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UNUSUALLY HIGH CONCENTRATIONS OF MAGNETITE AT CARAÍBA AND OTHER Cu-SULFIDE DEPOSITS IN THE CURAÇÁ VALLEY, BAHIA, BRAZIL

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ABSTRACT

The Curaçá Valley, in Bahia, Brazil, contains several pyroxenite-hosted Cu-sulfide deposits. They have unusually high Cu and low Ni contents (Cu/Ni up to 2500), with chalcopyrite and bornite being the dominant sulfides (Cu/S up to 3.5). Oxides (magnetite and lesser ilmenite) constitute approximately 50% of the opaque phases. Most other magmatic Cu–Ni-sulfide deposits contain between 2 and 15% oxides. The only other known magmatic sulfide deposits with comparable Cu/Ni values, at Okiep, South Africa, also have elevated contents of magnetite. There, the oxides have been interpreted as a result of oxidation and desulfurization of primary sulfides, resulting in a high abundance of pure magnetite. In the Curaçá Valley, reaction-replacement of sulfides to form magnetite is not apparent: the magnetite contains up to 14 wt% Cr_2O_3, 2% V_2O_3, 7% TiO_2, and 1% ZnO, and is generally replaced by chalcopyrite and bornite. However, the composition of the oxides seems to have been modified by equilibration with associated orthopyroxene, in response to high-grade metamorphism. The metamorphism could also have led to significant S-loss of the sulfides, reflected by relatively low S/Se values of the rocks (200–1500). As at Okiep, a large proportion of the oxides seems to have been a product of replacement of primary sulfides.

Keywords: magnetite, copper, S-loss, pyroxenite, Curaçá Valley, Caraíba, Brazil.

SOMMAIRE

La vallée de Curaçá, dans l'état de Bahia, au Brésil, contient plusieurs gisements de sulfures de cuivre dans un hôte pyroxénitique. Le minerai est fortement enrichi en Cu et remarquablement appauvri en Ni (le rapport Cu/Ni atteignant 2500); chalcopyrite et bornite sont les sulfures dominants (Cu/S jusqu'à 3.5). Les oxydes (magnétite surtout, avec ilménite accessoire) constituent environ 50% des phases opaques. La plupart des autres gisements de sulfures de Cu–Ni contiennent entre 2 et 15% d'oxydes. Les seuls gisements de sulfures magmatiques connus ayant une valeur Cu/Ni comparable se trouvent à Okiep, en Afrique du Sud; ils sont aussi enrichis en magnétite. Dans ce cas, on a interpreté la proportion élevée en magnétite pure en termes d'oxydation et de perte de soufre des sulfures primaires. Dans la vallée de Curaçá, un remplacement des sulfures par la magnétite ne semble pas évident. La magnétite contient jusqu'à 14% (poids) de Cr_2O_3, 2% de V_2O_3, 7% de TiO_2 et 1% de ZnO, et semble plutôt remplacé par la chalcopyrite et la bornite. Toutefois, la composition des oxydes semble avoir été modifiée par équilibrage avec l'orthopyroxène associé, en réponse à un métamorphisme de forte intensité. Cet épisode de métamorphisme aurait pu déstabiliser les sulfures et causer une perte en soufre, comme l'indique le faible rapport S/Se des roches (200–1500). Tout comme à Okiep, une proportion importante des oxydes semble s'être formée par remplacement des sulfures primaires.

(Traduit par la Rédaction)

Mots-clés: magnétite, cuivre, perte en soufre, pyroxénite, vallée de Curaçá, Caraíba, Brésil.

INTRODUCTION

More than 200 intrusive bodies of gabbro, norite, pyroxenite, minor peridotite, and amphibolitized equivalents occur in granulite-facies gneiss and migmatite of the Curaçá Valley, located toward the northern margin of the São Francisco Craton of Brazil (Fig. 1). Most of the pyroxenitic bodies contain Cu-sulfides. The Caraíba body is currently Brazil's largest Cu-deposit, with reserves originally amounting to 130 Mt, averaging 1% Cu (De Deus *et al.* 1982). The Surubim, Vermelhos, Angico, and Terra do Sal (Fig. 1) occurrences are at present considered uneconomic.

Whereas the mineralization of the Curaçá Valley pyroxenites is generally considered to be of magmatic origin (Lindenmayer 1981, Mandetta 1982, Oliveira 1990, Oliveira & Tarney 1995), the deposits are unusual in two main respects: (i) the sulfide assem-

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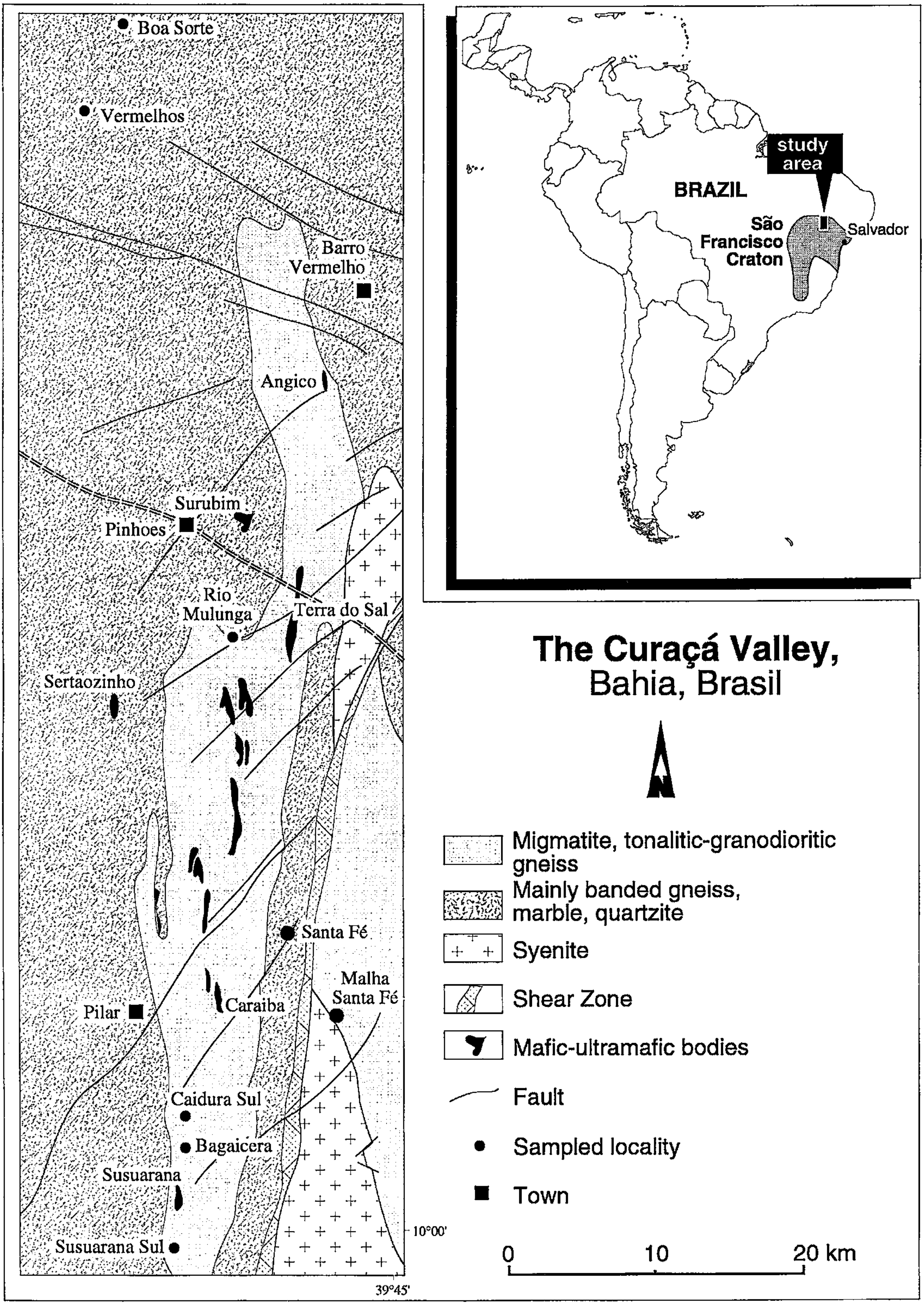
Boa Sorte
Vermelhos
Barro Vermelho
Angico
Surubim
Pinhoes
Rio Mulunga
Terra do Sal
Sertaozinho
Santa Fé
Malha Santa Fé
Caraiba
Pilar
Caidura Sul
Bagaicera
Susuarana
Susuarana Sul
10°00'
39°45'
study area
BRAZIL
São Francisco Craton
Salvador
The Curaçá Valley, Bahia, Brasil
Migmatite, tonalitic-granodioritic gneiss
Mainly banded gneiss, marble, quartzite
Syenite
Shear Zone
Mafic-ultramafic bodies
Fault
Sampled locality
Town
0
10
20 km

blage consists of bornite and chalcopyrite, resulting in high Cu/S values, and (ii) the ore contains about equal proportions of sulfides and oxides. In most other magmatic sulfide deposits, oxides average between 2 and 15% of the ore (Naldrett 1969). In the Sudbury intrusive complex, for example, the proportion of magnetite in the ore ranges between 5 and 15%, reaching 25% in some samples (Naldrett 1969, Naldrett & Hewins 1984). At Kambalda, Western Australia, magnetite constitutes between 2 and 10% of the ore (Ewers & Hudson 1972). The only other known magmatic sulfide deposit dominated by bornite and chalcopyrite, at Okiep, in South Africa, also has high contents of oxide. Here, we compare the mode of occurrence and composition of the Curaçá Valley oxides to those at Okiep and other magmatic sulfide deposits, and highlight the fact that variations in oxide contents of magmatic sulfide deposits remain unexplained. The origin of the Cu-mineralization in the Curaçá Valley also is discussed.

REGIONAL GEOLOGY

The Curaçá Valley is a granulite-facies terrane, dominated by different varieties of migmatitic gneiss, charnockite, and calc-silicate, as well as granite and syenite (Delgado & Souza 1981, De Deus *et al.* 1982, Figueiredo 1989, Wirth *et al.* 1990, Oliveira & Tarney 1995). The mafic–ultramafic bodies form part of the Caraíba Group (Figueiredo 1980) and have been described by several authors (Lewis 1966, Townend *et al.* 1980, De Deus *et al.* 1982, Silva *et al.* 1988, Figueiredo 1989, Wirth *et al.* 1990, D'el Rey Silva *et al.* 1994). The Caraíba Group has yielded a wide range of ages; Rb–Sr determinations on gneiss (Brito Neves *et al.* 1980, Sato 1986) yielded Archean (3012, 2850, and 2500 Ma) to Transamazonian ages (2000 – 2144 Ma). U/Pd data on zircon (Gaal *et al.* 1987) and K/Ar data on biotite (Brito Neves *et al.* 1980) from granite and tonalite in the region also yielded Transamazonian ages. Sm–Nd ages on orthopyroxenite dykes are slightly younger (1900 Ma, Oliveira 1990). However, the intense folding and shearing of the orthopyroxenite dykes indicate that they were emplaced before the peak orogenic and metamorphic event, distinguished by three main phases of deformation during the Transamazonian period (D'el Rey Silva *et al.* 1994).

DESCRIPTION OF THE PYROXENITE BODIES

This study focuses on the pyroxenite bodies in the Curaçá Valley, mainly because the sulfides are almost exclusively hosted by pyroxenite, with minor concentrations in norite. Other rock types are generally barren. This also applies to peridotite, amphibolite, and gabbro, which may occur as distinct bodies or as inclusions within pyroxenite. Some calc-silicate units and rare felsic breccias adjacent to the intrusive bodies may be mineralized, but these sulfides are interpreted as a result of local remobilization of sulfides from the pyroxenite.

The pyroxenite bodies generally are sill-like, reaching a thickness of some 10 m at Caraíba mine (in the fold hinges, the thickness of the sills may be multiplied). They do not appear to be closely associated with other mafic–ultramafic rock types, but they commonly contain subrounded inclusions of other mafic–ultramafic rocks, generally several cm or dm in diameter, and devoid of Cu-sulfides. Modal or cryptic layering in the pyroxenite is not observed, except for a tendency of the sulfides to be concentrated at the lower contact of the body.

PETROGRAPHY

Mineral modes of 13 samples of pyroxenite from six localities in the Curaçá Valley were determined by counting between 350 and 450 points per sample with a Swift point counter. The pyroxenite samples contain between 50 and 95% silicates (Fig. 2A). Orthopyroxene is the dominant silicate, reaching 90 modal %. Orthopyroxene shows a granoblastic texture, subgrain formation and undulatory extinction, reflecting the effects of high-grade metamorphism, estimated to have reached granulite-facies conditions, *i.e.*, between 700 to 850°C and 6.5 to 8 kbar (Figueiredo 1980, 1989, Jardim de Sá *et al.* 1982, Bello 1986, Ackermand *et al.* 1987). Plagioclase and phlogopite are the major additional silicates. Plagioclase occurs interstitially to orthopyroxene, as irregularly embayed inclusions within orthopyroxene, and as subhedral mesocrysts, up to 2 mm in length. Phlogopite commonly shows a preferred orientation and is associated with orthopyroxene. In several samples, it is highly deformed. It locally constitutes more than 60 modal % of the rock, essentially yielding

FIG. 1. Simplified geological map of the Curaçá Valley, with localities of sampling sites. Map is compiled from Delgado & Souza (1981).

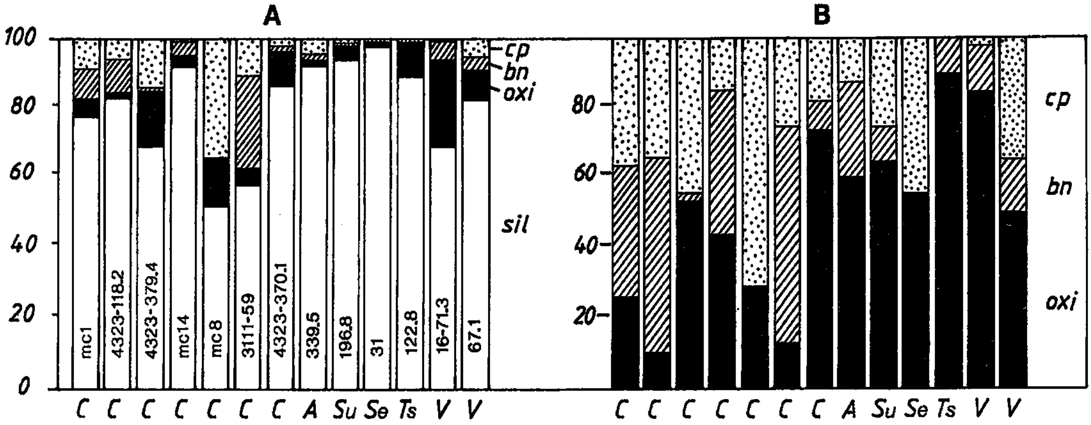

FIG. 2. Modal proportions of (A) silicates and opaque phases, and (B) oxides, bornite and chalcopyrite (normalized to 100% sulfides and oxides) in representative samples of pyroxenite from the Curaçá Valley. Symbols: C: Caraíba, A: Angico, Ts: Terra do Sal, V: Vermelhos, Su: Susuarana, Se: Sertaozinho. Sample numbers are shown inside the columns.

a glimmerite (Schoch & Conradie 1990). Apatite occurs as isolated, rounded crystals and in granoblastic aggregates. In some cases, it may constitute up to 15 modal % of the rock. Additional accessory minerals include (i) amphibole, chlorite, and epidote, all of which occur mainly at grain boundaries of, and in fractures within orthopyroxene, (ii) quartz that is dispersed throughout the rock, (iii) zircon, particularly in domains enriched in phlogopite, and (iv) titanite, which has been observed in two samples of pyroxenite and one of peridotite.

Oxides and sulfides occur in approximately equal proportions (Fig. 2B). We observed three main textural varieties of sulfides: (i) disseminated grains interstitial to silicates and oxides, (ii) massive aggregates and layers, commonly toward the base of the bodies and in the fold hinges (D'el Rey Silva *et al.* 1994), and (iii) veins and veinlets that may invade associated gabbro, gneiss and calc-silicate units. Chalcopyrite and bornite are the dominant sulfide minerals in all of the pyroxenite bodies of the Curaçá Valley. The two phases occur in varying proportions, but on average, their relative abundance is about equal (Fig. 2B). They are commonly intergrown in a symplectitic way. Accessory sulfides include digenite, pyrrhotite, pentlandite, covellite, pyrite, and cubanite. Pentlandite occurs predominantly at grain boundaries of bornite and chalcopyrite and in veins and veinlets. Digenite commonly replaces bornite at the grain boundaries and also occurs in microfractures within silicate grains and along cleavage planes. Millerite, heazlewoodite, carrollite, and melonite are accessory phases that we identified by semiquantitative electron-microprobe analysis.

Approximately 80–90% of the oxide fraction is magnetite, the remainder being ilmenite, and minor chromite. The latter was only identified at the Vermelhos deposit, where it is found as an isolated subhedral grain. Hematite is absent from most samples examined. We distinguish five main textural types of magnetite: (i) distinctly spherical grains included within orthopyroxene, (ii) euhedral or subhedral polygonal grains, interstitial to silicates (Fig. 3A), (iii) massive aggregates, mainly but not always associated with sulfide veins, (iv) finely dispersed aggregates in microfractures and along cleavage planes. In all of the above textures, magnetite may be partly replaced by bornite and chalcopyrite along microfractures (Fig. 3B) or {111} planes (Fig. 3C). (v) In a few samples, magnetite forms a rim around bornite (Fig. 3D), pyrrhotite and, less commonly, chalcopyrite. This type may be comparable to that described by Glassley (1983), Cameron (1993), and Cawthorn & Meyer (1993) from various other granulite terranes, and interpreted to result from a replacement phenomenon caused by oxidation of the sulfides.

Ilmenite is present in most samples. It occurs principally as trellis-type solid-solution intergrowths parallel to {111} within magnetite (Figs. 3A, C). Less commonly, sandwich-type lamellae are observed. These lamellae are believed to have formed by oxidation of the ulvöspinel component rather than by exsolution (Buddington & Lindsley 1964), as indicated by: (i) their concentration near grain boundaries (Fig. 3C), cleavages and cracks within magnetite and, (ii) a decrease in lamella thickness inward from grain boundaries, *i.e.*, toward the unoxidized areas of the grain. Apparently, the degree of oxidation was highly variable. Within individual samples, one finds domains free of lamellae that are enriched in the ulvöspinel component, and others

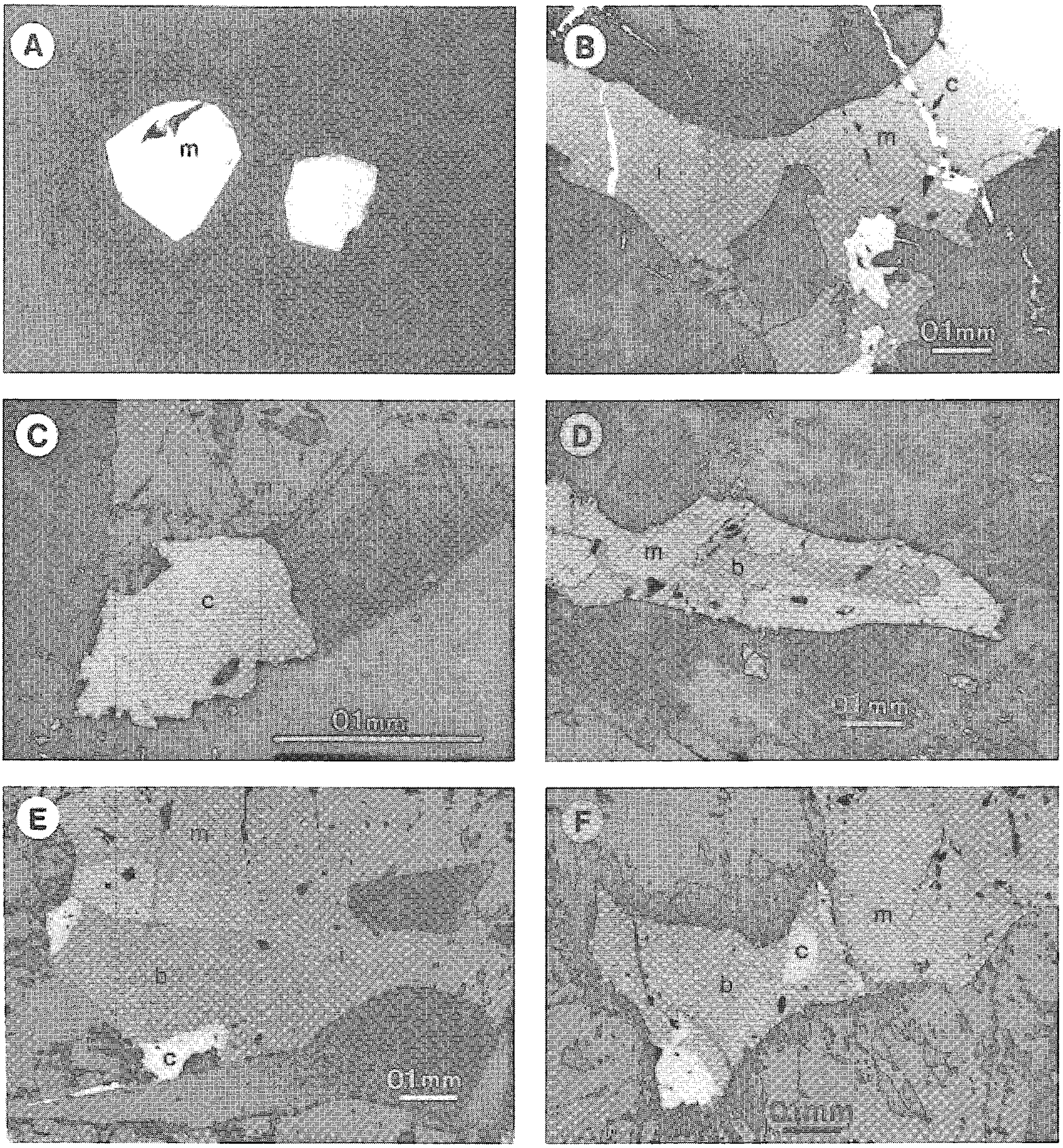

FIG. 3. Reflected-light photomicrographs of ore assemblages in the Curaçá Valley. (A) Euhedral magnetite, showing trellis-type lamellae of ilmenite parallel $\{111\}$. (B) Replacement of magnetite by chalcopyrite (c) along microfractures (i: ilmenite). (C) Replacement of magnetite by chalcopyrite (c) along $\{111\}$ planes. (D) Magnetite (m) replacing bornite (b) from the grain boundaries. (E) Corona of ilmenite (i) around bornite (b). (F) Alteration selvage in silicate bounding on sulfides (bornite: b, chalcopyrite: c). Note that silicates are fresh where in contact with magnetite (m).

where lamellae are abundant. Composite-type ilmenite grains (*i.e.*, granular ilmenite of either primary or secondary origin; Haggerty 1991) may reach 25% of the oxides in some samples. Where magnetite is replaced by sulfides, ilmenite may form a corona around magnetite (Fig. 3E).

The grain boundaries between silicates and oxides are generally smooth, and the silicates are unaltered (Fig. 3F). In contrast, where silicates are in contact with sulfides, they commonly show a narrow alteration selvage, and the grains of sulfide have highly irregular boundaries (Fig. 3F).

Mineral and Whole-Rock Chemistry

Ninety-one samples of the most common rock-types, sampled at 15 different localities in the Curaçá Valley, were analyzed for mineral and whole-rock compositions. Whole-rock compositions in terms of the major elements as well as Cu, Cr, V, and Zn were determined by X-ray-fluorescence analysis, and S by Leco titration, at McGill University, Montreal. Concentrations of the platinum-group elements (PGE) were determined at the Université du Québec à Chicoutimi (UQAC) by the Ni-sulfide fire-assay method followed by instrumental neutron activation (INAA), with sample irradiation being done at École Polytechnique, Montreal. Concentrations of the other trace elements, including Au, were determined at

TABLE 1. AVERAGE COMPOSITION OF SAMPLES OF COMMON ROCK TYPES, CURAÇÁ VALLEY, BRAZIL

Rock Type	Per	Px	Mn	No	Gb	Am	Gl	Cs	Sy	Gd	Gn
n	9	36	5	7	8	3	2	7	1	1	1
SiO2 wt%	47.18	46.08	41.67	52.29	48.35	47.89	36.47	31.46	61.74	74.06	72.96
TiO2	0.63	0.82	1.69	1.30	1.34	0.81	3.09	1.05	0.81	0.28	0.31
Al2O3	6.45	6.04	11.20	20.56	14.12	11.97	13.70	15.62	14.99	13.17	13.90
Fe2O3	12.56	24.57	21.78	6.89	14.63	13.11	17.14	11.28	4.94	1.55	1.89
MnO	0.20	0.34	0.25	0.08	0.26	0.24	0.10	0.18	0.07	0.02	0.02
MgO	21.48	16.80	12.19	3.23	8.11	10.33	11.65	12.83	1.59	0.37	0.55
CaO	8.83	1.37	2.41	7.09	9.85	12.48	1.50	1.45	3.42	0.80	2.00
Na2O	0.57	0.60	1.22	4.69	1.94	1.89	0.70	1.96	3.30	2.05	2.80
K2O	0.23	1.09	2.17	1.22	1.22	0.91	5.46	0.41	6.80	7.15	4.88
P2O5	0.06	0.17	0.31	0.78	0.12	0.17	0.28	0.00	0.68	0.06	0.08
S	0.09	2.42	1.35	0.25	0.05	0.01	0.78	3.11	0.02	0.00	0.00
Fe(S)	ns	1.91	1.31	ns	ns	ns	ns	3.75	ns	ns	ns
LOI	1.96	0.39	0.14	0.35	0.52	0.64	2.36	5.60	0.53	0.43	0.39
Cr ppm	2302	3028	2483	166	266	265	2443	1290	23	2	4
Ni	1099	1125	1292	162	121	187	1227	354	27	<20	<20
Co	96	124	174	34	56	56	128	65	11	2	4
Sc	30	43	40	17	46	49	25	23	11	2	2
V	156	113	427	132	263	199	740	72	20	10	19
Cu	249	44984	19717	4345	380	192	24067	31792	174	46	59
Zn	159	1184	1974	571	167	172	4417	372	124	58	69
As	<1	<1	<1	<1	<1	<1	<1	18	<1	<1	<1
Se	0.3	28.6	14.9	7.8	4.1	1.3	12.4	34.0	1.7	2.7	2.0
Sb	0.05	0.01	0.01	0.13	<0.1	<0.1	<0.1	0.08	<0.1	<0.1	<0.1
Re	0.19	0.08	0.03	0.11	0.54	0.10	<0.1	<0.1	<0.1	<0.1	<0.1
Rb	7	53	80	50	37	30	379	24	128	133	122
Ba	411	304	559	617	435	743	1987	271	10912	3681	2685
Ta	0.06	0.25	0.55	0.51	0.45	0.21	1.01	0.78	0.32	0.58	0.00
Hf	1.36	4.91	2.93	14.16	7.30	2.08	1.59	6.21	3.96	5.71	3.27
Zr	18	188	158	704	434	52	<50	295	274	263	213
Th	1.24	8.56	0.74	15.20	0.87	2.23	0.64	8.22	2.25	6.59	1.09
La	10.52	27.02	11.41	70.45	10.33	48.54	8.51	82.29	135.45	45.83	29.70
Ce	26.47	53.06	20.19	155.60	23.45	119.30	19.44	171.35	298.00	64.65	43.80
Nd	17.28	25.93	10.57	92.10	16.15	73.58	16.91	89.76	177.00	17.64	17.70
Sm	3.29	5.05	2.00	15.37	3.90	12.45	2.78	14.09	21.02	2.04	1.90
Eu	1.04	0.58	0.80	2.92	1.28	2.37	0.56	2.18	5.48	2.34	1.86
Tb	0.50	0.68	0.33	1.70	0.83	1.45	0.29	1.62	1.56	0.11	0.17
Yb	0.94	1.22	0.93	1.18	2.52	2.49	0.41	2.76	1.12	0.00	0.09
Lu	0.16	0.27	0.17	0.32	0.44	0.41	0.10	0.45	0.19	0.04	0.04
Os ppb	0.4	0.6	0.3	<5	0.1	0.3	<5	0.3	<5	<5	<5
Ir	0.56	1.23	0.94	0.06	0.13	0.19	0.69	0.81	0.17	<0.02	<0.02
Ru	3	5	7	1	<5	1	4	6	<5	<5	<5
Rh	1	1	2	<0.2	<0.2	<0.2	1	1	<0.2	<0.2	<0.2
Pd	6	92	93	3	11	9	49	77	4	<2	<2
Pt	7	181	64	10	11	13	217	42	<3	<3	27
Au	1	184	195	4	1	1	150	185	<1	<1	5
Ag	58	2818	167	68	50	<50	822	890	440	<50	<50

Symbols: Per: peridotite, Px: pyroxenite, Mn: melanorite, No: norite, Gb: gabbro, Am: amphibolite, Gl: glimmerite, Cs: calc-silicates, Sy: syenite, Gd: granodiorite, Gn: gneiss, n: number of samples, ns: not significant, Fe(S): Fe in sulfide.

UQAC, by INAA of 2 g of whole-rock powder (Bédard & Barnes 1990). Au determinations based on the fire-assay method were systematically two to three times lower than those based on analysis of whole-rock powder, probably owing to Au loss during the dissolution step of the fire assay. Therefore, we have more confidence in the whole-rock Au results than those obtained by the fire-assay method.

Average whole-rock compositions of various rock-types are listed in Table 1. Most of the Cr, V, Zn, and Ti is hosted by magnetite, as suggested by the electron-microprobe analyses of orthopyroxenes and oxides, to be discussed later. In the presence of sulfides, Au normally behaves as a chalcophile element. Surprisingly, the concentration of Au does not show a good correlation with that of S (Fig. 4), but, instead, with that of Cr and Zn, elements believed to be controlled by magnetite. This suggests that Au is equally controlled by magnetite. Magnetite control of Au has also been observed in calc-alkaline volcanic rocks of the Japanese arc (Togashi & Terashima 1996). The possibility that Au is controlled by magnetite prompted us to prepare a magnetite separate and determine its composition by INAA. We selected a sample characterized by relatively little intergrowth between oxides and sulfides. The sample was first crushed and sieved to yield a grain fraction between 170 and 230 mesh (*i.e.*, 60–90 μm), and then thoroughly washed in distilled water to remove dust. The dry powder was then repeatedly run through a Frantz L1 isodynamic magnetic separator. The concentrations of selected elements in the whole-rock sample and the separate are compared in Table 2. The concentration of Au in the separate is approximately twice that in the whole-rock sample, indicating that Au is indeed controlled by magnetite. The reduction in Se content in the separate clearly shows that Au is not hosted by inclusions of sulfide in the magnetite. Surprisingly, Sc contents also are depressed in the separate, suggesting that Sc is principally hosted by the pyroxenes.

The Cu and Ni contents of the Curaçá Valley pyroxenites and associated country-rocks, including other mafic and ultramafic rock-types, are plotted in Figure 5. Note that the high Cu contents of some of the non-pyroxenitic rocks reflect the presence of sulfide veins. It is apparent that Ni contents of the pyroxenite samples are remarkably constant, not exceeding 2000 ppm anywhere in the Curaçá Valley, but Cu varies by two orders of magnitude. This results in considerable variation in Cu/Ni ratio, between 2 and 100 in disseminated ore, and up to several thousand in massive ore and veins.

Se contents of the pyroxenites are *ca.* 30 ppm on average (Table 1). Se is incompatible in silicates and oxides, but highly compatible into sulfides (D = 1770, Peach *et al.* 1990). Therefore, Se shows a good correlation with S and Cu (Fig. 6). However, it is also seen in Figure 6 that S/Se values (*ca.* 850, on average) are markedly lower than those of primordial mantle (3000–4500, Eckstrand *et al.* 1989), and those of many other magmatic sulfide deposits. For example, the Noril'sk ores have S/Se values between 1000 and 7000 (M. Zientek, unpubl. data), ores of the Thompson Nickel Belt, between 1700 and >8000 (Eckstrand *et al.* 1989), and the Merensky Reef of the Bushveld Complex, 1500 (O.R. Eckstrand, unpubl. data). Interestingly, the Okiep deposits are the only major occurrences with similarly low S/Se values as the ones observed in the Curaçá Valley (Cawthorn & Meyer 1993).

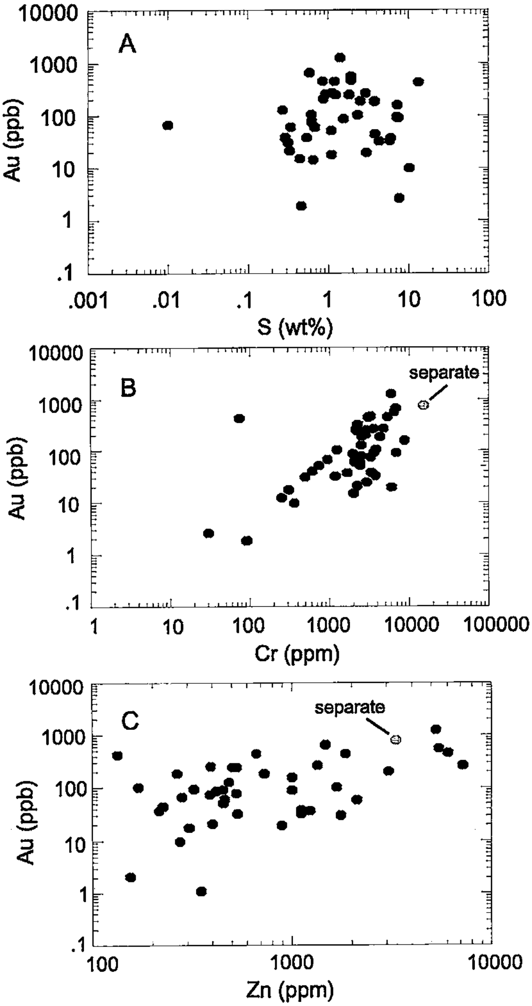

FIG. 4. Binary plots of element concentrations. (A) Au *versus* S, (B) Au *versus* Cr, and (C) Au *versus* Zn.

All electron-microprobe analyses were done on a ARL–SEMQ instrument at UQAC, using a defocused

TABLE 2. CONCENTRATION OF SELECTED ELEMENTS IN WHOLE-ROCK POWDER AND MAGNETITE SEPARATE OF SAMPLE VERMELHOS 16–71.3

	whole-rock powder	magnetite separate
FeO (wt%)	28.32	71.29
Cr_2O_3	0.7	1.75
Ni (ppm)	669	1013
Zn	555	3172
Co	123	175
Se	56	26
Sc	34	12
Au (ppb)	420	763

beam. Representative compositions of orthopyroxene from various localities and rock types in the Curaçá Valley are listed in Table 3. Orthopyroxene grains in pyroxenite have a Mg# [Mg/(Mg + Fe)] between 0.57 and 0.73, and contain between <0.1 and 0.28 wt% Cr_2O_3 (with one grain containing 0.37 wt%), between 0.1 and 0.15% TiO_2, and between 1 and 4.8 wt% Al_2O_3. The orthopyroxene of peridotite inclusions in pyroxenite and that of distinct peridotite bodies elsewhere in the Valley have generally higher Mg# and Al contents, but similar Cr contents. These compositions are unusual when compared to those of cumulus orthopyroxene from layered intrusions, such as the Bushveld Complex; there, Cr contents vary between 0.2 and 0.55% Cr_2O_3, Al contents between 0.7 and 1.3% Al_2O_3, and Ti contents between 0.1 and 0.35% TiO_2 (Maier 1995). The high Al contents in the orthopyroxene of the Curaçá Valley are interpreted to reflect the high-grade metamorphism. The Al content of orthopyroxene generally increases with increasing temperature and pressure (Wood & Banno 1973). Indeed, orthopyroxene samples from other granulite terranes contain up to 10 wt% Al_2O_3 (Grew 1981, Horrocks 1983, Harley *et al.* 1990). The observed low Ti and Cr contents (Table 3) are equally typical of metamorphic orthopyroxene (*e.g.*, Kihle & Bucher-Nurminen 1992, Pattison & Bégin 1994) and may be caused by expulsion of Ti^{4+} and Cr^{3+} from the structure at high pressure, and inclusion into phlogopite or ulvöspinel. This interpretation is supported by particularly elevated Ti and Cr contents of oxides that are included in orthopyroxene (see discussion below).

Core compositions of plagioclase megacrysts and interstitial plagioclase fall between An_{37} and An_{55}. Inclusions of plagioclase in orthopyroxene reach An_{79}. All types of plagioclase are generally reversely zoned.

Biotite from the Caraíba mine has a Mg# of 0.55 and contains up to 5 wt% TiO_2 (Figueiredo 1980, Oliveira & Tarney 1995). Notably, Townend *et al.* (1980) reported elevated (but unspecified) Cu contents in the biotite (as well as other silicates, with the exception of orthopyroxene).

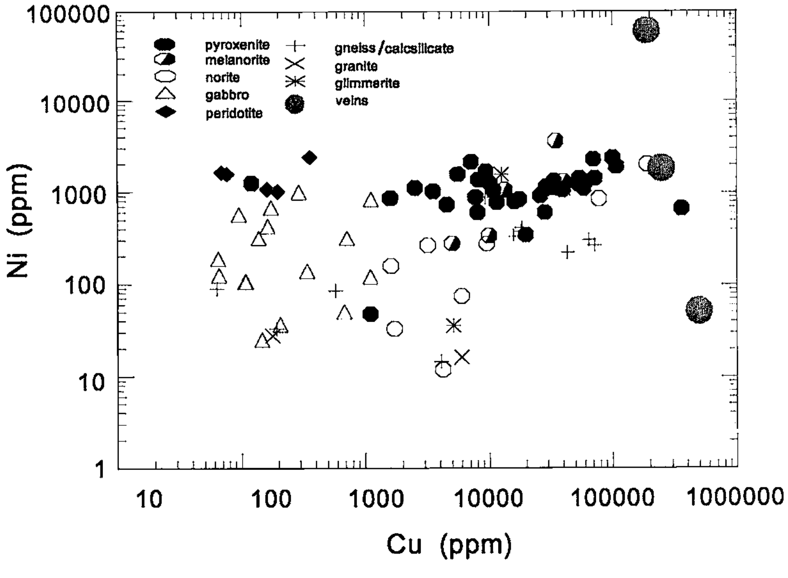

FIG. 5. Binary plots of concentration of Ni *versus* that of Cu in rocks of the Curaçá Valley.

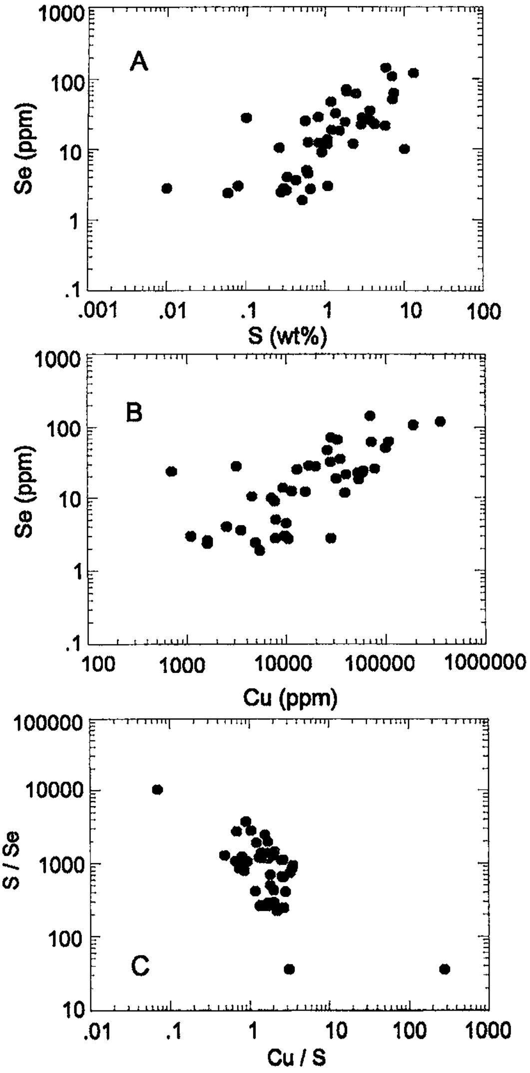

FIG. 6. Binary plots of element concentrations, showing positive correlation between (A) Se and S, and (B) Se and Cu. (C) A negative correlation in a plot of S/Se *versus* Cu/S may indicate S loss of the sulfides (see text for discussion).

Representative compositions of magnetite, as well as one composition of chromite, are listed in Table 4. The individual types of magnetite show marked compositional variation. All of types (i) to (iii) are Mg-free, but contain significant amounts of Cr, Ti, V, Zn, and Al. However, type (i), *i.e.*, magnetite that is included in orthopyroxene, has particularly elevated Ti (up to 7.2% TiO_2), Al (up to 5.75% Al_2O_3), and Zn (up to 1.1% ZnO) contents, whereas Cr contents are similar, and V and Ni contents seem to be lower than those of types (ii) and (iii). Magnetite in veinlets (type iv) and magnetite that rims bornite (type v, Fig. 3D) is Cr-, Al- ,Ti-, and V-free. In terms of Fe^{3+}–Cr^{3+}–Al^{3+}, and compared with magnetite from Australian komatiite-hosted Ni sulfide ores, there is a marked Al-enrichment in the Curaçá Valley oxides (Fig. 7). In contrast, Cr contents seem to cover a similar range. The same applies to Ti contents (Groves *et al.* 1983), although a limited number of determinations, mainly of type-(i) magnetite, have a markedly higher ulvöspinel component than the examples of magnetite in other massive sulfide deposits cited by Groves *et al.* (1983). Interestingly, magnetite separates at Okiep also have up to 6% TiO_2 (Cawthorn & Meyer 1993), but Cr contents of the magnetite (3.6% Cr_2O_3 in the separate) appear to be somewhat lower than in the Curaçá Valley.

Zn contents of the Curaçá Valley oxides reach 1.1% ZnO. In comparison, ferroan chromite from the Thompson Belt, Manitoba, contains 1.77 wt% ZnO (Groves *et al.* 1983), and chromite from sulfide-bearing Australian komatiites, 1.86 wt% ZnO (Groves *et al.* 1983). Exsolved spinel within magnetite from norite – orthopyroxenite bodies from Okiep has up to 14% ZnO (Stumpfl *et al.* 1976), and chromite from sulfide-bearing ultramafic rocks in Finland, between 1 and 3 wt% ZnO (Papunen *et al.* 1979). Groves *et al.* (1983) suggested that elevated Zn contents may be diagnostic of oxides in magmatic sulfide deposits. This does not rule out a magmatic origin of the Curaçá Valley oxides, since the Zn levels observed here are in the range of those found elsewhere in this type of deposits.

V contents in the Curaçá Valley oxides are slightly higher than those in chromite from sulfide-bearing komatiites at Kambalda, Australia (0.59 wt% V_2O_3, Frost & Groves 1989), and are similar to those of magnetite from Okiep (up to 0.71 wt% V_2O_3, Cawthorn & Meyer 1993).

DISCUSSION

The factors that govern the magnetite content of magmatic sulfide-oxide ores are poorly understood. It has been demonstrated that the intrinsic oxygen fugacity of mafic magmas lies around the QFM buffer (Fudali 1965, Sato & Wright 1966). Under these conditions, sulfide melts fall into the field of stability of magnetite in the system Fe–O–S (Naldrett 1969). Magnetite would be expected to crystallize from the sulfide melt before pyrrhotite, yielding an ore in which magnetite occurs in excess of cotectic proportions (*i.e.*, >30%). However, most natural sulfide ores fall into a relatively narrow field in the system Fe–O–S (Fig. 8), in which pyrrhotite is the principal liquidus phase, and magnetite is of lesser importance. The

TABLE 3. COMPOSITION OF ORPHOPYROXENE FROM ROCKS OF THE CURAÇÁ VALLEY, BRAZIL*

Locality	Car	Car	Sur	Sus	Ver	MSF	Ser	Bag	Car	Car	Bag
Sample	379.4	8	28.6	196.8	67.1	20	32	27	6	8	26
Rocktype	Px	Px	Px	Px	Px	Per	Per	Per	Per	Am	Gb
SiO2	52.75	52.83	51.32	52.20	53.12	54.15	53.81	54.55	54.25	53.68	50.42
TiO2	0.11	0.11	0.17	0.09	0.05	0.12	0.20	0.18	0.22	0.06	0.10
Al2O3	2.17	4.07	3.51	2.74	1.77	4.81	4.51	4.26	3.48	5.22	1.69
FeO	19.19	18.68	24.31	21.28	20.68	11.46	12.13	12.53	10.66	13.05	28.95
MgO	23.10	23.55	19.16	21.72	22.28	28.94	27.82	28.00	29.15	27.16	16.32
MnO	0.65	0.65	0.64	0.75	0.51	0.42	0.43	0.00	0.48	0.47	0.81
CaO	1.20	0.28	0.21	0.38	0.41	0.60	0.52	0.41	0.55	0.40	0.79
Cr2O3	0.18	0.15	0.26	0.23	0.17	0.16	0.08	0.09	0.09	0.16	<0.1
NiO	0.20	0.17	<0.05	0.05	<0.05	0.05	0.14	0.19	0.14	0.10	<0.05
Total	99.55	100.50	99.57	99.44	98.98	100.71	99.63	100.21	99.03	100.30	99.07
En	0.68	0.69	0.58	0.65	0.66	0.82	0.80	0.80	0.83	0.79	0.50

See Figure 1 for localities. Symbols: Px: pyroxenite, Per: peridotite, Am: amphibolite, Gb: gabbro, Car: Caraiba, Sur: Surubim, Sus: Susuarana, Ver: Vermelhos, MSF: Malha Santa Fe, Ser: Sertaozinho, Bag: Bagaicera.

reason for the contrast between the experimental data and natural ores is not apparent. Naldrett (1989) and Doyle & Naldrett (1987) suggested that the stability field of pyrrhotite may be expanded by the presence of other components in the sulfide melt, such as Ni and Cu. Pyrrhotite may then crystallize first, upon which the sulfide melt would lose much of its oxygen content owing to buffering of $f(O_2)$ and $f(S_2)$ by the silicate host magma (Naldrett 1969), resulting in minor crystallization of magnetite. The relatively high levels of Ni and low oxide contents of most magmatic sulfide ores, compared to the Curaçá Valley ores, lend support to this model. In contrast, in the Curaçá Valley, magnetite occurs in above-cotectic proportions if the pure system Fe–S–O is applied (Fig. 8). Primary fields of stability in the Cu-bearing system, however, remain uncertain owing to the lack of experimental data.

For the same reason, the high Cu contents of the

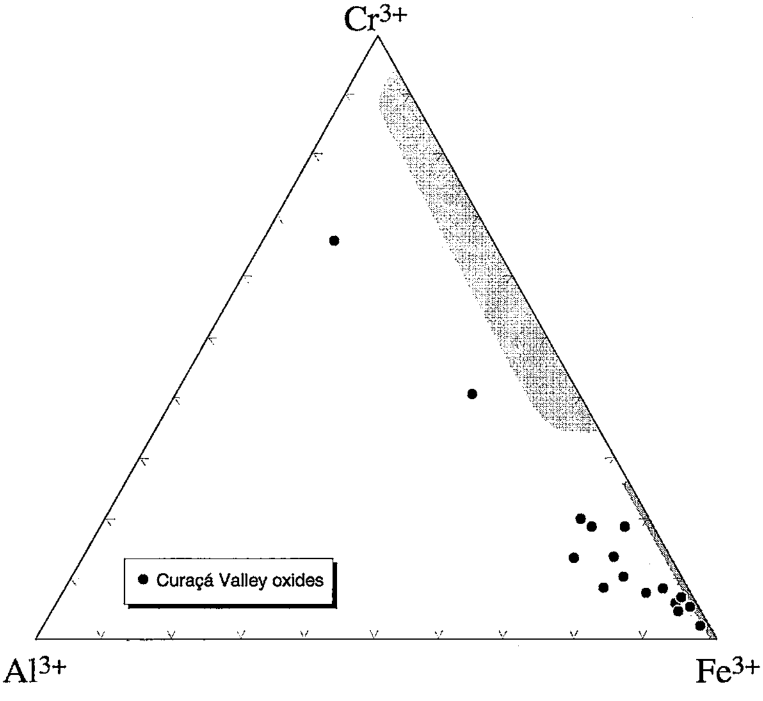

FIG. 7. Composition of magnetite from the Curaçá Valley, plotted in terms of Cr^{3+}–Al^{3+}–Fe^{3+}, and compared to the composition of chromian magnetite (solid line) and chromite (shaded field) from Western Australian sulfide-bearing komatiites (Groves *et al.* 1983).

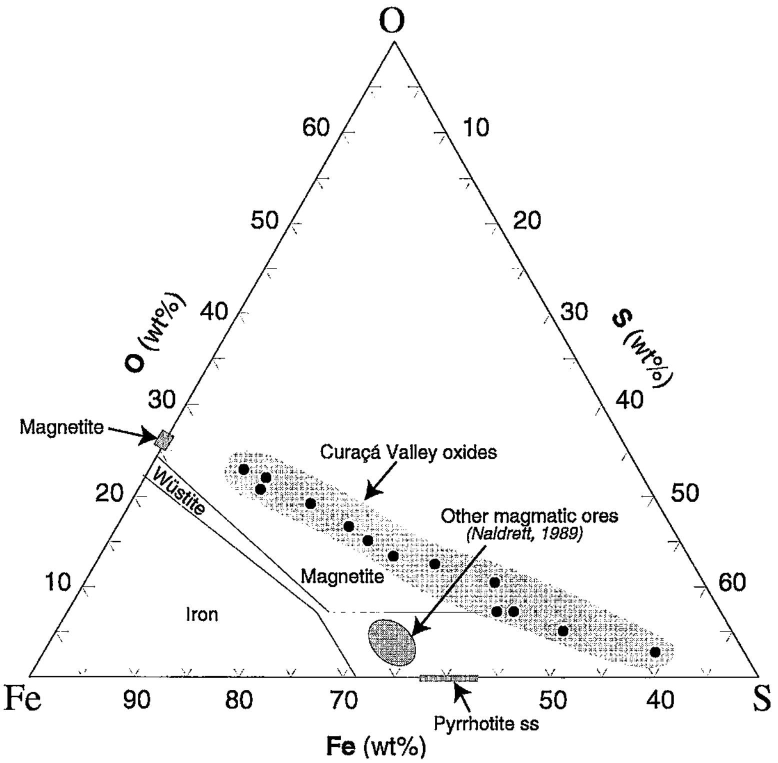

FIG. 8. The composition of Curaçá Valley ores plotted into the system Fe–S–O. Liquidus field-boundaries are from Naldrett (1969). Note that the field of magmatic ores represents an average bulk-composition, whereas the field of the Curaçá Valley ores reflects compositional variation among individual samples. The average of the Curaçá Valley ores falls into the stability field of magnetite. The linear trend reflects variation in the modal proportion of oxides and sulfides.

Curaçá Valley deposits remain difficult to explain. It has been stressed that the sulfide assemblage is dominated by bornite and chalcopyrite, with a bulk Cu/S value reaching 3.5. Stability fields of phases in the system Fe–Cu–S at atmospheric pressure (Kullerud *et al.* 1969) show that fractionating sulfide melts will become enriched in Cu owing to the incompatibility of Cu into early crystallizing monosulfide solid-solution (*mss*; Li *et al.* 1996). However, the Cu enrichment of the melt will cease once its Cu content reaches *ca.* 30%, owing to the appearance of intermediate solid-solution (*iss*) on the liquidus. Major crystallization of bornite from sulfide melt can only occur if initial Cu contents exceed *ca.* 35%. Assuming that the partition coefficient of Cu into sulfide melt is *ca.* 1000 (Peach *et al.* 1990), the silicate parental melt must, in this case, contain a minimum of 350 ppm Cu. Such levels appear to be too high if a tholeiitic parental melt is considered, but may be reached by fractionation of a calc-alkaline magma (Stolper & Newman 1994).

The abundance of bornite points to a hydrothermal addition of the Cu. However, this interpretation is not supported by our observations: (i) silicate alteration is restricted to narrow selvages along sulfide-infilled microfractures and veinlets; (ii) the mineralization is confined to the pyroxenites, with country-rock gneisses as well as xenolithic inclusions of gabbro and peridotite being barren; (iii) hydrothermal ores generally do not contain Ir, Ru, and Rh, and Au is hosted by sulfides rather than by oxides (*e.g.*, Tarkian & Koopmann 1995).

Notably, the only other magmatic sulfide deposit with abundant bornite, at Okiep, South Africa, also has elevated oxide contents. Precise modal analyses have not been published, but Stumpfl *et al.* (1976) observed oxide contents in the rock of up to 25% at Nababeep, one of the mines in the Okiep district. Cawthorn & Meyer (1993) and Boer *et al.* (1994) suggested

TABLE 4. COMPOSITION OF SPINEL FROM PYROXENITE SAMPLES OF THE CURAÇÁ VALLEY, BRAZIL

Type	i	i	ii	ii	ii	ii	ii	ii	ii	ii	ii	iii
Locality	Ver	Car	Ser	Ser	Car	Sus	Sus	MSF	MSF	Ang	Ang	TS
Sample	65	118.2	31	31	1720	196.8	196.8	23	23	339	339	122.8
TiO2	6.25	7.24	1.51	0.94	0.09	0.19	1.13	<0.1	0.24	<0.1	1.17	0.25
Al2O3	5.75	5.10	5.19	4.89	0.32	0.98	2.29	1.28	1.19	2.49	3.13	1.23
V2O3	0.75	1.06	2.36	2.31	1.45	1.43	1.04	0.38	0.5	1.09	0.97	1.1
Cr2O3	7.46	10.21	13.21	14.18	3.87	6.23	5.92	5.05	4.3	8.63	7.45	4.73
FeOp	75.04	71.88	75.18	75.02	86.99	84.19	83.4	87.79	87.51	83.37	82.34	88.71
FeOc	37.09	38.30	33.82	33.22	30.87	30.80	32.14	31.48	31.53	31.58	32.28	32.05
Fe2O3	42.17	37.32	45.96	46.46	62.37	59.33	56.96	62.58	62.21	57.55	55.64	62.97
MgO	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1.	<0.1
NiO	0.10	<0.1	0.3	0.17	0.1	0.20	0.28	0.13	<0.1	0.18	0.2	0.36
ZnO	1.09	0.42	0.36	0.53	<0.1	0.41	0.18	0.02	<0.1	0.56	0.79	<0.1
Total	100.67	99.72	102.72	102.69	99.07	99.58	99.95	100.92	99.97	102.08	101.8	102.69

Type	iii	iii	iii	iii	iii	iii	iii	iv	iv	v	v	chromite
Locality	Ver	Ver	Ver	Ver	Car	Car	Car	Car	Car	TS	TS	Ver
Sample	65	16-71.3	16-71.3	16-71.3	118.2	379.4	379.4	379.4	379.4	303.4	303.4	65
TiO2	0.39	0.35	0.56	2.53	3.39	0.11	<0.1	<0.1	<0.1	<0.1	1.14	0.20
Al2O3	3.3	0.89	1.36	3.71	5.38	1.56	2.48	0.21	<0.1	0.23	0.11	12.66
V2O3	0.99	1.07	0.97	1.02	0.97	0.78	0.65	<0.1	<0.1	<0.1	0.52	na
Cr2O3	8.21	3.47	3.57	3.17	8.64	7.84	9.27	<0.1	<0.1	<0.1	<0.1	52.91
FeOp	82.74	89.58	88.59	85.22	76.53	83.88	81.62	92.67	92.02	93.14	91.93	19.94
FeOc	32.29	32	32.26	34.28	34.47	31.2	30.98	30.64	30.37	31.12	32.12	13.62
Fe2O3	56.06	63.99	62.61	56.61	46.78	58.54	56.28	68.94	68.51	68.92	66.47	7.02
MgO	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	13.37
NiO	0.08	0.2	<0.1	0.1	0.25	0.42	0.56	0.54	0.46	<0.1	0.09	na
ZnO	0.26	<0.1	<0.1	0.3	0.91	0.12	0.27	<0.1	<0.1	0.09	0.09	na
Total	101.59	101.97	101.4	101.72	100.75	100.57	100.49	100.34	99.35	100.43	100.54	99.79

See Figure 1 for localities. Symbols: Ver: Vermelhos, Sus: Susuarana, MSF: Malha Santa Fe, Car: Caraiba, TS: Terra do Sal, Ser: Sertaozinho, Ang: Angico, FeOp: electron-microprobe value, FeOc: recalculated value assuming stoichiometry, na: concentration not determined.

that a primary magmatic pyrrhotite – chalcopyrite assemblage was oxidized and desulfurized, to yield secondary magnetite and bornite, according to the following equation:

$$5CuFeS_2 + 5FeS + 6H_2O + 8O_2 = Cu_5FeS_4 + 3Fe_3O_4 + 6H_2S\uparrow + 5SO_2\uparrow$$

Whereas direct petrographic evidence for replacement of pyrrhotite by magnetite appears to be rare at both the Okiep and the Curaçá Valley deposits, Cawthorn & Meyer (1993) argued that the occurrence of pure, presumably secondary, magnetite support their model for the Okiep district. In the Curaçá Valley, the amount of pure (Cr-, Ti-, and V-free) magnetite is negligible in all but a few samples. Typically, Cr-, Ti-, and V-enriched magnetite is replaced by sulfides. Hematite, a phase that we would expect as a product of reaction under relatively oxidizing conditions, is exceedingly rare.

However, there is reason to doubt the primary nature of these magnetite compositions. Archean plutonic rocks are expected to have exsolved most of their ulvöspinel component due to oxidation. The elevated ulvöspinel component observed in some of the magnetite in the Curaçá Valley suggests that ilmenite lamellae were partially resorbed during high-grade metamorphism, and that Ti re-entered the magnetite (Buddington & Lindsley 1964). If this is true, complete post-peak metamorphic re-equilibration apparently has been prevented, possibly owing to relatively rapid uplift and cooling of the rocks. This model is supported by the heterogeneous distribution of ilmenite lamellae within the rocks, the low Cr and Ti contents of orthopyroxene as compared with cumulus orthopyroxene from the Bushveld Complex, and by the work of Groves *et al.* (1977), who have shown that Cr contents of spinel from Australian komatiites increase with metamorphic grade.

It is of particular interest, in this regard, that both the Okiep and the Curaçá Valley ores underwent high-grade (granulite-facies) metamorphism, and that both deposits not only have elevated magnetite contents but also unusually low S/Se values. Furthermore, there is a good correlation between levels of S and Se, as well as of Cu and S contents. These correlations reflect the fact that those samples having a relatively low S/Se value contain the most bornite, and suggest that these samples suffered considerable loss of S. Comparison of the S/Se value in the Curaçá Valley samples with that of primary mantle allows us to estimate the S loss at between 70 and 80%, a value that is in approximate agreement with that proposed by Cawthorn & Meyer (1993) for the Okiep deposits.

It therefore appears that the desulfurization model of Cawthorn & Meyer (1993) is equally applicable to the Curaçá Valley deposits, and that a large proportion of the oxides are of secondary nature. However, whereas the desulfurization model is able to explain the high oxide and Cu contents of the ore, it fails to explain the low Ni values. Normalization of the Curaçá Valley ore to 100% sulfides yields a maximum Ni content of *ca.* 6000 ppm in the sulfides (if all Ni is hosted by sulfides). Assuming a partition coefficient for Ni between silicate melt and sulfide melt of 250 (Naldrett 1989), Ni levels of the parental magma may be estimated to have reached 25 ppm at the most. Assuming an additional S loss of up to 80%, the parental magma would have had a Ni content of less than 10 ppm. This represents an extremely low value for a basalt, although similarly low levels of Ni have been reported in calc-alkaline magmas (Stolper & Newman 1994). Furthermore, the mass-balance problem may be partly reconciled if recently published experimental data on fractionating sulfide melts are considered. Karup-Møller & Makovicky (1993) have shown that the partition coefficient of Ni into *Mss* is temperature-dependent. Barnes *et al.* (in press) point out that it increases from *ca.* 1 at 1000°C to 2 at 900°C. Ni may therefore be relatively depleted in fractionating Cu-sulfide melts.

CONCLUSIONS

The Cu-sulfide deposits in the Curaçá Valley share a number of features with the South African Okiep deposits: (i) sulfides are hosted by pyroxenite and norite, (ii) the sulfide assemblage is dominated by bornite and chalcopyrite, (iii) the rocks have a relatively low S/Se value, (iv) the ores contain a relatively high proportion of Cr–Ti-enriched magnetite, and (v) both deposits underwent high-grade metamorphism. These features suggest that the two occurrences formed by similar mechanisms. We support the model proposed by Cawthorn & Meyer (1993) for the Okiep deposits: a primary sulfide assemblage dominated by pyrrhotite and chalcopyrite was oxidized and desulfurized to yield secondary bornite and magnetite. However, the variation in the Ni/Cu ratio within the Curaçá Valley ores cannot be explained by S loss, and suggests that *mss* fractionation also occurred.

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