

VIOLARITE IN SOME NICKEL ORES FROM LYNN LAKE AND THOMPSON, MANITOBA, AND SUDBURY, ONTARIO, CANADA

R. G. ARNOLD AND O. P. MALIK*

Saskatchewan Research Council, Saskatoon, Saskatchewan, Canada

ABSTRACT

Violarite has been identified in small inclusions in pentlandite from the Lynn Lake, Manibridge and Soab Lake mines in Manitoba, and from the Frood Mine, Sudbury, Ontario. Violarite in inclusions probably represents the first stage of supergene alteration of pentlandite. The distribution of violarite in inclusions in the deposits is not known.

Violarite frequently coexists with monoclinic pyrrhotite and more rarely with pyrite in inclusions. Identification of violarite and associated phases was accomplished by microscopic, electron microprobe and x-ray powder diffraction procedures. The violarites are deficient in nickel and sulphur with respect to stoichiometric violarite.

Massive supergene violarite in extensively weathered specimens from the Whistle property and the Discovery site in the Sudbury area were analysed by electron microprobe for comparison with the analyses of violarite in inclusions.

INTRODUCTION

An examination of nickel ores from Lynn Lake, Manibridge and Soab Lake mines in Manitoba, and from the Frood, Levack and Garson mines, Sudbury, Ontario, has revealed small scattered inclusions in pentlandite grains. The phases in the inclusions were generally too small to identify reliably by microscopic methods, but electron microprobe and x-ray diffraction studies indicate that the inclusions contain violarite and/or iron sulphides.

The majority of samples examined in this study were collected on two Geological Association of Canada field excursions. Samples from Lynn Lake, and from the Manibridge and Soab Lake mines at Thompson, Manitoba, are grab samples collected from surface pits in September 1970. Samples from the Whistle property and the Discovery site were collected from weathered outcrops in the Sudbury area in May 1971. The Frood, Levack and Garson mine samples were obtained from the mineral collection of the Department of Geological Sciences, University of Saskatchewan, and the original mine

sample locations are unknown. Consequently, the extent of development and distribution of violarite in the various ore bodies is not known.

RESULTS

The inclusions in pentlandite (Fig. 1) are variable in shape and collectively can occupy up to 10 volume per cent of a pentlandite grain. A few inclusions are as large as 60 μm across but the majority are less than 25 μm across. Some inclusions are elongated and appear to be crystallographically oriented and others show a tendency to be triangular in shape. Some inclusions are polycrystalline, anisotropic and have the colour and reflectivity of pyrrhotite. These inclusions are readily etched by chromic and hydriodic acid. X-ray diffraction studies of inclusions removed from polished sections indicate that these inclusions are monoclinic pyrrhotite. If other species of iron sulphides exist in the inclusions they are present in minor amounts. Some inclusions are isotropic, have a slightly higher reflectivity than those mentioned above and are not appreciably etched by the above acids. Electron microprobe and x-ray diffraction studies indicate that these inclusions contain violarite. Some inclusions have a mottled appearance, are partly anisotropic and are only partly etched by acids. These inclusions contain fine-grained mixtures of violarite and monoclinic pyrrhotite. Inter-connections between inclusions, and between inclusions and pentlandite grain boundaries, are not apparent in unetched sections, but some inter-connections in the form of narrow cracks become apparent after etching. Inclusions containing violarite generally contain and are partly bounded by narrow cracks which are interpreted to be shrinkage cracks developed during the formation of the inclusions.

To aid in the identification of the inclusions they were analysed with a MS 64 Acton-Cameca electron microprobe equipped with four spectrometers which permitted the measurements of iron, nickel, cobalt and sulphur simultaneously. Synthetic $(\text{Fe,Ni,Co})_{1-2}\text{S}$ phases were used as standards and corrections were made with Ruck-

* Present address: Department of Geology, University of Toronto.

ledge & Gasparrini's (1969) EMPADR VII program.

Figure 1 shows a relatively large inclusion that was analysed by electron microprobe together with *x*-ray distribution photographs for nickel, iron and cobalt. The results of the analyses and their interpretation are summarized in Table 1. The circles in Figure 1 represent the approximate areas from which the analyses were obtained and the numbers refer to the analysis of each site in Table 1. The phase assemblage indicated for each site was deduced from the analysis. Analyses with > 17 and < 3 atomic per cent Ni and an appropriate amount of iron and sulphur were interpreted to indicate violarite and monoclinic pyrrhotite, respectively. For

TABLE 1. SUMMARY OF ANALYSES OF THE INCLUSION SHOWN IN FIGURE 1

Site	Phase(s)	Atomic %			
		Fe	Ni	Co	S
1	monoclinic pyrrhotite	43.3	2.5	0.1	54.1
2	monoclinic pyrrhotite	42.6	2.9	0.3	54.2
3	monoclinic pyrrhotite	44.0	1.5	0.1	54.4
4	monoclinic pyrrhotite(vioiarite)	38.6	6.7	0.8	53.9
5	monoclinic pyrrhotite(vioiarite)	35.5	8.8	1.4	54.3
6	monoclinic pyrrhotite(vioiarite)	31.4	9.9	2.3	56.4
7	vioiarite(monoclinic pyrrhotite)	23.6	14.7	4.0	57.7
8	vioiarite(monoclinic pyrrhotite)	25.5	13.3	4.2	57.2

The phase assemblage at each site was interpreted from the analysis. The phase in brackets constitutes less than one-half of the mixture

example, sites 1 to 3 contain relatively low nickel and cobalt and consist of monoclinic pyrrhotite. Sites 4 to 8 contain more nickel and cobalt than can be attributed to monoclinic pyrrhotite but not sufficient for violarite, conse-

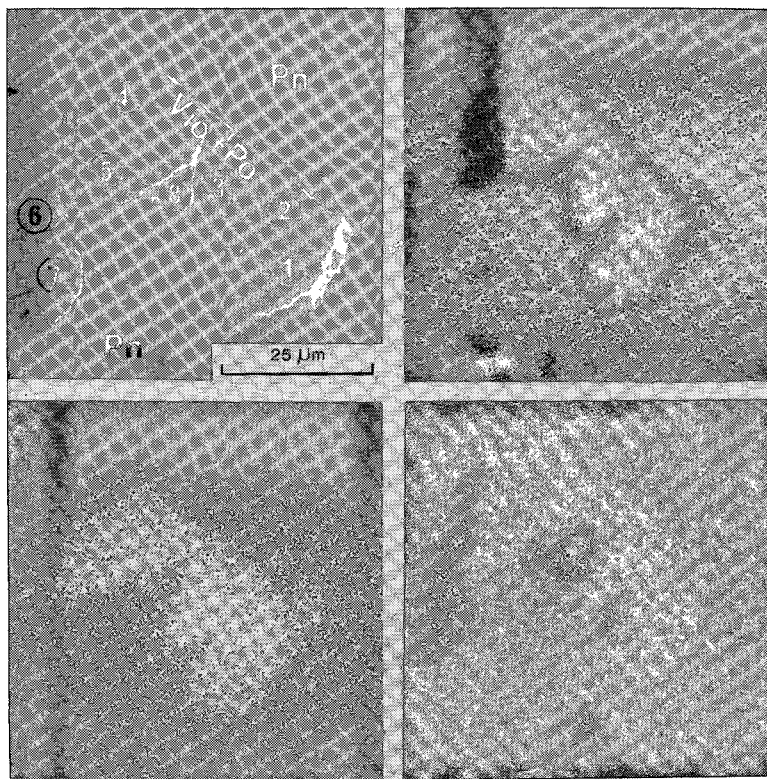


FIG. 1. Upper left. Inclusion in pentlandite from the Manibridge mine, Thompson, Manitoba, containing a fine-grained mixture of violarite and monoclinic pyrrhotite. The inclusion contains and is bounded by shrinkage cracks. The circles represent the approximate area ($\approx 6 \mu\text{m}$ diam.) of sites analysed by electron microprobe. The grains of violarite and pyrrhotite are sufficiently small that only mixtures of the two phases were analysed. (Table 1). (Crossed nicols). Upper right. NiK α x-ray distribution. Areas, 6, 7 and 8 are relatively high in nickel and indicate violarite. Lower left. FeK α x-ray distribution. Areas 6, 7 and 8 are relatively high in iron and indicate a low pyrrhotite content. Lower right. CoK α x-ray distribution. Areas high in cobalt indicate violarite.

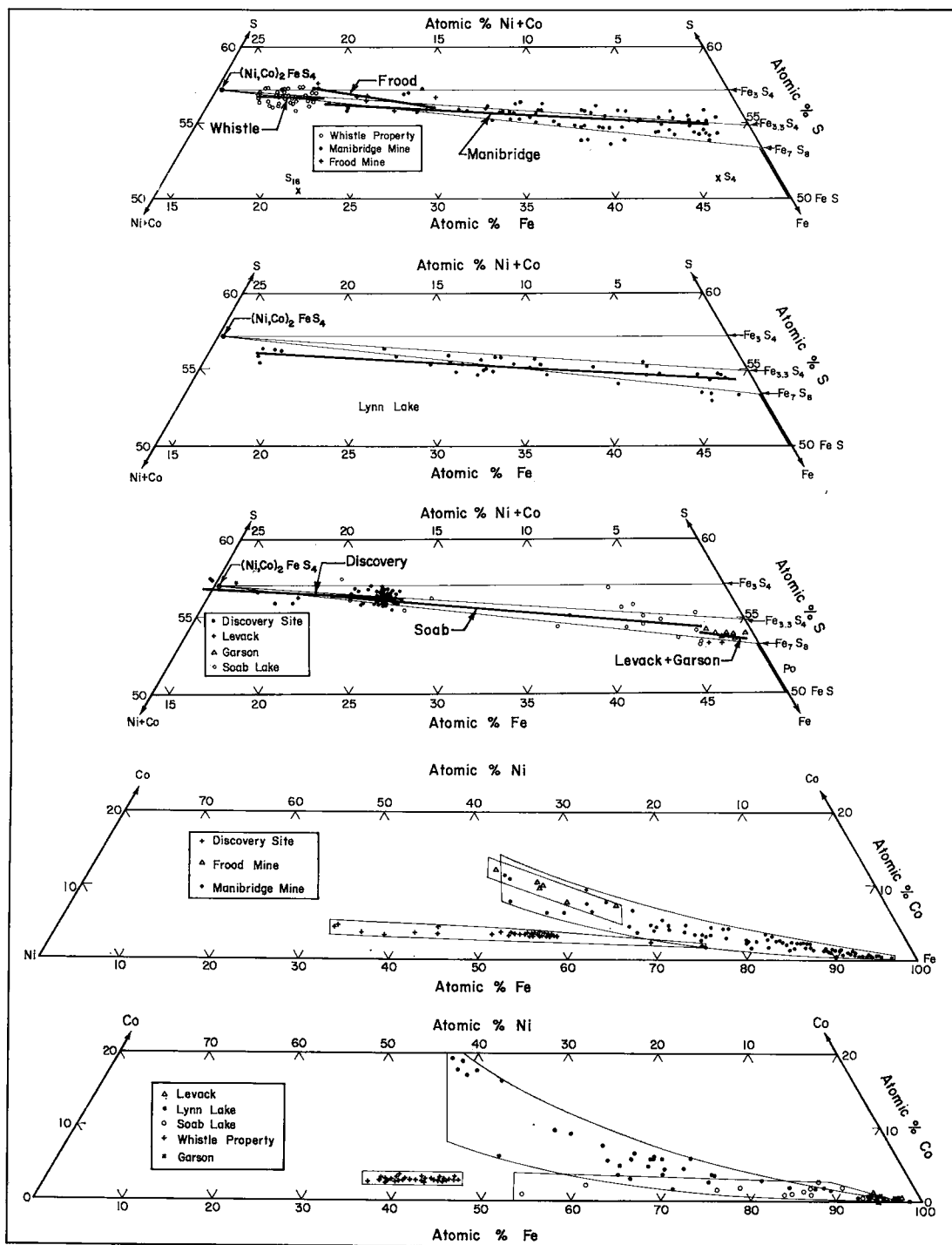


FIG. 2. The three upper diagrams summarize electron microprobe compositions of violarite in Discovery site and Whistle property samples and of inclusions in pentlandite in other samples. The inclusions contain violarite, violarite + monoclinic pyrrhotite or monoclinic pyrrhotite. Nickel and cobalt have been combined for convenience of presentation. The two lower diagrams summarize the iron, nickel and cobalt data for the same analyses after recalculating the metals to 100%.

TABLE 2. COMPOSITION OF END POINTS OF LINEAR REGRESSIONS (FIG. 2) FITTED TO ELECTRON MICROPROBE DATA FOR THE VARIOUS SAMPLES*

Locality	Assemblage	Ni-rich end of regression (atomic %)					Fe-rich end of regression (atomic %)				
		Fe	Ni	Co	S	metal/sulphur	Fe	Ni	Co	S	metal/sulphur
Whistle property	<i>pyrrhotite</i>	16.6±1.0	25.4±0.6	1.3±0.1	56.7±0.5	.764±.020	19.8±1.0	22.3±0.6	1.3±0.1	56.6±0.5	.767±.007
Discovery site		13.5±1.1	27.6±0.6	1.6±0.1	57.3±0.5	.745±.014	25.0±1.1	17.3±0.6	1.5±0.1	56.2±0.5	.779±.006
Frood	<i>violarite+pyrrhotite</i>	19.5±1.6	18.1±0.7	5.0±0.2	57.4±0.6	.742±.010	26.8±1.6	13.8±0.7	3.3±0.2	56.1±0.6	.783±.009
Manbridge		21.2±1.7	17.4±1.1	4.9±0.2	56.5±0.8	.770±.018	43.4±1.7	1.8±1.2	0.1±0.1	54.7±0.8	.828±.009
Lynn Lake	<i>pyrrhotite</i>	17.0±1.7	18.7±1.0	8.0±0.3	56.3±0.7	.776±.020	44.5±1.7	1.2±1.2	0.1±0.1	54.2±0.7	.845±.010
Soab Lake		21.1±3.0	21.3-18.2	1.2-4.3	56.4±1.2	.773±.039	42.5±3.0	2.8±2.1	0.2±0.1	54.5±1.2	.835±.018
Levack & Garson	<i>pyrrhotite</i>	43.3±0.7	2.8±0.2	0.3±0.2	53.6±0.3	.866±.004	45.6±0.7	0.7±0.3	0.1±0.1	53.6±0.3	.866±.004
Composition of stoichiometric phases for reference											
FeNi ₂ S ₄ (violarite)							14.29	28.57	---	57.14	0.750
Fe ₇ S ₈ (monoclinic pyrrhotite)							46.67	---	---	53.33	0.875
Fe ₃ S ₄ (smythite)							45.21	---	---	54.79	0.825
Fe ₃ S ₄ (greigite)							42.86	---	---	57.14	0.750

*The results can be explained in terms of three assemblages: violarite, violarite + monoclinic pyrrhotite, and monoclinic pyrrhotite as indicated. Uncertainties in metals and sulphur were estimated from the goodness of fit of the regressions.

quently these sites are interpreted to contain mixtures of the two phases. Other inclusions examined in the same manner contained pyrite, pyrite and violarite, monoclinic pyrrhotite, monoclinic pyrrhotite and violarite.

Routine analysis of inclusions in pentlandite from the various deposits, excluding data for pyrite in inclusions, are summarized in Figure 2. Regressions fitted to the data for each deposit represent the best estimate of the compositions. The data for Manbridge, Lynn Lake and Soab Lake inclusions range from near ideal violarite to near the iron-sulphur binary and are interpreted to represent mixtures of violarite and monoclinic pyrrhotite in varying proportions. The compositions of the two phases are estimated from the ends of each regression and are

summarized in Table 2. Inclusions in pentlandite from the Levack and Garson mines contain only monoclinic pyrrhotite. The estimated sulphur contents of iron sulphides in some of the inclusions are greater than expected for monoclinic pyrrhotite, but the estimates are within the expected error of analysis (3 atomic per cent of amount detected). The iron sulphides are not smythite because of their ease of etching by acids (Nickel 1971) and because of a total absence of smythite lines in x-ray powder camera diffraction patterns.

The relationship between iron, nickel and cobalt in the inclusions is shown in ternary plots in the lower portion of Figure 2. Data for pyrite in inclusions together with data for the pentlandite matrix, non-inclusion pyrite and mono-

TABLE 3. COMPOSITIONS OF PHASES IN SAMPLES ADDITIONAL TO THOSE CITED IN TABLE 2*

		No. of Grains or Points	Atomic %					Fe Ni+Co	metal sulphur
			Fe	Ni	Co	S			
Manbridge mine	Pn - matrix	114	23.4±0.4	30.2±0.4	0.6±0.1	45.9±0.6	0.76	9:7.62	
	Po - non-inclusion	93	47.4±0.5	0.5±0.1	0.004**	52.1±0.9		0.919	
	Py - non-inclusion	5		0.8±0.6	±0.3				
	Py - inclusion	28		3.8±0.6	2.4±0.5				
Lynn Lake	Pn - matrix	140	24.2±0.3	28.5±0.2	1.3±0.1	46.0±0.2	0.81	9:7.67	
	Po - non-inclusion	60	46.6±0.4	0.4±0.1	<0.01	53.0±0.9		0.887	
	Py - inclusion	15		4.5±0.9	3.4±0.3				
Soab Lake	Pn - matrix	72	24.0±0.3	28.9±0.3	0.7±0.1	46.4±0.2	0.81	9:7.79	
	Po - non-inclusion	72	46.5±0.5	0.4±0.1	0.005**	53.2±0.3		0.882	
	Py - non-inclusion	1		<0.01	0.9				
	Py - inclusion	13		3.7±1.3	2.9±1.1				
Whistle property	Po - matrix	2	47.0±0.4	0.5±0.1	<0.02	52.6±0.2		0.903	
	Marcasite-alteration	1		1.3	<0.02				
Discovery site	Pn - residual cores	6	25.3±0.2	27.6±0.1	1.5±0.1	45.7±0.2	0.87	9:7.56	
	Po - non-inclusion	18	46.3±0.5	0.4±0.1	<0.02	53.4±0.4		0.868	
Frood	Pn - matrix	4	24.2±1.1	28.4±0.8	0.2±0.2	47.2±0.4	0.85	9:8.04	
	Po - non-inclusion	2	45.7±0.1	0.7±0.1	<0.01	53.6±0.1		0.866	
	Py - non-inclusion	2		3.2±0.1	0.4±0.2				
Levack	Pn - matrix	4	24.1±0.6	27.9±0.3	0.5±0.1	47.3±0.5	0.85	9:8.11	
	Po - non-inclusion	5	44.9±0.8	1.4±0.8	0.1±0.1	53.6±0.2		0.866	
	Py - non-inclusion	2		<0.01	0.6±0.5				
Garson	Pn - matrix	5	25.7±1.4	26.5±0.7	0.8±0.1	46.9±0.5	0.94	9:7.96	
	Po - non-inclusion	2		0.5±0.1	< 0.01				
	Py - non-inclusion	2		<0.01	1.1±0.1				

* Data are given for pentlandite (Pn), non-inclusion monoclinic pyrrhotite with minor hexagonal pyrrhotite (Po), non-inclusion and inclusion pyrite (Py). Pyrite and marcasite have been assumed to be stoichiometric, therefore only their Ni and Co contents are presented. The stated uncertainties are standard deviations. The numbers of individual grains or points measured are indicated.

**Values determined by atomic absorption methods.

clinic pyrrhotite associated with minor hexagonal pyrrhotite that coexist with pentlandite in the samples are summarized in Table 3.

Violarite from the Discovery site and the Whistle property in the Sudbury area are massive replacements of pentlandite and were analysed for comparison with the analyses of inclusion violarite. The Discovery site and Whistle property are described by Guy-Bray & Peredery (1971) and Naldrett *et al.* (1971), respectively. Photomicrographs of violarite from the two localities are shown in Figure 3 and the analyses are summarized in Table 2 and are plotted in Figure 2. The majority of the Discovery site and Whistle property violarites show approximately the same degree of nickel and sulphur deficiency as inclusion violarite, there-

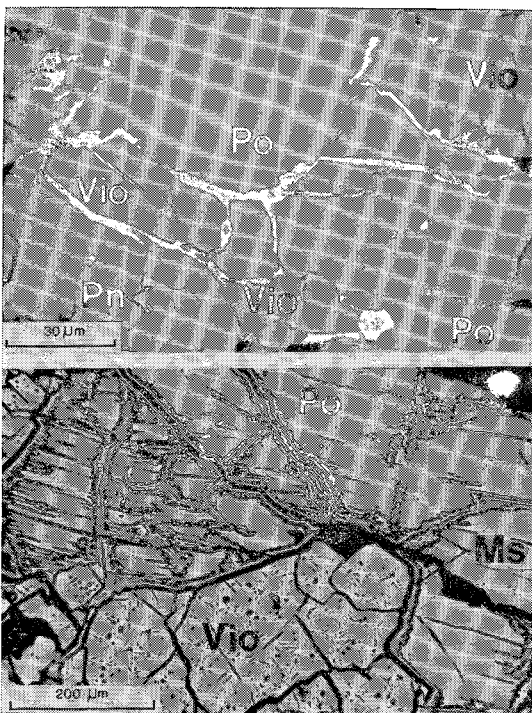


FIG. 3. Upper. Discovery site material showing grains of violarite (Vio) with associated shrinkage cracks in a matrix of monoclinic pyrrhotite (Po). Several residual cores of unreplaced pentlandite (Pn) and dark bands and patches of impurities occur in some violarite grains (plane light).

Lower. Whistle property material showing violarite (Vio) grains with associated shrinkage cracks in a matrix of monoclinic pyrrhotite (Po). Violarite grains show an internal cubic structure that is probably inherited from replaced pentlandite. Monoclinic pyrrhotite is partly altered to narrow bands of marcasite (Ms) along cracks and partings (plane light).

by confirming the reliability of the violarite analyses from inclusions. The bands of impurities in the Whistle property violarite, which consist of silica and iron oxides (Fig. 3), were avoided in selecting sites for analysis.

The occurrence of violarite in pentlandite in the various samples was confirmed by x-ray diffraction studies of pentlandite grains containing inclusions which were removed from the surface of polished sections and from pentlandite concentrates. A Philips powder diffraction camera (114.59 mm diameter) was used in conjunction with Mn-filtered Fe radiation. Silicon was used as an internal standard. Pentlandite, monoclinic pyrrhotite, violarite and occasionally pyrite diffraction lines were obtained from all samples judged to contain violarite on the basis of electron microprobe studies. Diffraction lines of other species of iron and nickel sulphides were looked for but were not detected. Only the three strongest lines of violarite were detected (113, 044 and 115) because of the small concentrations involved. The d -values show the following ranges: $d(113)$ — 2.845 to 2.863 Å; $d(044)$ — 1.674 to 1.697 Å; $d(115)$ — 1.815 to 1.825 Å. These values compare favourably with the values for the corresponding three strongest lines (2.85, 1.674 and 1.820 Å) given for violarite from the Vermilion mine, Sudbury, by Berry & Thompson (1962), and with the three strongest lines of violarite from Bindura (1.857, 1.676, 1.826 Å, unpublished data), Whistle property (2.864, 1.675, 1.823 Å, this study) and Discovery site (2.860, 1.681, 1.817 Å, this study). Because of the variable and relatively large cobalt content of violarites that tends to reduce the unit dimensions (Craig 1971), no estimates of the Fe:Ni ratios of violarites were attempted using powder diffraction data.

X-ray powder diffraction and etching studies indicate that non-inclusion pyrrhotite is predominantly monoclinic pyrrhotite with minor amounts of hexagonal pyrrhotite.

The composition of pentlandite (Table 2) from the Frood and Levack samples show nearly stoichiometric metal:sulphur ratios of 9:8.04 and 9:8.11, respectively, whereas these ratios for pentlandites from the remaining deposits range from 9:7.56 to 9:7.79 and indicate somewhat sulphur-deficient compositions. The Fe:Ni + Co ratios of all pentlandites range from 0.76 to 0.94.

A comparison of the nickel and cobalt contents of non-inclusion pyrite and inclusion pyrite (Manibridge, Lynn and Soab Lake, Table 2) indicates a significant enrichment of these metals in inclusion pyrite. Similarly, mono-

clinic pyrrhotite in inclusions on average contains more nickel and considerably more cobalt than non-inclusion monoclinic pyrrhotite. If the concentrations of both nickel and cobalt in inclusion minerals and the pentlandite matrix are considered, the phases in order of decreasing concentration of the elements are, for nickel: pentlandite, violarite, pyrite, monoclinic pyrrhotite; and for cobalt: violarite, pyrite, pentlandite, monoclinic pyrrhotite.

DISCUSSION OF RESULTS

The violarites analysed in the present study show metal-to-sulphur ratios ranging from near stoichiometric proportions, $(\text{Fe,Ni,Co})_8\text{S}_{4.04}$ (Frood Mine) to sulphur-deficient compositions, $(\text{Fe,Ni,Co})_8\text{S}_{3.85}$ (Discovery site). The majority of violarites analysed are sulphur-deficient, which conforms with published analyses (Buchan & Blowes 1968; Graterol & Naldrett 1971; Nickel 1973; Desborough & Czamanske 1973). None of the violarites analysed is as sulphur-deficient as $M_8\text{S}_{1.1}$ (Desborough & Czamanske 1973).

The Fe:Ni+Co ratios for violarites in Table 1 are generally greater than the ideal ratio of 0.50:1, and range from 0.62 to 0.95:1 with the exception of violarite from the Discovery site which has ratios ranging from 0.46:1 to 1.33:1. The latter high value may be due to disseminated iron oxides in some analysed sites (Fig. 3). Violarites with ratios greater than 0.50:1 are common in published analyses (Short & Shannon 1930; Buchan & Blowes 1968; Nickel 1973; Desborough & Czamanske 1973).

In contrast to published analyses of violarite which are generally deficient in sulphur and high in iron, the analysis of massive violarite replacing pentlandite from the Old Vermilion mine, Sudbury (L. J. Cabri, personal communication 1973) indicates a nearly ideal metal: sulphur ratio of 0.752 and a deficiency of iron (Fe:Ni+Co = 0.43:1). The analysis of this violarite is (atomic %): 29.44 Ni, 12.88 Fe, 0.61 Co, 57.07 S.

The Ni:Co ratios of massive violarite replacing pentlandite are generally relatively large and have the same order of magnitude as for the pentlandite it replaces. For example, the Ni:Co ratios of violarite from the Whistle property and Discovery site range between 11.5 and 19.5 and for the Old Vermilion mine it is 48.3. The Ni:Co ratios for pentlandites associated with violarite from all but the Frood deposits range between 18.3 and 51.0; Frood pentlandite has a very high average value of 142. In contrast, Ni:Co ratios for inclusion vio-

larite are less than 4.2 with the exception of one high value of 17.8 for an inclusion in Soab Lake pentlandite. The lower Ni:Co ratios for inclusion violarite is due to a lower nickel and a higher cobalt content relative to that in massive violarite.

The development of violarite in surface exposures at the Whistle property and Discovery site is clearly due to the supergene alteration of pentlandite as described for other Sudbury deposits by Wandke & Hoffman (1924), Lindgren & Davy (1924), Short & Shannon (1930), Michener & Yates (1944). It is of interest to note that violarite can develop within 25 years as an alteration product of pentlandite in fresh core exposed to the northern Ontario climate (Michener & Yates 1944).

The occurrence of violarite in inclusions in the various deposits has not been systematically studied, but A. L. DeCarle of Sherritt Gordon Mines Limited (personal communication 1974) believes that violarite in the Lynn Lake nickel deposit has a supergene origin as oxidation zones are developed in the upper portion of the orebody. This conclusion is supported by the absence of violarite inclusions in pentlandite in fresh ore specimens from the 2000 foot level of this mine, which indicates that there is no general development of primary violarite throughout the ore body.

Violarite in small inclusions is a common occurrence in the Australian Kambalda nickel deposits and is referred to as "micronsize flecks" (Woodall & Travis 1970) and "small nuclei" (Nickel 1973); however, the occurrence of additional sulphides coexisting with violarite in inclusions, such as occur in the Canadian ores, was not indicated. The violarite inclusions in the Australian deposits occur in the lower portion of the transition zone in which the initial alteration of pentlandite takes place (Woodall & Travis 1970). As alteration proceeds the small violarite grains increase in size and coalesce and eventually replace pentlandite completely.

ACKNOWLEDGEMENTS

We wish to thank Dr. C. Duesing for a number of suggestions concerning this work. Dr. Hiko Shimazaki assisted in the laborious task of removing violarites from inclusions and x-raying them.

REFERENCES

- BERRY, L. G. & THOMPSON, R. M. (1962): *X-ray Powder Data for Ore Minerals. The Peacock Atlas*. Geol. Soc. Amer. Mem. 85.

- BUCHAN, R. & BLOWES, J. H. (1968): Geology and mineralogy of a millerite nickel ore deposit. Marbridge No. 2 mine, Malartic, Quebec. *CIM Bull.* **61**, 529-534.
- CRAIG, J. R. (1971): Violarite stability relations. *Amer. Mineral.* **56**, 1303-1311.
- DESBOROUGH, G. A. & CZAMANSKE, G. K. (1973): Sulfides in eclogite nodules from a kimberlite pipe, South Africa, with comments on violarite stoichiometry. *Amer. Mineral.* **58**, 195-202.
- GRATEROL, M. & NALDRETT, A. J. (1971): Mineralogy of the Marbridge No. 3 and No. 4 nickel-iron sulfide deposits with some comments on low temperature equilibration in the Fe-Ni-S system. *Econ. Geol.* **66**, 886-900.
- GUY-BRAY, J. & PEREDERY, W. V. (1971): Field Guide for Excursion 1, Sudbury Basin. *Guide Book, Mineral. Assoc. Can. Mtg.*, Sudbury.
- LINDGREN, W. & DAVY, W. M. (1924): Nickel ores from Key West mine, Nevada. *Econ. Geol.* **19**, 309-319.
- MICHENER, C. E. & YATES, A. B. (1944): Oxidation of primary nickel sulphides. *Econ. Geol.* **39**, 506-514.
- NALDRETT, A. J., ARMSTRONG, T., HEWINS, R. H., PATTISON, E. F. & PHIPPS, D. (1971): Field Guide to the Sudbury Nickel Irruption. *Guide Book, Mineral. Assoc. Can. Mtg.* Sudbury.
- NICKEL, E. H. (1972): Nickeliferous smythite from some Canadian occurrences. *Can. Mineral.* **11**, 514-519.
- (1973): Violarite — a key mineral in the supergene alteration of nickel sulphide ores. *Aust. Inst. Min. Met.*, Western Australia Conference, 111-116.
- RUCKLIDGE, J. & GASPARRINI, E. L. (1969): Electron micro-probe analytical data reduction — EMPADR VII. *Dept. Geol., Univ. Toronto.*
- SHORT, M. N. & SHANNON, E. V. (1930): Violarite and other rare nickel sulphides. *Amer. Mineral.* **15**, 1-22.
- WANDKE, A. & HOFFMAN, R. (1924): A study of Sudbury ore deposits. *Econ. Geol.* **19**, 169-204.
- WOODALL, R. & TRAVIS, G. A. (1970): The Kambalda nickel deposits, Western Australia. *Mining & Petrol. Geol. Commonw. Mining Met. Congr.* (9th), *Publ. Proc.* **2**, 517-533.

Manuscript received November 1973, emended February 1974.