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ARGENTIAN PENTLANDITE, $(Fe,Ni)_8AgS_8$, FROM BIRD RIVER, MANITOBA

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Abstract

Argentian pentlandite from the Ore Fault claims of Bird River Mines, Manitoba, occurs as small patches in chalcopyrite and is very similar to that described by Shishkin *et al.* (1971) from Russia and Vuorelainen *et al.* (1972) from Finland. The mineral is reddish-brown and isotropic in reflected light, contains 13.1 to 14.0 wt % Ag, has a mean Vickers micro-indentation hardness of 164 kg/mm² using a 100 g load, and has mean spectral reflectances of (in %) 25.5 at 470 nm, 32.8 at 546 nm, 33.7 at 589 nm and 39.6 at 650 nm. The mineral is cubic with $a = 10.52(1)$Å and has a powder *x*-ray diffraction pattern similar to normal pentlandite.

The chemical formula of argentian pentlandite may be written as $(Fe,Ni)_{8+x}Ag_{1-x}S_8$ and is consistent with the observation of Hall & Stewart (1973) that Ag replaces Fe and Ni only in the octahedral sites of pentlandite.

Introduction

Argentian pentlandite is a newly-discovered variety of pentlandite which contains up to 14.8 wt % silver and has a considerably larger cubic cell edge (10.5Å) than normal pentlandite (10.1Å). The mineral was first described by Shishkin *et al.* (1971) from two massive copper-nickel sulphide deposits and a nickel-cobalt skarn deposit in the U.S.S.R. and by Vuorelainen *et al.* (1972) from Outokumpu-type copper sulphide deposits and magmatic nickel-copper deposits in Finland. In these deposits, argentian pentlandite is commonly found in chalcopyrite as small blebs or exsolution bodies with or without normal pentlandite. Other closely associated sulphides include pyrite, pyrrhotite, sphalerite, galena and cubanite.

Earlier, Michener (1940; see also Hawley 1962) reported a pentlandite containing approximately 3.8 wt % silver intergrown with normal pentlandite from the Frood mine, Sudbury. Its optical properties as described by Michener are similar to those of argentian pentlandite but it had a much smaller cell edge (9.55Å) than either argentian pentlandite or normal pentlandite. In an attempt to synthesize this silver-rich pentlandite Knop *et al.* (1965) heated a synthetic charge of $Fe_4Ni_4AgS_8$ composition in an evacuated silica tube and produced, along with normal pentlandite, a face-centred cubic phase of unknown composition with $a = 10.499$Å. This new phase was probably argentian pentlandite.

In this paper we present data on the first documented Canadian occurrence of argentian pentlandite, from the Ore Fault claims of Bird River Mines Co. Ltd., Township 17, Range 15E, southeastern Manitoba. The argentian pentlandite was identified during routine examination of a polished section provided by Dr. E. H. Nickel, formerly of the Mines Branch, Department of Energy, Mines and Resources, Ottawa and was subsequently found in samples provided by Mr. John Donner of Bird River Mines. In the following paper, Hall & Stewart (1973) present the refined crystal structure of another sample of argentian pentlandite from the same locality.

Occurrence

The geology and mineralogy of the nickel-copper sulphide deposits of the Bird River area have recently been described by Karup-Møller &

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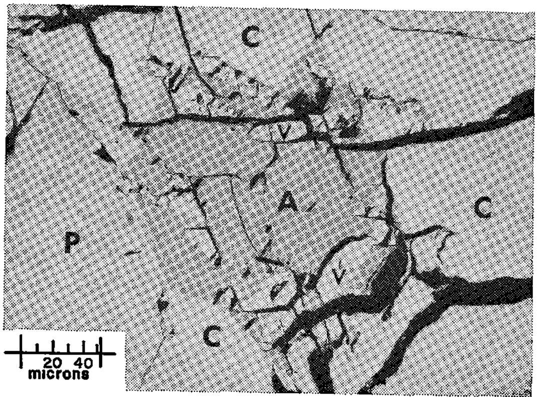

FIG. 1. Argentian pentlandite (A) with lamellae of violarite (V) enclosed in a matrix of chalcopyrite (C) and in contact with pyrrhotite (P). The black cracks are gangue. (Photograph courtesy of D.C. Harris, Mines Branch, Ottawa).

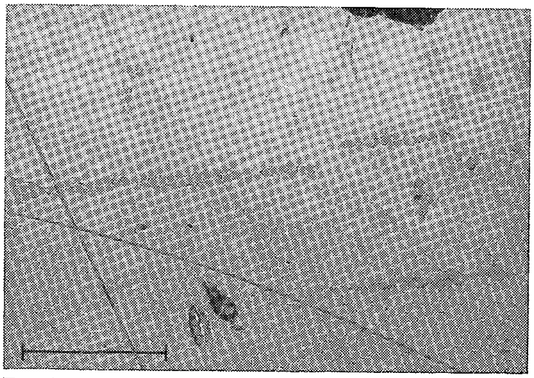

FIG. 2. Parallel set of poorly-developed dendrites of argentian pentlandite in chalcopyrite. Bar is 50 µm.

FIG. 3. Large grain of argentian pentlandite (A) in chalcopyrite (C) rimmed and cut by blades of alteration products consisting of unidentified Ag-Fe-Ni sulphides(s) (light and dark grey) and a few with cores of acanthite (white). Material between the alteration products and argentian pentlandite plucked out during polishing. V and similar appearing lamellae are violarite. Small, light-grey, triangular bodies in argentian pentlandite are chalcopyrite. Bar is 100 µm.

Brummer (1971). The massive sulphide deposits occur near, but not in, the ultrabasic Bird River sill. According to Karup-Møller & Brummer the deposits are not typical magmatic nickel-copper sulphides but were emplaced under the influence of regional metamorphism accompanying the main orogeny of the area. The mineralization of the Ore Fault claims, in which the argentian pentlandite was found, occurs in a fault zone offsetting the Bird River sill (personal communication from D. T. Anderson, University of Manitoba).

The argentian pentlandite from Bird River commonly occurs as small anhedral patches up to 200 µm across and occasional larger masses within or in contact with chalcopyrite (Fig. 1). In places it forms parallel sets of poorly-developed dendrites (Fig. 2) suggesting that some of it may have exsolved from chalcopyrite. Associated sulphides include sphalerite, violarite, bravoite, pyrrhotite, smythite (see Nickel 1972) and pyrite; normal pentlandite was not found in our samples but it is a common mineral in the deposit. In one highly altered (supergene?) sample an unidentified Ag-Fe-Ni sulphide(s) and acanthite rim argentian pentlandite and form blades cutting it in a crystallographically-controlled array (Fig. 3). Similar alteration was described by Vuorelainen *et al.* (1972) from the Finnish samples.

PROPERTIES

Optical and physical

Argentian pentlandite from Bird River has a reddish-brown colour in reflected light and tarnishes slowly in air to a slightly darker colour. It is isotropic and has no internal reflection. As pointed out by Shishkin *et al.* (1971) it looks very similar to freshly-polished bornite.

Our samples do not contain any discernible cleavage, in agreement with Shishkin *et al.* (1971). However, cleavage has been reported in argentian pentlandite by Vuorelainen *et al.* (1972) from the Finnish deposits and by A. E. Johnson, Mines Branch, Ottawa (personal communication 1973) from the Burnt Basin lead-zinc skarn prospect in southern British Columbia.

The spectral reflectance of our argentian pentlandite was measured using an Evans Model 165 Digital Microphotometer. Values for four wave-

TABLE 1. REFLECTANCE OF BIRD RIVER ARGENTIAN PENTLANDITE

Wavelength nm	No. of meas.	Reflectance % (s.d. in brackets) argent. pent.	SiC standard
470	5	25.5(3)	20.95
546	7	32.8(6)	20.6
589	5	33.7(6)	20.2
650	5	39.6(8)	20.0

lengths measured in air relative to a SiC standard are in Table 1. Three reflectances are very close to those given by Vuorelainen *et al.* (1972) but their value of 37.4% at 546 nm appears to be anomalously high. Direct comparison with the Russian argentian pentlandites is difficult because Shishkin *et al.* (1971) used a different standard (silicon). Our data agree at 650 nm but Shishkin *et al.'s* reflectances are 2 to 3% greater than ours at shorter wavelengths.

The Vickers micro-indentation hardness measured by D. C. Harris, Mines Branch, Ottawa on a Leitz Durimet with a 100 g load, ranges from 159 to 173 kg/mm² for six indentations, with a mean of 164 kg/mm². Vuorelainen *et al.* (1972) obtained VHNs of 132 to 154 kg/mm² (50 g load) and Shishkin *et al.* (1971) obtained 162 and 173 kg/mm² (30 g load).

Composition

The Bird River argentian pentlandite was analyzed by electron microprobe (ARL-EMX) using as standards synthetic pyrrhotite (62.00 wt % Fe) and millerite and silver, copper and cobalt metals. Raw data were reduced using the EMPADR VII computer routine of Rucklidge & Gasparrini (1969). Our analyses together with those from other sources are in Table 2.

The Bird River analyses give a constant composition approximating $(Fe_5Ni_3)_{\Sigma=8}\,Ag_1S_8$. The Russian and Finnish analyses have a wider range in Fe and Ni content so the ratio of 5Fe to 3Ni from the Bird River analyses is not characteristic of all argentian pentlandites.

Analyses 1,3,5,6,7,9,11,12 and 13 in Table 2 give ratios of total metals to sulphur in excess of the stoichiometric ratio for pentlandite of 9:8. A similar phenomenon is found in analyses of normal pentlandite (Harris & Nickel 1972) and it is uncertain whether this represents real non-stoichiometry or is due to inaccuracies in the analyses.

The assignment of a special position for the one atom of silver in the formula of argentian pentlandite from Bird River is based on the suggestion of Shishkin *et al.* (1971) and the demonstration by Hall & Stewart (1973) that the replacement of Fe and Ni by Ag occurs only in the octahedral (4*b*) lattice sites of pentlandite. The slight excess of Ag in the Bird River and Russian analyses can probably be ascribed to analytical errors. However, the analyses by Vuorelainen *et al.* (1972) demonstrated that argentian pentlandite can contain significantly less than one atom of silver, presumably resulting in Fe and Ni occupying some of the octahedral sites. These data suggest that the general formula for argentian pentlandite should be written as $(Fe,Ni)_{8+x}Ag_{1-x}S_8$. The lower limit of silver content is as yet unknown but we have in progress dry synthesis and hydrothermal recrystallization experiments which should answer this question as well as others on the composition and stability of argentian pentlandite.

X-ray diffraction

Powder *x*-ray diffraction data for the Bird River argentian pentlandite are in Table 3. They were obtained using a 57.3 mm Debye-Scherrer camera with Mn-filtered Fe radiation and were corrected for film shrinkage. All reported argentian pentlandites have similar patterns and, as verified by Hall & Stewart (1973), have the same *f.c.c.* structure as normal pentlandite.

DISCUSSION

Argentian pentlandite has been found in eleven deposits at widely separated localities and has formed under a variety of geological conditions. It is the main source of silver in the investigated nickel sulphide ores and, because it is easily con-

TABLE 2. MICROPROBE ANALYSES OF ARGENTIAN PENTLANDITE

Sample	Elements (wt. %)							(Fe+Ni+Co+Cu):Ag:S
	Fe	Ni	Ag	Co	Cu	S	Total	
1	33.8(2)	21.9(2)	13.7(8)	n.d.	n.d.	31.4(4)	100.8	7.99:1.04:8
2	33.5(1)	21.8(1)	14.0(3)	n.d.	n.d.	31.4(2)	100.7	7.93:1.06:8
3	33.8(2)	22.4(1)	13.9(1)	0.08(2)	0.04(2)	30.6(1)	100.8	8.28:1.08:8
4	33.0(5)	22.7(2)	13.1(4)	---	---	31.3(1)	100.1	8.00:0.99:8
5	33.3	22.1	13.6	---	---	31.0	100.0	8.04:1.04:8
6*	38.24	17.05	13.77	0.07	0.50	31.18	100.81	8.09:1.05:8
7	36.66	19.05	14.77	0.03	0.06	30.70	101.27	8.23:1.16:8
8	30.33	23.83	14.22	0.03	0.10	30.91	99.42	7.89:1.09:8
9	37.0	20.0	11.3	0.1	0.1	31.5	100.0	8.19:0.85:8
10	37.2	20.0	11.1	0.1	0.2	31.8	100.4	8.16:0.83:8
11	37.1	20.4	10.7	0.1	0.4	31.7	100.4	8.25:0.80:8
12	37.9	19.7	10.2	0.1	0.3	31.5	99.7	8.31:0.77:8
13	34.7	22.6	10.3	0.1	0.4	31.4	99.5	8.25:0.78:8

1,2,3: Bird River, Manitoba (this study): Elvira Gasparrini, analyst. n.d. = not determined; s.d. in parentheses.
4 : Bird River, Manitoba (Hall & Stewart 1973).
5 : Average of Bird River analyses normalized to 100%.
6,7,8: Russian occurrences (Shishkin *et al.* 1971).
9-13 : Finnish occurrences (Vuorelainen *et al.* 1972).

*The coefficient for Fe in the formula for sample 44 is misprinted in Table 2 of Shishkin *et al.* (1971). It should read 5.63.

TABLE 3. *X*-RAY POWDER DATA FOR ARGENTIAN PENTLANDITE FROM BIRD RIVER, MANITOBA (a=10.52(1) Å).

hkl	*I*	d_{meas}	d_{calc}
111	1	6.13	6.07
002	1	5.27	5.26
022	1	3.72	3.72
113	10	3.171	3.172
222	5	3.035	3.037
004			2.630
133			2.413
024	1	2.353	2.352
224	1/2	2.150	2.147
115, 333	3	2.025	2.025
044	8	1.861	1.860
135			1.778
244	1/2	1.758	1.753
335	1	1.600	1.604
226			1.586

hkl	*I*	d_{meas}	d_{calc}
444			1.518
117, 155			1.473
137, 355	1	1.370	1.370
008	1/2	1.317	1.315
337			1.285
157, 555	1/2	1.211	1.215
266			1.207
139			1.103
448	2	1.073	1.074
0.0.10			1.052
159, 377	1/2	1.015	1.017

fused with bornite in reflected light, it has probably been overlooked in many other deposits.

Argentian pentlandite contains close to one silver atom per formula unit and, as shown in the following paper by Hall & Stewart (1973), the silver replaces iron and nickel only in octahedral and not tetrahedral sites. Because of this we are of the opinion that it should not be considered as a member of an isomorphous series with normal pentlandite but, rather, it is a distinct mineral species, albeit of variable iron and nickel, and to a lesser degree, silver content.

Acknowledgements

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