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NICKELIFEROUS SMYTHITE FROM SOME CANADIAN OCCURRENCES [1]

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ABSTRACT

Nickeliferous smythite [$(Fe,Ni)_{3.3}S_4$] has been found in four Canadian localities, associated with pentlandite and monoclinic pyrrhotite The nickel content of the smythite, which has been found to vary between 1.7 and 7.5% Ni, is consistently higher than that of the co-existing monoclinic pyrrhotite.

INTRODUCTION

Smythite was first described by Erd *et al.* (1957), from an occurrence at Bloomington, Indiana, and since that time only a few additional occurrences of the mineral have been reported : the Kerch Peninsula, U.S.S.R. (Chukhrov *et al.* 1965) ; Boron, California (Morgan & Erd 1969) ; and Cobalt, Ontario (Taylor 1970). These few reported occurrences would appear to indicate that smythite is a very rare mineral. However, Taylor (1970) and Nickel & Harris (1971) have suggested that, because of the mineral's similarity to pyrrhotite, smythite may actually be much more common than the paucity of reported observations suggests. At the same time, Nickel & Harris presented criteria (reflectance and microhardness) to assist in the distinguishing between the two minerals. Subsequently, the author has been engaged in an investigation of low-grade nickel deposits in Canada, during the course of which he found an additional four occurrences of smythite which are reported herewith.

SAMPLES

1. Lorraine Mine, Gaboury Township, Quebec. The ore is reported to occur as disseminations, stringers and almost massive forms, at the contact of andesite and gabbro (Kish 1965). The ore samples examined consist chiefly of pyrrhotite and chalcopyrite in a matrix of quartz, chlorite, calcite, and feldspar. Other ore minerals in the samples include smythite, pentlandite, violarite, pyrite, marcasite, and magnetite.

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2. Nicopor Mine, 8 miles north of Schreiber, Ontario, on the Canadian Pacific Railway. The ore occurs along the contact between amphibolite and granite (Thomson 1957). The samples investigated consist of disseminated sulphides in a siliceous matrix. The principal ore minerals are pyrrhotite, pyrite, and magnetite; chalcopyrite, smythite, and violarite are present in small amounts. Quartz and feldspar comprise most of the gangue minerals although chlorite, amphibole, and mica are also present.

3. Bird River Mines, (Ore Fault Group Claims, Township 17, Range 15E) in the Lac du Bonnet area of Manitoba. The ore occurs along a fault zone displacing the Bird River ultrabasic sill. (D. T. Anderson, personal communication). The samples used for this study consist of disseminated to massive sulphides, including pyrrhotite, chalcopyrite, pyrite, sphalerite, pentlandite, smythite, marcasite, and violarite. The principal non-metallic minerals are amphibole, quartz and chlorite.

4. Atikokan Iron Mine, Hutchinson Township, Ontario. The ore occurs in lenses and irregular masses in a highly altered gabbro (Hawley 1930). The samples examined consist of a matrix of talc, chlorite, amphibole, and carbonates containing irregular masses of sulphides and magnetite. The sulphide minerals include pyrrhotite, pyrite, chalcopyrite, pentlandite, smythite, and sphalerite.

MICROSCOPIC OBSERVATIONS

The smythite has a characteristic occurrence in all the samples in which it has been found — as flame-like forms in monoclinic pyrrhotite, extending inward from the margins of the pyrrhotite grains (Nickel & Harris 1971) and, where it is particularly abundant, as "flames" within the pyrrhotite itself (Fig. 1).

The smythite always has a slightly higher reflectance than the associated pyrrhotite, as pointed out previously by Nickel & Harris (1971) and can be recognized quite readily in good polished sections. The contrast can be greatly enhanced by etching with hydriodic acid for about half a minute. This etches the pyrrhotite strongly, but does not appreciably affect the smythite (Fig. 1).

It should, perhaps, be noted here that the hydriodic acid also etches monoclinic and hexagonal pyrrhotite differentially, monoclinic pyrrhotite being less susceptible to attack than the hexagonal variety (Schwarz & Harris 1970).

COMPOSITION

The smythite was analyzed with a Materials Analysis Company (M.A.C.) electron-probe microanalyzer, using synthetic pyrite as a standard for iron and sulphur, and metallic nickel as a standard for nickel. Corrections were made using Rucklidge's (1967) computer program. The results of the analyses are shown in Table 1.

The analyses in Table 1 show that the total metal content exceeds 3 atoms per formula in every case, in conformity with observations made on the Silverfields smythite by Taylor (1970) and by Nickel & Harris (1971). The nickel content of the smythite exhibits a wide variation, indicating that nickel can substitute for iron over a considerable range.

Table 2, which gives the results of nickel analyses made on co-existing smythite and pyrrhotite, shows that smythite consistently carries more nickel than the co-existing pyrrhotite. The ratio of nickel in smythite to that in pyrrhotite varies between 2.3 and 3.1 in the samples analyzed. The values shown in Table 2 are averages obtained from a number of deter-

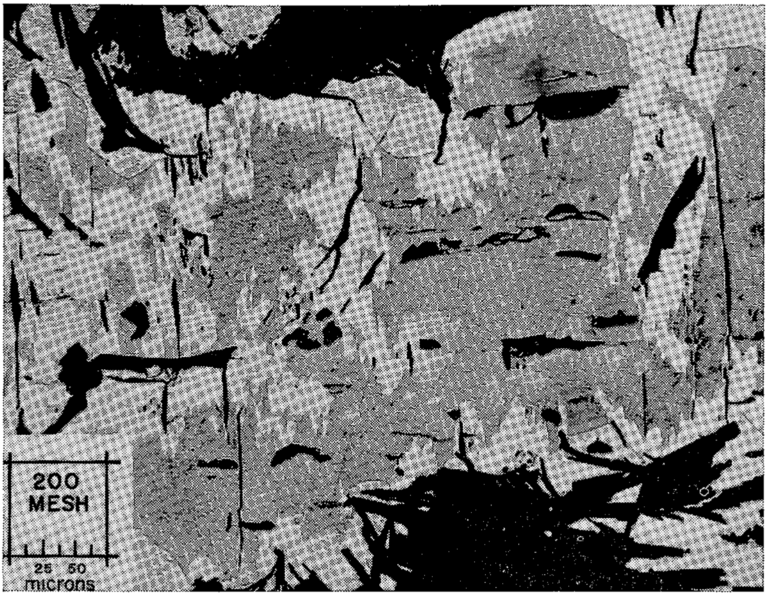

FIG. 1. Photomicrograph, in oil immersion, of a polished section from Bird River Mines, etched with HI. The pyrrhotite is etched (grey) and the smythite is unetched (white). Black areas represent gangue minerals and fractures. Note that the smythite is concentrated around the margins of the pyrrhotite and along fractures.

minations. Individual values show a much wider spread. For example, the smythite in Table 1 with the highest nickel content (7.5%) adjoins pyrrhotite with 0.8% nickel, giving a ratio of about 9:1.

Composition of pentlandite associated with pyrrhotite

Pentlandite is known to vary in composition, depending on the associated minerals (Graterol & Naldrett 1971). The analyses of pentlandites from the samples containing smythite (Table 3) show that all pentlandite compositions have an Fe:Ni ratio between 0.76 and 0.78, which is appro-

TABLE 1. MICROPROBE ANALYSES OF SMYTHITE.

Sample	Weight Percent			Atomic Proportions	
	Fe	Ni	S	Fe + Ni	S
Nicopor mine, Schreiber, Ontario	56.8	1.7	41.1	3.264	4.000
Bird River mine, Manitoba	56.3	1.9	41.1	3.246	4.000
Atikokan Iron Mine, Ontario	56.9	2.8	41.2	3.315	4.000
Lorraine mine, Ontario (Ave. of 17)	56.4	2.2	40.5	3.317	4.000
Lorraine mine, Ontario (Max. Ni)	50.9	7.5	40.7	3.271	4.000

TABLE 2. DISTRIBUTION OF NICKEL BETWEEN CO-EXISTING SMYTHITE AND PYRRHOTITE.

Sample	Wt. % Nickel		Ratio
	Smythite	Pyrrhotite	$Ni_s : Ni_p$
Nicopor	1.7	0.6	2.8
Bird River	1.9	0.8	2.4
Atikokan	2.8	1.2	2.3
Lorraine	2.2	0.7	3.1

TABLE 3. COMPOSITIONS OF PENTLANDITES ASSOCIATED WITH SMYTHITE.

Sample	Fe	Ni	Co	S	Fe : Ni At. ratio
Nicopar	28.5	38.3	0.7	32.6	0.78
Bird River	26.8	37.2	2.8	33.0	0.76
Atikokan	27.8	38.2	—	32.3	0.76
Lorraine	27.9	38.4	—	33.6	0.76

ximately in the middle of the pentlandite composition range, and should be in equilibrium with pyrite below 135°C, according to the tentative phase diagram proposed by Graterol & Naldrett (1971).

CONCLUSIONS

Nickeliferous smythite, with a composition approximating $(Fe, Ni)_{3.3}S_4$ apparently exists in equilibrium with monoclinic pyrrhotite and pentlandite of intermediate composition. The nickel content of smythite consistently predominates over that of the co-existing pyrrhotite, indicating a greater tolerance for this element.

Phase equilibrium studies in the synthetic Fe-Ni-S system have so far not demonstrated the existence of nickeliferous smythite as a stable phase. Since smythite has the appearance of a secondary phase, it may be formed by the late-stage, low-temperature sulphurization of monoclinic pyrrhotite, during which the nickel content becomes re-equilibrated between the two phases. The reason for nickeliferous smythite not having been found in studies of synthetic systems may be due to the very long times required for it to form at the presumably low temperatures. Experiments are currently underway in these laboratories in attempts to elucidate the stability relations of the mineral.

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