

## SYNTHESIS, STABILITY, AND PHASE RELATIONS OF ARGENTIAN PENTLANDITE IN THE SYSTEM Ag-Fe-Ni-S

Z. L. MANDZIUK AND S. D. SCOTT

Department of Geology, University of Toronto, Toronto, Ontario M5S 1A1

### ABSTRACT

Argentian pentlandite is a stable phase in the Ag-Fe-Ni-S system below 455°C. At 400°C it has a solid-solution field from Fe/Ni=1.12 to 3.21 (atomic ratio) compared to 0.45 to 1.95 for normal pentlandite at the same temperature. Silver solubility at 400°C ranges from 4.20 to 5.88 at. %. The latter corresponds to a crystallographic limit of one atom of Ag per formula unit due to Ag saturation of octahedral sites. At 300°C the composition limits are Fe/Ni=1.07 to 4.10 and Ag=3.80 to 5.88 at. %. The mineral coexists with Ag or Ag<sub>2</sub>S below ~358°C and with Ag at higher temperatures.

Crystal-chemical models of Rajamani & Prewitt (1973) and Nickel (1970) predict the stoichiometric composition of argentian pentlandite saturated with one atom of Ag per formula unit to be (Fe<sub>2</sub>Ni<sub>3</sub>)Ag<sub>1</sub>S<sub>8</sub>. This corresponds to the most stable composition as determined by experiment and to the average composition found in nature. Ag-saturated compositions with Fe/Ni ratios other than 5/3 exhibit metal/sulfur ratios other than 9/8 by cation addition-omission solid solution.

Associations and textures in magmatic sulfide ores suggest that most argentian pentlandite was exsolved from late-crystallizing massive chalcopyrite. These Cu-rich zones probably were residual sulfide melts into which Ag was fractionated.

### SOMMAIRE

La pentlandite argentifère est une phase du système Ag-Fe-Ni-S qui est stable en-dessous de 455°C. A 400°C, elle possède un domaine de solution solide s'étendant de Fe/Ni=1.12 à 3.21 (proportion atomique) alors qu'il s'étend de 0.45 à 1.95 pour la pentlandite normale à la même température. La solubilité de l'argent à 400°C s'étend de 4.20 à 5.88% atomique. Cette dernière correspond à une limite cristallochimique d'un atome d'Ag par formule correspondant à l'occupation complète des sites octaédriques par Ag. A 300°C, les limites de composition sont Fe/Ni=1.07 à 4.10 et Ag=3.80 à 5.88% atomique. Le minéral coexiste avec Ag ou Ag<sub>2</sub>S en-dessous de ~358°C et avec Ag seulement aux températures plus élevées.

Les modèles cristallochimiques de Rajamani & Prewitt (1973) et de Nickel (1970) prévoient que la composition stoechiométrique de la pentlandite argentifère saturée d'Ag est (Fe<sub>2</sub>Ni<sub>3</sub>)Ag<sub>1</sub>S<sub>8</sub>. Ceci correspond à la composition la plus stable déterminée expérimentalement et s'accorde avec la com-

position moyenne observée dans la nature. Les pentlandites saturées d'Ag étayant une proportion Fe/Ni différant de 5/3 présentent des proportions métal/soufre différant de 9/8 en raison d'une solution solide par addition ou omission de cation.

Les associations et les textures des minerais sulfurés magmatiques suggèrent que la plus grande partie de la pentlandite argentifère provient de chalcopyrites massives dont la cristallisation s'est faite tardivement. Ces zones riches en Cu étaient probablement des sulfures liquides résiduels dans lesquelles Ag s'est concentré.

(Traduit par la Rédaction)

### INTRODUCTION

Argentian pentlandite, (Fe,Ni)<sub>8+z</sub>Ag<sub>1-z</sub>S<sub>8</sub>, is an important silver-bearing sulfide mineral which has been recognized in nickel ores of various types from Finland (Vuorelainen *et al.* 1972), the Soviet Union (Shishkin *et al.* 1971) and Canada (Scott & Gasparrini 1973; Karpenkov *et al.* 1973). Published descriptions of the mineral and measurements of its spectral reflectances, hardness and unit-cell parameters are consistently similar. Argentian pentlandite has a cinnamon, foxy-red, bronze or reddish brown color in reflected light with a very similar appearance to freshly polished bornite, but slowly tarnishes in air to a slightly darker color.

The mineral was discovered by Michener (1940), who described an "argentiferous pentlandite" as intergrowths with normal pentlandite in the Froid mine, Sudbury. Unfortunately, Michener erred in his measurement of the cell edge of this mineral so his data do not agree with more recent values and his contribution was overlooked. We have re-analyzed Michener's Debye-Scherrer X-ray powder pattern and have ascertained a pentlandite structure with  $a_0=10.47\text{\AA}$  which corresponds with current determinations. Knop *et al.* (1965) were probably the first to synthesize the mineral; they annealed under vacuum a composition 4Fe:4Ni:1Ag:8S which yielded normal pentlandite ( $a_0=10.119\text{\AA}$ ) and a greater portion of an unidentified *fcc* phase with  $a_0=10.499\text{\AA}$  which we suspect was argentian pentlandite.

TABLE 1. MICROPROBE ANALYSES OF ARGENTIAN PENTLANDITE  
Z.L. Mandziuk, Analyst

Sample	Composition, wt%				Total	Atomic ratio*		
	Fe	Ni	Ag	S		Fe : Ni	Ag : S	: S
1	31.9(3)*	23.7(4)	13.2(6)	31.5(1)	100.3	4.66	3.28	.99 8
2	35.1(3)	21.1(4)	12.8(6)	31.5(2)	100.5	5.11	2.92	.97 8
3	37.9(6)	17.9(1)	13.2(2)	31.1(3)	100.1	5.59	2.52	1.01 8
4	39.3(2)	16.1(1)	14.1(9)	30.9(1)	100.4	5.84	2.27	1.09 8
5	37.0(4)	18.1(2)	14.1(2)	31.1(4)	100.3	5.47	2.55	1.08 8
6	38.9(5)	16.6(5)	13.9(9)	31.1(3)	100.5	5.74	2.32	1.06 8

1. Bird River, Manitoba.

2. Burnt Basin, B.C. Sample courtesy A.E. Johnson.

3. Talnakh, U.S.S.R. Sample courtesy A.D. Genkin.

4. Outokumpu, Finland. Sample courtesy H. Papunen.

5,6. Kerimäki, Finland. Samples courtesy H. Papunen.

\* parenthesized figure represents the sample standard deviation in terms of least units cited for the value to their immediate left, i.e. 31.9(3) indicates a standard deviation of 0.3.

Published analyses to 1972 of natural argentine pentlandites are summarized in Scott & Gasparrini (1973). In addition, Karpenkov *et al.* (1973), and Cabri & Laflamme (1976) have provided analyses from Sudbury. Table 1 gives six new analyses, including three from Finnish occurrences previously investigated by Vourelainen *et al.* (1972). Scott & Gasparrini (1973) found that argentine pentlandite from Bird River, Manitoba approximated  $(\text{Fe}_8\text{Ni}_8)\text{Ag}_5\text{S}_8$ . Although Soviet and Finnish analyses give wider ranges in Fe/Ni ratios and exhibit slightly different silver contents, this composition lies close to the mean for all natural analyses. Natural argentine pentlandites exhibit a range in Fe/Ni atomic ratio of 1.34 to 2.57 and an M/S atomic ratio\* which ranges from 1.096 to 1.173 as opposed to the ideal  $M_8S_8$  stoichiometric ratio of 1.125 for pentlandite.

The single atom of silver has been assigned a special position in the formula pursuant to the suggestion of Shishkin *et al.* (1971) and the demonstration by Hall & Stewart (1973) that Ag replaces Fe and Ni only in the octahedral 4b sites of the pentlandite structure.† Analyses of Finnish samples by Vourelainen *et al.* (1972) have been taken as evidence that the mineral can occur with slightly less than one (0.77 to 0.85) atom of silver in the formula, resulting in Fe and Ni occupancy of some octahedral sites. On this basis Scott & Gasparrini proposed the general formula  $(\text{Fe,Ni})_{8+x}\text{Ag}_{1-x}\text{S}_8$  for argentine pentlandite and considered the mineral to be a distinct species rather than a member of an isomorphous series with normal pentlandite.

The present study was undertaken to synthesize argentine pentlandite, to determine its phase equilibria in the quaternary system Ag-Fe-Ni-S and to comment on the geological occurrence and significance of the mineral assemblages encountered. Phase relations involving argentine

pentlandite and its solubility limits have been examined mainly at 400° and 300°C by dry synthesis, but runs at other temperatures and DTA results are also presented. As well, recent investigations of the crystal chemistry, stability and solid-solution limits of natural and synthetic pentlandite phases (Knop *et al.* 1965; Rajamani & Prewitt 1973) are augmented by similar data presented here on argentine pentlandite. An abstract of our results has been published (Mandziuk & Scott 1975) and further details are in Mandziuk (1975).

## EXPERIMENTAL PROCEDURES

Our research mainly involved determination of phase relationships in that part of the Ag-Fe-Ni-S system in which argentine pentlandite occurs as a stable member of an equilibrium assemblage. Bulk compositions within and surrounding the stability field of argentine pentlandite were prepared by combination of the elements Ag, Fe, Ni, and S or by a two-step process similar to that described by Craig (1971): (1) stocks of monosulfide solid solution (*Mss*) with variable Fe/Ni ratios were prepared by direct reaction of the elements Fe, Ni, and S at 800°C, with one regrinding under acetone, followed by annealing for one week at 800°C; (2) the finely ground *Mss* was reacted at the temperature of investigation with the appropriate amount of silver. All experimental runs were prepared from starting materials of 99.999% spectral purity.

Experimental charges were reacted in evacuated silica-glass tubes in the manner described by Kullerud (1971). Temperatures were controlled within  $\pm 3^\circ\text{C}$  or better as measured on calibrated chromel-alumel thermocouples. Because of sluggish reaction rates at the relatively low temperatures of these experiments, it was necessary to modify standard annealing techniques (see also Ripley 1972, p. 35-39; Misra & Fleet 1973a) by partly melting all starting compositions at 850°C for 3 days. The charges were then quenched before annealing (without regrinding) at subsolidus temperatures. This method promoted solid-state reaction, homogenization of phases, and coarsening of grains through the achievement of more pervasive and intimate diffusion of elements in the presence of a melt. After annealing 3 to 20 weeks, charges were rapidly quenched by immersion in cold water.

### Differential thermal analysis

Ten DTA experiments designed to test the thermal stability of argentine pentlandite in the presence of vapor were conducted on a Mettler

\*M is the sum of all metals in the compound.

†See note added in proof at end of text.

Recording Vacuum Thermoanalyzer at the Department of Mineralogy and Geology of the Royal Ontario Museum. Various compositions close to or within the argentine pentlandite field were reacted at 350°C and then heated in evacuated silica tubes in the DTA apparatus at a constant rate of 8°C/min from room temperature to approximately 700°C.  $Al_2O_3$  was used as an inert standard and thermal events were calibrated against the  $\alpha$ - $\beta$  inversion of quartz (573°C). Endothermic peaks corresponding to the breakdown of argentine pentlandite near 450°C failed to reappear as exothermic deflections during cooling maintained at rates of 8 to 1.5°C/min, because the solid-state renucleation of argentine pentlandite is very sluggish. As a result, the breakdown products of argentine pentlandite ( $Mss$ +pentlandite+Ag), as determined by reversed appearance-of-phase experiments, were preserved metastably.

#### ANALYSIS OF EXPERIMENTAL PRODUCTS

Products of experimental runs were examined by reflected light microscopy, X-ray powder dif-

fraction and electron microprobe analysis. Recognition of phases in polished grain mounts under reflected light was uncomplicated. Freshly polished synthetic argentine pentlandite is indistinguishable from the natural mineral and exhibits similar tarnishing in air to darker shades in a few months. Tarnished specimens often develop reticulate or crystallographically-controlled octahedral patterns of oxidation which can be removed by light polishing.

#### X-ray diffraction

Routine identification of phases was made with  $FeK\alpha$  radiation on a Philips X-ray diffractometer equipped with a graphite single-crystal monochromator. Cell edges were calculated from the (113) spacings of several argentine pentlandites. The  $d(113)$  was measured against an internal standard of sodium chloride previously calibrated against metallic Si ( $a_0=5.4306\text{\AA}$ ; Kissin 1974, p. 32). At least four sets of two upward and two downward scans of the sodium chloride (200) [at  $58.118^\circ 2\theta$  for  $FeK\alpha$ ] and argentine pentlandite (113) X-ray reflections were obtained.

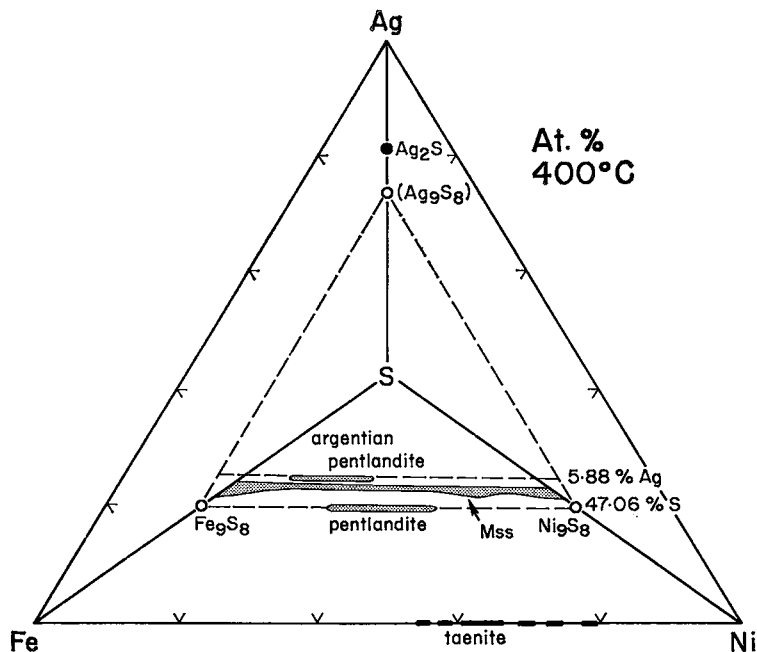


FIG. 1. Schematic representation of solid-solution limits and compositions of phases encountered in the lower central part of the system Ag-Fe-Ni-S as they appear at 400°C. The dashed line outlines a triangular plane at 47.06 at. % S of the hypothetical  $M_9S_8$  components  $Ag_9S_8$ ,  $Fe_9S_8$  and  $Ni_9S_8$ . Pentlandite compositions straddle the bottom of this plane on the Fe-Ni-S base. The solid-solution field of argentine pentlandite occurs mainly within the  $M_9S_8$  plane at a height of 4.20-5.88 at. % Ag above the Fe-Ni-S base. The plane Ag-Fe-Ni forms the front face of the tetrahedron.

### Electron microprobe

Analyses were performed on an ARL-EMX microprobe. Operating conditions were as follows: electron beam potential 25 kV; beam current  $5 \times 10^{-7}$  amp.; specimen current  $3 \times 10^{-8}$  amp.; counting time 10 seconds. Detector crystals were LiF for  $\text{FeK}\alpha$  and  $\text{NiK}\alpha$  and ADP for  $\text{AgL}\alpha$  and  $\text{SK}\alpha$ . Standards were synthetic *Mss* containing (wt. %) 41.75 Fe, 20.00 Ni and 38.25 S for Fe, Ni and S, and pure Ag metal. Raw microprobe data were reduced by EMPADR VII (Rucklidge & Gasparrini 1969).

In the analyses of synthetic samples, sulfur was not analyzed directly but was derived as the difference between the sum total of analyzed metals and 100% (similar to oxygen determination in microprobe analyses of silicate minerals). For matrix corrections, an approximate sulfur value was computed for each analysis and entered into the EMPADR routine. This value was then discarded and sulfur was determined by difference. The practice was adopted in order to avoid the typical low precision of microprobe analyses for sulfur when standards closely approximating the compositions of the unknowns are not available (e.g. see Czamanske 1974) and to facilitate rapid and precise operation on a three-spectrometer microprobe. The technique

was checked by first conducting total analyses for Fe, Ni, Ag and S on several homogeneous synthetic argentian pentlandites of different compositions. These same samples were subsequently re-analyzed for metals only and sulfur was determined by difference. When results of the two sets of analyses were compared, the differences in elemental concentrations between the two methods were consistently less than 0.1 wt. %.

Sulfur in all natural samples was determined directly. Values for all elements in Table 1 are averages of 5 separate spot analyses per sample, each spot counted 6 times.

### EXPERIMENTAL RESULTS

We have examined phase relations and solubility limits in the lower central part of the Ag-Fe-Ni-S system from 92 separate experiments principally near 600°, 400° and 300°C, and with a few runs at intervening temperatures and at 650°C. The phases encountered are shown schematically in Figure 1; argentian pentlandite becomes stable below approximately 455°C. Most of our efforts were expended on the 400°C isotherm where all of the univariant equilibria were reversed. At 300°C, sluggish reaction rates pro-

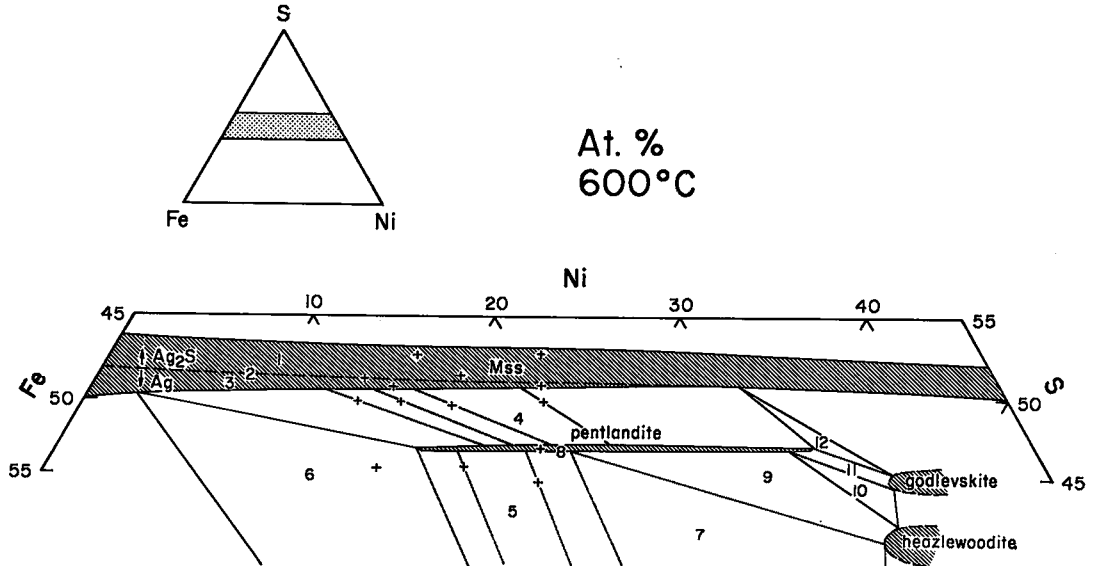


FIG. 2. Projection of phase relations from Ag onto the central part of the ternary Fe-Ni-S base in the system Ag-Fe-Ni-S at 600°C. The dashed line traces the position of the Ag/Ag<sub>2</sub>S buffer across the *Mss* field. Crosses locate bulk compositions of experimental runs. Numbers identify equilibrium assemblages given below. The right of the diagram is from Misra & Fleet (1973a). Vapor coexists with all phases. (1) Ag<sub>2</sub>S+*Mss*; (2) Ag<sub>2</sub>S+Ag+*Mss*; (3) Ag+*Mss*; (4) Ag+*Mss*+pentlandite; (5) Ag+pentlandite+taenite; (6) Ag+*Mss*+pentlandite+taenite; (7) Ag+pentlandite+taenite+heazlewoodite; (8) Ag+pentlandite; (9) Ag+pentlandite+heazlewoodite; (10) Ag+pentlandite+heazlewoodite+godlevskite; (11) Ag+pentlandite+godlevskite; (12) Ag?+*Mss*+pentlandite+godlevskite.

hibited many reversals and produced metastable relationships.

Compositions of coexisting phases produced at 400°C and 300°C are given in Table 2. Results of appearance-of-phase experiments at these two temperatures for which there are no microprobe analyses, as well as all results from other temperatures, may be obtained at nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

600° isotherm

Compositions of some of the coexisting phases at 600°C are presented in Figure 2. The solubility of Ag in the phases encountered (Mss, pentlandite, taenite) is below microprobe detection limits (i.e. less than ~0.05 wt. %). Silver in quantities of up to 14 at. % did not alter the solid-solution limits or tie-line relationships within the Fe-Ni-S ternary at 600°C. Consequently, Figure 2, a projection from Ag onto the Fe-Ni-S face of the Ag-Fe-Ni-S system, depicts known

TABLE 2. COMPOSITIONS OF COEXISTING PHASES AT 400°C AND 300°C

		Composition, wt.% (standard deviation in parenthesis)													
		Argentian Pentlandite				Mss			Pentlandite			Taenite			
Point in Fig.5	Assemblage* (including apn + V)	Ag	Fe	Ni	S	Fe	Ni	S	Fe	Ni	S	Fe	Ni		
Temperature = 400°C (Fig.5a)															
1	Mss+pn	10.5(4)	34.3(9)	23.0(1)	32.2	45.8(5)	17.1(1)	37.2	39.9(3)	26.1(7)	34.0	-	-		
2	Mss+pn	11.1(9)	29.4(2)	27.6(7)	31.9	31.5(1)	31.3(5)	37.2	30.5(1)	36.2(5)	33.3	-	-		
3	Mss+pn	9.6(2)	39.8(4)	17.9(7)	32.7	38.0(5)	24.4(1)	37.6	35.9(1)	30.8(2)	33.3	-	-		
4	Ag+Mss+pn	13.0(4)	29.4(3)	26.3(7)	31.3	30.0(3)	33.0(3)	37.1	29.7(5)	36.9(7)	33.5	-	-		
5	Ag+Mss+pn	12.8(9)	29.0(3)	26.5(1)	31.7	30.1(2)	32.8(7)	37.0	29.4(7)	37.0(3)	33.5	-	-		
6	Mss+pn	11.1(6)	30.0(4)	27.2(2)	31.7	32.7(6)	30.2(1)	37.1	30.9(3)	36.0(4)	33.1	-	-		
7	Ag+Mss+pn	13.2(8)	29.3(1)	26.2(5)	31.2	30.0(4)	32.9(5)	37.1	29.7(4)	37.1(4)	33.2	-	-		
8		13.0(9)	32.7(6)	23.0(5)	31.3	-	-	-	-	-	-	-	-		
9		12.8(7)	37.5(5)	18.0(2)	31.7	-	-	-	-	-	-	-	-		
10	Ag+pn	11.9(9)	35.6(8)	20.7(6)	31.7	-	-	-	38.7(2)	27.6(2)	33.7	-	-		
11	Mss+pn	9.9(9)	42.7(7)	14.9(5)	32.6	47.5(4)	15.3(5)	37.2	40.8(8)	25.7(3)	33.5	-	-		
12	Mss+pn	9.6(4)	34.0(3)	23.9(7)	32.5	38.4(3)	24.3(5)	37.3	35.8(2)	30.9(3)	33.2	-	-		
13		13.0(8)	34.1(7)	21.3(4)	31.5	-	-	-	-	-	-	-	-		
14		13.0(8)	40.9(6)	14.5(1)	31.5	-	-	-	-	-	-	-	-		
15	Mss+pn+tn	12.0(8)	42.5(5)	13.9(8)	31.7	61.0(5)	2.4(3)	36.6	43.3(3)	23.4(6)	33.3	31.7(5)	62.9(4)		
16		13.2(8)	37.5(6)	17.9(4)	31.4	-	-	-	-	-	-	-	-		
17	Ag+tn	10.9(7)	40.6(7)	16.3(4)	32.1	-	-	-	-	-	-	34.4(4)	65.6(6)		
18	Ag+pn+tn	11.3(8)	35.1(4)	22.0(2)	31.6	-	-	-	38.7(5)	28.7(3)	32.7	32.9(4)	67.1(4)		
19		10.4(8)	35.1(6)	22.8(3)	31.6	-	-	-	-	-	-	-	-		
Temperature = 300°C (Fig.5b)															
20	Ag <sub>2</sub> S+Mss+pn	12.1(3)	28.3(6)	28.0(4)	31.5	29.9(3)	32.7(2)	37.4	31.2(6)	35.5(2)	33.2	-	-		
21	Ag+Mss	13.2(8)	34.1(7)	21.4(4)	31.3	40.3(4)	22.4(3)	37.4	-	-	-	-	-		
22	Ag+Mss	13.0(4)	41.1(3)	14.4(5)	31.5	48.6(5)	14.3(3)	37.1	-	-	-	-	-		
23	Mss+pn+tn	11.8(4)	44.8(5)	11.5(5)	32.0	61.6(5)	1.7(3)	36.6	44.5(2)	22.2(3)	33.3	37.0(4)	63.0(6)		
24	Mss+Ag <sub>2</sub> S	13.2(7)	30.6(5)	25.0(2)	31.2	35.8(3)	26.7(1)	37.5	-	-	-	-	-		
25		13.0(2)	41.1(3)	14.4(3)	31.5	-	-	-	-	-	-	-	-		
26		8.7(6)	37.9(6)	21.3(1)	32.1	-	-	-	-	-	-	-	-		
27		8.7(5)	37.1(4)	22.2(3)	32.0	-	-	-	-	-	-	-	-		
28		10.6(9)	35.9(1)	22.3(1)	31.2	-	-	-	-	-	-	-	-		
29		9.2(4)	40.9(6)	17.3(3)	32.7	-	-	-	-	-	-	-	-		
30		11.7(8)	38.1(1)	18.6(2)	31.6	-	-	-	-	-	-	-	-		
31		8.7(6)	34.4(2)	24.9(5)	32.0	-	-	-	-	-	-	-	-		
32		9.1(4)	32.3(1)	26.6(4)	32.0	-	-	-	-	-	-	-	-		
33	Ag+Mss+Ag <sub>2</sub> S	13.2(9)	33.0(4)	22.5(5)	31.3	38.6(3)	24.0(2)	37.4	-	-	-	-	-		
34	Ag <sub>2</sub> S+Mss	13.2(8)	29.7(2)	25.8(3)	31.3	34.8(1)	27.7(4)	37.5	-	-	-	-	-		
35	Ag+pn	13.2(8)	36.3(5)	19.2(3)	31.3	-	-	-	38.8(4)	27.8(2)	33.5	-	-		

\*Abbreviations: apn - argentian pentlandite; Mss - monosulfide solid solution; pn - pentlandite; tn - taenite; V - vapor.

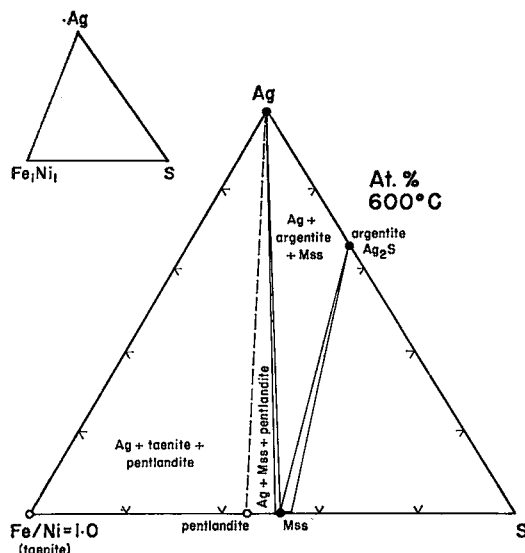


FIG. 3. A representative isopleth section through Figure 2 at  $\text{Fe/Ni}=1$  (atomic ratio). The section has been distorted into an equilateral triangle. The true shape of the section is shown in the insert. Solid symbols and lines represent composition of phases and tie-lines within the isopleth section. Open circles and the dashed line are projections onto the section (see text). Vapor coexists with all phases.

phase relationships of the central part of the Fe-Ni-S system, with the additional stable phases Ag and/or  $\text{Ag}_2\text{S}$  (argenite) which occur in regions of appropriate ambient fugacity of  $\text{S}_2(f_{\text{S}_2})$  over a given assemblage. The 600°C isothermal data are in general agreement with those of Kullerud (1963a), Naldrett & Craig (1966), Naldrett *et al.* (1967), Shewman & Clark (1970) and Misra & Fleet (1973a).

The dashed line in Figure 2 represents the intersection of the divariant volume  $\text{Ag}+\text{Ag}_2\text{S}+\text{Mss}+\text{V}$  (see Fig. 3) with the Fe-Ni-S ternary base. This measured position of the  $\text{Ag}/\text{Ag}_2\text{S}$  buffer within the *Mss* field is close to that predicted from binary fugacity data for  $\text{Ag}/\text{Ag}_2\text{S}$  and  $f(\text{S}_2)$  isobars in the *Mss* field at 600°C as measured by Naldrett *et al.* (1967). Such agreement is expected because of low quaternary solid solutions in Ag,  $\text{Ag}_2\text{S}$  and *Mss*.

Phase relations in the Ag-Fe-Ni-S system at 600°C are very similar to those documented by Taylor (1970) for the system Ag-Fe-S in the temperature range 320°-607°C, indicating that phase relations in the central portion of the Ag-Fe-Ni-S system at 600°C approximate a projection of the tie-triangle  $\text{Ag}+\text{Ag}_2\text{S}+\text{pyrrhotite}+\text{V}$  of the Ag-Fe-S system into the quaternary. This

consistency of phase relations is due to the ideality of Fe-Ni substitution in the *Mss* field (Scott *et al.* 1974). Taylor's (1970) data on the position of the  $\text{Ag}/\text{Ag}_2\text{S}$  buffer in the  $\text{Fe}_1\text{-S}$  field have been incorporated in our study.

One major difference between Taylor's Ag-Fe-S data and Figure 3, an isopleth at  $\text{Fe/Ni}=1$  in the Ag-Fe-Ni-S system, arises from the presence of pentlandite to the sulfur-deficient side of *Mss* in the system Fe-Ni-S. The orientation of tie-lines between *Mss* and pentlandite in Figure 2 is such that the pentlandite which coexists with Ag and an *Mss* composition along the  $\text{Fe/Ni}=1$  isopleth is considerably more Ni-rich than the *Mss*. Consequently, in Figure 3, the pentlandite composition has been projected onto the isopleth and the tie-line from Ag is dotted as it also does not lie on the isopleth. Similarly, pentlandite in the plane of the isopleth with  $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$  stoichiometry coexists with a taenite which is more Ni-rich ( $\text{Fe}_{0.3}\text{Ni}_{0.7}$ ) on its S-poor side and with *Mss* that is more Fe-rich on its S-rich side. Therefore, only that part of the system involving  $\text{Ag}+\text{Ag}_2\text{S}+\text{Mss}+\text{V}$  can be considered as pseudo-ternary in the isopleth section.

#### 400°C isotherm

The 400°C isotherm is shown in Figure 4a. Relative to normal pentlandite, the field of argenite pentlandite has a smaller range in Fe/Ni ratio and is displaced towards more Fe-rich compositions. The midpoints of the fields of argenite pentlandite and pentlandite are at  $\text{Fe/Ni}=2.2$  and 1.0, respectively.

Compositions of argenite pentlandites encountered at 400°C (Table 2) are plotted on the  $\text{M}_2\text{S}_3$  plane in Figure 5a. The solid-solution field extends from  $\text{Fe/Ni}=1.12$  to 3.21 (at. ratio) and  $\text{Ag}=0.7$  to 1.0 atom per unit formula. The silver contents of coexisting pentlandite, taenite and *Mss* were below detection limits of the electron microprobe.

Three univariant prisms impinge upon the argenite pentlandite field at 400°C and are shown in Figure 4a from left to right: (1) argenite pentlandite+*Mss*+pentlandite+taenite+V; (2) argenite pentlandite+Ag+pentlandite+taenite+V; (3) argenite pentlandite+Ag+*Mss*+pentlandite+V. It is evident from Figure 4a that the divariant field of argenite pentlandite+*Mss*+pentlandite+V extends across the entire bottom part of the argenite pentlandite solubility field with an ever-increasing slope of tie-lines between argenite pentlandite+pentlandite and argenite pentlandite+*Mss* as the Fe/Ni ratio decreases. Since argenite pentlandite is always in equilibrium with a pentlandite of lower Fe/Ni ratio, it follows that the substitution of

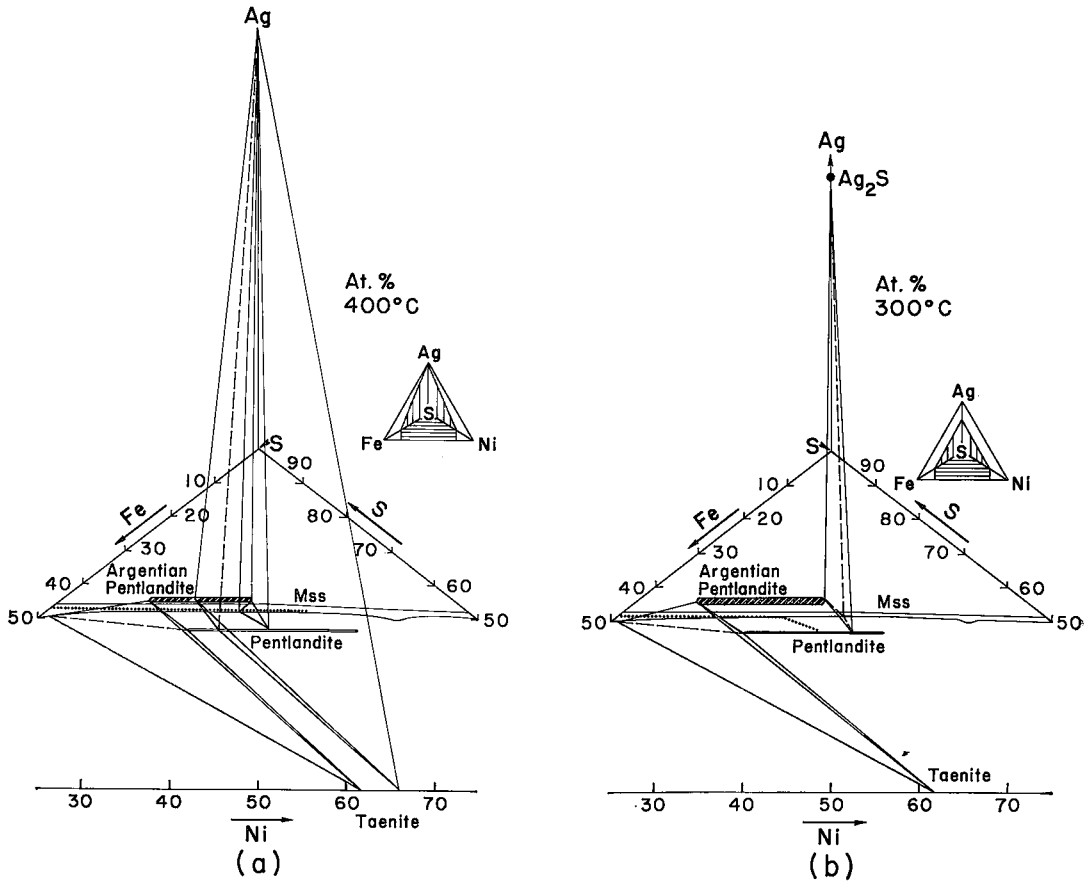


FIG. 4. Solubility limits and phase relations involving argentian pentlandite in the lower central part of the Ag-Fe-Ni-S system. Tie-lines "hidden" beneath the prisms are dashed. The dotted lines trace the projected position of the Ag/Ag<sub>2</sub>S buffer on the ternary Fe-Ni-S base as determined by appearance-of-phase experiments. The right side of the Fe-Ni-S base is from Craig (1973) and Misra & Fleet (1973a). (a) 400°C. Three univariant prisms are shown: (1) argentian pentlandite+Mss+pentlandite+taenite+V; (2) argentian pentlandite+Ag+pentlandite+taenite+V; and (3) argentian pentlandite+Mss+pentlandite+Ag+V. (b) 300°C. Two univariant prisms are shown: argentian pentlandite+Mss+pentlandite+taenite+V, and argentian pentlandite+Ag<sub>2</sub>S+Mss+pentlandite+V. Other expected prisms were not located (see text).

Ag into the pentlandite structure lowers the activity of FeS in argentian pentlandite relative to that in pentlandite of the same Fe/Ni ratio.

As at 600°C, the projected location of the Ag/Ag<sub>2</sub>S buffer at 400°C (dotted line in Fig. 4a) is confined within the Mss field for the bulk compositions investigated. As a result, the trivariant assemblage Ag+Mss+V precludes equilibrium coexistence of Ag<sub>2</sub>S (argentite) with argentian pentlandite, pentlandite, and taenite or other phases on the S-poor side of the Ag/Ag<sub>2</sub>S buffer at 400°C in the condensed system.

300°C isotherm

Part of the 300°C isotherm is shown in

Figure 4b and compositions of selected argentian pentlandites (Table 2) in Figure 5b. The solubility limits of argentian pentlandite are wider at 300°C than at 400°C and are likewise displaced towards more Fe-rich compositions than are found for normal pentlandite. Fe/Ni atomic ratio ranges from 1.07 to 4.10 and Ag content from 0.65 to 1.0 atoms per unit formula. As was the case for all other temperatures that we have investigated, silver was not found by electron microprobe in the coexisting pentlandite, taenite or Mss.

Univariant prisms occur at either end of the argentian pentlandite field: argentian pentlandite+Mss+pentlandite+taenite+V at the Fe-

saturated end and argentian pentlandite+ $\text{Ag}_2\text{S}$ + $Mss$ +pentlandite+V at the Ni-saturated end. We were not able to determine phase relations involving argentian pentlandite of intermediate compositions because of sluggish reaction rates. Therefore, the location of other expected univariant prisms involving combinations of three of Ag,  $\text{Ag}_2\text{S}$ , pentlandite and taenite with argentian pentlandite and vapor are not known. However,

coexistence of argentian pentlandite with  $Mss$ + $\text{Ag}_2\text{S}$ +Ag+V (point 33 in Table 2) allowed us to approximate the position of the Ag/ $\text{Ag}_2\text{S}$  buffer below the S-poor boundary of  $Mss$  in Figure 4b and serves to separate argentian pentlandite assemblages containing  $\text{Ag}_2\text{S}$  from those containing Ag. At 300°C only Ni-rich argentian pentlandite ( $\text{Fe}/\text{Ni}<1.54$ ) encounters a sufficiently high  $f(\text{S}_2)$  to coexist with  $\text{Ag}_2\text{S}$  (Fig. 4b).

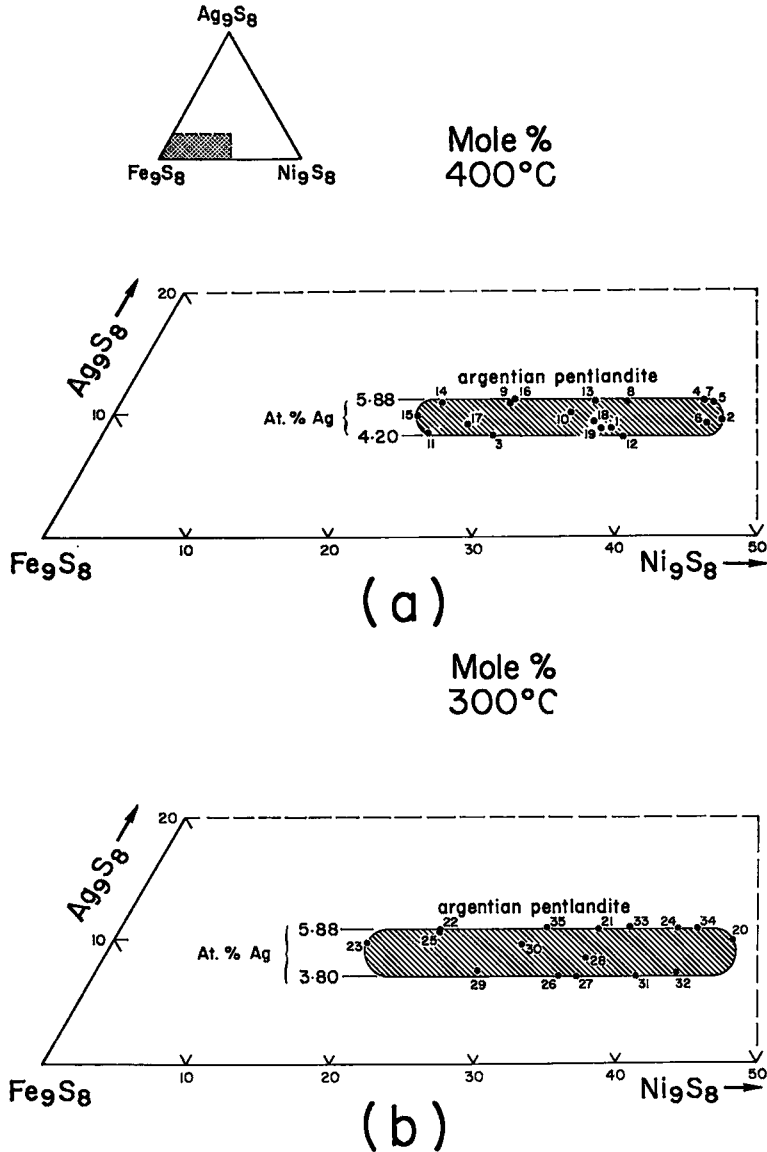


FIG. 5. The solid-solution field of synthetic argentian pentlandite in the  $M_0S_8$  plane of the Ag-Fe-Ni-S system at (a) 400°C and (b) 300°C. Numbered dots locate projections of compositions of argentian pentlandites from experimental runs as determined by microprobe analyses (Table 2).



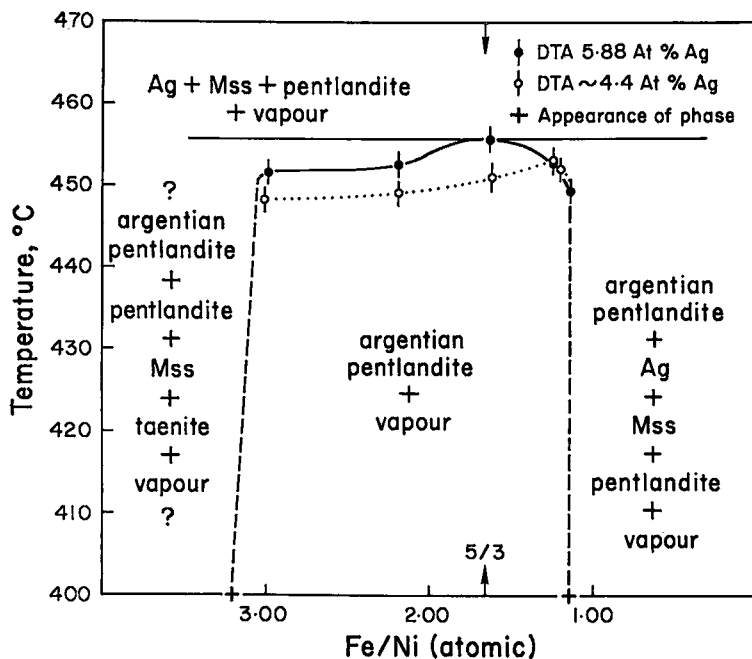


FIG. 6. Results of DTA experiments locating the upper thermal stability of argentic pentlandite. The solid curve and solid points are for argentic pentlandites with 1 atom Ag per unit formula; the dotted curve and open points are for compositions with 0.7 atom Ag per unit formula. Vertical bars are estimated precisions of the temperature at which exothermic breakdown reactions began. Crosses are from the 400°C isotherm (Fig. 4a). It is uncertain which of several possible phase assemblages are intersected on the Fe-rich side of the argentic pentlandite field.

#### Upper thermal stability of argentic pentlandite

The upper thermal stability of argentic pentlandite is a function both of Fe/Ni ratio and of Ag content, as shown by DTA experiments in Figure 6. Endothermic deflections used to construct Figure 6 were generally broad and with rounded shoulders, resulting in considerable uncertainty in locating precise temperatures at which breakdown of argentic pentlandite was initiated. The ultimate breakdown products of argentic pentlandite are Ag+Mss+pentlandite (Figs. 2 and 4). However, only the unique composition of approximately  $(\text{Fe}_5\text{Ni}_3)\text{Ag}_1\text{S}_8$  gave these products directly. Other compositions went through an intermediate series of reactions in which Fe/Ni ratio in argentic pentlandite approached approximately 5/3 and Ag approached 1 atom per unit formula. This can be seen by considering an Ag-saturated argentic pentlandite and the univariant prisms argentic pentlandite+pentlandite+Mss+taenite+V and argentic pentlandite +Ag+Mss+pentlandite+V in Figure 4a which occur at either end of its solid-

solution field. As temperature increases near the upper stability limit, these prisms approach one another until they meet in an invariant point near 455°C involving argentic pentlandite+Ag+Mss+pentlandite+taenite+V and in which the composition of the argentic pentlandite is  $(\text{Fe}_5\text{Ni}_3)\text{Ag}_1\text{S}_8$ . Thus, in the DTA experiments, an argentic pentlandite which is not initially of this invariant composition encounters one of the univariant prisms as temperature increases and undergoes progressive change in its Fe/Ni ratio by exsolving other phases until the invariant point is reached or until the starting composition lies outside the prism concerned. Similarly, Ag-deficient argentic pentlandites adjust not only their Fe/Ni ratio but also increase Ag content by exsolving pentlandite as temperature is raised. As a result, DTA deflections are expected to be broad except for the  $(\text{Fe}_5\text{Ni}_3)\text{Ag}_1\text{S}_8$  composition which did, in fact, give a sharp break.

The breakdown temperature of Fe-rich argentic pentlandite which is undersaturated with

Ag (i.e. less than 1 atom per formula unit) is slightly lower than for Ag-saturated argentic pentlandite. For example, in Figure 6 the dotted breakdown curve of argentic pentlandite with 0.7 atoms Ag per formula unit,  $(\text{Fe,Ni})_{8.3}\text{Ag}_{0.7}\text{S}_8$ , lies well below that of argentic pentlandite with 1.0 atom Ag per formula unit (solid curve) for  $\text{Fe/Ni} > 1.25$ . For more Ni-rich compositions, the breakdown temperature appears to be independent of Ag content. Furthermore, as the Ag content of argentic pentlandite decreases, the composition of the maximum thermal stability becomes more Ni-rich. An explanation of this phenomenon is offered in the section on crystal chemistry.

### DISCUSSION

The compositional range of synthetic argentic pentlandites produced in our experiments is considerably wider than that of natural argentic pentlandites, both in Fe/Ni atomic ratio (1.07-4.10 at 300°C vs. 1.34-2.57) and in number of Ag atoms per formula unit (0.65-1.0 at 300°C vs. approximately 0.8-1). A similar phenomenon is observed in normal pentlandites (Harris & Nickel 1972) and probably reflects the limited range of bulk composition or sulfur fugacities encountered in nature.

The maximum thermal stability limit of Ag-saturated argentic pentlandite is at a considerably lower temperature (455°C) and different Fe/Ni atomic ratio (5/3) than for pentlandite (610°C and 1/1, respectively; Kullerud 1963b). The very large thermal expansion of the pentlandite structure (Rajamani & Prewitt 1975) suggests that the thermal stability and probably the silver content of argentic pentlandite is strongly influenced by pressure as is the case of the former for normal pentlandite (Bell *et al.* 1964). We have not investigated this hypothesis experimentally but have estimated  $\Delta V$  for the breakdown reaction of  $(\text{Fe}_5\text{Ni}_3)\text{Ag}_5\text{S}_8$  at 455°C to be negative and large at approximately  $-22 \text{ cm}^3/\text{mole}$  (calculated from the data of Robie & Waldbaum 1968; Skinner 1966; Misra & Fleet 1973b). The  $\Delta H$  of the reaction is not known nor can it be estimated from our DTA curves. However, the breakdown reaction is endothermic in which case  $\Delta H$  is positive and, from the Clapeyron equation,  $dT/dP$  is negative. In other words, pressure lowers the upper stability of argentic pentlandite by an amount that is unknown but is expected to be large relative to other sulfide reactions. The effect of minor impurities (mainly Co and Cu; see Scott & Gasparrini 1973, Table 2) on the upper stability of argentic pentlandite also is not known but is not expected to

be significant because the amounts are small and Vaasjoki *et al.* (1974) found no effect for  $< 1 \text{ wt. } \% \text{ Co}$  in solid solution in normal pentlandite.

The Ag/Ag<sub>2</sub>S buffer has not been located in detail for bulk compositions more Ni-rich than Fe/Ni=1. However, available data in Figure 4 show that equilibration above 300°C of natural nickeliferous Ag-bearing sulfide assemblages (with bulk compositions on the Fe-rich side of Fe/Ni=1) will result in silver values which occur predominantly as argentic pentlandite with minor or trace amounts of native Ag or Ag<sub>2</sub>S depending on the prevailing local  $f(\text{S}_2)$  during final equilibration. Primary Ag<sub>2</sub>S has not been observed in magmatic Cu-Ni ores and indicates ambient  $f(\text{S}_2)$  below the Ag/Ag<sub>2</sub>S buffer (e.g. less than  $10^{-10} \text{ atm}$  at 400°C). On the other hand, primary Ag<sub>2</sub>S (as acanthite) is observed in argentic pentlandite-bearing skarn deposits (e.g. Burnt Basin, B.C., A. E. Johnson, pers. comm. 1974; Khovuaksa, U.S.S.R., Shishkin *et al.* 1971) and either acanthite or native Ag are found as alteration products of argentic pentlandite (Vuorelainen *et al.* 1972; Scott & Gasparrini 1973; this study).

Figure 7 illustrates selected sulfidation curves and stability fields in the Ag-Fe-Ni-S system. Phase relations at 400°C and 300°C indicate that the assemblage argentic pentlandite+*Mss*+pentlandite+V is stable along the entire bottom part of the argentic pentlandite stability field allowing estimation of  $f(\text{S}_2)$  over the assemblage from experimental data on the S-poor boundary of the *Mss* field at 400°C (Naldrett & Craig 1966). The proportions of phases in the naturally occurring assemblage argentic pentlandite+*Mss*+pentlandite suggest that most bulk compositions on the microscale of such systems contain less than  $\sim 3 \text{ at. } \% \text{ Ag}$ . In Figure 7 the greater portion of the stability field of argentic pentlandite+*Mss*+pentlandite lies within the stability field of Ag (stippled area). Ag<sub>2</sub>S first becomes co-stable with Ni-rich argentic pentlandite+*Mss*+pentlandite at  $\sim 358^\circ\text{C}$  where the Ag/Ag<sub>2</sub>S buffer intersects this field. At lower temperatures Ag<sub>2</sub>S continues to be co-stable with *Mss*, pentlandite, and a relatively restricted range of argentic pentlandite compositions (cross-hatched area in Fig. 7), whereas the greater part of the argentic pentlandite+*Mss*+pentlandite field lies within the stability field of Ag.

Some genetic distinctions between Ag-bearing argentic pentlandite assemblages in magmatic Cu-Ni ores and Ag<sub>2</sub>S-bearing assemblages in skarn deposits are apparent from Figure 7. For example, coexistence of Ag<sub>2</sub>S with argentic pentlandite+*Mss*+pentlandite at a final equili-

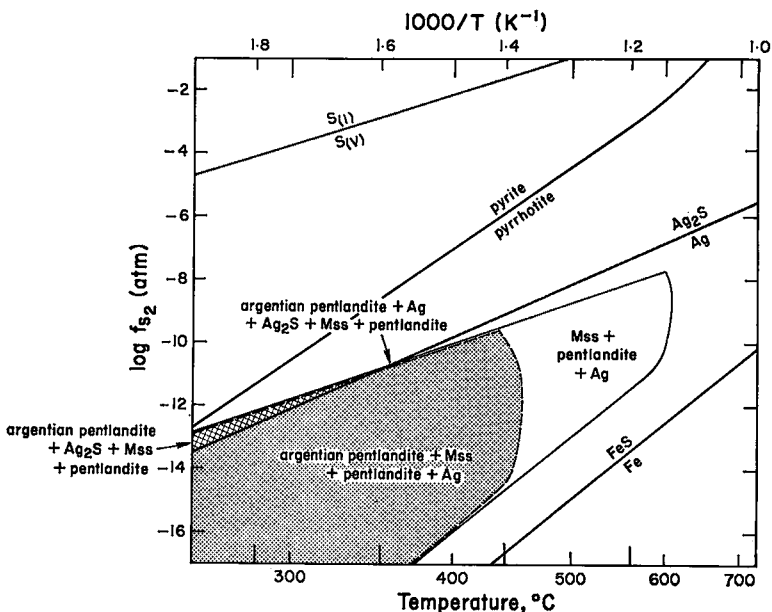


FIG. 7. Selected sulfidation curves and stability fields in the Ag-Fe-Ni-S system. Ag/Ag<sub>2</sub>S and Fe/FeS are from Robie & Waldbaum (1968), S<sub>v</sub>/S<sub>l</sub> from Braune *et al.* (1951) and pyrrhotite/pyrite from Scott & Barnes (1971). The field of Mss+pentlandite+Ag is estimated from the data of Naldrett & Craig (1966). The invariant point involving Ag+Ag<sub>2</sub>S+argentic pentlandite+Mss+pentlandite+V is estimated to occur at 358°C. Vapor coexists with all solid phases.

bration temperature near 300°C is only possible if  $f(S_2)$  is maintained within a very narrow range near  $10^{-12}$  atm and if the bulk composition of the assemblage is relatively Ni-rich. Our experiments imply that reaction rates in the solid state decrease significantly in this system somewhere in the range 200°-300°C, so it is possible that roughly similar temperatures might apply to the final equilibration of dry magmatically-derived Cu-Ni sulfide assemblages in which argentic pentlandite occurs. Consequently, in the micro-environment containing argentic pentlandite and Ag,  $f(S_2)$  must have been below the Ag/Ag<sub>2</sub>S buffer but within the stability field of argentic pentlandite+Mss+pentlandite. On the other hand, coexistence of Ag<sub>2</sub>S with these phases, as observed in nickeliferous skarn-type deposits, is probably the result of equilibration of argentic pentlandite-bearing sulfide assemblages down to much lower temperatures than are possible in most magmatically derived ores owing to the circulation of mineralizing hydrothermal fluids which act as fluxes for sulfide equilibration. As shown in Figure 7, equilibration to lower temperatures allows a greater portion of the stability field of Ag<sub>2</sub>S to intersect the field of argentic pentlandite+Mss+pentlandite, resulting in a

wider range of  $f(S_2)$  values and of bulk compositions over which these phases can coexist.

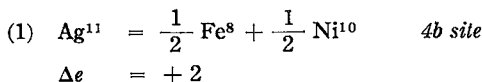
#### CRYSTAL CHEMISTRY OF ARGENTIAN PENTLANDITE

Rajamani & Prewitt (1973) have proposed that a cube cluster of tetrahedrally-coordinated metal atoms stabilizes the pentlandite structure and, for a random distribution of cations in the octahedral 4b and tetrahedral 32f sites, fixes the total number of non-bonding (with respect to metal-sulfur) outer shell electrons in the unit cell to a uniform value of 260. Because Fe( $d^6$ ), Co( $d^7$ ) and Ni( $d^8$ ) have different numbers of 3d electrons, nonstoichiometry is expected over the compositional range of pentlandite via cation addition-omission solid solution in order to maintain this uniformity. As a result, the metal/sulfur ratio in pentlandites in general cannot be constant over the entire solubility field but must be a function of Fe/Ni ratio.

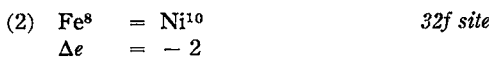
This theory also applies intrinsically to argentic pentlandite. The prediction of the ideal  $M_3S_8$  stoichiometric quaternary pentlandite composition (in terms of Fe/Ni ratio) in the system Ag-Fe-Ni-S can be reduced to two equations in

two unknowns as follows: consider a stoichiometric silver-saturated argentian pentlandite ( $\text{Fe}_x\text{Ni}_y\text{Ag}_1\text{S}_8$ ). First, since  $M/S=9/8$ , it follows that  $x+y=8$  (equation 1). Summing electrons in the outer shells of the cations yields 11 for each Ag atom ( $d^{10}s^1$ ), 8 for each Fe ( $d^8s^2$ ) and 10 for each Ni ( $d^8s^2$ ) or a total of  $(1 \cdot 11 + 8x + 10y)$  of which 16 are assigned to bonds with 8 S atoms. This leaves  $(8x + 10y - 5)$  non-bonding electrons per formula unit or  $4(8x + 10y - 5)$  in the unit cell. Thus  $32x + 40y - 20 = 260$  (equation 2). Solving for  $x$  and  $y$  in equations 1 and 2 gives  $x=5$ ,  $y=3$ . Therefore,  $(\text{Fe}_5\text{Ni}_3)\text{Ag}_1\text{S}_8$  represents the stoichiometric and most stable composition of argentian pentlandite when there is one Ag atom per unit formula. In other words, when octahedral sites are completely filled with  $\text{Ag}(d^{10}s^1)$  under conditions of stoichiometry ( $M/S=9/8$ ), the structure is stabilized at a greater Fe/Ni ratio (5/3) than normal stoichiometric pentlandite (1/1).

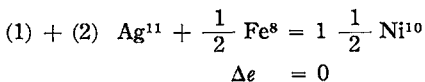
The above result can also be obtained by consideration of coupled replacement reactions such as described by Nickel (1970) for the triarsenides of Co-Fe-Ni which exhibit strikingly similar limits of solid solution to those observed in Co-Fe-Ni pentlandites. Assuming a random distribution of Fe and Ni in octahedral  $4b$  sites of a stoichiometric Fe-Ni pentlandite (Hall & Stewart 1973) of composition  $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$ , the hypothetical replacement of one atom of Ag is given by:



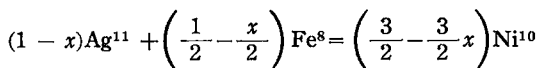
This results in gain of 2 electrons which can be simultaneously compensated for by adjustment in the Fe/Ni ratio via substitution of Fe into the tetrahedral sites:



The net coupled replacement is then:



The net changes in Ag, Fe and Ni atoms per formula unit are +1.0, +0.5 and -1.5, respectively, relative to  $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$  and the new stoichiometric formula is  $(\text{Fe}_5\text{Ni}_3)\text{Ag}_1\text{S}_8$ . A general formula of the net coupled replacement which can be used to predict stoichiometric compositions for Ag-deficient argentian pentlandites is given by



where  $x = (1 - \text{the number of Ag atoms / unit$

formula) and from our experimental results ranges from 0.0 to 0.35.

Just as normal pentlandites exhibit nonstoichiometry for compositions on either side of Fe/Ni=1/1, Ag-saturated argentian pentlandites on either side of Fe/Ni=5/3 are nonstoichiometric as indicated in Figure 8. The scatter of data points about the expected theoretical variation in composition of argentian pentlandite in Figure 8 is most likely caused by analytical errors. In the discussion of Figures 2 and 4 we noted that the solid-solution field for normal pentlandite is wider than that of argentian pentlandite. Our crystal-chemical arguments suggest that this is because both  $4b$  and  $32f$  sites can be enriched in either Fe or Ni in normal pentlandite whereas, in argentian pentlandite, the  $4b$  site is occupied by Ag.

DTA results (Fig. 6) confirm the crystal-chemical argument that  $(\text{Fe}_5\text{Ni}_3)\text{Ag}_1\text{S}_8$  is the most stable composition of Ag-saturated argentian pentlandite, just as  $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$  is the most stable normal pentlandite. Also, the above general equation for coupled replacement between  $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$  and stoichiometric argentian pentlandite predicts that argentian pentlandite with less than one atom of Ag per unit formula will have a  $M/S$  ratio of 9/8 when Fe/Ni is less than 5/3. Accordingly, the most stable composition should be Ni-rich with respect to Fe/Ni=5/3 for Ag-deficient compositions. DTA results confirm this for compositions with 0.7 atoms per unit formula (Fig. 6). Ag-deficient argentian pentlandites would be represented in Figure 8 by a parallel set of curves lying above that shown for Ag-saturated argentian pentlandite.

#### Cell edge of argentian pentlandite

Shewman & Clark (1970) have shown that  $d(115)$  of synthetic  $(\text{Fe},\text{Ni})_9\text{S}_8$  varies appreciably with composition as given by the relationship  $d(115) = (1.9407 - 0.0023R + 0.0077R^2)\text{\AA}$ , where  $R$  is the Fe to Ni weight ratio at a fixed S content of about 33.0 wt. %. They attributed non-linearity in this equation to a disordering of atoms on either side of the  $(\text{Fe}_{4.5}\text{Ni}_{4.5})\text{S}_8$  composition and considered the solid solution to be of the substitutional type where Ni replaces Fe atom for atom. In Figure 9 we show the relationship between cell edge and composition of argentian pentlandites synthesized at 300°-350°C. A least-squares fit through our data at each Fe/Ni ratio extrapolates very closely to cell edges determined by Shewman & Clark (1970) for normal pentlandite. Because the family of lines in Figure 9 is regular, parallel, and displays gradients of  $\Delta a_c / \Delta(\text{Fe}/\text{Ni})$  independent of  $x$ , it follows that Shewman & Clark's relationship for  $d(115)$  vs.

composition is valid for argentine pentlandites of any given silver content so long as a term is added to account for cell expansion from silver substitution. This result confirms Hall & Stewart's (1973) observation that Ag enters only the octahedral  $4b$  sites of the pentlandite structure. Significant substitution of Ag into tetrahedral  $32f$  sites would produce curvature of the lines in Figure 9, prohibiting their linear extrapolation to cell edges of normal pentlandite.

The facts that (a) Ag substitution into the pentlandite structure has an effect on  $a_0$  which is simply additive onto the effect derived by Shewman & Clark (1970) for Fe-Ni substitution and (b) Ag substitution at fixed Fe/Ni ratio produces a linear variation in  $a_0$  (unlike the exponential variation for Fe-Ni substitution; Knop *et al.* 1965), demonstrate two distinct types of solid solution in argentine pentlandite:

(1) For fixed Ag contents, complex substitutional plus omission-addition solid solution occur in the tetrahedral  $32f$  sites; i.e. Fe and Ni replace each other atom for atom and coupled with this substitution is cation-addition into normally unoccupied tetrahedral sites for Fe-rich compositions (with respect to the stoichiometric  $M_5S_8$  formula) or cation-omission for Ni-rich compositions. Cation addition-omission is necessary in order to preserve uniform electron concentration in the unit cell at the expense of ideal  $M_5S_8$  stoichiometry and explains the non-linear varia-

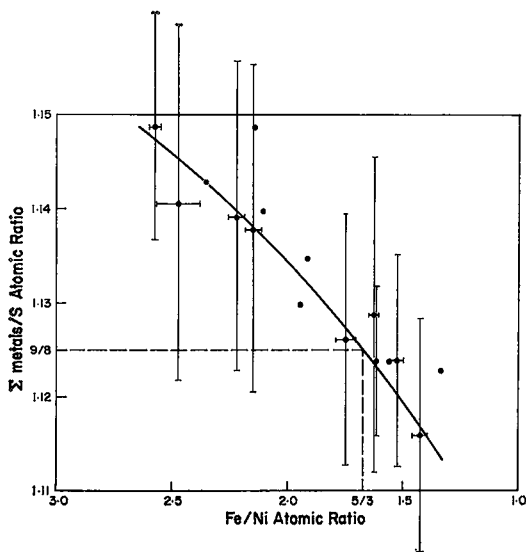


FIG. 8. Variation of metal/sulfur atomic ratios with Fe/Ni atomic ratios in natural argentine pentlandites containing one or close to one atom of Ag per unit formula. Solid curve represents the expected theoretical variation in composition (Rajamani & Prewitt 1973). Bars are one standard deviation calculated for those ratios for which there is sufficient information.

tion of  $a_0$  with composition of normal Fe-Ni pentlandites.

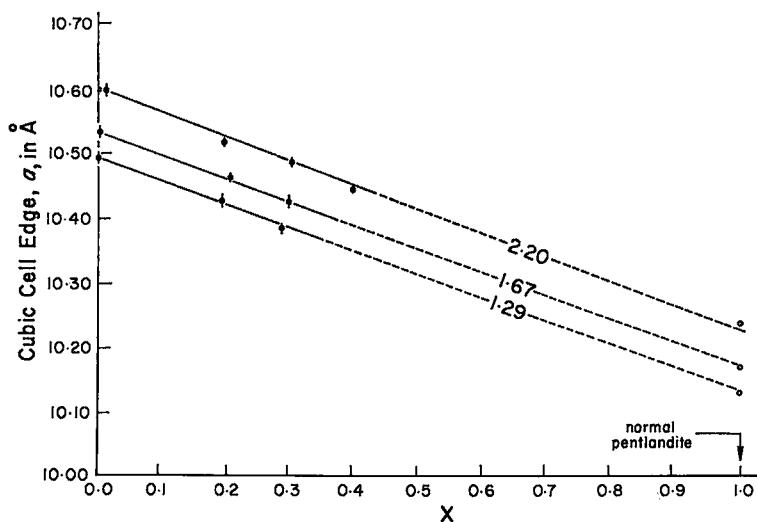


FIG. 9. Variation in  $a_0$  of synthetic argentine pentlandite. Vertical bars represent one standard deviation. Lines are least-square fits to our data at given Fe/Ni atomic ratios. Open circles are calculated values of  $a_0$  for Ag-free pentlandites of the same Fe/Ni ratios as the synthetic argentine pentlandites (Shewman & Clark 1970).  $x$  is the deficiency of Ag in atoms per unit formula.

(2) For fixed Fe/Ni ratios, substitutional solid solution occurs in octahedral 4*b* sites in which Ag replaces both Fe and Ni (Hall & Stewart 1973) with concomitant adjustment in the *M/S* ratio by cation addition-omission as in (1).

Non-recoverable or irreversible expansion of  $a_c$  by approximately 0.6% has been observed in natural Fe-Ni pentlandites (Knop *et al.* 1965; Rajamani & Prewitt 1975) annealed at 150°-200°C. Rajamani & Prewitt suggested that this phenomenon is the result of disordering of Fe and Ni leading to slight enrichment of high-spin Fe<sup>2+</sup> in octahedral 4*b* sites relative to its occupancy in the natural case. We have not tested for irreversible cell expansion of natural argentinean pentlandite nor do we expect to find it when 4*b* sites are saturated with Ag because Ag does not enter the tetrahedral 32*f* site. Thus, no disordering of either Ag into 32*f* sites or of Fe into 4*b* sites can occur, and the cell parameter of silver-saturated argentinean pentlandite should be independent of thermal history. However, silver-deficient argentinean pentlandites (less than 1 atom Ag/unit formula) could allow enrichment of high-spin Fe<sup>2+</sup> in 4*b* sites on annealing and give rise to a small component of irreversible cell expansion.

#### CONCLUSIONS

Dry-synthesis experiments show that argentinean pentlandite exists over a range of Fe/Ni ratios which overlap and extend beyond those of Fe-rich normal pentlandites. Ag content varies with equilibrium assemblage from 0.65 (at 300°C) atoms per unit formula to 1.0, the saturated value representing complete filling of octahedral 4*b* sites in the pentlandite structure. The upper thermal stability limit of argentinean pentlandite varies with Fe/Ni ratio and Ag content. The most stable composition is (Fe<sub>8</sub>Ni<sub>8</sub>)Ag<sub>8</sub>S<sub>8</sub> which, from our DTA experiments, breaks down to Ag + *Mss* + pentlandite at about 455°C. This composition is close to the mean for all analyzed natural samples and is also the stoichiometric composition predicted for the Ag-saturated phase by our application of the crystal-chemical models of Rajamani & Prewitt (1973) and Nickel (1970) to Ag-Fe-Ni-S pentlandites. Other metals such as Pt, Pd, Ru and Rh can also occur in pentlandites (Knop *et al.* 1965; Genkin *et al.* 1973, 1974) and we expect that the crystal-chemical models can be extended to include these phases.

The reason for the existence of a solvus between argentinean pentlandite and normal pentlandite is not understood and, in fact, crystal-chem-

ical modelling suggests that continuous solid solution should be possible. However, both natural pentlandites and our synthetic products contain less than the limit of Ag detectable by electron microprobe (<0.05 wt. %), even when coexisting with argentinean pentlandite or other silver-bearing phases. For this reason, we do not believe that argentinean pentlandite is simply a member of an isomorphous solid-solution series with normal pentlandite and agree with Scott & Gasparrini (1973) that argentinean pentlandite is a distinct mineral species.

Natural argentinean pentlandite is invariably associated with chalcopyrite. It is restricted to the Cu-rich zones of magmatic Cu-Ni sulfide ores where it is in direct contact with chalcopyrite and, in some samples, shows textures suggestive of exsolution from chalcopyrite (Scott & Gasparrini 1973, Fig. 2). Ag enrichment by as much as two orders of magnitude in the Cu concentrate relative to the Ni concentrate from some Sudbury ores (M. B. Sizgoric, pers. comm. 1974) indicates a strong partitioning of Ag into the massive chalcopyrite ore zones compared with the Ni-rich pyrrhotite-pentlandite zones. This enrichment probably takes place at magmatic temperatures during the separation of a residual Cu-rich sulfide melt (Keays & Crockett 1970). Such a melt would crystallize Cu<sub>2</sub>Fe<sub>7</sub>S<sub>2-2</sub> intermediate solid solution (Kullerud *et al.* 1969; Cabri 1973) containing appreciable Ag in solid solution (Boyle 1968; G. K. Czamanske, pers. comm. 1973). Subsequent subsolidus reaction below 455°C between this *Iss* (or chalcopyrite) and Fe-Ni sulfides could produce argentinean pentlandite either at grain boundaries or as exsolved bodies in *Iss* (chalcopyrite) — both textures are seen in ores.

At Sudbury, where approximately 1.5 million ounces of silver are recovered annually, Ag in solid solution with chalcopyrite, considered by Hawley to be the best host, averages 180 ppm (Hawley 1962) and cannot account for the total production. Similarly, Ag solubilities in other sulfides from the massive chalcopyrite zones along with the rare occurrences of native Ag, hessite (Ag<sub>2</sub>Te) and schapbachite (AgBiS<sub>2</sub>) fail to make up the deficit. However, it is possible that considerable argentinean pentlandite has been misidentified as bornite in many magmatic Cu-Ni sulfide ores and is probably a very significant repository of Ag in these deposits.

#### ACKNOWLEDGMENTS

We gratefully acknowledge the generous help of many people: J. C. Rucklidge (University of Toronto) and O. P. Malik (formerly University

of Toronto) for provision, maintenance and advice on the electron microprobe facility; F. J. Wicks and D. McKinnon (Royal Ontario Museum) for provision and operation of the DTA facility; A. J. Naldrett, J. C. Rucklidge, V. Rajamani (University of Toronto) and L. J. Cabri (CANMET, Ottawa) for critical comments at various stages of our research; D. Alcock and M. B. Sizgoric (INCO) for information on natural occurrences of argentine pentlandite; B. Buchan (Falconbridge Research Laboratory), J. Donner (Bird River Mines), A. E. Johnson (CANMET, Ottawa), A. D. Genkin (IGEM, Moscow) and H. Papunen (Turku University, Finland) for their kind donation of samples.

Our paper has benefited from an incisive review by V. Rajamani. Figures were drafted by W. M. Jurgeneit and photographed by B. O'Donovan.

Financial support for this study was provided by the National Research Council of Canada through a post-graduate scholarship to Z. L. Mandziuk and operating grant A7069 to S. Scott. Scott thanks the Department of Economic Geology, University of Adelaide for providing office space and facilities during the final preparation of the manuscript while on sabbatical leave.

#### Note added in proof

Recent discussions with Professor S. Takeuchi of Tokyo University have brought to our attention two Japanese studies of argentine pentlandite. Imai *et al.* (1975) have described argentine pentlandite from the Falconbridge mine at Sudbury. The mineral has the characteristic physical properties of other natural occurrences and an average structural formula based on three microprobe analyses from a single grain of  $(\text{Fe}_{5.30}\text{Ni}_{12.81}\text{Cu}_{0.04})\text{Ag}_{0.99}\text{S}_8$ . Of greater concern to our results, however, is an earlier report in Japanese (Mariko *et al.* 1973) of an "argentine pentlandite" containing 1.56 atoms Ag per formula unit from an iron-copper skarn in the Kamaishi mine, Japan. The average structural formula of this mineral, from electron microprobe analyses, is  $(\text{Fe}_{5.68}\text{Ni}_{11.87}\text{Cu}_{0.01})\text{Ag}_{1.56}\text{S}_8$ . Powder X-ray diffraction data correspond to those of Vuorelainen *et al.* (1972) and an fcc structure with  $a$  10.59 Å. The Vickers hardness is approximately 40 to 70 higher than previously reported for argentine pentlandites.

The relationship of the Kamaishi "argentine pentlandite" to those discussed in our manuscript is enigmatic. It is unlikely that the mineral is stable above 300°C or we would have encountered it in our synthesis experiments. The structural formula indicates that Ag in excess of one

atom preferentially replaces Ni, but whether the Ag is in tetrahedral or octahedral coordination is uncertain. The cell edge is approximately 0.33 Å smaller than that obtained from extrapolation of our Figure 9 for an argentine pentlandite with 1.56 atoms of Ag in the formula unit ( $x = -0.56$ ) and  $\text{Fe}/\text{Ni} = 3.02$ . The small cell edge and the higher microhardness suggest that, despite the similarity of powder X-ray diffraction patterns, the mineral has a different structure from that determined by Hall & Stewart (1973) for argentine pentlandite. Nevertheless, the composition of the Kamaishi "argentine pentlandite" satisfies our general formula for net coupled replacement. In other words, it fulfills the condition of stoichiometry in that the  $\text{Fe}/\text{Ni}$  and  $M/S$  ratios are the expected values (i.e. 3.02 and 1.136, respectively) for a pentlandite which contains 1.56 atoms of Ag per formula unit. Clearly, single-crystal X-ray diffraction data are needed for this mineral.

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