmas which were emplaced over a prolonged period of time into a region undergoing deformation and high-grade metamorphism. The original magma was modified in zones of mixing, assimilation and fractional crystallization at the crust-mantle boundary or in the deep lower crust. Later modification occurred at the level of emplacement through differentiation and metamorphism. Crustal contamination can explain the origin of the elevated δ^{18} O values and the high levels of Rb and low K/Rb ratios.

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