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Sulfides in Eclogite Nodules from a Kimberlite Pipe, South Africa, with Comments on Violarite Stoichiometry[1]

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Abstract

An unusual assemblage composed of four sulfides of Fe, Ni, and Cu occurs in rounded eclogite nodules which were inclusions in the kimberlite pipe at the Roberts Victor diamond mine, 45 miles ENE of Kimberley, South Africa. The polymineralic sulfide aggregates commonly are spherical and are composed of similar proportions of individual phases; they are interpreted to have developed from an immiscible liquid phase.

Electron microprobe, X-ray diffraction, and reflectivity data indicate that the dominant sulfide phase in the aggregates is a new mineral, approximate formula $(Fe, Ni)_9S_{11}$, typically containing 2.4 to 3.2 wt percent Ni; the higher Ni concentrations occur in 1 mm wide lamellae. Additional phases are Ni-bearing pyrite, a new, violarite-like, $(Fe, Ni)_9S_{11}$ phase, and stoichiometric chalcopyrite.

The complex sulfide assemblage, considered to have developed on cooling from a homogeneous liquid, is apparently metastable because it contains phases not reported in synthetic studies of the Cu-Fe-Ni-S system.

Introduction

Examination of 18 eclogite nodules[2] from the Roberts Victor diamond mine, South Africa, showed that a few specimens have sulfide accessory minerals. Specimen USNM 110607 contains the freshest, abundant sulfide. This nodule is essentially bimineralic, consisting of about 60 percent subhedral garnet grains 0.5-6 mm in diameter which occur as solitary grains or clots of grains, intergrown with coarser omphacite. Subsequent study by Dr. George Switzer (oral communication, 1969), indicating that this specimen contains the freshest omphacite, is in agreement with our impression that secondary processes may be responsible for alteration and removal of sulfides from more altered material.

Unpublished analyses of the dominant silicate phases in USNM 110607 are reported in Table 1. A. T. Anderson (oral communication, 1969), in an earlier study of similar Roberts Victor samples, found no ilmenite or magnetite, but did find accessory chromite having compositions (wt percent) in the range $MgAl_2O_4$, 2.6-16.1; $MgCr_2O_4$, 42.5-47.3; $FeCr_2O_4$, 25.9-36.0; Fe_2TiO_4, 1.8-5.6; and Fe_3O_4, 7.4-10.6.

In all sulfide-containing specimens examined, the sulfide occurs as aggregates which are mostly semirounded and elongated blebs between silicate grains, and also as nearly spherical inclusions within single crystals of garnet, omphacite, and phlogopite. Sulfides constitute about 0.2 percent by volume of specimen 110607. Individual aggregates are from 0.05 to 1 mm in greatest dimension and invariably consist of at least four phases, listed in order of decreasing abundance: (1) $(Fe,Ni)_9S_{11}$, with 2.4 to 3.2 wt percent Ni; (2) an isotropic, violarite-like mineral, also of $(Fe,Ni)_9S_{11}$ stoichiometry, with 21.5 to 30.0 wt percent Ni; (3) stoichiometric chalcopyrite, and (4) pyrite containing 0.6 to 4.8 wt percent Ni. Secondary alteration in the rock has resulted in deposition of minor amounts of Ni-free pyrite which is restricted to areas interstitial to the silicates and shows no apparent relationship to the four-phase sulfide assemblage.

Because of its strong magnetism and appearance in polished section, the major $(Fe,Ni)_9S_{11}$ phase can easily be misidentified as pyrrhotite. The intergrowth of this phase with the subordinate high-Ni $(Fe,Ni)_9S_{11}$ mineral of higher reflectivity is also similar to some pyrrhotite-pentlandite intergrowths or to replacement of pyrrhotite by marcasite (Fig. 1).

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[1] Publication authorized by the Director, U.S. Geological Survey.

[2] The nodules are in the collection of Dr. George Switzer, U.S. National Museum, Washington, D. C.

TABLE 1. Chemical Analyses of Omphacite and Garnet from Roberts Victor Eclogite, USNM 110607

Omphacite					Garnet				
Oxide	Wt.%[a]	Cation	Proportion[b]		Oxide	Wt.%[c]	Cation	Proportion[b]	
SiO_2	55.42	Si	1.97	2.00	SiO_2	40.7	Si	5.86	5.90
TiO_2	0.37	Al	0.03		TiO_2	0.4	Ti	0.04	
Al_2O	8.89	Al	0.34	1.10	Al_2O_3	23.9	Al	4.07	4.07
Fe_2O_3	1.35	Ti	0.01		FeO[d]	16.3	Fe^{2+}	1.97	6.15
FeO	3.41	Fe^{3+}	0.04		MnO	0.4	Mn	0.05	
MnO	0.10	Mg	0.61		MgO	15.7	Mg	3.44	
MgO	11.57	Fe^{2+}	0.10		CaO	4.5	Ca	0.69	
CaO	13.75	Na	0.35	0.87	Sum	101.9			
Na_2O	5.00	Ca	0.52						
K_2O	0.15								
		Components:					Components:		
$H_2O(+)$	n.d.								
		Acmite		4			Pyrope		55.9
$H_2O(-)$	0.02	Jadeite		31			Almadine		32.0
		Tschermakite		3			Spessartine		0.1
		Hedenbergite		10			Grossular		12.0
Sum	100.03	Diopside		50					

a/ Wet chemical analysis by E. Jarosewich.
b/ Calculated on the basis of six and 24 oxygens for omphacite and garnet, respectively.
c/ Microprobe analysis by George Switzer using close standards, corrected for background and drift.
d/ Fe = 12.6; all Fe assumed to be Fe^{2+}.

We (Czamanske and Desborough, 1968) have previously suggested the formula $(Fe,Ni)_3S_4$ for the dominant, low-Ni phase, but now believe that this formula is incorrect.

Microprobe analyses of sulfides in eclogitic material have been made by White (1966) and Meyer and Brookins (1971). For a compositionally zoned sulfide grain in an ultramafic inclusion in Hawaiian basalt, White reported (Table 8a and p. 293): Fe, 48.5-50.9; Ni, 12.8-10.8; and S, 37.9-38.0. Meyer and Brookins (1971) report finding chalcopyrite, pyrrhotite, and apparent pentlandite from the Stockdale Kimberlite, Kansas.

Four-Sulfide Assemblage Mineralogy

Aggregate blebs contain fairly uniform proportions of the four phases, and the phases are everywhere distributed in a characteristic pattern (Fig. 1a). At the center of each bleb is the low-Ni, $(Fe,Ni)_9S_{11}$ phase which comprises 60 to 80 percent of the whole. Peripheral to, and as marginal lamellae within this phase is the violarite-like, high-Ni $(Fe,Ni)_9S_{11}$ phase. Within both of these phases, Ni-bearing pyrite is found as subhedral grains as large as 25 μm across. Chalcopyrite, in small amounts, is typically found only at the margin of blebs (Fig. 1a).

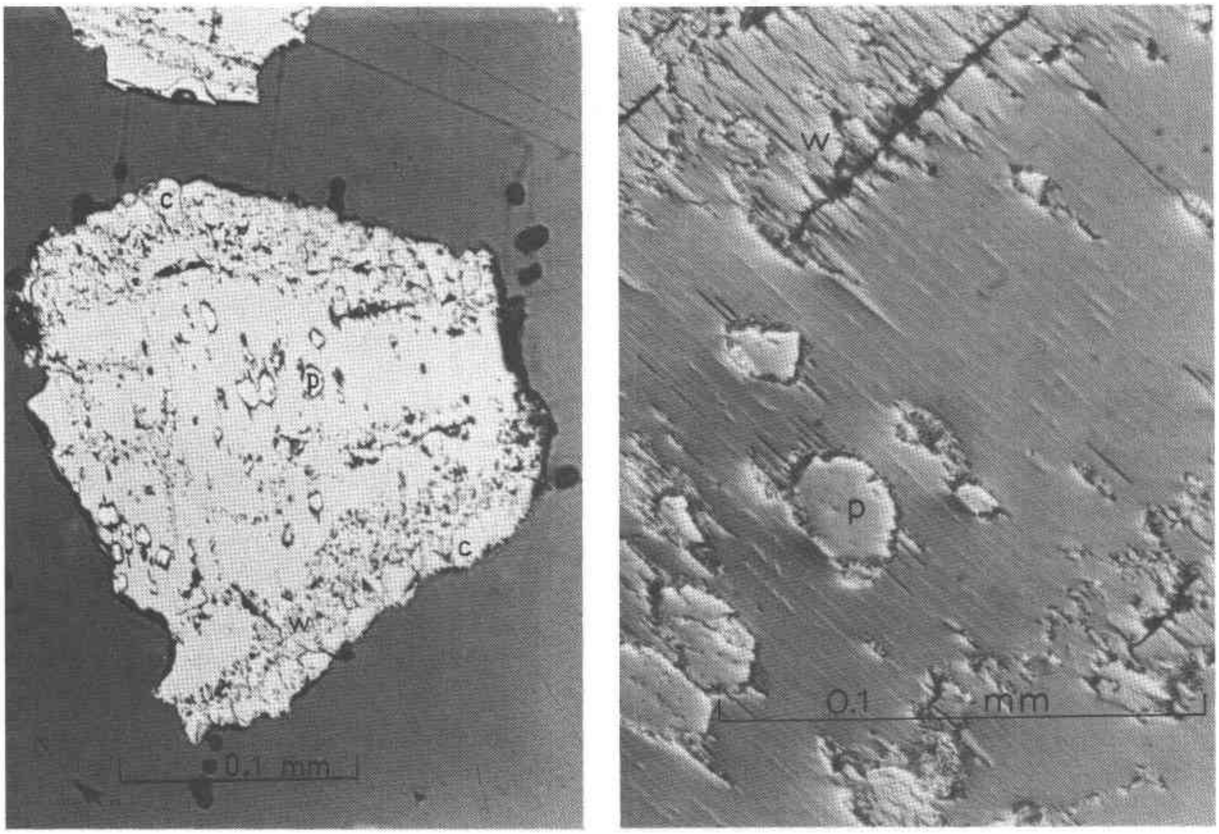
Quantitative electron microprobe analyses were performed on these phases in the U.S. Geological Survey laboratories in Washington, D. C., and Denver, Colorado. Ten synthetic sulfides of appropriate composition were used as reference standards. Appropriate standards were occupied both before and after analysis of the samples. Weight percentages of elements in our unknown phases were calculated by the USGS B-890 computer program.

Low-Ni, $(Fe,Ni)_9S_{11}$. Quantitative microprobe analysis was difficult due to problems of surface imperfections and beam overlap onto lamellae of a more Ni-rich phase (see Fig. 1). However, our best analyses of this phase have shown satisfying concordance for three distinct analytical efforts on two microprobes. We reanalyzed this phase carefully on three occasions because of shortcomings in our early analyses in which the three principal elements could not be measured simultaneously, and because of concern over suggesting 9:11 stoichiometry.

Our ultimate analysis of the low-Ni phase is presented in Table 2; the formula $(Fe,Ni)_3S_4$, with comparable Ni content, would require 43.3 wt percent sulfur (*cf* Table 5). Therefore we were in error in reporting our early data as evidence of a new $(Fe,Ni)_3S_4$ phase. Simultaneous determinations of Fe and Ni consistently show a lesser standard deviation for the sums of these two elements than for the individual elements, clearly indicating mutual substitution over a small range.

A maximum of 7.9 wt percent Ni was measured on marginal, fine lamellae of the major low-Ni $(Fe,Ni)_9S_{11}$ phase which projected into the high Ni-phase; the scattering of X-rays from the high-Ni phase may be partially responsible for this high value, but the extent of this contribution is unknown. As is shown below, the concentration of Co in these lamellae shows them to be atypical.

As much as 1.3 wt percent Co was measured in the lamellae of the major low-Ni $(Fe,Ni)_9S_{11}$ phase which project into the high-Ni, violarite-like phase. In general the highest Co values were obtained on areas adjacent to the violarite-like phase. Among 25 determinations on central areas of four grains, only 11 indicated Co above 0.1 wt percent, and only four contained more than 0.4 wt percent Co. From 0.2-0.6 wt percent Cu is present in the major low-Ni phase. Probably neither Cu nor Co is essential to the structure of $(Fe,Ni)_9S_{11}$.



(a) (b)

FIG. 1. (a) Typical polymineralic grain from eclogite mounted in epoxy (reflected light). Pyrite and similar high-relief central grains = p, chalcopyrite and similar grains = c, white, high-Ni, $(Fe,Ni)_9S_{11}$ and continuous submarginal fractured material = w; the major central phase is low-Ni, $(Fe,Ni)_9S_{11}$.

(b) Enlarged portion of grain in (a) showing parallel 1μm wide lamellae in major low-Ni, $(Fe,Ni)_9S_{11}$. (Nomarski objective, reflected light.)

TABLE 2. Electron Microprobe Analyses (in weight percent)[a] and Calculated Formulas for Low- and High-Nickel 9:11 Phases

	Low-Nickel Phase		High-Nickel Phase	
	Range[b/]	Mean	Range[c/]	Mean
Fe	55.2-56.4	55.5(9)	29.2-40.5	32.3(29)
Ni	2.4-3.2	2.8(6)	21.5-30.0	27.4(22)
Fe+Ni	--	58.3(5)	57.4-61.2	59.7(12)
S	40.1-41.6	40.9(7)	39.1-41.6	40.8(7)
Total		99.2		100.5
Formula[d/]	$(Fe_{8.575}Ni_{0.414})_{8.989}S_{11}$		$(Fe_{4.999}Ni_{4.035})_{9.034}S_{11}$	

a/ Estimated standard deviations (enclosed in parentheses) refer to the last decimal place cited. Thus 32.3(29) indicates an estimated standard deviation of 2.9. This convention will also be followed in the text and in subsequent tables.
b/ Eighteen determinations on 10 grains.
c/ Fifteen determinations on five grains.
d/ Totals normalized to 100.0

Unfortunately, the small size and finely intergrown mineralogy of the sulfide blebs have made it impossible to obtain completely satisfactory X-ray, reflectivity, and hardness data for even the major low-Ni phase. Judging from its polishing characteristics relative to the other sulfides present, it is apparently about the same hardness as pyrrhotite. Its color and anisotropism also may best be described as indistinguishable from those of monoclinic pyrrhotite.

Reflectivity data on this new phase were measured by B. F. Leonard in plane-polarized light by means of a Reichert photoelectric microphotometer. The U.S. primary germanium standard calibrated by the National Physical Laboratory, Teddington, England, was used as the standard for comparison. Values for the germanium standard are 47.0, 51.3, and 52.0 percent at 470, 546, and 589 nm. Values for the mineral, determined on three grains of suitable size and polish, are:

	470	546	589 nm
Rg′	38.1	40.5	41.1
Rm	—	37.4	—
Rp′	31.0	35.9	36.9
Rg′-Rp′	7.1	4.6	4.2
$\bar{R}$	34.6	37.7	38.6

The probable values for Rg and Rp are indicated by primes because one cannot be certain that these few grains truly show principal reflectivities. Values for $\bar{R}$, the midrange of all values for apparent maximum and minimum reflectivity at the standard wavelengths, are reproducible with a precision of 0.1–0.2 percent. Reconnaissance in the critical part of the spectrum suggests that the reflectivity curves have a single broad peak at or very close to 589 nm. Reflectivity at 650 nm was not determined, owing to the insensitivity of the photoreceptor at that wavelength. These reflectivity values are slightly higher than those for hexagonal pyrrhotite, but distinctly lower than those reported by Nickel and Harris (1971) for smythite of similar stoichiometry from Cobalt, Ontario. Reflectivity data for well-documented monoclinic pyrrhotite are not available.

At the three standard wavelengths, Rp′ is parallel to the trace of elongate exsolution(?) bodies of both the higher Ni (*i.e.,* 7.0 wt percent) lamellae and the white, isotropic Ni-Fe sulfide; Rg′ is perpendicular thereto. The presence of a nearly constant intermediate value of reflectivity, corresponding to Rm, shows that the mineral is optically biaxial.

X-ray powder diffraction investigation of several grains of this material was conducted utilizing Mn-filtered Fe radiation and also Fe-filtered Co radiation. The intimate nature of the intergrowth with the isotropic, high-Ni phase precluded extraction of a single phase. However, the fine-grain size and preferred orientation of the intergrowth aided in discrimination of the powder lines of each phase. The symmetry of the dominant, low-Ni, $(Fe,Ni)_9S_{11}$ phase could not be deduced from X-ray powder data. Attempts at indexing the X-ray powder lines for a hexagonal or tetragonal model were unsuccessful; the phase is thus either orthorhombic, monoclinic, or triclinic, as we later determined also from the quantitative reflectivity data.

X-ray powder lines of the minerals in the polymineralic sulfide assemblage are shown in Table 3. A powder pattern of the entire sulfide assemblage is shown in the second column. The third column lists powder lines obtained from a microprobe-analyzed, single crystal fragment extracted from the polished surface. (The data are representative of those obtained from several additional mounts and films.) This crystal was chiefly low-Ni, $(Fe,Ni)_9S_{11}$ with minor amounts of the intergrown white, high-Ni, $(Fe,Ni)_9S_{11}$ sulfide. The spottiness of the film lines associated with the major phase contrast with the smooth lines of the minor fine-grained phase to permit discrimination of these minerals. Column one of Table 3 lists powder lines of material containing neither chalcopyrite nor pyrite, and consisting entirely of the low-Ni and high-Ni sulfides. The major, low-Ni, $(Fe,Ni)_9S_{11}$ phase is indicated in the line-identity column of Table 3 by triple asterisks. The strongest lines of this phase are distinctive enough to permit identification and have *d*-values of 1.73Å, 2.56Å, 2.24Å, 1.98Å, and 1.90Å.

Numerous attempts by Howard T. Evans, U.S. Geological Survey, to produce interpretable single crystal photographs by both X-ray and electron dif-

TABLE 3. X-Ray Powder Camera Data for Sulfides in Eclogite

$(Fe,Ni)_9S_{11}$ plus White Ni-Fe sulfide spindle 3, Co/Fe[2]		Sulfide aggregate capillary tube, Fe/Mn[3]		$(Fe,Ni)_9S_{11}$ plus White Ni-Fe sulfide spindle 2, Fe/Mn[3]		
d(Å)[4]	I	d(Å)[4]	I	d(Å)[4]	I	Line Identity[5]
5.47	w	5.45	mw	----		WNiFeS
3.33	m	3.32	s	3.35	w	WNiFeS
----		3.12	w	----		py
----		3.03	s	----		cpy
2.989	m	2.99	w	2.99	w	***
2.847	m	2.84	vs	2.85	m	WNiFeS
2.810	m	----		----		***
----		2.70	m	----		py
2.561	ms	2.55	mw	2.56	m	***
2.466	w	2.47	w	----		***
----		2.42	mw	----		py
2.362	mw	2.36	s	2.37	w	WNiFeS
2.244	m	2.25	vw	2.23	w	***
----		2.21	mw	----		***
2.150	m	2.15	w	2.16	w	***
----		2.01	w	2.02	w	***
1.981	m	1.98	m	1.98	w	***
1.901	m	1.92	mw	1.905	w	***
----		1.85	w	----		cpy
1.818	vw	1.818	m	----		WNiFeS
1.730	vs	1.730	m	1.730	s	***
1.666	mw	[6]1.668	ms	----		WNiFeS
----		1.635	mw	----		py
----		1.590	vw	----		cpy
1.548	vw	1.562	vw	1.567	w	***
----		1.502	w	----		***
----		1.450	w	----		***
----		1.423	w	----		***
1.303	w	----		----		***
1.275	vw	[6]1.260	w	----		***
1.200	vw	[6]1.210	vw	----		***
1.181	vw	[6]1.183	mw	----		WNiFeS
1.100	ms	[6]1.102	w	----		***
----		[6]1.091	vw	----		***
----		[6]1.043	mw	----		py
----		[6]1.007	w	----		py
----		[6]0.999	w	----		py(?)
0.9852	w	[6]0.986	w	----		***

[1] 114.6 mm diameter powder camera. Relative intensities of lines are visual estimates where w = weak, m = medium, s = strong.

[2] Co/Fe = Fe filtered $Co_{K\alpha}$ radiation.

[3] Fe/Mn = Mn filtered $Fe_{K\alpha}$ radiation.

[4] Corrected for film shrinkage.

[5] WNiFeS = white, isotropic Ni, Fe sulfide intergrown with $(Fe,Ni)_9S_{11}$; cpy = chalcopyrite; py = pyrite; *** = $(Fe,Ni)_9S_{11}$.

[6] Very broad line due to large spindle diameter.

fraction techniques were unsuccessful, due to the presence of small domains and more than one phase.

Taylor (1970) and Nickel and Harris (1971) have reported on smythite from Cobalt, Ontario, which has a chemical composition almost identical to that of our low-Ni $(Fe,Ni)_9S_{11}$ phase (see also last section of the present report and Table 5). We emphasize that Buerger precession patterns obtained by Evans in one of the original descriptions of smythite (Erd *et al,* 1957), and from *both* Taylor's (1970) smythite and our low-Ni $(Fe,Ni)_9S_{11}$ phase clearly show that our phase is not smythite.

High-Ni, $(Fe,Ni)_9S_{11}$. This white, isotropic phase occurs chiefly as a sub-marginal rim (Fig. 1a), separating the dominant, low-Ni phase from the host silicate or chalcopyrite. The high-Ni phase has a distinctly higher reflectivity than the other sulfides and appears to be fractured on a fine scale (Fig. 1b), but this feature may be due to plucking during polishing. The high-Ni phase commonly projects into the low-Ni $(Fe,Ni)_9S_{11}$ phase as lamellae, 2-10μm wide (Fig. 1), that are similar in texture to some pyrrhotite-pentlandite intergrowths, or to the replacement of pyrrhotite by marcasite.

Microprobe analyses for Fe, Ni, and S were conducted simultaneously and the results are shown in Table 2. Measured variations in Fe, Ni, and S are shown on Figure 2; cobalt is not considered in this figure because its concentration is less than 1 wt percent. The average composition of this phase, like that of the low-Ni phase, corresponds most closely to $(Fe,Ni)_9S_{11}$, with variations in Fe and Ni due to mutual substitution. Some of the variability may be due to electron beam placement on the fine intergrowths.

Because of the slight difference in atomic weight between Fe and Ni, a $(Fe,Ni)_3S_4$ phase containing 27 wt percent Ni will have an S content of 42.8 wt percent. When normalized to totals of 100 percent, the microprobe analyses for the high- and low-Ni phases show the expected weight percentage changes in Ni+Fe and S values as a function of Ni content.

The high-Ni, $(Fe,Ni)_9S_{11}$ phase is always in contact with the low-Ni, $(Fe,Ni)_9S_{11}$ phase, but never adjacent to Ni-bearing pyrite. We believe this to indicate that the high-Ni phase did not react directly with the grains of Ni-bearing pyrite which were protected in the low-Ni phase. This interpretation is consistent with the fact that the sulfur contents of the two phases differ only to the extent required by their differing Fe:Ni ratios.

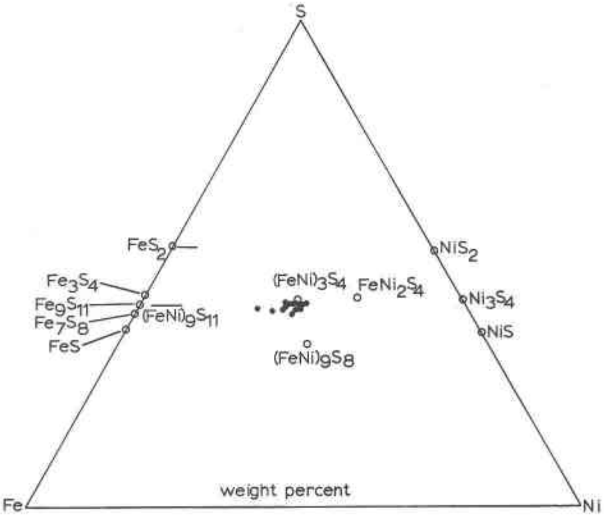


FIG. 2. Some of the stable phases in the Fe-Ni-S system. The new low-Ni, $(Fe,Ni)_9S_{11}$ phase and the coexisting Ni-pyrite are plotted with their compositional ranges shown by short horizontal lines. Small filled circles represent the white, isotropic high-Ni, $(Fe,Ni)_9S_{11}$ sulfide which is similar in structure to violarite.

The intimate intergrowth of high-Ni, $(Fe,Ni)_9S_{11}$ with the low-Ni $(Fe,Ni)_9S_{11}$ phase and with chalcopyrite prohibited unequivocal elucidation of its X-ray powder pattern. However, the seven lines labeled in Table 3 as white, isotropic Ni,Fe sulfide (WNiFeS) correspond closely to the strongest X-ray powder lines of violarite (Berry and Thompson, 1962). It is noteworthy that although both the structure and composition are very similar to those of violarite, this phase does not correspond to a known phase in the Fe-Ni-S system (Fig. 2).

Ni-bearing pyrite and chalcopyrite. The pyrite disseminated in $(Fe,Ni)_9S_{11}$ as subhedral to euhedral grains (Fig. 1) ranges in Ni content from 0.6 to 4.9 wt percent and in Co content from less than 0.1 to 0.55 wt percent; the average Ni content determined for 16 pyrite grains is 2.1 wt percent. Simultaneous analyses of Fe and Ni for 14 grains distributed among five separate polymineralic sulfide aggregates demonstrates that Ni is substituting for Fe. Nine of 16 grains contained less than 0.1 wt percent Co, the limit of detection for the conditions of analysis. Cobalt values greater than 0.1 wt percent were found only in pyrite grains with more than 1.5 wt percent Ni; however, there is no linear correlation between Ni and Co contents of pyrite.

The chalcopyrite at the sulfide bleb-silicate interface has been determined by microprobe analysis to be of stoichiometric composition.

Distribution of S, Fe, Ni, and Cu. To supplement our detailed mineralogical study, we have also attempted to determine the sulfur and sulfide-bound metal content of eclogite USNM 110607 and of a somewhat less sulfide-rich specimen, USNM 110586. Sulfur determinations by X-ray fluorescence on bulk powders gave respective values of 0.20 and 0.10 percent for these specimens. Sulfide-bound metal analyses were made by treating ground eclogite with bromine water (Czamanske and Ingamells, 1970) and analyzing the resulting solution for metals by atomic absorption techniques. Specimen 110607 was leached twice to check the efficiency of the leaching process. Values presented in Table 4 show that more than 97 percent of three sulfide-bound metals were extracted by the initial leach and give a picture of the overall transition-metal distribution in the nodules. Total sulfide-bound metals determined on the initial leach were 2,340 ppm for USNM 110607 and 709 ppm for USNM 110586. Metal proportions were, respectively, Fe:Ni:Cu—63.5:27.0:9.5 and Fe:Ni:Cu—61.0:24.1:14.9. All analyses on specimen 110607 are considered superior because it is less altered than specimen 110586; nevertheless, there is general agreement of ratios between the two.

Discussion

Carter and MacGregor (1969) reported trace element data for coexisting garnets and clinopyroxenes from Roberts Victor eclogites. Their values (in ppm) from eclogites of the 110607 type are for garnet Ni, 44 to 155; Cu, 0.1 to 22; Co, 55 to 134; and for omphacite Ni, 122 to 1,000; Cu, 1.2 to 39; Co, 32 to 51. On the basis of our work, we believe that their analyses are probably upper limits for metal concentrations in the silicate phases because of possible sulfide inclusions; they did not note sulfides.

There is thus the suggestion, in comparing our best data (USNM 110607) with those of Carter and MacGregor (1969), that where S is present under conditions of eclogite formation, the chalcophile metals are quantitatively to be found as sulfides. John Gurney (1971, written communication) indicates that a search for sulfides among 500 samples from Roberts Victor revealed them in nearly all specimens. Systematic investigation of the presence and nature of sulfides in a broad spectrum of materials of deep origin should be made.

TABLE 4. Distribution of Fe, Ni, Cu, and Co in Two Roberts Victor Eclogite Nodules on the Basis of Parts per Million in the Whole Rock

	USNM 110607				USNM 110586			
	Whole Rock	First Leach	Second Leach	Leached Rock	Whole Rock	First Leach	Second Leach	Leached Rock
Fe	--	1480	33	--	--	430	—	--
Ni	680	630	14	25	390	170	—	230
Cu	240	220	8	12	120	105	—	11
Co	N.D.	10	0.5	N.D.	N.D.	4	—	N.D.
Total		2340	55.5			709		

* Analyst, Neil Elsheimer. N.D. signifies "not detected" and -- indicates "not analyzed for."

The roundness, distribution, and similar relative proportions of phases of the sulfide aggregates suggest an origin by liquid immiscibility within a silicate melt. Both the sulfur and sulfur-bound metal values that we have obtained for these aggregates indicate sulfur contents for sulfides in excess of those for sulfide associated with sulfide immiscibility in basalts under surface conditions (Desborough *et al.,* 1968; Skinner and Peck, 1969). In marked contrast to the sulfides in basalts reported by Desborough *et al* (1968) and Skinner and Peck (1969), these eclogite sulfides lack an iron oxide phase and posses higher Ni content.

The effects of pressure on sulfur solubility and fractionation, the sulfur content of the mantle, and the metal-sulfur redistribution associated with possible eclogite-to-basalt transitions are topics of considerable interest toward which we are here able to contribute only meager data. Eclogite nodule USNM 110607 shows strong fractionation of the typical chalcophile elements, Co, Ni, and Cu, toward the sulfide fraction, and the sulfidation state of the minerals described is not minimal. In particular, the exsolution of pyrite is somewhat surprising and indicates a sulfide liquid richer in sulfur than would be expected for a typical surficial mafic rock with appreciable concentrations of chalcophile elements. It seems likely that the rather high sulfur and sulfur-bound metal values which we report can be explained in terms of lower oxygen fugacities during crystallization than are associated with crystallization of previously described mafic sulfide occurrences (see MacLean, 1969). The absence of iron oxide phases from our material supports this theory.

Because of the unknown effect of pressure on the Fe-Ni-Cu-S system and our observation of two phases unknown in extensive synthetic studies, it seems pointless to try to follow a crystallization history for the four-phase assemblage we report. We believe that the four phases have evolved from an originally homogeneous sample of immiscible sulfide liquid.

Comments on Violarite Stoichiometry

The apparent departure of the composition of our sulfides from $(Fe,Ni)_3S_4$ warrants discussion of the problem of the composition of violarite-like minerals.

At least two other investigators have reported iron sulfides with apparent 9:11 stoichiometry. Taylor (1970) and Nickel and Harris (1971) report analyses of smythite from Cobalt, Ontario, as $Fe_{3.25}S_4$. Their analyses are compared in Table 5 with ideal 3:4 and 9:11 stoichiometry.

TABLE 5. Comparison of Cobalt Smythite (Taylor, 1970, and Nickel and Harris, 1971) with Theoretical Stoichiometry

	Cobalt Smythite		Fe_3S_4	Fe_9S_{11}
	Taylor	Nickel and Harris		
Fe	58.3	58.6	56.64	58.76
Ni	0.45	0.1	...	...
S	41.2	41.5	43.36	41.24

On the basis of Craig's (1971) study, Czamanske sulfidized homogeneous Mss (monosulfide solid solutions) ranging in composition from $Fe_{61.0}S_{39.0}$ to $Fe_{20.45}Ni_{43.00}S_{36.56}$. We attempted 3:4 and 9:11 syntheses at four low-Ni compositions, plus a composition of Fe,Ni content equivalent to violarite. We experimented at 200° and 296°C in runs to 6 months in length. Reactions in the low-Ni experiments produced considerable pyrite and yielded no phases suitable for microprobe examination.

We have analyzed our own synthetic violarite-like materials, a synthetic violarite supplied by Craig, and a natural violarite from Sudbury, Ontario (USNM, R-699), furnished by B. F. Leonard. All have an X-ray pattern typical of violarite, although the first three of our materials listed in Table 6 show traces of Mss as well.

The material provided by Craig and considered to be synthetic $FeNi_2S_4$ contains traces of both unreacted Mss and pyrite (or $(Fe,Ni)S_2$) which are visible microscopically at 1625 magnifications using an oil immersion objective. Electron microprobe analysis of the major phase, presumably $FeNi_2S_4$, gives a sulfur content of 41.8(4) wt percent, instead of 42.5 wt percent as expected for stoichiometric $FeNi_2S_4$.

Microscopic study of the four violarite-like materials analyzed for sulfur (Table 6) revealed the presence of unreacted Mss in the interior of virtually all grains. Traces of pyrite and/or $(Fe,Ni)S_2$, as well as a gray phase within the reaction rim, were also detected.

The accuracy of our analytical method for the determination of sulfur content may be evaluated in Table 6. For Runs I, II, and III, all values for sulfur in the cores (Mss) are within one standard deviation of the starting composition—*i.e.,* 36.56 wt percent sulfur. The product of Run IV contains only very small remnants of Mss plus some very small but conspicuous pyrite grains; these factors may have contributed to poor electron beam placement on Mss and thus the slightly higher results for sulfur. None of the sulfur contents determined for the prepared products are within one standard deviation of either $FeNi_2S_4$ or $Fe_3Ni_6S_{11}$, which have S contents of 42.54 and 40.42, respectively. However, the value 41.6(5), which includes all of our data in Table 6 for reacted material, is identical to that obtained for Craig's presumed synthetic $FeNi_2S_4$.

Natural violarite from Sudbury, Ontario, as shown by 20 analyses on 10 grains of the material, contains only 41.0(3) wt percent sulfur. This value is not directly comparable with the value 40.8(7) wt percent sulfur obtained for our high-Ni $(Fe,Ni)_9S_{11}$ phase, but it is intriguing that the sulfur values for the two natural phases are distinctly lower than those for the synthetic materials.

The analytical sulfur data for materials which have the X-ray diffraction pattern of violarite, including natural violarite, synthetic violarite provided by Craig, and our synthetic violarites, force us to conclude that "violarite" is generally not stoichiometric $FeNi_2S_4$.

Additional evidence supporting this conclusion is found in reports on the Marbridge ore bodies, Quebec, by Buchan and Blowes (1968) and Graterol and Naldrett (1971). Both papers report several

TABLE 6. Microprobe Analysis of Sulfur on Synthetic Fe–Ni–S Products, Using Two Spectrometers Simultaneously*

Run No.	Temperature and intended product	Sulfur content (wt. percent, std. dev.)			
		Margins of grains		Monosulfide solid solution in core of grains	
		Spectrometer		Spectrometer	
		1	2	1	2
I	200°C, $Fe_3Ni_6S_{11}$	41.3(6)	41.4(6)	36.3(5)	36.4(4)
II	296°C, $Fe_3Ni_6S_{11}$	41.1(4)	41.8(5)	36.4(4)	36.3(3)
III	200°C, $FeNi_2S_4$	41.8(3)	42.0(4)	36.2(4)	36.3(9)
IV	296°C, $FeNi_2S_4$	41.7(5)	42.1(7)	37.1(3)	37.6(7)

* Analyst G. A. Desborough using two spectrometers simultaneously at 6 kV according to the method of Desborough et al. (1971). Estimated standard deviations (in parenthesis) are in terms of the last decimal place cited.

analyses of "violarites," all of which have a metal: sulfur ratio greater than 3:4. Specifically, Buchan and Blowes identify three types of "violarite" with an average metal:sulfur ratio of 3.24:4 or 8.91:11. Graterol and Naldrett report four analyses averaging 3.35:4 or 9.22:11 (excluding one apparently inferior analysis with S = 37.1 wt percent, 3.28:4 or 8.96:11). In each of these studies, the authors ascribe deviations from 3:4 stoichiometry to difficulties in polishing and resolving fine "violarite" intergrowths. We believe that this explanation is erroneous and obscures the fact that "violarite" is not strictly a 3:4 compound. Clearly, a problem arises concerning the proposed solid solution between violarite and polydymite (*e.g.*, Graterol and Naldrett, Fig. 8). On the basis of our study, that of Graterol and Naldrett, and that of Buchan and Blowes (see their Fig. 6), it seems more reasonable to propose an extensive solid solution series that contains throughout a proportion of sulfur more clearly corresponding to 9:11 than 3:4 stoichiometry and ranges from compositions richer in Fe than violarite toward polydymite (compositions richer in Ni than violarite).

We propose that synthetic material previously assumed to be synthetic $FeNi_2S_4$ contained traces of pyrite and/or traces of $(Ni,Fe)S_2$, a suggestion compatible with the phase diagram of Craig (1968) at temperatures below 450°C. Trace quantities of these two additional phases, as well as traces of unreacted Mss cores, would change the sulfur content of presumed violarite. Such small quantities are not detected in routine X-ray diffraction studies of a bulk product and may go unnoticed in microscopic investigations unless extreme care is taken. Furthermore, only the most careful microprobe study, with well-known, homogeneous standards of close composition, is able to document unequivocally the observed deviation from stoichiometry.

In any case, the nickel-rich violarite-like material we report in eclogite contains 40.8(7) wt percent sulfur but is apparently indistinguishable from the mineral referred to as violarite. It has the X-ray pattern reported for violarite, but does not have M_3S_4 stoichiometry.

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