

ARGENTIAN PENTLANDITE FROM SOME FINNISH SULFIDE DEPOSITS

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ABSTRACT

Argentian pentlandite is a high-silver variety of pentlandite with an average composition of $Ag_{0.61}Ni_{2.22}Fe_{0.41}S_8$. The mineral has so far been identified as an accessory constituent in seven sulfide deposits in Finland. Of them, four are of the Outokumpu copper ore type, the rest being early magmatic nickel-copper mineralizations or occurrences related to them. Argentian pentlandite is cubic with $a = 10.50 \text{ \AA}$. Its space group is probably the same as that of pentlandite proper, i.e., $O_4 - Fm\bar{3}m$, $Z = 4$, with a calculated density of 4.66 g/cm^3 . The strongest lines of the X-ray powder pattern are 3.170 (10) (113), 2.018 (4) (115,333), 1.858 (10) (044), and 1.072 (3) (448).

The mineral is isotropic and reddish-brown in reflected light. Its microhardness values range from 132 to 154 kg/mm^2 with a 50 g load.

INTRODUCTION

In 1958 while one of us (YV) was carrying out ore microscopic studies on the Outokumpu copper ore, a reddish sulfide mineral was observed in intimate association with chalcopyrite. Since then the mineral has been encountered occasionally in polished sections of the Outokumpu ore. On the basis of precious metal analyses and its mode of occurrence, the mineral was suspected to be a carrier of silver. However, due to its rarity and small grain size, the composition and crystal structure of the mineral remained unknown until 1969-1970 when grains large enough for accurate electron microprobe analysis were detected.

In connection with the microscopic studies on the ores of the Vuonos deposit, discovered in 1965 about 6 kilometers east of Outokumpu, 50 to 200 microns diameter grains of the silver-bearing sulfide mineral were observed. X-ray diffraction and semiquantitative X-ray fluorescence studies showed the mineral to be an isometric sulfide of silver, nickel, and iron and probably a variety of pentlandite.

In addition to the Outokumpu and Vuonos deposits, argentian pentlandite was identified during the first half of 1970 in five other deposits. Of these, two are of the Outokumpu copper ore type (Huhma

and Huhma, 1970) and the others either nickel-copper ores or closely related to them.

OCCURENCE

Argentian pentlandite has so far been encountered in four deposits of the Outokumpu type, *i.e.*, in Outokumpu (Long. 29°0'E, Lat. 62°44'N), Vuonos (Long 29°03'E, Lat. 62°45'N), Miihkali (Long. 29°03'E, Lat. 62°57'N), and Hietajärvi (Long. 29°06'E, Lat. 62°16'N), all of which are in East Finland. The mineral occurs as exsolution bodies in chalcopyrite, either in the contacts of the orebodies or in the mineralized zones parallel to them. In addition to chalcopyrite, the major paragenetic minerals are pyrrhotite and cobalt pentlandite or pentlandite with a variable cobalt tenor. Also pyrite, siegenite, sphalerite, stannite, mackinawite, and cobaltite-gersdorffite belong to the association as well as occasional melonite. The oxides are eskolaite and zincian chromite with a zinc percentage of up to 10.8. Normal pentlandite is often observed in association with argentian pentlandite either as inclusions or exsolution bodies.

Microscopic studies suggest that the sulfide minerals crystallized in the following order:

- pyrite
- siegenite and cobaltite-gersdorffite
- pyrrhotite and pentlandite
- chalcopyrite, sphalerite and stannite
- argentian pentlandite
- mackinawite

In the Outokumpu, Vuonos, and Miihkali deposits the average silver content of the ore is approximately constant, 9 ppm, most of which is apparently incorporated in argentian pentlandite.

In the Hitura nickel deposit in western Finland (Long. 25°03'E, Lat. 63°51'N), which has ultramafic rocks as host (Papunen, 1970), argentian pentlandite has been encountered in copper-rich apophyses in the mica gneiss wall rock of the deposit. The paragenetic minerals are chalcopyrite, pyrrhotite, pentlandite, mackinawite, and rare cubanite.

The mineral has also been identified in a nickel ore at Ranua (Long. 26°07'E, Lat. 66°06'N) in North Finland. The ore body, which has a gabbroic host rock, is cut in its lower part by a sulfide vein of extraneous origin containing abundant sphalerite, galena, chalcopyrite, and pyrrhotite. Mixing of the two sulfide assemblages in the vein obviously gave rise to the formation of argentian pentlandite, which occurs there

not only in chalcopyrite but also in association with sphalerite and galena.

In a nickel-copper mineralization in a noritic body at Kerimäki (Long. 28°59'E, Lat. 61°58'N), SE-Finland, argentian pentlandite occurs as inclusions in chalcopyrite in the copper-rich contacts of the mineralized rock with its host rock. The associated minerals are pentlandite and pyrrhotite.

CHEMISTRY

Argentian pentlandite grains from four localities, *i.e.*, Outokumpu, Vuonos, Miikkali, and Kerimäki, were large enough to warrant reliable electron microprobe analyses. The analytical data obtained with a Geoscan microprobe are listed in Table 1. As standards, the following compounds were used: pure metals for nickel, cobalt, silver, and copper; troilite for iron; and chalcopyrite for sulfur. In the Hitura, Ranua, and Hietajärvi deposits, the grains were too small for accurate analysis. Consequently, the analytical data pertinent to them are not included in Table 1.

The chemical composition of the mineral suggests that it is a derivative of pentlandite in which mainly nickel but also to some extent iron have been replaced by silver. The silver percentage appears to be fairly constant with only a slight fluctuation from 10.2 to 11.3 percent Ag. The data available at present are not comprehensive enough for far-reaching conclusions. However, it seems likely that abundance of silver in the argentian pentlandite of the copper ores of the Outokumpu type is somewhat lower than that of the nickel-copper ores of early magmatic type.

A remarkable feature of the argentian pentlandites in the Outokumpu type of copper deposits is their low cobalt content, *i.e.*, 0.1 percent Co. This is even more surprising if it is remembered that the

Table 1. Electron microprobe analyses of argentian pentlandite from four Finnish sulfide deposits. 25 kV; 0.1 A, LiF and mica crystals.

Element	Kerimäki (%)	Kerimäki (%)	Miikkali (%)	Outokumpu (%)	Vuonos (%)	Average (%)	SD (%)	Range (%)
Ag	11.3	11.1	10.7	10.2	10.3	10.72	0.48	10.2-11.3
Ni	20.0	20.0	20.4	19.7	22.6	20.54	1.18	19.7-22.6
Fe	37.0	37.2	37.1	37.9	34.7	36.78	1.22	34.7-37.9
Co	0.1	0.1	0.1	0.1	0.1	0.10	-	0.1-0.1
Cu	0.1	0.2	0.4	0.3	0.4	0.28	0.13	0.1-0.4
S	31.5	31.8	31.7	31.5	31.4	31.58	0.16	31.4-31.8
Total	100.0	100.4	100.4	99.7	99.5	100.00		

composition of pentlandites in these deposits ranges from the pure nickel-iron end member, which has only 0.02 percent Co, to the cobalt pentlandite proper. In the latter, the abundance of cobalt has been observed to reach values as high as 49 percent (Kouvo *et al.*, 1959). In general, however, the abundance of cobalt in these pentlandites fluctuates between 10 and 35 percent. The lack of cobalt in argentic pentlandite may be due to the fact that the mineral was

Table 2. X-ray powder diffraction data for argentic pentlandite, pentlandite and cobalt pentlandite.

Argentic pentlandite a = 10.50 Å				Pentlandite a = 10.07 Å			Co-pentlandite a = 9.973 Å		
hkl	I	d (meas)	d (calc)	hkl	I	d (calc)	hkl	I	d (calc)
111	2	6.06	6.062	111	2	5.81	111	6	5.76
002	2	5.25	5.250	002	$\frac{1}{2}$	5.03	002	2	4.986
022	2	3.71	3.712	022	1	3.56	022	2	3.527
113	10	3.170	3.167	113	6	3.04	113	10	3.007
222	2	3.024	3.031	222	2	2.91	222	6	2.879
004	$\frac{1}{2}$	2.610	2.625	004	1	2.52	004	$\frac{1}{2}$	2.493
133	1	2.41	2.409	133	3	2.31	133	5	2.288
024	1	2.350	2.348				024	$\frac{1}{2}$	2.230
224	2	2.150	2.143						
115,333	4	2.018	2.021	115,333	4	1.938	115,333	8	1.919
044	10	1.858	1.856	044	10	1.781	044	10	1.763
				135	$\frac{1}{2}$	1.702	135	2	1.686
335	2	1.602	1.601	335	1	1.536	335	4	1.521
226	1	1.584	1.583	226	1	1.518	226	4	1.503
				444	$\frac{1}{2}$	1.454			
				117,155	$\frac{1}{2}$	1.410			
137,355	2	1.369	1.367	137,355	3	1.311	137,355	5	1.298
008	1	1.315	1.313	008	3	1.259	008	5	1.246
				337	$\frac{1}{2}$	1.230			
157,555	$\frac{1}{2}$	1.212	1.212	157,555	3	1.162	157,555	4	1.152
				266	$\frac{1}{2}$	1.155			
				139	2	1.056	139	4	1.045
448	3	1.072	1.072	448	5	1.028	448	6	1.018

Argentic pentlandite (Table 1. Vuonos)

Pentlandite (Berry and Thompson, 1962)

Cobalt pentlandite (Kouvo *et al.*, 1959)

obviously exsolved from chalcopyrite which seems to be incapable of taking appreciable amounts of cobalt in solid solution.

The average composition in Table 1 gives $(\text{Ag}, \text{Ni}, \text{Fe})_{9.05}\text{S}_8$ as a formula for the mineral. The slight excess of metals over the ideal 9:8 ratio may be due to analytical errors but could also be real in a manner analogous to that reported by Papunen (1970) for pentlandites. When cobalt and copper are added to iron, $\text{Ag}_{0.81}\text{Ni}_{2.84}\text{Fe}_{5.41}\text{S}_8$ is obtained as the formula for the average argentinean pentlandite. If idealized, the content of a unit cell may be approximated by $\text{Ag}_3\text{Ni}_{11}\text{Fe}_{22}\text{S}_{32}$.

CRYSTAL GEOMETRY

The powder pattern of argentinean pentlandite was recorded by the camera technique using a 114.6 mm camera and Ni-filtered $\text{CuK}\alpha$ -radiation (1.542 Å). The diffraction data are compiled in Table 2, together with the corresponding data for pentlandite and cobalt pentlandite. On account of the replacement of nickel and iron by silver, the length of the unit cell edge of argentinean pentlandite has somewhat increased compared with that of the normal pentlandite (10.50 Å as against 10.07 Å). Otherwise, apart from some differences in the intensities, the powder data for the minerals listed in Table 2 bear considerable resemblance to each other.

The precession photographs of argentinean pentlandite were recorded with $\text{MoK}\alpha$ -radiation. The investigated crystal fragment, with a diameter about 0.2 mm, was taken from a polished section. The two a -axes were used as precession axes. Zero, first, and second layers were recorded in one direction, zero and first layers in the other. The mineral has a face-centered cubic structure and its space group is one of the following: $Fm\bar{3}m$, $F\bar{4}3m$, or $F432$. Thus the mineral may have the same space group as normal pentlandite, *i.e.*, $O_4 - Fm\bar{3}m$ with $Z = 4$. The cell edge was measured as 10.495 (± 0.008) Å from the precession photograph calibrated by a silicon standard. The volume of the unit cell is $V_0 = 1157.6 \text{ \AA}^3$.

PHYSICAL AND OPTICAL PROPERTIES

Under a binocular microscope the mineral is bronze-brown in color. Euhedral crystals, with well-developed (111) faces, have been observed as well as a cleavage parallel to (111).

Argentinean pentlandite is isotropic and reddish-brown in reflected light. The spectral reflectance was measured with a Leitz MPV microscope photometer on various parts of a rather large crystal both in air and in oil using a SiC standard (Nr. 87 Physical Laboratory). The values on four wavelengths are given in Table 3.

Table 3. Reflectances for argentican pentlandite, in percent.

Wavelength nm	In air	In oil	Ref. ind. of oil
470	26.3	23.7	1.5247
546	37.4	23.5	1.5185
589	33.0	26.5	1.5160
650	39.8	25.0	1.5133

Values are averages of five measurements

The microindentation hardness, measured with a Leitz Durimeter ranges from 132 to 154 kg/mm² for a 50 g weight. Accordingly, the mean Vickers hardness and reflectance of argentican pentlandite are fairly close to those of naumannite.

Etch reactions: HNO₃ stains brown, KCN produces a very weak brown staining, practically negative, HCl, HgCl₂, FeCl₃, KOH, and H₂O₂ all negative. The polishing hardness of argentican pentlandite is *B* and the mineral takes an easy polish. Under the microscope it resembles and may easily be mistaken for bornite, especially if it has been exposed to the air for several days, during which time argentican pentlandite acquires a brownish tarnish. In a freshly polished section the mineral has a slightly higher reflectance than bornite.

The rarity of the mineral and its small grains size have prevented the direct determination of its density.

The calculated value, based on the average chemical composition presented in Table 1 and the unit cell edge of 10.50Å, is 4.66 g/cm³.

ALTERATION

In supergene environments the mineral alters readily into ill-defined products. The initial stages of alteration develop along fractures and grain boundaries (Figs. 1 and 2). The X-ray scanning images and electron microprobe profiles, run across the alteration products, suggest that in the process silver and iron are depleted from argentican pentlandite. Nickel remains in situ and apparently produces cubic nickel sulfide. Silver and iron are expelled almost completely, the former being enriched in the boundary zones between unaltered argentican pentlandite and the alteration products, where its abundance may reach values twice as high as those encountered in fresh minerals. Most of the iron migrates out of the system.

DISCUSSION

Argentian pentlandite has been found as a minor constituent in several sulfide deposits. It seems to be the main carrier of silver in the Outokumpu-type deposits as well as in the copper-nickel deposits associated with ultramafic and mafic igneous rocks. Silver is evidently enriched like zinc in the copper sulfide accumulations. Argentian pentlandite therefore belongs to the chalcopyrite-rich mineral assemblage which invades the contacts or wall rocks of the main sulfide mineralization as apophyses, veins, and stringers.

An argentiferous pentlandite from the lower levels of the Froid

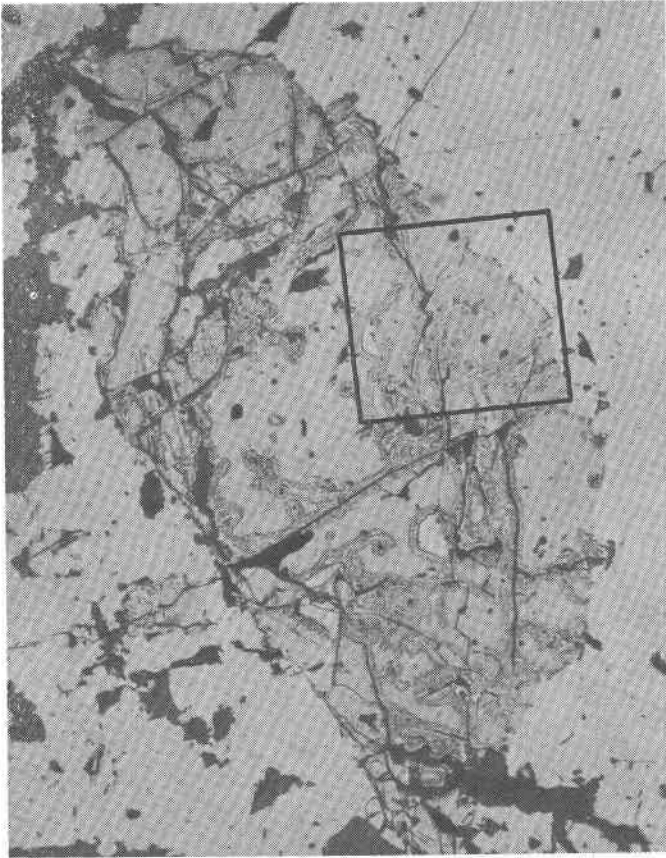
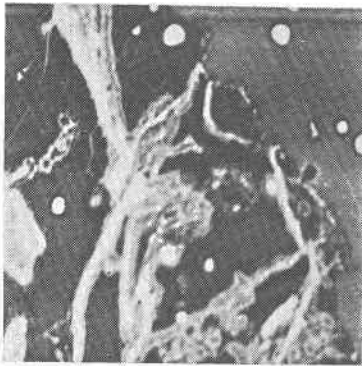


FIG. 1. A grain of argentian pentlandite embedded in chalcopyrite. The sample is from the Kerimäki nickel-copper mineralization close to the surface. The supergene alterations are clearly visible. The 165 x 180 micron rectangle marked in the figure indicates the area and location of the scanning images reproduced in Fig. 2.



S.C. IMAGE

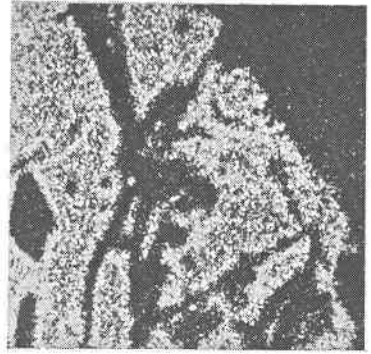
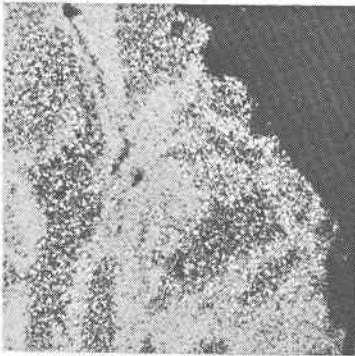
Ag L_{α} Ni K_{α} Fe K_{α}

FIG. 2. Part of the area of Fig. 1 showing specimen current and element fluorescent X-ray images. The incipient alteration proceeds along fractures in argentic pentlandite giving rise to secondary minerals of which nickel sulfide is perhaps the most characteristic.

mine, Sudbury, has been reported by Michener (Hawley, 1962). According to him, it occurred in oriented intergrowths with normal pentlandite and also as small grains, less than a millimetre in diameter, associated with galena and normal pentlandite. An approximate chemical analysis indicated that the mineral contained 3.8 percent silver. This is about one third of the percentage encountered in the argentic pentlandites described in this paper. The fox-red color of the Frood silver-bearing pentlandite well matches the color of the argentic pentlandite. However, the length of the unit cell edge is clearly shorter for the former than the latter (9.55 Å as against 10.50 Å). If

the value reported for the unit cell edge of the Froid silver-bearing pentlandite is correct, then the mineral can hardly be the same as that identified in Finland.

On the basis of Michener's observations, Knop *et al.* (1965) studied the existence of argentine pentlandite by preparing samples with the composition $\text{Fe}_4\text{Ni}_4\text{AgS}_8$ by dry synthesis in vacuo. The result was a π phase with $a = 10.119 \text{ \AA}$ and a dominating cubic face-centered phase with $a = 10.499 \text{ \AA}$ whose composition remained unknown. Compared with the data of the present study, the prevalent phase of the above-mentioned synthesis was probably a silver-bearing π phase thus obviously corresponding the mineral described here.

After the completion of the present paper Professor V. A. Frank-Kamenetskii of Leningrad University drew the attention of the authors to the fact that argentine pentlandite has recently also been encountered in Talnakh, Siberia (Shishkin, Mitnikov, *et al.*, 1971). Consequently, it must be concluded that this variety was simultaneously discovered in Finland and the USSR.

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