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**PETROCHEMISTRY OF THE OKIEP COPPER DISTRICT
BASIC INTRUSIVE BODIES,
NORTHERN CAPE PROVINCE,
SOUTH AFRICA**

R.G. CAWTHORN and F.M. MEYER

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by

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ABSTRACT

Copper mineralization is associated with noritic and pyroxenitic rocks in the granulite-facies metamorphic terrane in the Okiep District of Namaqualand, in the northern Cape Province of South Africa. These bodies have been interpreted as post-metamorphic and the mineralization has been inferred to be magmatic. However, the sulphide mineralogy of many of the ore bodies is dominated by bornite, whereas immiscible magmatic sulphide ores contain pyrrhotite and chalcopyrite. Hence, the Okiep ores cannot be primary magmatic sulphides. Geochemical evidence is presented to demonstrate that the ores have undergone an extensive oxidative event in which pyrrhotite and chalcopyrite were converted to magnetite and bornite. Up to 90% of the sulphur has been lost in the case of some samples from Carolusberg Mine. The high $\text{Fe}_2\text{O}_3/\text{TiO}_2$ and Cu/S , and low S/Se ratios of whole rock samples, and their variation in different ore bodies provide quantitative evidence for this process. It is possible to recalculate the original sulphide from these data, and a Cu content of approximately 10% is indicated. However, these ores only contain in the order of hundreds of ppm Ni, and so the Cu/Ni ratio is extremely high compared to most sulphide ores derived from a differentiated basic magma.

In many of the mines, a later low-temperature hydrothermal alteration has obliterated the textural and mineralogical evidence for these reactions and relations which are best preserved in samples from the Carolusberg Mine.

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PETROCHEMISTRY OF THE OKIEP COPPER DISTRICT BASIC INTRUSIVE BODIES, NORTHERN CAPE PROVINCE, SOUTH AFRICA

INTRODUCTION

Copper mineralization was first reported in 1685 in what is now referred to as the Bushmanland Subprovince of the $\pm 1100\text{Ma}$ Namaqua-Natal Metamorphic Province shown in Figure 1 (Hartnady *et al.*, 1985). In the region (Fig. 2) a sequence of metasedimentary rocks (the Okiep Group) is intruded by two periods of syntectonic granites, the Nababeep and Modderfontein granitic gneisses (the Klein Namaqualand Suite) at $1213 \pm 22\text{Ma}$ and the

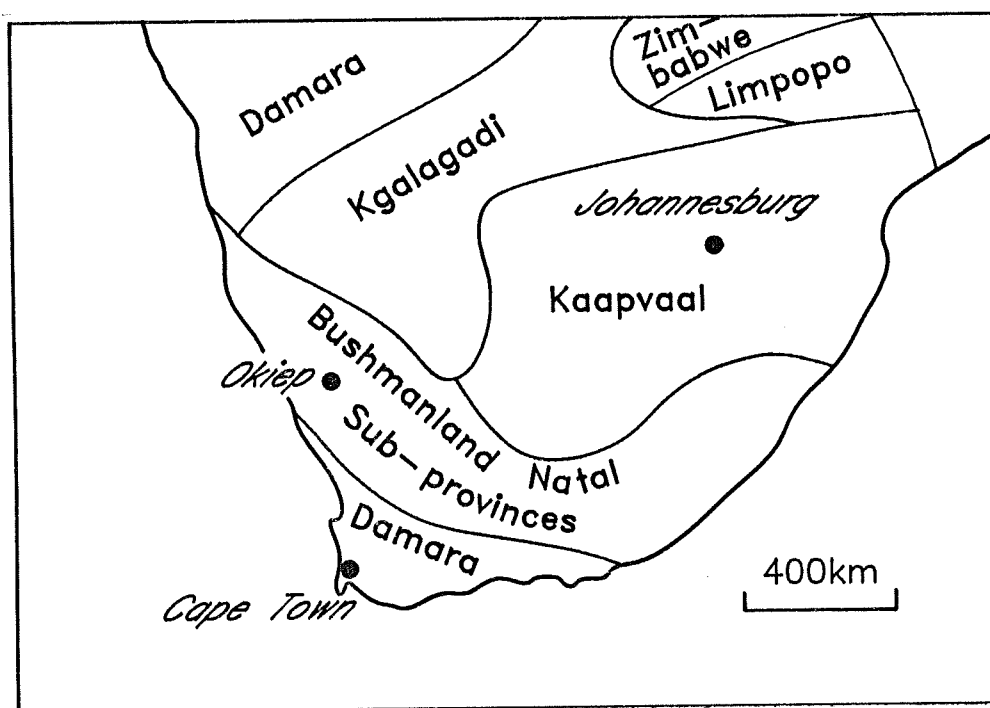


Figure 1: Regional tectonic setting of the Okiep Copper District in southern Africa (after Hartnady *et al.*, 1985).

Rietberg and Concordia granites (the Spektakel Suite) at $1166 \pm 26\text{Ma}$ (Clifford *et al.*, 1975). The former was associated with a subhorizontal deformation (D2) producing recumbent folding, and the latter with upright, gentle open folding (D3) which produced the Springbok anticline (Joubert, 1986). Related to the latter event is the formation of "steep structures", which possibly developed along periclinal axes or as piercement folds parallel to the Springbok anticline, in which an intense vertical fabric is locally developed (Joubert, 1986). These are narrow, laterally persistent zones, many of which contain intrusive basic bodies, referred to as the Koperberg Suite. Rocks range from pyroxenite to anorthosite to diorite and glimmerite, and are collectively referred to as noritoids. These basic dykes have been dated at $1070 \pm 20\text{Ma}$ by Clifford *et al.* (1975). Most authors have therefore concluded that these basic bodies are post-metamorphic (Conradie and Schoch, 1986a; Schoch and Conradie, 1990). However, McIver *et al.* (1983) argued that they were syn-metamorphic and had been recrystallized under granulite-facies metamorphism producing a mineralogy, but not a texture, indistinguishable from magmatic rocks.

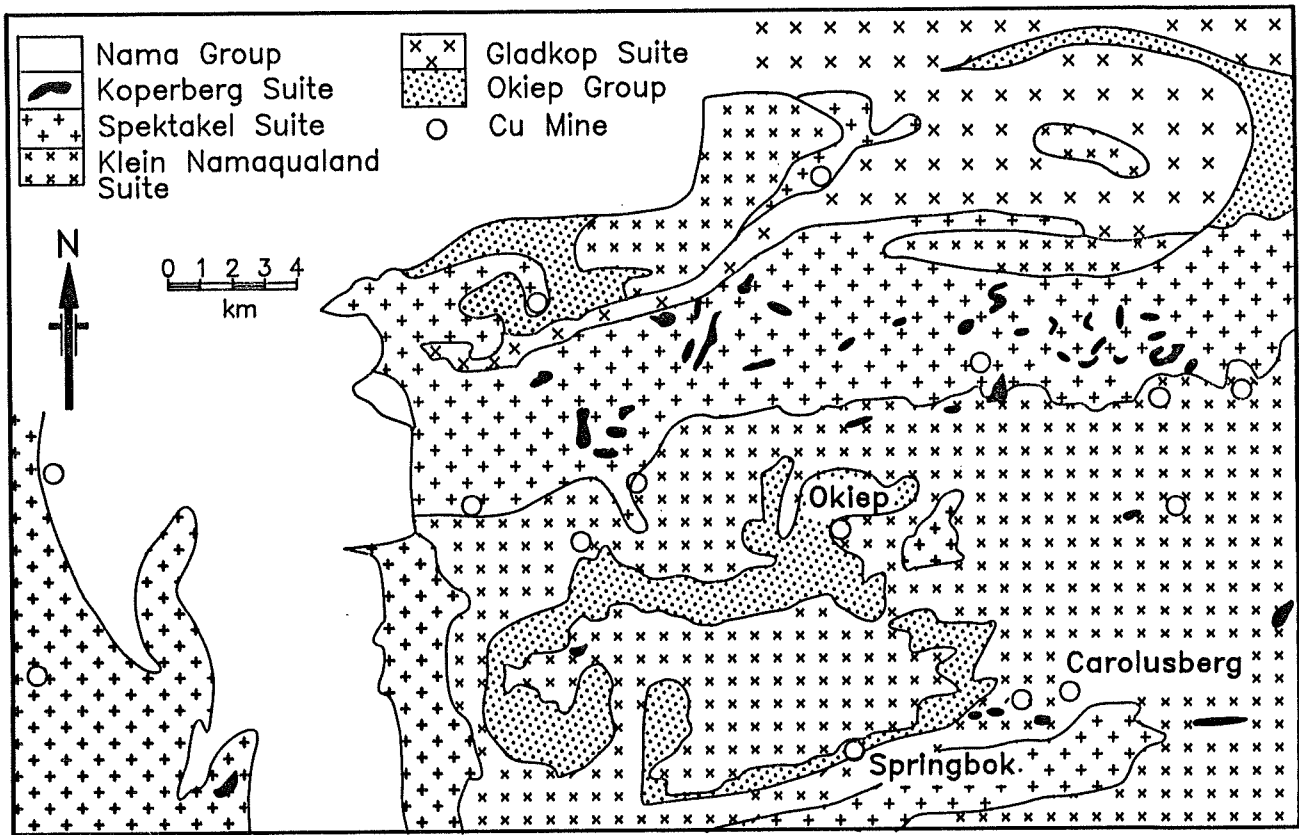


Figure 2: Geological map of the Okiep Copper District, after Joubert (1986).

The sulphides are generally regarded as having formed by immiscibility of sulphide liquid from a basic magma since the studies of Latzky (1942) and Van Zyl (1967). In contrast, Stumpfl *et al.* (1976) suggested that the sulphides formed from late-stage, magmatically derived hydrothermal fluids. In a refinement of this model Clifford *et al.* (1990) recognised two end-member types of mineralization, the Carolusberg-type which was syngenetic and the Hoits-type where Cu had undergone local remobilization, redistribution and recrystallization. They related the latter process to the 500-550Ma Pan-African event.

In order to further investigate the origin of the sulphides, with special reference to the debate on the timing of the igneous and mineralizing events, suites of samples were collected from three mines, which displayed a range of sulphide mineralogies, and these have been investigated petrographically and geochemically.

GEOLOGICAL SETTING

The regional geology and locations of the three mines discussed here are presented in Figure 2. The three mines are located in Nababeep granitic gneiss of the Spektakel Suite, and a frequent geometrical relation in these and many other mines is that the mineralization and basic bodies occur just above the Springbok Quartzites of the Okiep Group. The

geometry of the basic bodies on Carolusberg Mine is shown in Figure 3, where the podiform shape, frequent lateral displacement and relation to the steep structures are apparent. Samples were collected from the deep ore body as alteration decreases with depth and were taken from a horizontal borehole. Pyroxenite and norite are interbanded on a scale of 1-10m. There is no chilled margin against country rocks, a feature typical of all the Koperberg Suite. The geometry of the Okiep mines has been documented by Van Zyl (1967) and is shown in Figure 3.

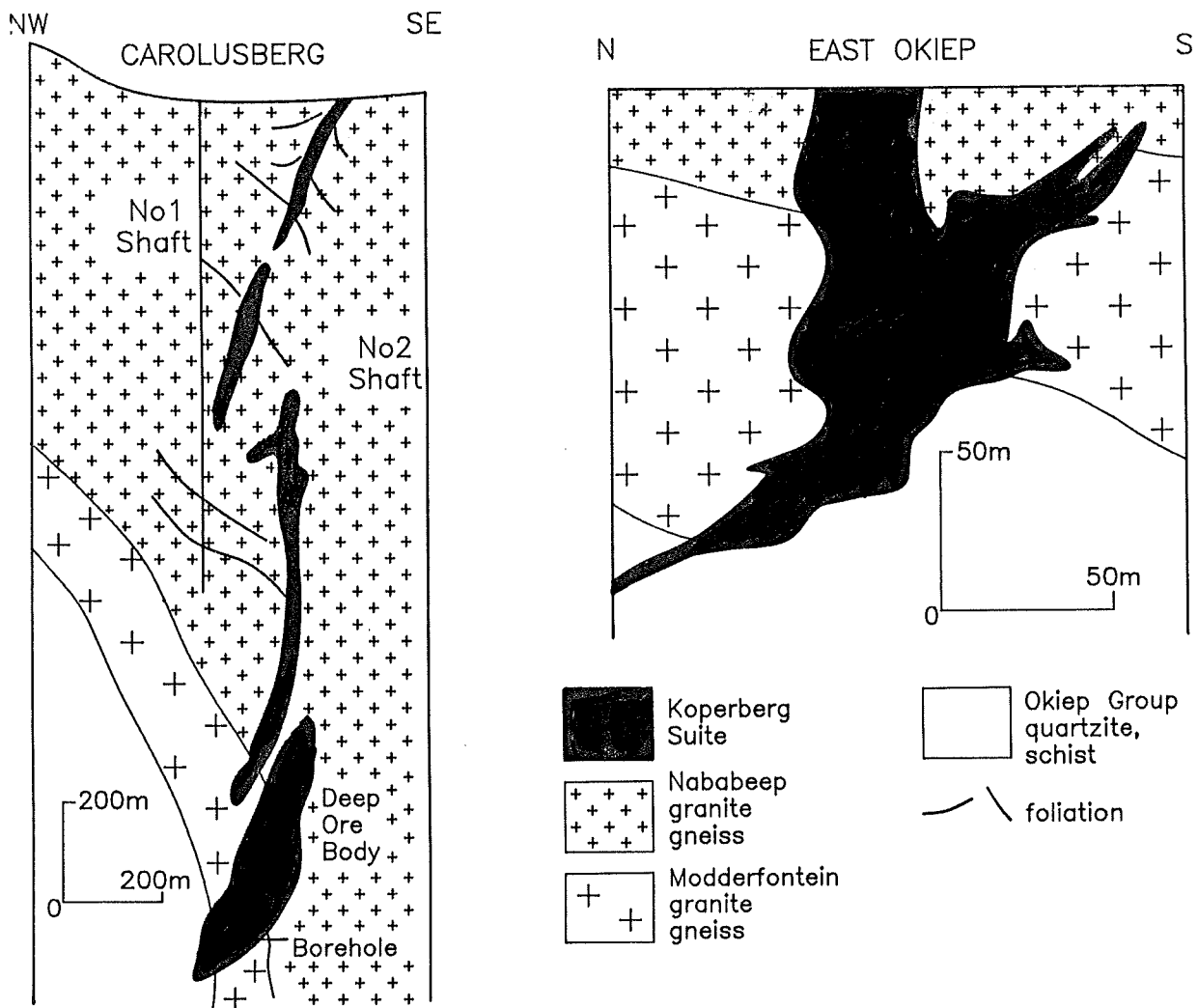


Figure 3: Section through the Carolusberg and East Okiep Mines.

PETROGRAPHY

The mineralogy and textures of the basic bodies have been documented in great detail by McIver *et al.* (1983) and Conradie and Schoch (1986a) and will not repeated here. The mineralization generally occurs in the more mafic facies of the intrusions, namely pyroxenites

and norites and less commonly diorites. Their textures have been described as igneous (Van Zyl, 1967), metamorphic (McIver *et al.*, 1983) or displaying characteristics of both (Conradie and Schoch, 1986a). The rocks are dominated by orthopyroxene and plagioclase with magnetite and biotite being variably abundant. Minor minerals include ilmenite, apatite, quartz and anhydrite. Some intrusions are very mica-rich but have not been investigated here. Clinopyroxene is remarkable by its almost complete absence. The textures of the oxide minerals from a variety of localities has been reviewed by Conradie and Schoch (1986b), while the sulphides have been described by Latzky (1942), Van Zyl (1967, 1978) and Stumpfl *et al.* (1976).

Here it is intended to highlight some of the features which are of specific reference to explaining the differences in opaque mineralogy in the different mines and to the origin of these ores. Most attention will be devoted to the samples from the deep ore at Carolusberg, as they have not been extensively documented previously.

Samples from Carolusberg range from pyroxenites to norites and nearly all contain some mineralization. Indeed, pyroxenites without sulphides are rare in the entire region. The dominant sulphide is bornite, which shows infrequent patchy replacement to chalcocite on the edges and within grains. It may occur as angular to polygonal grains (Fig. 4A and B). These have straight to gently curved mutual grain boundaries with pyroxene. In other examples bornite and magnetite coexist (Fig. 4C), where straight edges to pyroxene and between oxide and sulphide are evident. Frequently when magnetite abuts bornite, the former is idioblastic against the sulphide (Fig. 4D).

Magnetite frequently displays a polygonal shape (Fig. 4E) indicating textural re-equilibration with pyroxene. Also of significance in this photograph is the absence of exsolution in the magnetite. Other grains of magnetite do contain ilmenite exsolution (Fig. 4F), and examples of both textural types of magnetite may be found in contact. Ilmenite contains extremely well developed exsolution of hematite (Fig. 4G and H). Grains of ilmenite and magnetite may be in contact, with the former showing abundant exsolution, while the latter may be totally homogeneous (Fig. 4I). These textures and the sulphide mineralogy are extremely unusual for magmatic sulphides. Furthermore, the silicates seen in these photographs are all extremely fresh and argue against the possibility of late-stage hydrothermal processes being responsible for the mineralization (Stumpfl *et al.*, 1976), at least for the Carolusberg ore body.

The above features are in contrast to the more common ores from other mines, where silicates show alteration and the sulphide textures indicate remobilisation (Stumpfl *et al.*, 1976). Typical textures from the Okiep mines are shown in Figures 4J-L. Figure 4J shows chalcopyrite and bornite intergrown with chlorite derived from pyroxene and muscovite, while Figure 4K shows chalcopyrite growing along cleavage planes in mica. Conversion of bornite to chalcopyrite is often noted (Fig. 4L).

The major sulphide and oxide mineralogies of the West and East Okiep and Carolusberg mines are summarized in Table 1. Information for the Okiep mines is from Van Zyl (1967 and 1978), and for Carolusberg mine is from this study and Van Zyl (1978). These differences indicate different histories for each of the ore bodies, and that regionally

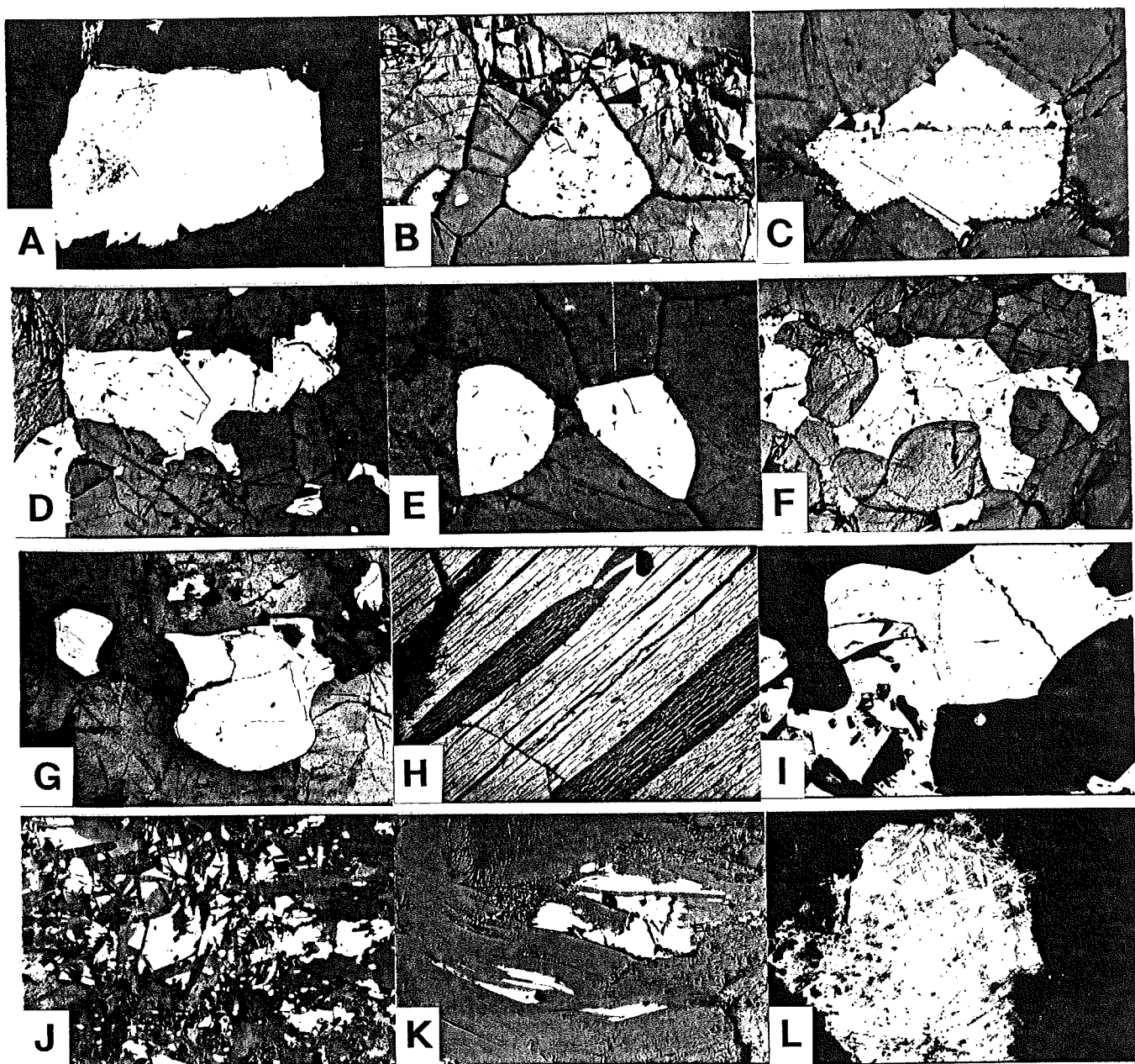


Figure 4: Reflected light photomicrographs of sulphide and oxide textures from the Koperberg Suite. Photomicrographs A-I are from Carolusberg mainly from pyroxenite; J-L are from Okiep mines. A. Polygonal grain of bornite (showing alteration on left to chalcocite) intergrown with orthopyroxene. B. Bornite and orthopyroxene showing well-developed triple junctions. C. Magnetite, devoid of exsolution (above) with a straight boundary to bornite, showing alteration to bright white chalcocite (below). 120° junctions are clearly seen. D. Idioblastic homogeneous bornite (left) in contact with irregular bornite (right), surrounded by orthopyroxene. E. Polygonal homogeneous magnetite and orthopyroxene. F. Magnetite showing few exsolution lamellae of dark ilmenite (NW-SE) with 120° junctions to orthopyroxene. G and H. Two scales of exsolution between hematite and ilmenite. I. Ilmenite-hematite exsolution (right) in contact with magnetite (lower left) showing no exsolution. J. Intergrowth between chlorite and mica with bornite and chalcopyrite in altered diorite. K. Precipitation of chalcopyrite along cleavage traces in deformed mica in biotite-rich diorite. L. Growth of chalcopyrite (bright white) flames in bornite in altered diorite. Widths of fields of view: A, C, E, H, I and L - 2mm; B, D, J and K - 4mm; F and G - 8mm.

TABLE 1: Opaque Mineralogy from Different Mines

MINERAL	CAROLUSBERG	WEST OKIEP	EAST OKIEP
Magnetite	Very common (Some grains have ilmenite exsolution others homogeneous)	Common (ilmenite exsolution)	Common (ilmenite exsolution)
Ilmenite	Present	Present	Present
Pyrrhotite	Absent	Absent	Present
Chalcopyrite	Very rare	Common	Very common
Pentlandite	Absent	Absent	Rare
Bornite	Very common	Very common	Rare
Chalcocite	Present	Absent	Absent

Data on Okiep mines from Van Zyl (1967 and 1978), Stumpfl *et al.* (1976) and this study; Carolusberg Mine Van Zyl (1978) and this study.

applicable models are an oversimplification of the real situation.

GEOCHEMISTRY

In this study, three mines have been specifically chosen as representing the two possible end-members of Clifford *et al.* (1990), namely Carolusberg and East Okiep; and an intermediate example (West Okiep) in terms of their oxide and sulphide mineralogies (Table 1). However, a substantial data base has been accumulated on other mines and also on unmineralized basic bodies from the area, and these are incorporated into the diagrams and discussion.

Representative material has been analysed for major and trace elements by X-ray fluorescence spectrometry; for ferrous iron by wet chemistry; for sulphur and water by Leco analyser; and for selenium by inductively coupled plasma mass spectrometry. Further, pure separates of magnetite and orthopyroxene were obtained from samples crushed to 125-250 μ . Magnetite was analysed for TiO₂, V₂O₅ and Cr (Cawthorn and McCarthy, 1980); and pyroxene for major and trace elements by X-ray fluorescence. The results for whole rocks, magnetite and pyroxene are presented in Tables 2, 3 and 4.

Whole-Rock Data

Major oxide and trace element analyses of samples from all three mines are presented in Table 2. Most samples are dominated by the minerals orthopyroxene and plagioclase. This is demonstrated by the good inverse correlation between MgO and Al_2O_3 , in Figure 5. There is a continuum of compositions from pyroxenite to anorthosite. The typical compositional range of the pyroxene and plagioclase in pyroxenite and norite is from En_{70-60} and An_{55-60} (this study and Conradie and Schoch, 1986a), but such changes do not drastically affect the position of the tie-line as shown in Figure 5. Variations in the proportion of brown

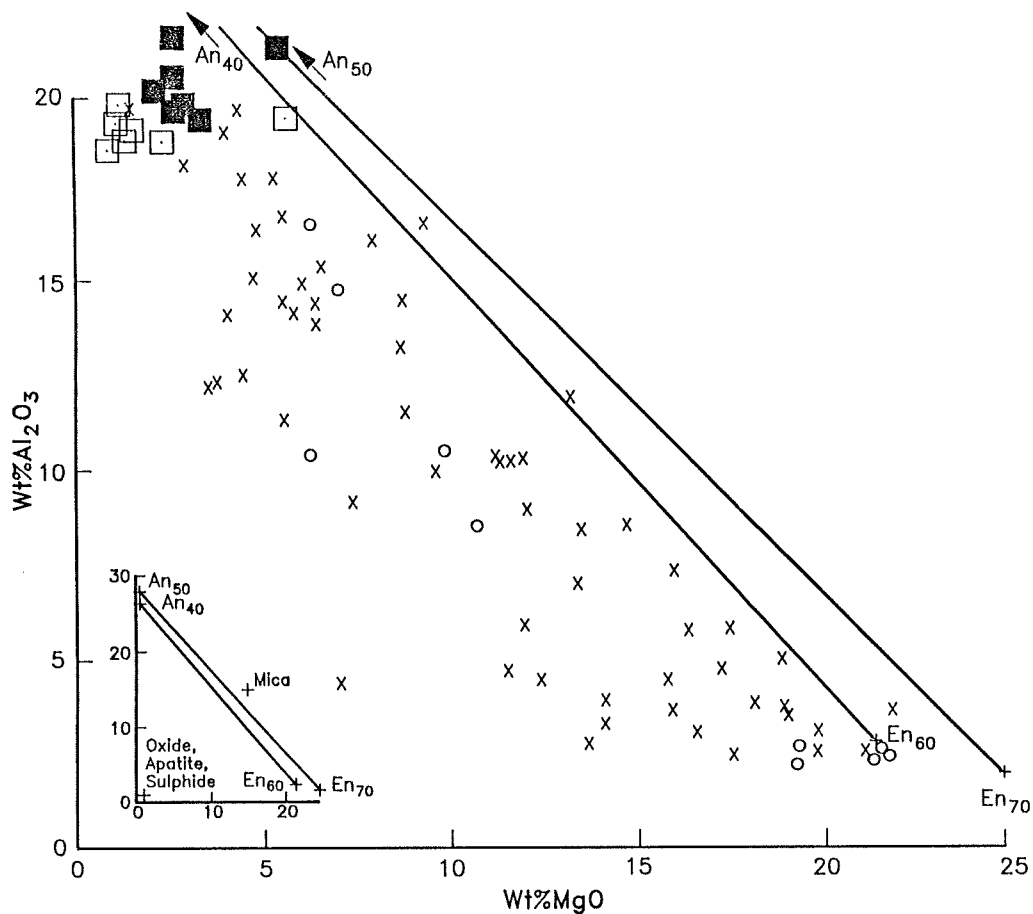


Figure 5: Plot of MgO versus Al_2O_3 for whole rocks. Inset shows the compositions of the different minerals comprising this rock suite, indicating that the analyses are dominated by plagioclase and orthopyroxene. Brown mica is variably present, but does not greatly affect the colinearity observed. The presence of oxides, sulphide and apatite cause the data to plot below the binary mixing lines shown which trend from $\text{En}_{70}\text{-An}_{50}$ and $\text{En}_{60}\text{-An}_{40}$. Analyses from Carolusberg Mine are shown by open circles; West Okiep by open squares; East Okiep by solid squares; crosses indicate data from the unpublished data base of Gold Fields of South Africa, McIver et al. (1983), Conradie (1983) and Conradie and Schoch (1986a), covering numerous basic bodies. Mineral compositions are from this study and from Conradie and Schoch (1986a).

TABLE 2. Whole-rock Analyses of Koperberg Suite Samples

	CW19.05	CW26.62	CW27.10	CW27.60	CW29.30	CW36.90	CW50.30	CW50.8	CW57.7	CW58.2	CB3	WO1	WO2	WO3
SiO ₂	42.95	41.28	40.80	38.03	44.38	42.27	41.94	45.56	46.62	46.48	41.86	40.92	40.04	39.67
TiO ₂	.79	2.95	3.84	3.99	2.52	3.43	.92	.55	.39	.37	1.25	1.45	1.50	1.72
Al ₂ O ₃	2.73	13.29	10.59	8.65	16.61	14.76	2.33	2.39	2.59	2.55	19.88	19.95	18.65	19.03
Fe ₂ O ₃	7.57	5.01	8.70	16.63	9.87	6.82	7.79	6.17	9.57	6.54	22.44	13.22	9.77	13.16
FeO	16.43	14.04	15.10	10.70	5.80	11.01	16.30	16.20	13.01	15.30	9.09	10.97	10.97	9.99
MnO	.34	.24	.28	.33	.16	.21	.35	.38	.37	.38	.07	.14	.10	.18
MgO	19.47	8.13	10.08	10.79	6.26	7.12	19.48	21.37	21.79	21.68	2.07	1.14	.99	1.48
CaO	1.21	6.42	5.25	4.79	7.17	6.61	1.22	.83	.62	.66	5.62	6.92	6.08	6.68
Na ₂ O	.10	3.10	2.06	1.58	3.23	3.03	.01	0	0	0	4.16	3.43	2.59	2.93
K ₂ O	.15	.28	.17	.28	.27	.28	.02	0	0	.01	1.74	.75	1.04	.72
P ₂ O ₅	.29	.67	.73	1.02	.67	.89	.38	.13	.01	.02	.05	.69	.58	.69
S	1.27	.88	.82	.80	.36	.90	2.18	1.78	1.31	1.36	.25	1.12	.37	.37
Cu	48796	18508	23904	31386	13407	23481	68630	55470	33658	36195	3198	7362	41663	12890
Total	98.17	98.14	100.81	100.59	98.64	99.68	99.76	100.90	99.62	98.97	99.46	98.67	97.59	97.90
Se	20						24	21		24			17	7
Cr	3534	692	1125	1413	595	614	3109	3210	2959	2992	161	320	324	367
V	358	280	445	508	281	386	330	256	276	261	403	732	711	789
Ni	791	241	331	382	171	253	844	767	715	727	139	173	396	218
Rb	17	9	8	13	7	7	8	5	6	7	105	38	60	41
Sr	24	471	381	292	687	566	10	10	2	2	529	674	626	640
Y	14	48	64	85	48	72	26	14	8	11	8	52	50	54
Zr	35	496	592	682	497	673	27	26	18	28	219	19	41	47
Ba	59	108	117	106	197	201	28	20	20	21	426	263	293	249

	WO4	WO5	WO6	WO7	WO8A	WO8B	EO1	EO2	EO3	EO4	EO5	EO6	EO7	EO8
SiO ₂	40.55	38.64	38.74	42.23	52.52	51.48	45.11	46.66	46.22	50.77	47.26	47.43	44.20	47.61
TiO ₂	1.26	1.62	1.55	1.37	.19	.30	1.16	1.21	1.20	1.87	1.18	1.02	1.36	.83
Al ₂ O ₃	19.26	18.82	18.95	19.63	21.16	19.48	21.31	22.02	22.38	20.20	22.68	19.87	19.38	20.45
Fe ₂ O ₃	9.30	14.10	14.31	8.83	2.96	10.41	5.69	4.32	5.41	4.48	4.69	6.64	8.72	6.47
FeO	9.22	10.22	10.16	9.01	4.29	10.41	4.85	5.61	4.86	5.45	4.51	6.54	7.47	5.49
MnO	.11	.16	.17	.15	.15	.22	.07	.07	.05	.09	.03	.12	.12	.12
MgO	1.02	2.22	1.26	2.58	3.99	5.66	2.59	2.74	2.47	2.17	2.48	3.06	3.34	2.73
CaO	6.43	5.95	6.67	6.80	7.00	6.47	7.05	7.23	7.79	6.43	7.95	6.95	6.62	7.02
Na ₂ O	2.85	2.68	2.80	3.42	3.57	3.23	3.74	4.37	3.46	3.08	3.51	3.46	3.28	3.76
K ₂ O	.73	.62	.72	.67	.57	.56	1.53	1.67	1.68	1.88	1.73	.75	1.47	.82
P ₂ O ₅	.50	.72	.70	.52	.09	.15	.52	.51	.53	.45	.53	.42	.66	.39
S	1.40	.30	.30	1.37	.54	.54	1.24	1.25	1.12	1.25	1.05	1.26	1.19	1.47
Cu	42628	5919	9140	32341	9432	5040	11675	10225	9990	4513	9529	12264	8213	13294
Total	96.89	96.63	97.24	99.81	97.99	98.47	96.01	98.67	98.16	98.56	98.55	98.74	98.62	98.47
Se	11						7	9					7	7
Cr	436	386	371	243	165	138	42	34	45	38	34	38	56	29
V	572	917	863	505	91	139	227	216	227	127	203	248	308	210
Ni	434	249	209	371	145	151	173	172	100	114	94	83	137	83
Rb	41	43	41	37	11	14	86	92	93	47	92	83	82	20
Sr	667	552	644	661	636	583	710	699	746	582	741	629	594	650
Y	37	43	54	36	16	24	17	23	17	34	16	35	34	31
Zr	16	19	12	30	28	25	31	33	23	447	19	499	316	475
Ba	251	153	252	231	174	160	853	992	867	1044	886	242	666	256

mica cannot be seen on this diagram as its composition plots close to the plagioclase-pyroxene join. However, samples from the present study do not contain much biotite. All compositions plot below this join due to the presence of variable proportions of oxides, sulphides and apatite. The very broad, but continuous spread of the major element data suggests that these rocks are cumulates as has been argued by McIver *et al.* (1983), and that these analyses are not representative of magma compositions.

The contribution made by oxide minerals in these rocks can be seen in a plot of TiO_2 versus Fe_2O_3 , as all other minerals are depleted in these two components. The only exception is mica which contains 3-6% TiO_2 (Conradie and Schoch, 1986a), but this is scarce in the samples studied here. Fe_2O_3 has been determined by difference between ferrous iron determined wet chemically and total iron by X-ray fluorescence. The results are shown in Figure 6A, where it can be seen that these rocks contain very high concentrations of Fe_2O_3 . A plot of all pyroxenites and norites from the Koperberg Suite is presented in Figure 6B, and indicates that high Fe_2O_3 contents are a general feature of the Koperberg Suite.

The samples studied here are variably mineralized, and their Cu and S contents are plotted on Figure 7. The dashed lines indicate the trends predicted for samples containing only bornite or chalcopyrite, and the solid diagonal line indicates compositions of a rock containing sulphide with 10% Cu in 100% sulphide. This would correspond to the most Cu-rich ores associated with mafic magmatic rocks, such as Noril'sk (Naldrett, 1981). Samples from Carolusberg and West Okiep plot very close to the trend for bornite, while the data for East Okiep plot close to the chalcopyrite line. Thus, these rocks are highly enriched in Cu for the amount of sulphur present compared to typical magmatic sulphide ores.

The Cu:Ni ratio of all samples is shown in Figure 8. Figure 8A refers to samples from this study, while Figure 8B includes pyroxenites and norites from the entire Copper District. The band encloses samples with a Cu/Ni ratio from 100 to 50. This is extremely high for a magmatic sulphide associated with mafic rocks (Naldrett, 1981).

The S/Se ratio is highly variable from 500 to 20,000 (Table 1), with each ore body having a different range of ratios. The Se content of the ore may be quite high for magmatic sulphides (up to 24ppm). For all the samples there is a negative correlation between the S/Se ratio and the Cu/S ratio (Fig. 9), with the Carolusberg ore body having the lowest ratio for S/Se and increasing values being recorded in West Okiep and East Okiep. The samples with the lowest Se content (and hence subject to the largest percentage error) have high S/Se ratios (10000 - 20000) similar to typical magmatic sulphides (Naldrett, 1989). The samples with the highest Se content and least uncertainty are those from Carolusberg Mine which have the atypically low ratios which are discussed below.

Mineral Data

The orthopyroxene in this study (Table 3) ranges from En71-66, which is at the magnesian end of the range reported by Conradie and Schoch (1986a). Those from the pyroxenite are more magnesian than those from the norite, with a distinct gap between En67.5-69.5. This bimodality is even more pronounced for the Cr data, where the pyroxenites contain minerals with 739-914 ppm Cr, compared to the range of 196-244 ppm

TABLE 3. Analyses of Orthopyroxene from Carolusberg Mine

	CW19.05	CW26.62	CW27.10	CW27.60	CW29.30	CW36.90
SiO ₂	52.27	51.84	53.04	52.89	52.58	52.13
TiO ₂	.10	.73	.27	.12	.28	.15
Al ₂ O ₃	1.97	3.52	2.10	1.76	3.01	2.45
FeO(T)	19.23	19.30	20.59	20.45	19.56	19.92
MnO	.45	.72	.79	.66	.58	.58
MgO	24.81	21.18	22.92	23.91	21.41	22.95
CaO	.49	1.69	.95	.76	1.29	.77
Na ₂ O		.08	.01		.06	.02
Total	99.32	99.07	100.66	100.54	98.76	98.97
V	89	108	77	70	73	89
Cr	739	244	238	242	196	223
Co	146	144	152	160	144	152
Ni	534	349	393	398	356	434
Cu	3315	6030	4635	4567	5599	5546
mg	69.70	66.16	66.48	67.57	66.11	67.25

	CW50.30	CW50.80	CW57.70	CW58.20	J1
SiO ₂	52.80	54.30	51.44	53.08	52.67
TiO ₂	.46	.46	1.17	.20	.13
Al ₂ O ₃	2.35	2.34	2.24	2.21	2.01
FeO(T)	18.80	17.95	19.16	18.66	21.49
MnO	.58	.59	.47	.46	.64
MgO	24.78	24.19	24.58	25.29	23.41
CaO	.59	.61	.58	.49	.61
Na ₂ O	.03	.37			
Total	100.39	100.81	99.64	100.40	100.97
V	104	92	98	94	109
Cr	762	914	875	904	762
Co	148	153	148	149	132
Ni	564	582	553	547	544
Cu	4852	8063	4073	3381	973
mg	70.14	70.60	69.57	70.72	66.00

TABLE 4. Partial Analyses of Magnetite from Carolusberg and Okiep Mines

	CW19.05	CW26.62	CW27.10	CW27.60	CW29.30	CW36.90
TiO ₂ %	1.07	4.98	6.09	5.32	5.94	8.39
V ₂ O ₅ %	.50	.36	.39	.40	.38	.37
Cr ppm	31826	7918	8376	8852	7349	4934

	CW50.30	CW50.80	CW57.70	CW58.20	CB3	GA1444
TiO ₂	1.98	.99	1.37	1.34	1.47	6.33
V ₂ O ₅	.49	.45	.49	.45	.35	.18
Cr	29506	36650	34802	34169	930	80

	EO1	EO2	EO3	EO4	EO5	EO6
TiO ₂	1.83	1.74	1.50	2.56	1.53	1.58
V ₂ O ₅	.66	.68	.64	.40	.61	.60
Cr	730	751	713	1089	687	616

	EO7	EO8	WO1	WO2	WO3	WO4
TiO ₂	1.28	1.57	3.07	2.54	3.02	2.80
V ₂ O ₅	.58	.61	.72	.86	.74	.79
Cr	667	693	1666	2080	1593	1953

	WO5	WO6	WO7N	AVE CW	AVE EO	AVE WO
TiO ₂	2.72	2.97	2.65	3.75	1.70	2.47
V ₂ O ₅	.75	.73	.68	.43	.60	.66
Cr	1759	1643	1552	20438	743	1531

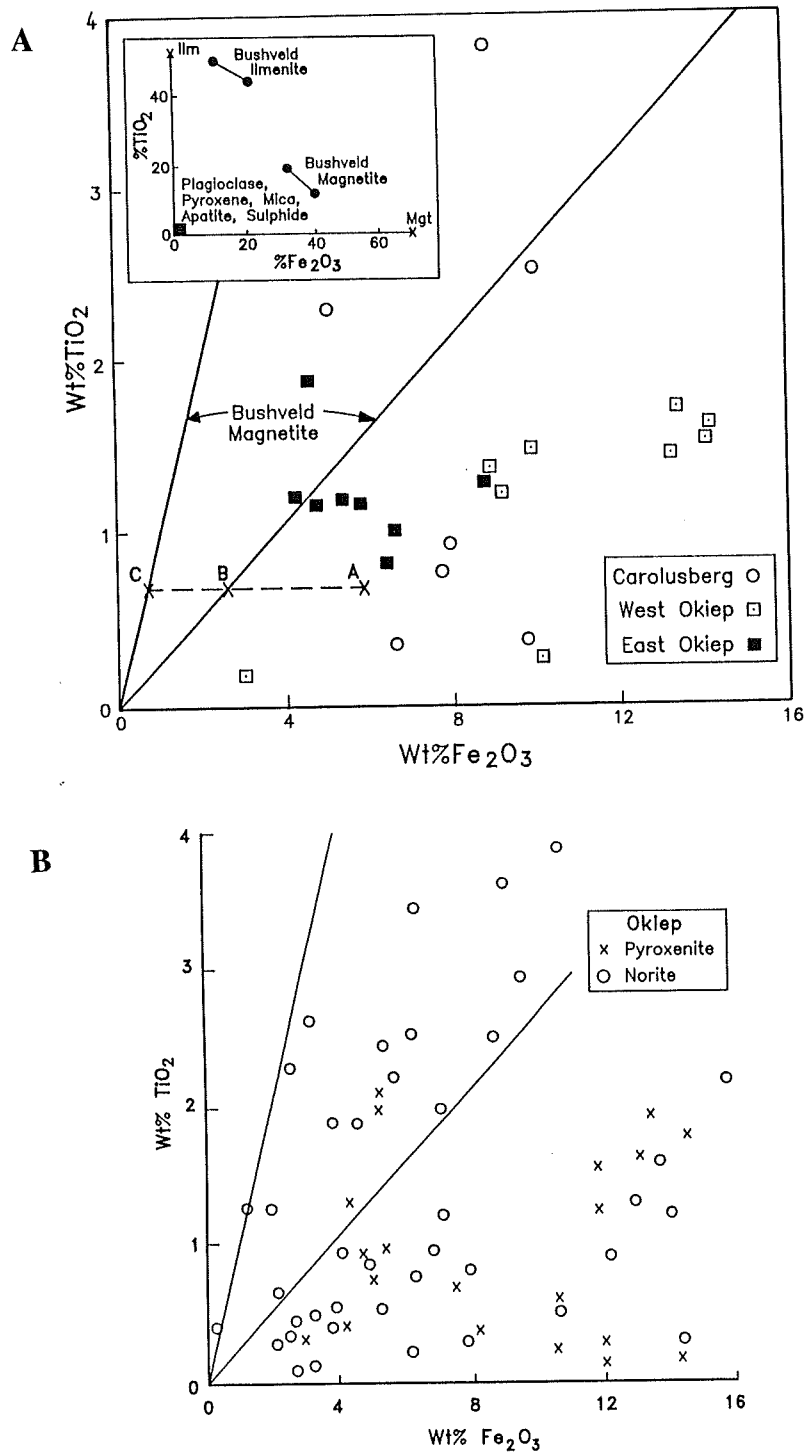
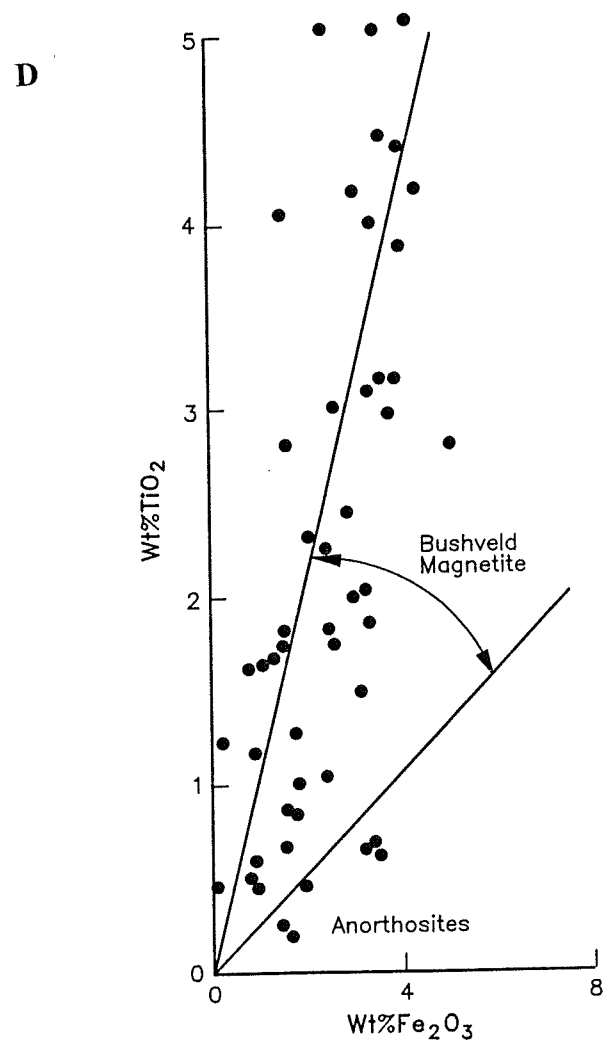
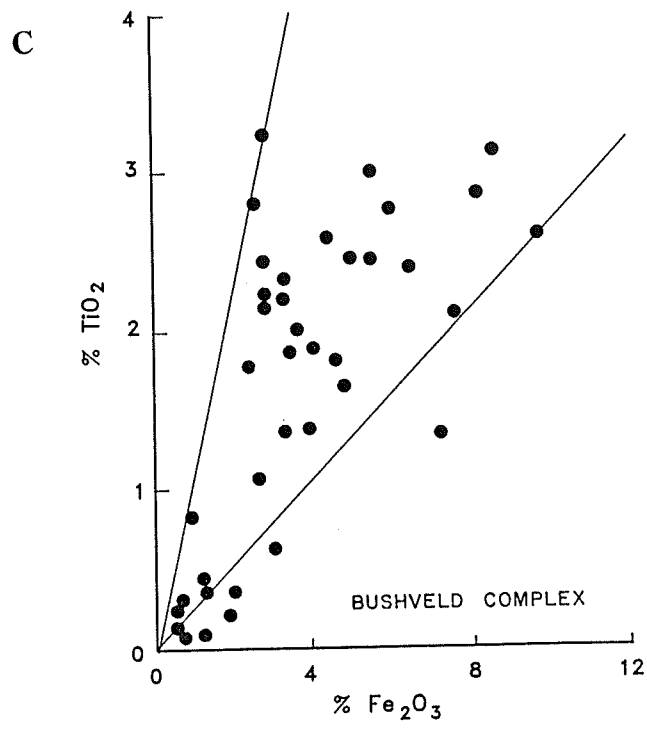


Figure 6: Plot of TiO₂ versus Fe₂O₃ (determined by difference between total iron and ferrous iron). Figure 6A shows data for the three ore bodies studied here. Points A, B and C are discussed in the text. Figure 6B covers the entire Okiep Copper District using the same data base as Figure 5. Figure 6C shows the same plot for data from the Upper Zone of the Bushveld Complex, and Figure 6D data for anorthositites taken from Hill (1988), Higgins and Doig (1986), Moreau et al. (1987), Kamineni (1986) and Emslie (1976). Analyses from Carolusberg Mine are shown by open circles; West Okiep by open squares; East Okiep by solid squares.



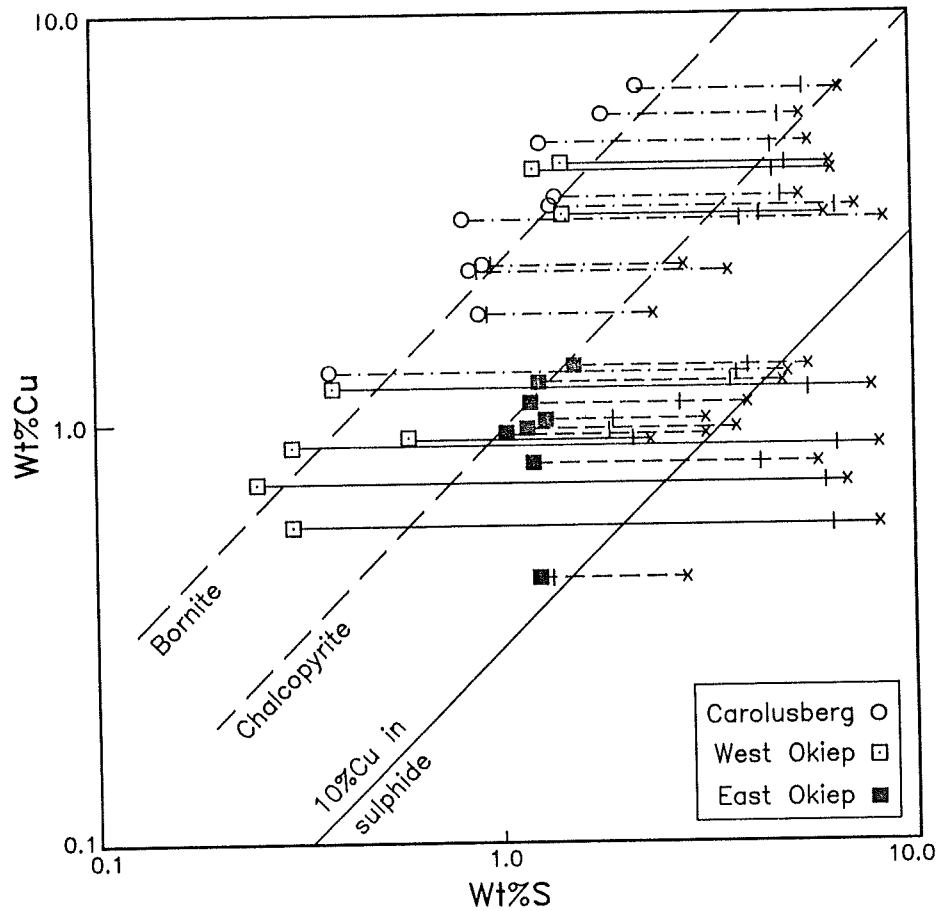


Figure 7: Plot of log Cu versus log S contents (in wt %) of samples from Carolusberg (circles), West Okiep (open squares) and East Okiep (solid squares). Hypothetical lines representing varying proportions of bornite, chalcopyrite and a sulphide with 10% Cu are shown. The horizontal lines indicate the possible original concentrations (cross represents maximum and short tick represents minimum calculated from Fig. 6A) of sulphur in the rock prior to oxidation. See text for discussion.

Cr for the norites. This range of compositions is comparable to that found from the bottom and top of the Main Zone of the Bushveld Complex (Mitchell, 1990). The other minor elements TiO_2 , Al_2O_3 and CaO do not display systematic differences between the two different rock types. Despite the close juxtaposition of samples of pyroxenite and norite in the borehole core, they appear to represent two different suites and are not merely related to each other by continuous fractionation in their present setting. The analyses of pyroxene yielded in the order of 3000-8000 ppm for Cu, which indicates that there are inclusions of sulphide present which were too small to remove during mechanical separation.

The magnetite has been analysed for its trace elements (Table 4). There has been prolonged development of coarse exsolution of ilmenite from some of the magnetite,

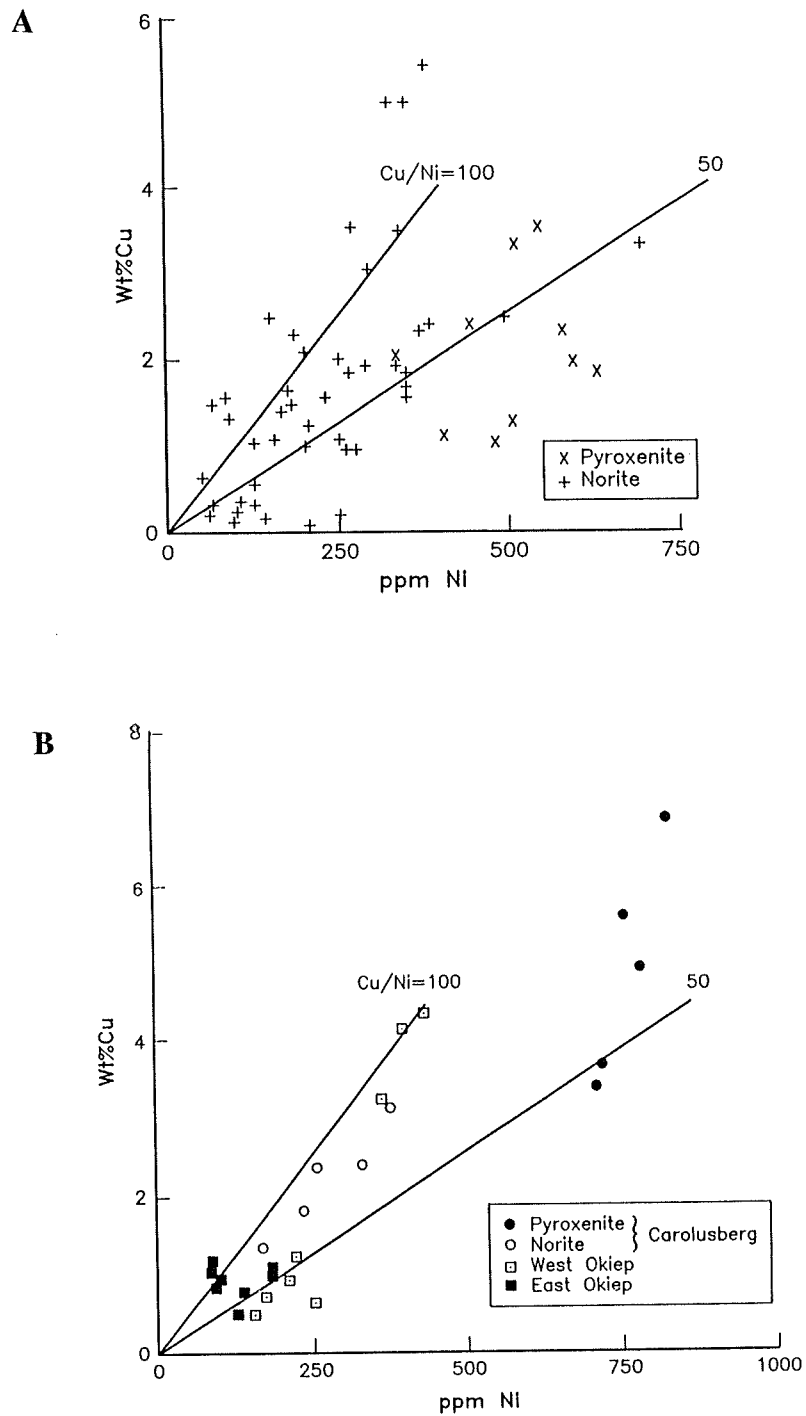


Figure 8: Plot of Cu (wt %) versus Ni (ppm). Figure 8A includes pyroxenites (crosses) and norites (pluses) from the Gold Fields' data base for the entire region. Figure 8B includes samples from this study; solid circles indicate pyroxenites open circles norites from Carolusberg; open squares from West Okiep; solid squares from East Okiep.

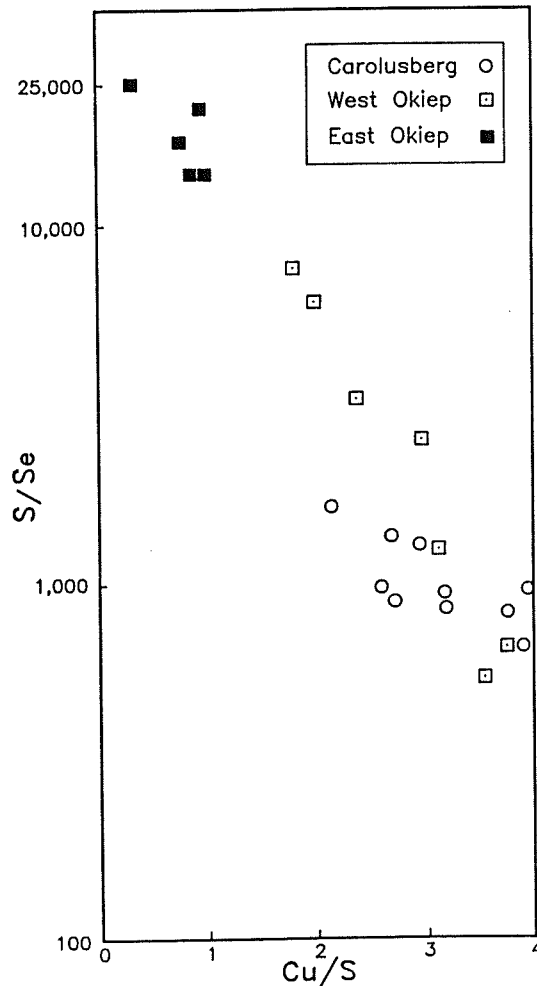


Figure 9: Plot of log S/Se ratio versus Cu/S ratio for different ore bodies. Carolusberg (circles), West Okiep (open squares) and East Okiep (solid squares).

especially from the Okiep mines (Conradie and Schoch, 1986b). Some of the coarse exsolved ilmenite would not be concentrated in the magnetic fraction, and hence these analyses do not represent the primary, magmatic composition. Typical TiO_2 contents are from 1 - 8%; this variation probably reflecting the coarseness of the exsolution, and how much of the ilmenite had segregated into discrete granules. However, it will also depend on the proportions of the two generations of magnetite identified petrographically, one having abundant exsolution and the other being devoid of exsolution. The lowest values for TiO_2 correspond to those reported by Conradie and Schoch (1986b) from electron microprobe analyses. Magnetite from pyroxenites from Carolusberg contains in the order

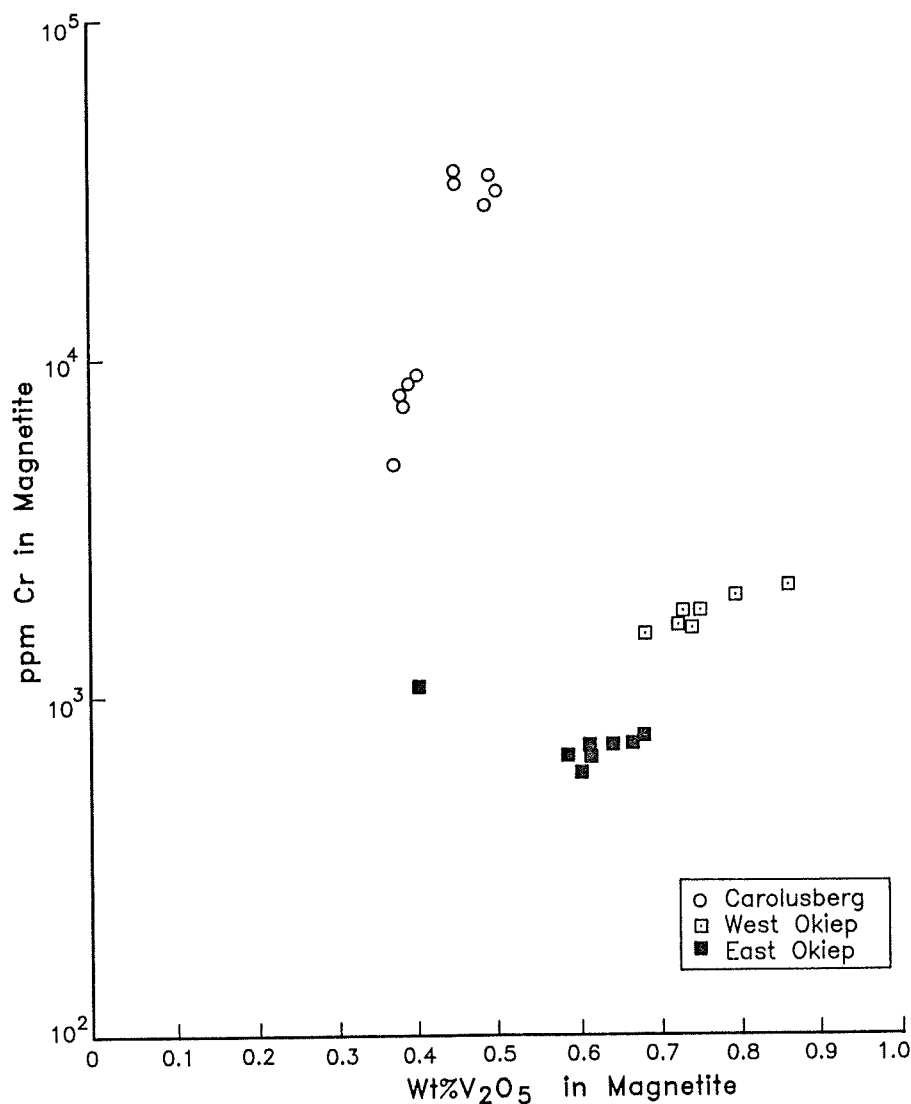


Figure 10: Plot of log Cr (ppm) versus V_2O_5 (wt %) for magnetite separates. Solid circles indicate pyroxenites, open circles norites from Carolusberg; open squares from West Okiep; solid squares from East Okiep.

of 30000 ppm of Cr (4.5% Cr_2O_3), whereas those from the norites contain 5000 - 9000 ppm. Samples from West and East Okiep contain about 1500 and 750 ppm Cr respectively. The magnitude of the differences for V_2O_5 are much smaller, but still can be recognised between each setting. The pyroxenites and norites from Carolusberg contain on average 0.46 and 0.38% V_2O_5 respectively, while from West and East Okiep they average 0.66 and 0.60% V_2O_5 respectively. The data of Conradie and Schoch (1986b) indicate very wide variation in this element even within single localities. For example, they quoted values from 0.46 to 3.42% V_2O_5 from West Okiep. The data are plotted in Figure 10 which shows that Carolusberg has higher Cr but lower V_2O_5 than the Okiep deposits. Individual samples from each ore body define a tight cluster, but between mine variation is very significant.

DISCUSSION

Sulphide Mineralogy

Typical magmatic sulphide deposits are dominated by pyrrhotite, with lesser chalcopyrite and pentlandite depending upon the composition of the host rocks. This assemblage is observed at East Okiep (Table 1), although the textures are not obviously those of a pristine magmatic sulphide, as there has been alteration of the silicate mineralogy and remobilization of the sulphides. However, the preponderance of bornite in ore from most mines indicates that this is not a typical magmatic sulphide. The oxygen fugacity of the magma will control the sulphur content of any immiscible sulphide (Shima and Naldrett, 1975), but it would not seem possible to produce an immiscible liquid with so little sulphur that no pyrrhotite forms. Even the most copper-rich magmatic sulphides, such as Noril'sk with $\pm 10\%$ Cu, produce an assemblage with abundant chalcopyrite, but not bornite. Furthermore, the nature of the silicate host minerals at Carolusberg and the absence of hydrothermal alteration precludes the model of Stumpfl *et al.* (1976) of concentration of sulphur in a late-stage hydrous fluid at the end-stages of differentiation (at least for Carolusberg).

Finally, the granular texture and polyhedral angles observed between the sulphide and pyroxene in many samples is not that of a typical immiscible sulphide which normally forms interstitial areas as the sulphide phase is the last to solidify in basic rocks. Thus the presently preserved sulphide mineralogy and texture of the freshest ore body, Carolusberg, are inconsistent with formation by liquid immiscibility.

Oxide Mineral Relationships

Conradie and Schoch (1986b) suggested that the exsolution textures seen in the ores indicated the most extreme case of slow cooling and re-equilibration ever recorded in an igneous body on the basis of the very low temperatures extrapolated from the magnetite-ilmenite compositions. The ilmenite shows extremely strongly pronounced exsolution features (Fig. 4). While this is also recorded in most magnetite grains from most unmineralized bodies, some of the sulphide-rich rocks contain magnetite with no exsolution at all. The physical proximity of highly exsolved ilmenite with homogeneous magnetite, and of both exsolved and homogeneous magnetite in the same sample, is difficult to explain by prolonged cooling of a magmatically derived rock. McIver *et al.* (1983) noted a parallel anomaly with the pyroxenes. While clinopyroxene is very rare in these rocks, occasionally coexisting orthopyroxene and clinopyroxene are observed, but they contain no exsolution lamellae. In a slowly cooled intrusion with coexisting pyroxenes this is again extremely atypical, if not impossible to explain. In some cases, (Fig. 4) the homogeneous magnetite occurs associated with the sulphide and so it could be argued that the magnetite formed from the immiscible sulphide liquid. However, there are many examples of homogeneous magnetite without associated sulphide. Also the proportion of homogeneous magnetite to sulphide is too high for the magnetite to be derived from a normal immiscible liquid, and so this mechanism of origin must be questioned.

Fe₂O₃-TiO₂ Ratios

The most significant feature of the whole-rock geochemistry is the extremely high Fe₂O₃ contents, for their TiO₂ levels (Fig. 6A and B). Such high contents of Fe₂O₃ are unknown in other igneous rocks, and no common igneous mineral can account for this high concentration. For comparison, the oxide-rich rocks of the Upper Zone of the Bushveld Complex are plotted on Figure 6C, where the range of ratios of TiO₂:Fe₂O₃ is generally higher and much more restricted than in the Koperberg Suite. The inset in Figure 6A shows the compositions of titaniferous magnetite and ilmenite from the Bushveld Complex, which are typical of mafic rocks. This range of compositions of Bushveld magnetite is indicated for reference on the other diagrams as two solid diagonal lines. Conradie and Schoch (1986a) suggested that the Koperberg Suite has affinities with anorthosites, rather than with tholeiitic layered complexes. Hence, data from anorthosites for which FeO and Fe₂O₃ have been separately analysed are plotted on Figure 6D. Again they show higher TiO₂ contents relative to Fe₂O₃ compared to the Koperberg and Bushveld rocks, as expected from their abundant ilmenite content. Thus the high Fe₂O₃ content of the Koperberg Suite is atypical.

Cu-S-Se Values

The sulphides themselves are chemically atypical of magmatic sulphides for two reasons. First, they have extremely high Cu/S ratios; this far exceeds that usually found in mafic rocks. This is manifested in the atypical assemblage dominated by bornite, with the almost total absence of pyrrhotite in many of the ore bodies. Second, the different mines have extremely variable S/Se ratios, some of which are among the lowest reported for magmatic sulphides (Naldrett, 1989). Each ore body has slightly different values for these two parameters (Fig. 9), with Carolusberg being the most extreme (lowest S/Se, highest Cu/S and also high Fe₂O₃/TiO₂) and East Okiep being more like other magmatic suites (as is also seen in its sulphide mineralogy in Table 1).

Sulphide-Oxide Relationships

In the plot of Fe₂O₃ against TiO₂, even the least titaniferous magnetite found in basic rocks cannot explain the high abundance of Fe₂O₃ in these samples. This demands that some of the magnetite is not magmatic in origin. Instead, it is suggested that it has formed by oxidation from pyrrhotite. It is this second generation of Ti-free magnetite which causes the high Fe₂O₃ content in these rocks without the increase in TiO₂ seen in Figure 6A and 6B. Being Ti-free this magnetite will not exhibit exsolution features. It is further suggested that the bornite results from oxidation of chalcopyrite. There are several ways in which this oxidation can be illustrated geochemically. In Figure 11 the modal proportion of oxides is plotted against the weight percent of Cu in the rocks and indicates that there is a positive correlation. In the suite from Carolusberg this trend would project back to 0% Cu at about 10 wt. % oxide. This could be interpreted as suggesting that there was about 10% primary magmatic oxide in these rocks, and that the second generation of magnetite formed from the oxidation of sulphide, the original proportion of which is qualitatively represented by the amount of Cu. Assemblages of bornite plus magnetite may represent original chalcopyrite-rich domains, while magnetite without associated sulphide could have been originally pyrrhotite rich.

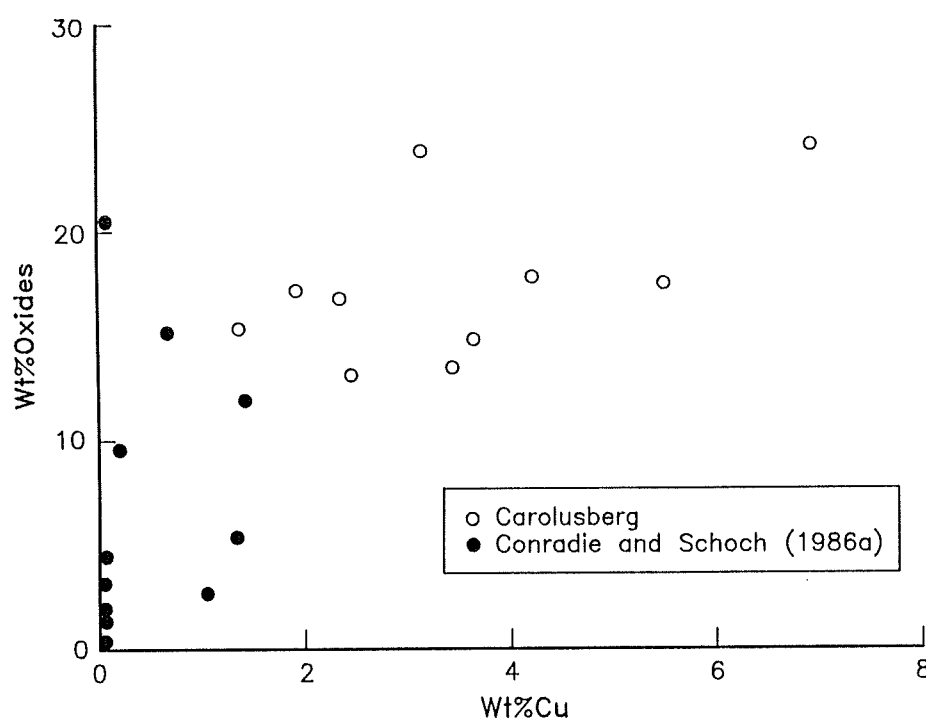


Figure 11: Plot of modal weight percent of oxide phases against weight percent Cu in samples from Carolusberg (open circles) and from the data of Conradie and Schoch (1986a) (solid circles).

The compositions of magnetite from the different ore bodies define discrete groups (Fig. 10). Those from West and East Okiep contain more V_2O_5 than those from Carolusberg and this could be interpreted to imply that they formed from a less differentiated magma. However, the compositions of the plagioclase from Okiep are An40-45, whereas those from Carolusberg are An50-53 (Conradie and Schoch, 1986a). This apparent contradiction is resolved if there has been oxidation of sulphide to produce secondary magnetite with no Cr or V. As Carolusberg is the most oxidised (Table 1 and Fig. 6) the V_2O_5 content of the bulk magnetite, which includes both generations of magnetite, will have been diluted by more than for the magnetite separates from the Okiep bodies. The wide variation in V_2O_5 content by electron microprobe analysis between grains from a single ore body reported by Conradie and Schoch (1986b) probably reflects analyses of primary and secondary magnetite grains.

Naldrett (1981) compared the composition of magmatic immiscible sulphide ores by recalculating analyses to 100% pure sulphide. This eliminates the diluting effect of gangue minerals and permits a quantitative comparison of the sulphide composition of different ore bodies. In the present study (Fig. 7) it is evident that the sulphides contain far more Cu than typical magmatic ore bodies. This is attributed to oxidation of the sulphide to magnetite with loss of sulphur, but not of Cu.

Original Sulphide Composition

It is possible to recalculate what the original composition of the sulphide was from the present data. This is achieved by determining the "excess Fe_2O_3 " produced during oxidation and reconvert it to sulphide. The calculation of "excess Fe_2O_3 " is illustrated in Figure 6a. Composition "A" contains more Fe_2O_3 than would be expected for its TiO_2 content by comparison with the range of other magmatic rocks. Its composition would be expected to plot between B and C. The difference "AB" is the minimum, and the difference "AC" is the maximum "excess Fe_2O_3 ". This "excess Fe_2O_3 " is assumed to result from oxidation of sulphide with loss of SO_2 . The "excess Fe_2O_3 " and volatilised S can then be added back into the rock to yield the original composition of the sulphide. This calculation is made by assuming that all Cu was originally present as chalcopyrite. The present Cu/S ratio indicates how much Cu is present as bornite and how much is present as chalcopyrite. The bornite is then converted to chalcopyrite by using some of the calculated "excess Fe_2O_3 " and adding sulphur. The remainder of the "excess Fe_2O_3 " is used to make pyrrhotite by adding further sulphur. From the reconstituted chalcopyrite and pyrrhotite the ratio of the original Cu/S is determined.

These results are plotted on Figure 7. Both maximum and minimum values for "excess Fe_2O_3 " as determined from Figure 6a are included to indicate the range of uncertainty in this calculation. It is apparent from Figure 7 that the derived ratios of Cu/S for samples using this calculation are significantly lower than the actual measured values and generally plot closer to the trend expected for a magmatic sulphide with 10% Cu in 100% sulphide. This recalculation therefore yields an original pure Cu sulphide close in composition to that observed at Noril'sk (Naldrett, 1981) and from the Upper Zone of the Bushveld Complex (Von Gruenewaldt, 1976). Published pyroxene and plagioclase compositions for these two settings (Von Gruenewaldt, 1973, Genkin *et al*, 1981) are similar to those reported from the Okiep District (Conradie and Schoch, 1986a), indicating similar degrees of fractionation of these bodies and hence comparable Cu/S ratios in the immiscible sulphide are to be expected. While these calculations can only indicate a range of possible Cu/S ratios for the original sulphide as shown in Figure 7, they demonstrate that a very plausible sulphide composition is obtained by such a calculation.

The ratio of S/Se in magmatic ores is highly variable (McGoldrick and Keays, 1981; Hoatson and Keays, 1989; Naldrett, 1989) in the range 1000 to 40000. However, in this instance there is a variation even for samples from within one ore body and this variation correlates with the Cu/S ratio, an observation which has not been previously reported. The above arguments suggest that variation in Cu/S is not the result of primary magmatic processes but is due to oxidation. Sulphur, but not Se, will be lost during this process. The effect of this oxidation on S/Se and Cu/S ratios is clearly demonstrated in Figure 9. The Carolusberg ores (with the highest Cu/S ratio) are interpreted to be the most oxidised and are seen in Figure 9 to have the lowest S/Se ratios. The West and East Okiep ores show progressively less oxidation and have higher S/Se ratios. Thus the overall trends through the entire suite can be attributed to variable volatilisation of S. The high Cu/S ratio (Fig. 7), low S/Se ratio (Fig. 9) and high "excess Fe_2O_3 " (Fig. 6A and 6B) of the Carolusberg ores suggests that up to 90% of the original sulphur may have been lost; while for East Okiep less than half of the sulphur has been lost.

Ni Content of Sulphide

Magmatic sulphides contain variable Ni content, the concentration depending on the extent of differentiation. The Koperberg Suite ores contain relatively little Ni (Table 2). Nickel may also be present in pyroxene. The data in Table 2 are illustrated in Figure 12. Samples plotting on the Ni-rich side of the plagioclase-pyroxene tie-line indicate samples which contain Ni in the sulphide. In view of the high Cu content in pyroxene in these mineral separates, there are probably small inclusions of sulphide and so not all the reported Ni need be in the pyroxene structure. It can be seen on Figure 12 that the abundance of Ni in excess of that in plagioclase-pyroxene assemblages does not exceed 500ppm. In view of the high Cu contents of these rocks, this yields a very high Cu/Ni ratio for these sulphides (Fig. 8). This exceeds the Cu/Ni ratio for sulphides in the Upper Zone of the Bushveld Complex, which is about 10 (Von Gruenewaldt, 1973). The reason for the very high ratio in the Koperberg ores is not apparent. However, it may be significant that the Cu/Ni ratio for the pyroxenes with their enclosed sulphides (Table 3) is close to 10, which may represent samples of original magmatic sulphide trapped in the pyroxene and shielded from oxidation.

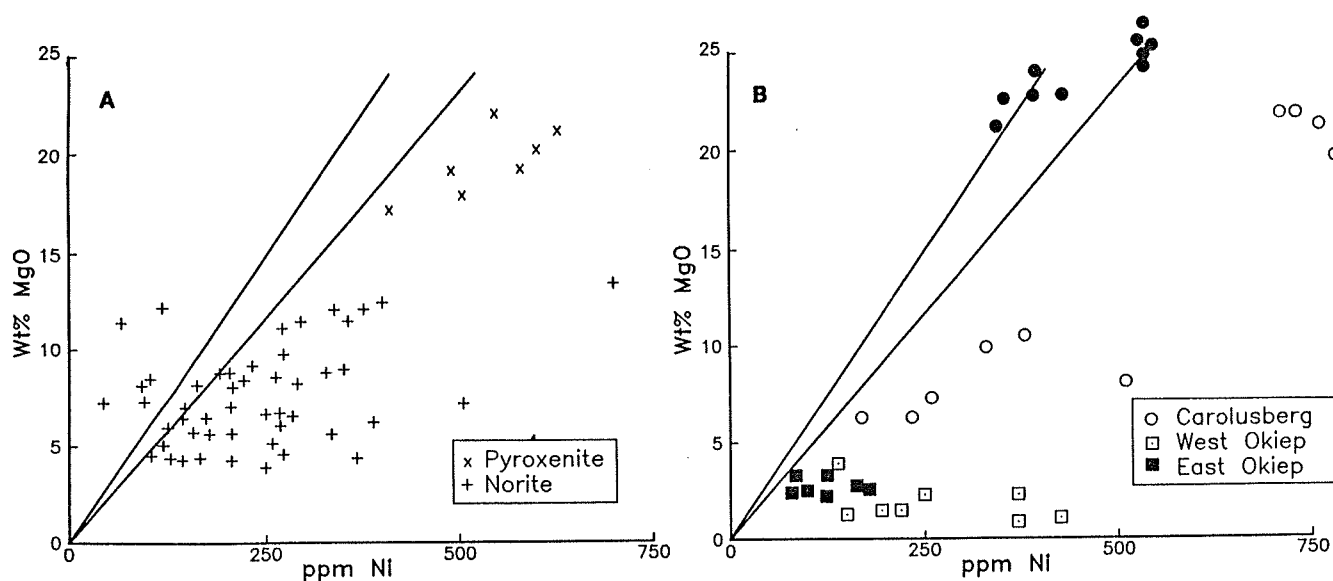


Figure 12: Plot of ppm Ni against wt % MgO in whole rock samples from the Okiep district. Figure 12A refers to analyses from the entire district and 12B to this study. Open circles samples from Carolusberg, open squares from West Okiep, solid squares from East Okiep. Solid circles are pyroxene analyses from Carolusberg (this study). Lines in Figure 12B join pyroxene and plagioclase compositions. These lines are also shown on Figure 12A.

Paragenesis of the Sulphide

There is a very strong tendency for the more mafic rocks to contain mineralization (Lombaard, 1986). However, there are also barren noritoid bodies. Others, such as Carolusberg, are very heavily mineralized throughout their entirety. In the case of Carolusberg the different $Mg/(Mg+Fe)$ and Cr content of the pyroxenes in the norite and pyroxenite (Table 3), even where the two are spatially closely related, suggests that each rock type may have resulted from emplacement of discrete pulses of magma. Both pulses are heavily mineralized, as can be seen from the Cu contents in Table 2. In other instances, sulphides occur along the hanging wall contacts of steeply dipping intrusives. These features suggest that there has been some pre-emplacement differentiation and accumulation of immiscible sulphide liquid, possibly analogous to that at Noril'sk (Genkin *et al.*, 1981). Given the small size and near vertical geometry of some bodies, in situ formation and gravity segregation of sulfide seems unlikely.

The present mineralogy and geochemistry of the sulphides argues very persuasively against these being a primary magmatic assemblage formed by immiscibility from a basic magma. However, the relationships between the oxides and sulphides, and such geochemical trends as Fe_2O_3/TiO_2 , Cu/S and S/Se indicate that there may have been an original magmatic Cu-rich sulphide which has undergone extensive oxidation. The highly annealed polygonal textures of magnetite and especially bornite shown in Figure 4, and the preservation of equilibrium orthopyroxene and plagioclase assemblages, especially at Carolusberg, suggest that this occurred during a high temperature metamorphism.

Textural relations (Fig. 4J-L) indicate that most of these ore bodies have undergone a later hydrothermal alteration causing break down of the pyroxenes to chlorite, and saussuritization of plagioclase, and the regrowth of chalcopyrite. Stumpfl *et al.* (1976) recognised that these were not magmatic textures and suggested that this remobilization of the sulphide occurred during the 550-500 Ma Pan-African event. Fortunately, the deep ore at Carolusberg has been relatively unaffected and permits recognition of the previous textural and chemical relationships of the sulphides.

CONCLUSIONS

The Cu sulphide mineralization associated with noritoid bodies of the Koperberg Suite in Namaqualand, South Africa has been regarded as originating as an immiscible magmatic sulphide liquid. However, the sulphide assemblage of bornite with lesser chalcopyrite or chalcocite makes this hypothesis untenable. Textural evidence indicates that these rocks have undergone a high-grade metamorphic recrystallization. Geochemical data, specifically high Fe_2O_3 contents, indicate that there has been strong oxidation associated with this metamorphism. This resulted in the oxidation of original magmatic pyrrhotite and chalcopyrite to Ti-free magnetite and bornite. The inverse correlation between S/Se and Cu/S ratios confirms this loss of S. Variations in the S/Se ratio show that up to 90% of original S may have been lost in the case of ore from Carolusberg Mine, whereas only 50% loss occurred for the Okiep mines. In the present interpretation three distinct events may be recognized. A primary magmatic sulphide-forming event; a period of high temperature oxidative metamorphism in which bornite and magnetite formed from chalcopyrite and

pyrrhotite, and finally a late, low-temperature hydrothermal alteration of silicates and recrystallization of sulphide in some ore bodies.

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