

## MERENSKYITE FROM THE SHEBANDOWAN NICKEL-COPPER MINE, NORTHWESTERN ONTARIO

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### ABSTRACT

Merenskyite occurs in chalcopyrite and pyrrhotite from Cu-rich ore, Shebandowan Ni-Cu mine (Inco Ltd.), northwestern Ontario. Reflectance in air was measured at fifteen wavelengths on two grains; interpolated average values at 470, 546, 589 and 650 nm are 59.7, 65.6, 67.7 and 70.4. Vickers microhardness is 158 kp/mm<sup>2</sup>. Electron microprobe analyses of eight grains in two specimens give a compositional range (weight %) of Pd 19.7-27.4, Pt 0.0-0.4, Fe 0.3-1.2, Ni 0.4-5.9, Cu 0.1-1.2, Ag 0.0-2.3, Sb 0.4-0.6, Bi 1.8-6.3, S 0.1, Se 0.0-0.1, Te 62.5-71.2. Grains enclosed by pyrrhotite are Ni-rich, whereas those in chalcopyrite are Cu-rich. Bi content in two specimens is about 2 and 6% and is lower than previously recorded for merenskyite. The merenskyite is interpreted to have exsolved from two different solid solutions which had been generated in the Cu-rich part of the Shebandowan magmatic sulfide body.

### SOMMAIRE

La mérenskyite se présente en inclusions dans la chalcopyrite et la pyrrhotine du minerai riche en Cu, à la mine Ni-Cu de Shebandowan (Inco Ltée), dans le Nord-Ouest de l'Ontario. La réflectance dans l'air mesurée à quinze longueurs d'onde sur deux cristaux donne des valeurs moyennes, interpolées à 470, 546, 589 et 650 nm, de 59.7, 65.6, 67.7 et 70.4. La microdureté Vickers est de 158 kp/mm<sup>2</sup>. Des analyses à la sonde électronique faites sur huit cristaux provenant de deux échantillons indiquent les domaines de composition suivants (% en poids): Pd 19.7-27.4, Pt 0.0-0.4, Fe 0.3-1.2, Ni 0.4-5.9, Cu 0.1-1.2, Ag 0.0-2.3, Sb 0.4-0.6, Bi 1.8-6.3, S 0.1, Se 0.0-0.1, Te 62.5-71.2. Les inclusions de mérenskyite dans la pyrrhotine sont nickelifères, tandis que, dans la chalcopyrite, elles sont riches en cuivre. La teneur en Bi, 2 et 6% dans deux échantillons, est plus faible que dans les mérenskyites étudiées précédemment. La mérenskyite serait un produit de la démixtion de deux solutions solides différentes, originaires de la

partie riche en cuivre du gisement de sulfures magmatiques de Shebandowan.

(Traduit par la Rédaction)

### INTRODUCTION

The presence of platinum-group elements (PGE) in nickel-copper sulfides from Shebandowan, Ontario, has been known since the work of Cross (1920) and Watson (1928). However, there are few published data on the PGE, the sulfides or the associated serpentinites and enclosing metavolcanic rocks other than those of Watkinson & Irvine (1964), Hodgkinson (1968) and Morin (1973). An investigation of the relationships between the various rock types and the Ni-Cu sulfide deposit at Shebandowan is being carried out by Morton and Watkinson. In routine microscopic examination of polished sections from the ore deposit, merenskyite was identified and characterized further at Carleton University and BRGM.

The Shebandowan mine is located about 80 km west of Thunder Bay, Ontario, within Archean rocks of the Shebandowan greenstone belt (Morin 1973). In the vicinity of the mine, basalt, andesite and pyroclastic dacite are intercalated with iron formation and mafic to ultramafic lenses that vary in composition from gabbro and diorite to peridotite. The Ni-Cu deposit is spatially related to one of these ultramafic lenses occurring at or near the contact with thinly banded basaltic flows and volcanoclastic rocks. Massive, breccia and stringer ore, consisting predominantly of pyrrhotite, chalcopyrite, pentlandite and pyrite, interdigitate with ultramafic rocks and basalt over a strike length of 4 km. The deposit and enclosing rocks have been deformed at least twice and intruded by the Shebandowan quartz-diorite stock and its apophyses. Metamorphic grade in the area is greenschist facies.

The sulfide-mineral assemblage corresponds to what is considered typical of magmatic sul-

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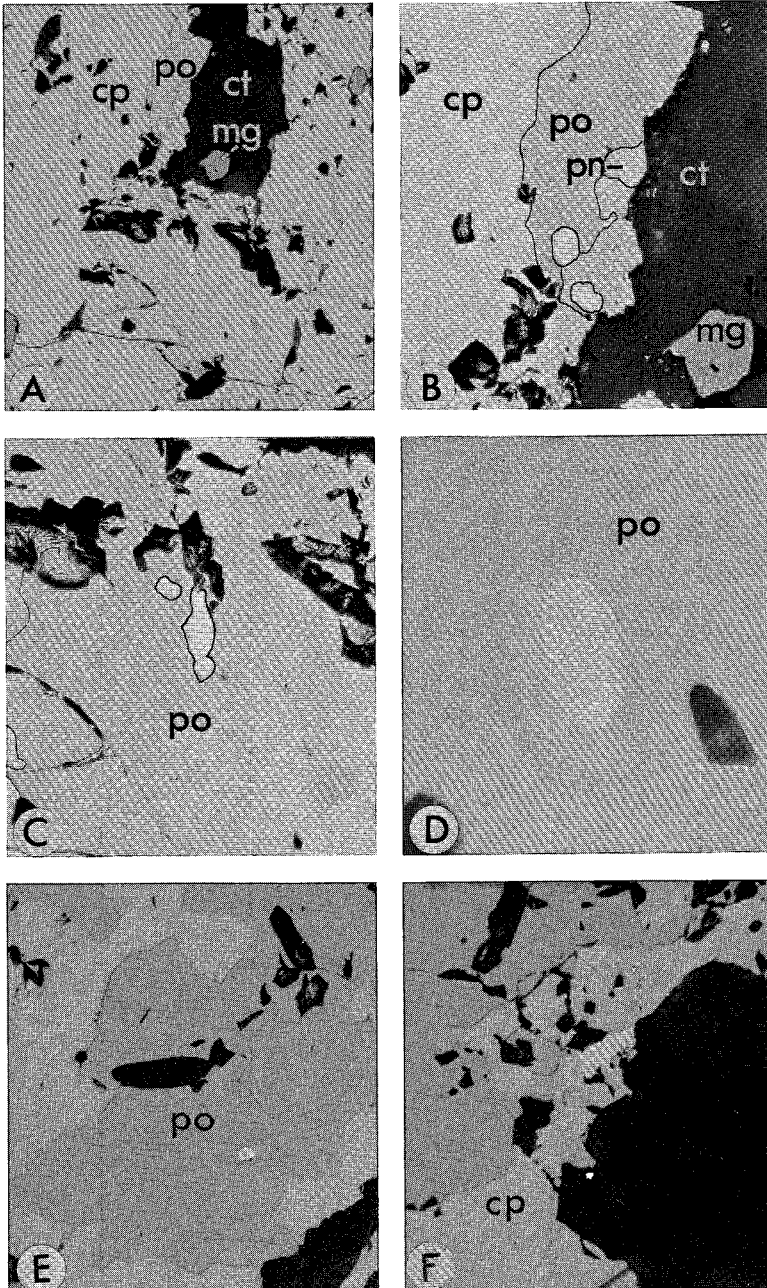


FIG. 1. Photomicrographs of merenskyite and associated chalcopyrite (cp), pyrrhotite (po), pentlandite (pn), magnetite (mg) and carbonate (ct) in SH-6. (A) Merenskyite 1 (Table 2) in pyrrhotite and 2 at pyrrhotite-chalcopyrite contact in upper part. Width of photo (W) 0.6 mm. (B) Enlargement of upper part of A with grains outlined. W 0.25 mm. (C) Enlargement of central part of A with grains outlined. W 0.25 mm. (D) Merenskyite in pyrrhotite. W 0.06 mm. (E) Merenskyite in recrystallized pyrrhotite enclosed by chalcopyrite. W 0.6 mm. (F) Merenskyite in chalcopyrite. W 0.6 mm.

TABLE 1. REFLECTANCE OF MERENSKYITE FROM SHEBANDOWAN

$\lambda$ nm	420	440	460	480	500	520	540	560	580	600	620	640	660	680	700
1	43.3	48.5	58.2	60.1	61.6	63.1	64.4	65.6	66.7	67.5	68.5	69.4	70.6	71.5	72.2
2	46.3	51.2	59.6	61.6	63.4	64.9	66.2	67.4	68.3	69.2	70.0	71.0	72.1	72.6	73.6
3	43.8	52.0	57.9	61.0	62.7	64.0	65.2	66.2	67.1	67.9	68.7	69.3	70.0	70.5	71.0

Average of four determinations at each wavelength. 1. Merenskyite 1 (R minimum); 2. Merenskyite 1 (R maximum); 3. Merenskyite 2 (isotropic grain).

TABLE 2. ELECTRON MICROPROBE ANALYSES\* OF MERENSKYITE FROM SHEBANDOWAN

	1	2	3	4	5	6	7	8
Pd	19.7	23.7	25.4	21.2	21.1	27.4	26.9	26.8
Pt	0.4	0.4	0.4	0.3	-	-	-	-
Fe	1.1	0.6	0.3	1.2	1.3	0.9	0.9	1.0
Ni	5.9	2.8	2.1	3.5	3.4	0.5	0.7	0.4
Cu	0.1	0.2	0.3	0.2	0.2	1.2	0.9	1.1
Ag	-	-	-	1.7	2.3	-	-	-
Sb	0.6	0.6	0.6	0.4	0.4	0.4	0.4	0.4
Bi	1.8	1.9	2.2	6.2	6.0	5.8	6.3	4.8
S	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Se	0.0	0.1	0.0	-	-	-	-	-
Te	71.2	68.8	68.6	62.5	65.1	65.1	64.6	64.4
Sum	100.9	99.2	100.0	97.3	99.9	101.4	100.8	99.0
Atomic Proportions Total of Three Atoms								
Pd	.63	.80	.85	.70	.70	.92	.90	.91
Pt	.01	.01	.01	.00	-	-	-	-
Fe	.07	.04	.02	.07	.08	.05	.06	.07
Ni	.34	.17	.13	.21	.21	.03	.05	.03
Cu	.00	.01	.02	.01	.01	.07	.05	.07
Ag	-	-	-	.06	.08	-	-	-
	1.05	1.03	1.03	1.04	1.08	1.07	1.06	1.08
Sb	.02	.02	.02	.01	.01	.01	.01	.01
Bi	.03	.03	.04	.11	.10	.10	.11	.08
S	.02	.01	.01	.01	.01	.00	.01	.01
Se	.00	.00	.00	-	-	-	-	-
Te	1.89	1.92	1.91	1.81	1.81	1.82	1.81	1.83
	1.96	1.98	1.98	1.94	1.93	1.93	1.93	1.93

\* in weight per cent. (1) in pyrrhotite, specimen SH-6; (2) in pyrrhotite at contact with chalcopyrite, SH-6; (3) in chalcopyrite at contact with serpentinized olivine, SH-6; (4) in pyrrhotite, SH-9; (5) in pyrrhotite, SH-9; (6) in chalcopyrite, SH-9; (7) in chalcopyrite, SH-9; (8) at contact between chalcopyrite and pyrrhotite, SH-9.

fide deposits but it is unusual in that (1) the Ni-Cu ratio is lower than that commonly recorded in magmatic sulfides associated with ultramafic rocks (Watkinson & Irvine 1964, Naldrett & Cabri 1976), and (2) the orebody is not always in direct contact with ultramafic rock; it is apparently devoid of disseminated ore.

TABLE 3. MICROPROBE ANALYSES OF PYRRHOTITE AND PENTLANDITE COEXISTING WITH MERENSKYITE FROM SHEBANDOWAN

	Pyrrhotite				Pentlandite		
	Weight Per Cent						
	1	2	3	4	5	6	7
Fe	59.8	60.5	60.4	60.5	28.8	29.0	30.0
S	39.0	39.4	39.4	39.1	34.5	34.4	33.1
Co	0.1	0.1	0.1	0.1	1.2	1.1	0.9
Ni	0.4	0.6	0.5	0.6	34.4	35.5	36.6
Cu	0.2	-	-	-	0.3	0.1	-
TOTAL	99.5	100.6	100.4	100.3	99.2	100.1	100.6
Atomic Per Cent							
Fe	46.6	46.6	46.6	46.8	23.4	23.5	24.5
S	52.9	52.9	53.0	52.8	48.9	48.4	47.0
Co	0.1	0.1	0.0	0.0	0.9	0.9	0.1
Ni	0.3	0.4	0.4	0.4	26.6	27.2	28.4
Cu	0.1	-	-	-	0.2	0.1	-

1, 5, 6 from SH - 9. 2, 3, 4, 7 from SH - 6

## MERENSKYITE: PHYSICAL AND CHEMICAL DATA

Merenskyite was identified in an assemblage of chalcopyrite-pentlandite-pyrite-pyrrhotite ore with magnetite, serpentine and carbonate. The specimens are from a chalcopyrite-rich section of breccia ore, 800+76 level. Typical ore is composed of pyrrhotite in grains 0.5-0.6 mm across having polygonal boundaries against chalcopyrite, pentlandite and other pyrrhotite grains. Pyrite grains are commonly about 0.06 mm across and occur at pyrrhotite grain boundaries. Pentlandite only rarely displays slight alteration to violarite. Where the ore occurs in stringers, pyrite is more abundant and two types are evident: white, euhedral coarse grains (Co content about 1.5%) and yellowish, Co-poor grains commonly in symplectitic intergrowth or sharing corroded boundaries with chalcopyrite. A few very small blebs of native gold were seen in chalcopyrite. Merenskyite is found within chalcopyrite and pyrrhotite in the centres and margins of sulfide grains (Fig. 1). Many grains are too small to characterize further. The largest merenskyite grain measures less than 50  $\mu$ m in longest dimension. In plane polarized light it is white in air but slightly creamy in oil. Its weak bireflectance, light grey to white, is more distinct in oil. Under crossed polarizers anisotropism is moderate to distinct from brown to grey with a slightly greenish tint. Reflectance measurements of grains 1 and 2 were made at fifteen wavelengths between 420 and 700 nm (Table 1) with a SiC standard. Vickers microhardness of these grains is 158 kp/mm<sup>2</sup> under a load of 7.6 g.

Electron microprobe analyses 4-8 (Table 2) were done with a Cambridge MK5 microprobe using the correction program of Rucklidge & Gasparrini (1969). The X-ray lines and standards used were PdL $\alpha$  and TeL $\alpha$  in PdTe; AgL $\beta$  and SbL $\alpha$  in Ag<sub>90</sub>Sb<sub>10</sub> alloy; FeK $\alpha$  and SK $\alpha$  in pyrite; BiM $\alpha$  in PdBi; CuK $\alpha$  in CuS; NiK $\alpha$  in pentlandite; PtL $\alpha$  in pure metal. All standards were synthetic except for pyrite; all analyses were done at 20 kV and 60 nA. Detection limits determined at the 95% confidence level were Sb 0.03, S 0.05, Fe 0.04, Ni 0.09, Cu 0.13, Pt 0.21, Ag 0.65.

Analyses 1-3 were done with a Cameca MS 46 microprobe and the ZAF correction program

at BRGM. X-ray lines (kV, standard) were PdL $\alpha$  (15,Pd), CuK $\alpha$  (25,Cu), NiK $\alpha$  (25,Ni), TeL $\alpha$  (15,Te), SeL $\alpha$  (15,Se), BiM $\alpha$  (25,Bi), PtL $\alpha$  (25,Pt), FeK $\alpha$  (15,FeS $_2$ ), SbL $\alpha$  and SK $\alpha$  (15,Sb $_2$ S $_3$ ). Traces of Co, Ge and Au were present in grain 1. As, Hg, Pb, Sn and Zn were specifically sought but not detected. Chemical compositions of sulfides coexisting with merenskyite in specimens SH-6 and SH-9 are given in Table 3.

#### DISCUSSION

The analytical data from two independent laboratories (Table 2) suggest that the ratio of Pd and other metallic elements to Te, Bi and other group V elements is close to but less than 1:2. However, this is probably within error of the analytical methods. One might explain the Fe and Cu contents of merenskyite as being the result of fluorescence from host pyrrhotite and chalcopyrite. Elimination of these data would mean that the stoichiometry would approach 1:2. However, it is possible that the compositions are real in that the grains contain negligible S. Certainly the Ni values are real: they are higher than values in enclosing grains.

Hoffman & MacLean (1976) have shown that synthetic merenskyites may exhibit a large range in Pd:Te ratio. The high Te contents preclude the coexistence of kotulskite with this merenskyite, in contrast to their coexistence in other deposits (*e.g.*, Bushveld: Kingston 1966, Sudbury: Cabri & Laflamme 1976, other Ontario occurrences: Rucklidge 1969). In fact, one very small grain gave an unusually high Te value in semiquantitative analysis, suggesting that it might be an intergrowth with tellurium or some mineral rich in Te. No other evidence for intergrowths was obtained.

The Bi:Te ratio is highly variable in synthetic merenskyite and this relation is consistent with the range of Bi contents of natural merenskyite. The grains analyzed in this study are lower in Bi than those previously reported. Although the correlations Pd-Ni and Bi-Te are negative, there is no apparent simple chemical relationship among the four elements in the available merenskyite data. Further discussion of possible extents of solid solution, with melonite or michenerite, for example, require more data, especially on the presence of coexisting phases containing Ni, Bi and Te.

Merenskyite and other platinum-group minerals (PGM) in magmatic sulfide ores are commonly thought to be directly related to the process producing the ore minerals chalcopyrite, pentlandite and pyrrhotite by either direct pre-

cipitation from a sulfide liquid, or more likely, by exsolution from a monosulfide solid solution. At Shebandowan, merenskyite occurs in very Cu-rich ore as inclusions in pyrrhotite and chalcopyrite; thus, it is apparently not a product of exsolution from a single mineral. The differences in Ni and Cu contents correlate with the nature of the host grain; *i.e.*, grains in chalcopyrite have higher Cu and lower Ni compared with those in pyrrhotite. If these values are not the result of contamination by the host mineral they may reflect the former presence of two solid solutions prior to PGM exsolution.

There is no direct evidence for the participation of aqueous fluids in the distribution, redistribution or differentiation of PGE in the specimens. Fluids have certainly affected the host silicates and sulfides during serpentinization and metamorphism; this has resulted in a variety of silicate-carbonate-oxide assemblages in serpentinites and the assemblage pyrite-millerite-chalcopyrite-magnetite in the very small amount of disseminated sulfides in serpentinites, presumably by partial oxidation of magmatic sulfides. However, the large orebody may have buffered oxidation to some extent and only minor pyrite, magnetite and violarite were formed. The distribution of PGE may have been slightly affected during oxidation.

The occurrence of PGM in copper-rich ore is common in many sulfide bodies (Stumpfl 1974). Copper-rich ore at Shebandowan may be the result of differential thermal diffusion of metals in a cooling orebody, of Cu enrichment during alteration or metamorphism, or of differential movement of chalcopyrite-rich material in the solid state upon deformation. The latter seems to be the most attractive hypothesis. Although we have found PGM in Cu-rich ore, it should be stressed that merenskyite in the specimens investigated occurs both in chalcopyrite and pyrrhotite.

The presence of merenskyite in minerals commonly thought to have been exsolved from monosulfide solid solution of primary magmatic origin (Naldrett 1969) and its apparent absence from pyrite or magnetite, interpreted by us to be formed for the most part upon serpentinization or metamorphism, suggest that merenskyite was exsolved as a discrete mineral during original cooling of either a monosulfide solid solution or of two coexisting solid solutions, one Cu-, the other Fe- and Ni-rich. On the other hand, these two solid solutions might well have been readily generated during metamorphism of Cu-rich parts of the sulfide body, and they could have exsolved PGM upon cooling.

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