# CHALCOGENIDES OF THE TRANSITION ELEMENTS. IV. PENTLANDITE, A NATURAL π PHASE[1]

OSVALD KNOP,[2] MOHAMMAD ANWAR IBRAHIM AND SUTARNO
*Department of Chemical Engineering, Nova Scotia Technical College,*
*Halifax, N.S., Canada*

## ABSTRACT

It is shown that pentlandite must be regarded as a natural $\pi$ (Fe,Co,Ni,S) phase in which the Fe:Co:Ni ratio may vary within wide limits. This conclusion is confirmed by the available analyses of mineral specimens. Since the crystal structure of pentlandite does not require a fixed ideal value of the ratio, the problem of the "true" Ni:Fe ratio is meaningless, except when it refers to a centroid for a particular ore body or area. The same holds for the lattice parameter, though all the classical, i.e., low-cobalt, pentlandites have been found to have $a$ between 10.034 and 10.067 Å.

When natural pentlandite is heated in vacuo or in argon its lattice parameter increases by about 1/2 of one per cent. The expansion of the unit cell, which takes place between 150 and 200° C., is not prevented by argon pressures up to 2000 atm.

## INTRODUCTION

The formula of pentlandite was settled by crystallographic argument only in 1936 by Lindqvist, Lundqvist & Westgren (abbreviated in the following to LLW). They showed that pentlandite was isostructural with synthetic $\pi$(Co,S),[3] $Co_9S_8$, and consequently wrote its formula as $(Fe,Ni)_9S_8$. Lundqvist (1947) later reported that the lattice parameter of $\pi$(Fe,Ni,S) did not change with the total sulphur content of the synthetic samples, and that the $\pi$ phase invariably contained 47.0 atomic per cent S, irrespective of the quenching temperature. He stated that the stability limits of synthetic $\pi$(Fe,Ni,S) below 200° C corresponded to the compositions

$$Fe_{5.22\pm0.18}Ni_{3.78\pm0.18}S_8 \quad (a = 10.195 \text{ Å [from kX]) and}$$
$$Fe_{3.78\pm0.18}Ni_{5.22\pm0.18}S_8 \quad (a = 10.095 \text{ Å [from kX]).}$$

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[1] Part III of this series appeared in Canadian Journal of Chemistry (Knop & MacDonald, 1961).

[2] Present address: Department of Chemistry, Dalhousie University, Halifax, N.S.

[3] The term "$\pi$ phase" was first used by Lundqvist (1947) to designate the synthetic $D8_9$-type phase of variable Ni:Fe ratio in the system Fe-Ni-S. Since then other binary and ternary phases of this type have been described, and it has been found convenient to retain Lundqvist's notation for such phases, regardless of their actual stoichiometry.

On this information (i) pentlandite is a $\pi$(Fe,Ni,S) phase of a formula $(Fe,Ni)_9S_8$; (ii) its atomic Ni:Fe ratio may vary from 0.725 to 1.38; (iii) the presence of faint pyrrhotite lines in the two synthetic pentlandites of LLW, $Fe_{4.5}Ni_{4.5}S_8$ and $Fe_6Ni_3S_8$, is not consistent with the constancy of the sulphur content reported by Lundqvist for his samples. Assuming thermal equilibrium, the presence of pyrrhotite would point to a higher $M$:S ratio than the ideal value 9:8.

Since pentlandite has traditionally been looked upon as a typical iron-nickel sulphide, no attention has been paid to the small amounts of cobalt that have been consistently found whenever the mineral was analysed for this element. The not negligible cobalt contents (up to 3 weight per cent) and the large variations reported for the Ni:Fe ratio prompted Eliseev (1955) to re-examine the evidence relevent to the composition and formula of pentlandite.

On reviewing the thirty-five analyses that he found in the mineralogical literature Eliseev dismissed all those (mostly quite old) showing Ni:Fe ratios lower than unity, as originating in mixtures of pentlandite and pyrrhotite, pyrite, or the secondary iron and nickel sulphides. To accommodate the remaining analyses he proposed the formula $Fe^{iv}_4Ni^{iv}_4$ $(Co,Ni,Fe)^{vi}_{0-1}S_8$, where the superscript iv refers to tetrahedral and vi, to octahedral co-ordination. This formula provides for a variable $M$:S ratio, 1 to 1.125, as well as for a variable Ni:Fe ratio, 0.80 to 1.25. Cobalt can be accommodated to a maximum extent of 1/9 of the total metal content, which corresponds to the formula $Fe_4CoNi_4S_8$ or 7.62 weight per cent Co.

Unfortunately not one of Chirkov's analyses (1940), which Eliseev considered reliable, and which he used to demonstrate the constancy of the $M$:S ratio of pentlandite within an ore body, gives an $M$:S ratio less than 1.15, so that the proposed formula can hardly be said to account for the analyses explicitly scrutinized in Eliseev's paper.

An investigation of the $\pi$ phase existing in the $M_9S_8$ section of the quaternary system Fe-Co-Ni-S (Ibrahim, 1959; Knop & Ibrahim,) 1961) indicated as early as 1957 that the traditional concept of pentlandite as an iron-nickel sulphide containing small accidental admixtures of cobalt cannot be maintained. Instead, pentlandite must be considered a natural $\pi$(Fe,Co,Ni,S) phase in which iron and nickel are completely replaceable by cobalt (Fig. 1). Soon afterwards our correspondence with Kouvo (1959) concerning the identity of an unknown sulphide from Outokumpu, Finland, which had been taken for valleriite (Vähätalo, 1953; Kouvo & Vuorelainen, 1959), was followed by a description of pentlandites containing up to 49 weight per cent Co

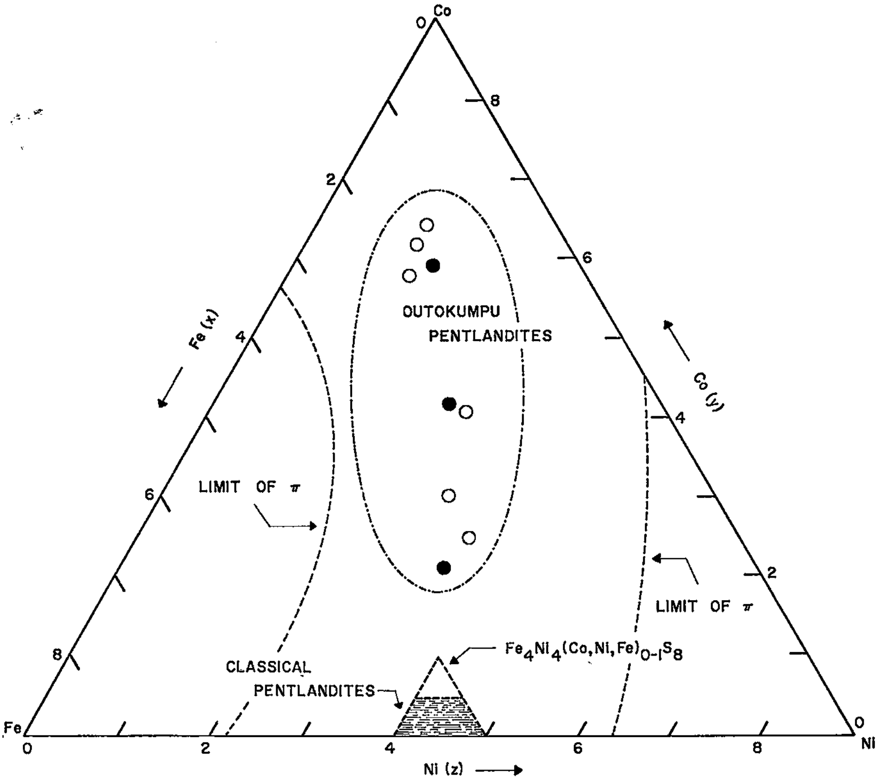

FIG. 1. Fe:Co:Ni ratios of natural pentlandites. The limits of $\pi$ refer to the estimated saturation boundaries of $\pi[(Fe,Co,Ni)_9S_8]$ (Knop & Ibrahim, 1961). Outokumpu pentlandites: open circles, chemical analysis (Kouvo, Huhma & Vuorelainen, 1959); full circles, microprobe (this work). The small shaded area is enlarged in Fig. 3.

(Kouvo, Huhma & Vuorelainen, 1959), thus confirming the above contention on the nature of pentlandite.

In the following the available analyses and crystallographic data of pentlandite, from the literature and our own, will be re-examined to provide a broader justification of the above view and possibly a comment on points (ii) and (iii). The paper will also describe certain phenomena that take place in natural pentlandite on heat treatment in vacuo or in an inert atmosphere under pressure.

## ANALYSES OF PENTLANDITE

The validity of Eliseev's comments on the older analyses is recognized. Thus while we reviewed all the analyses we could locate in the literature as pertaining to pentlandite, analyses showing atomic $M$:S ratios lower than 0.90 were discarded. The same holds for a few analyses showing a very large excess of iron over nickel. As will be shown later, a low Ni:Fe ratio *per se* is not a sufficient reason for discarding an analysis. But in practically all the discarded analyses the low Ni-Fe ratio was associated with a high sulphur content, both of which can be well accounted for by assuming the material to be a mixture of pentlandite and another iron-nickel sulphide.

Apart from these omissions Table 1 includes references to all the independent literature analyses. The selection is liberal; any material recognizably related to pentlandite is listed.

TABLE 1. STOICHIOMETRY OF PENTLANDITE

| | Atomic ratio[1] | | | $Fe_xCo_yNi_z$ | | | |
|---|---|---|---|---|---|---|---|
| No. | $\frac{Ni}{Fe}$ | $\frac{Co+Ni}{Fe}$ | $\frac{M^2}{S}$ | $x$ | $y$ | $z$ | Origin and Remarks[5] |
| | | | | *Theory*[3] | | | |
| a | 1 | 1 | 1.125 | 4.5 | — | 4.5 | $(Fe,Ni)_9S_8$, Ni:Fe = 1.00 |
| b | 1.10 | 1.10 | 1.125 | 4.28 | — | 4.72 | $(Fe,Ni)_9S_8$, Ni:Fe = 1.10 |
| c | 1 | 1.25 | 1.125 | 4 | 1 | 4 | $Fe_4CoNi_4S_8$ |
| | | | | *Alaska, Scotland, Norway and Switzerland* | | | |
| 1 | 0.62 | | 0.94 | | | | Bohemia Prospect, Yakobi Island, Alaska (Buddington). Po probably present. |
| 2 | 0.31 | | 0.95d | | | | Essochossan Glen, Inverary, Scotland (Greg & Lettsom). Po and Py present. |
| 3 | 0.21 | | 0.93 | | | | Essochossan Glen, Inverary, Scotland (Forbes). Po and Py present. |
| 4 | 0.19 | 0.21 | 0.93d | | | | Craigmuir mine, Loch Fyne, Inverary, Scotland (Forbes). |
| 5 | 0.42 | | 0.96d | | | | Espedalen, Gausdal, Norway (Scheerer). Pe and Po. The locality quoted for this material in Dana (1892) and elsewhere is Lillehammer. |
| 6 | 0.52 | | 0.97d | | | | |
| 7 | 1.04 | 1.05 | 0.99d | 4.39 | 0.06 | 4.55 | Eiterjord gård, Beiern River nr Tvervik, Norway (Vogt). |
| 8 | — | — | — | | | | Valle del Boschetto (see specimen A below). Microprobe. Ca 0.5 w/o Co; Cu very low if any. |

[1] Where copper determination is available the Fe and S contents have been corrected for chalcopyrite. [2] d, Sulphur determined directly. [3] Not included in the $M$:S ratios of Fig. 5. [4] Argentiferous pentlandite of Michener, see text. [5] Analytical figures given only for own analyses (except No. 39). Pe, pentlandite; Po, pyrrhotite; Py, pyrite; Cp, chalcopyrite; w/o, weight per cent.

TABLE 1.—*Continued*

| | Atomic ratio[1] | | | $Fe_xCo_yNi_z$ | | | |
|---|---|---|---|---|---|---|---|
| No. | Ni/Fe | (Co+Ni)/Fe | $M$[2]/S | $x$ | $y$ | $z$ | Origin and Remarks[5] |
| | | | | *Kola Peninsula and Petsamo* | | | |
| 9 | 1.10 | 1.15 | 1.19d | 4.19 | 0.21 | 4.60 | Monche Tundra, Kola Peninsula (Chirkov). |
| 10 | 1.07 | 1.10 | 1.17d | 4.28 | 0.14 | 4.57 | |
| 11 | 1.06 | 1.12 | 1.15d | 4.25 | 0.27 | 4.48 | |
| 12 | 1.01 | 1.10 | 1.19d | 4.29 | 0.38 | 4.33 | |
| 13 | 1.05 | 1.12 | 1.16d | 4.25 | 0.29 | 4.47 | |
| 14 | 1.06 | 1.12 | 1.19d | 4.25 | 0.22 | 4.53 | |
| 15 | 1.04 | 1.08 | 1.17d | 4.33 | 0.15 | 4.51 | |
| 16 | 1.05 | 1.09 | 1.18d | 4.30 | 0.18 | 4.53 | |
| 17 | 1.06 | 1.12 | 1.17d | 4.25 | 0.25 | 4.51 | |
| 18 | 1.05 | | 1.14 | 4.38 | | 4.62 | Kamikivitunturi, Finland (Michener & Yates). |
| | | | | *Outokumpu, Finland* | | | |
| 19 | 0.84 | 5.36 | 1.19d | 1.41 | 6.41 | 1.18 | Outokumpu, Finland (Kouvo, Huhma & Vuorelainen). Nos. 1-7 of the original paper. Corrected for Cp (less than 1 w/o of total sample); Fe, Co, Ni and S recalculated to 100% (Kouvo, 1959). |
| 20 | 0.75 | 4.56 | 1.13d | 1.62 | 6.17 | 1.21 | |
| 21 | 0.70 | 3.77 | 1.06d | 1.89 | 5.78 | 1.33 | |
| 22 | 1.29 | 3.16 | 1.15d | 2.16 | 4.06 | 2.78 | |
| 23 | 1.09 | 2.15 | 1.11d | 2.86 | 3.01 | 3.13 | |
| 24 | 1.22 | 2.06 | 1.12d | 2.94 | 2.49 | 3.58 | |
| 25 | 0.94 | 0.99 | 1.09d | 4.51 | 0.25 | 4.23 | |
| 26 | 1.05 | 1.68 | 1.11 | 3.36 | 2.12 | 3.52 | Outokumpu, Finland. Microprobe. 24.3 w/o Fe, 16.2 w/o Co, 26.8 w/o Ni; total metal content, 66.3 w/o. |
| 27 | 1.06 | 1.10 | 1.10 | 4.29 | 0.15 | 4.56 | Leppävirta, Finland. Microprobe. 30.8 w/o Fe, 1.2 w/o Co, 34.4 w/o Ni; total metal content, 66.4 w/o. |
| 28 | 1.00 | 4.78 | 1.10 | 1.55 | 5.90 | 1.55 | Outokumpu, Finland. Microprobe. 10.9 w/o Fe, 43.6 w/o Co, 11.4 w/o Ni; total metal content, 66.9 w/o. |
| 29 | 1.16 | 2.94 | 1.09 | 2.28 | 4.16 | 2.55 | Outokumpu, Finland. Microprobe. 16.2 w/o Fe, 31.2 w/o Co, 19.0 w/o Ni; total metal content, 66.4 w/o; see further notes below. |
| 30-33 | | | | | | | Unknown (Naldrett). Nos. S. Gen. 2-5 of the original paper. Co and Ni only. |
| | | | | *Sudbury, Ontario.* | | | |
| 34 | | 1.48 | 1.07d | (3.63) | | (5.37) | Mackenzie<br>Coarse Pe. Ni includes traces of Co. |
| 35 | 1.11 | | (0.95) | (4.27) | | (4.73) | Zurbrigg |
| 36 | 1.01 | | 1.19d | 4.49 | | 4.51 | Michener, 1940 |
| 37 | 1.06 | | 1.12 | 4.36 | | 4.64 | |
| 38 | 1.11 | 1.13 | 1.11d | 4.22 | 0.11 | 4.67 | Frood mine (Dickson) |
| 39[4] | 1.02 | | (0.91) | | | | Frood mine (Michener, 1940)<br>3.8 w/o Ag. Native Bi present. |
| 40 | | 1.10 | 1.06d | 4.27 | | (4.73) | Stobie mine (Browne)<br>Po present as fine dust. Ni plus Co. |

TABLE 1. *Stoichiometry of pentlandite—concluded*

| | Atomic ratio[1] | | | $Fe_xCo_yNi_z$ | | | |
|---|---|---|---|---|---|---|---|
| No. | $\frac{\mathrm{Ni}}{\mathrm{Fe}}$ | $\frac{\mathrm{Co+Ni}}{\mathrm{Fe}}$ | $\frac{M^2}{\mathrm{S}}$ | $x$ | $y$ | $z$ | Origin and Remarks[5] |
| 41 | | 1.08 | 1.01d | 4.30 | | (4.70) | Evans mine (Browne)<br>Po present as fine dust. Ni plus Co. |
| 42 | 0.87 | 0.92 | 0.96d | 4.68 | 0.27 | 4.06 | Garson mine (Michener, 1940) |
| 43 | 1.10 | 1.13 | 1.12d | 4.22 | 0.11 | 4.66 | Creighton mine (Dickson). |
| 44 | 1.08 | | 1.15 | 4.32 | | 4.67 | Creighton mine (Michener & Yates) |
| 45 | 1.13 | 1.14 | 1.09 | 4.20 | 0.06 | 4.74 | Creighton mine (see specimen S below) (Ibrahim)<br>30.00 w/o Fe, 0.45 w/o Co, 0.018 w/o Cu, 36.20 w/o Ni (plus probably most of Co). Average of 4 duplicate determinations. |
| 46 | 1.07 | 1.11 | 1.13d | 4.27 | 0.17 | 4.56 | Worthington mine (Walker) |
| 47 | 1.12 | 1.15 | 0.98d | 4.19 | 0.13 | 4.68 | No. 47: Pe plus polydymite? (Walker). |
| 48 | 1.10 | 1.12 | 1.10d | 4.24 | 0.11 | 4.66 | Worthington mine (Dickson) |
| 49[3] | 0.99 | | 1.24 | (4.51) | | (4.49) | Worthington mine (Mixer)<br>"Folgerite" |
| 50 | 0.96 | | 0.93 | (4.58) | | (4.42) | |
| 51[3] | 1.05 | | 0.73 | | | | |
| 52 | | 1.12 | 1.05d | 4.25 | | (4.75) | Copper Cliff mine (Browne) |
| 53 | | 1.10 | 1.09d | 4.29 | | (4.71) | Ni plus Co. |
| 54 | 1.08 | 1.10 | 1.09d | 4.28 | 0.11 | 4.61 | Copper Cliff mine (?) (Penfield). |
| 55-57 | | | | | | | McKim mine (Naldrett)<br>Nos. Sk 10, 46 and 47 of the original paper; Co and Ni only. |
| 58-59 | | | | | | | East mine (Naldrett)<br>Nos. SE 2 and 4 of the original paper; Co and Ni only. |
| 60-65 | | | | | | | Falconbridge mine (Naldrett)<br>Nos. SF 2, 4, 5, 7, 8, and 10 of the original paper; Co and Ni only. |
| 66-79 | | | | | | | Hardy mine (Naldrett)<br>Nos. SH 47, 50-53, 55, 58, 59, 61-65 and 67 of the original paper; Co and Ni only. |

TABLE 1. *Continued: Specimens used in the present work*

| No. | Origin | Remarks |
|---|---|---|
| S | Creighton mine, Sudbury<br>(Int. Nickel Co. of Canada, Ltd.) | Coarse crystalline ore. Large Pe grains intergrown with Po. Relatively little Cp. |
| F | Frood mine, Sudbury<br>(Dr. C. H. R. Gauthier, G.S.C.) | Intimately intergrown Pe, Po, Cp, Py, etc. |
| B | Falconbridge mine, Sudbury<br>(Falconbridge Nickel Mines Ltd.) | Almost massive ore. Very coarse Pe, Po, Cp, etc. |
| K | McKim mine, Sudbury<br>(Falconbridge Nickel Mines Ltd.) | Pe, Po, Cp, etc. disseminated in quartz. |
| L | Lynn Lake, Man.<br>(Sherritt Gordon Mines Ltd.) | Similar to F but Pe coarser. |

TABLE 1. *Specimens used in the present work—concluded*

| No. | Origin | Remarks |
|---|---|---|
| M | Moak Lake, Man.<br>(Int. Nickel Co. of Canada, Ltd.) | Basic rock with veins of Pe intergrown with Po. |
| R | Rankin Inlet, N.W.T.<br>(North Rankin Nickel Mines, Ltd.) | Massive ore, fine to medium grained. Pe and Cp in a matrix of Po. |
| P | Kaulatunturi, Petsamo<br>(Dr. A. Laitakari) | Massive ore with Pe inclusions up to 5 mm dia. |
| 26-29 | Outokumpu, Finland<br>(Dr. O. Kouvo) | For general mode of occurrence and association see Vähätalo; Kouvo, Huhma & Vuorelainen. No. 26: Outokumpu mine (Pe & Po in quartz matrix). No. 27: Leppävirta, Kotalahti, 250-level (almost massive ore, Pe & Po & Cp). No. 28: Outokumpu mine, No. 2 area, 285 Mpl/Oku (disseminated Pe & Po & Cp). No. 29: Outokumpu mine, No. 3X area, I/Oku (same as No. 28). |
| A | Valle del Boschetto nr Palagnedra, Centovalli, Switzerland<br>(Prof. F. de Quervain) | Same as No. 8. Material described by Friedenreich (1956). Grey-black hornblende peridotite containing macroscopic but very small Pe grains. Heavy-liquid separation; magnetic separation not feasible because of the strongly magnetic matrix. |
| V | Vlakfontein 902, N. W. Rustenburg District, Transvaal<br>(Prof. T. W. Gevers) | G. S. Unicn of S. Africa No. 3912. Massive fine-grained Po & Pe with Pe inclusions resembling those in P. |

To reinforce some of the following arguments several pentlandite grains were analyzed *in situ.* Results obtained in this manner are free from objections on grounds of incomplete separation of pentlandite from the associated sulphide minerals.

Of the five microprobe analyses listed in Table 1 four (Nos 26-29) were obtained through the kindness of Dr. J. V. P. Long of the Department of Mineralogy and Petrology, University of Cambridge, who provided these comments:

> "The analyses of Fe, Co and Ni are each the mean of several determinations. The standard error is estimated to be ±1% of the determined value except for the cobalt determination in No. 27, where it is probably nearer ±10%. The results have been corrected for absorption and fluorescence but not for the variation in the average atomic numbers between specimens and the pure-metal standards. The latter correction, if applied, would reduce the determined metal contents by probably less than 1%.
>
> Rough checks on the cobalt and nickel in the associated pyrrhotite and chalcopyrite of No. 29 showed that the metal content was in each case below 0.2 weight per cent."

The fifth microprobe analysis (No. 8) was a semiquantitative run on an Alpine pentlandite using a JXA-3 electron probe $x$-ray microanalyser of the Japan Electron Optics Laboratory Co., Ltd.

The mineral specimens are described in Table 1. The ore specimens used in this work (S to V) were usually coarsely crushed, handpicked, separated with a powerful magnet, the non-magnetic grains handpicked again, ground to pass 100 mesh or better, and fractionated a number of times on Frantz Isodynamic Separator Model L1 using the highest field strength obtainable. In some cases preliminary heavy-liquid separation with tetrabromoethane was repeatedly employed to remove excessive gangue.

## THE Fe:Co:Ni RATIO

Of the 79 analyses referred to in Table 1, fifty are sufficiently complete for a discussion of the stoichiometry of pentlandite. The atomic ratios Ni:Fe, (Co + Ni): Fe, and metal-to-sulphur are shown. Also shown are the atomic ratios Fe:Co:Ni expressed in terms of the assumed formula $Fe_xCo_yNi_zS_8$ with $x + y + z = 9$. The ratio $x$: $y$:$z$ provides a convenient basis for comparison while it in no way prejudices a discussion of the actual $M$:S ratio in the mineral.

Omitting the argentiferous pentlandite of Michener (No. 39) which will be dealt with separately, the Ni:Fe ratios of the 49 pentlandites are grouped in Fig. 2.[4] One sees that while the composite aggregate has a considerable width, ranging from about 0.2 to almost 1.5, the unimodal peaks for Sudbury and Monche Tundra are relatively narrow and center at 1.05—1.10. There is no well-defined peak for Outokumpu, but here the spread is accounted for by the high cobalt contents of some of the specimens, and even so the distribution centers around 1.01. The frequency distribution for the remaining analyses is confused.

When only analyses reported after 1930 (28 in all) are considered a unimodal peak of some width is obtained centering at 1.05. The cut-off year is of course arbitrary, but the elimination of the very low values does seem to indicate inadequacy of some of the older figures. It is noteworthy, however, that the positions of the centroids of this distribution and of the distribution for all analyses differ very little. The seemingly double peak in the latter distribution is almost certainly due to the small size of the statistical sample and may be disregarded.

[4] Where separate cobalt determinations were not available (Co + Ni): Fe ratios were used instead. This substitution may result in an appreciable shift, but the uncertainty should be considered in conjunction with the efficacy of the older separation procedures for cobalt and nickel, and with the fact that where only iron and nickel analyses are quoted, and plotted as such, the Ni:Fe ratio may in reality be an incomplete (Co + Ni): Fe ratio. This consideration is equally true of Fig. 3.

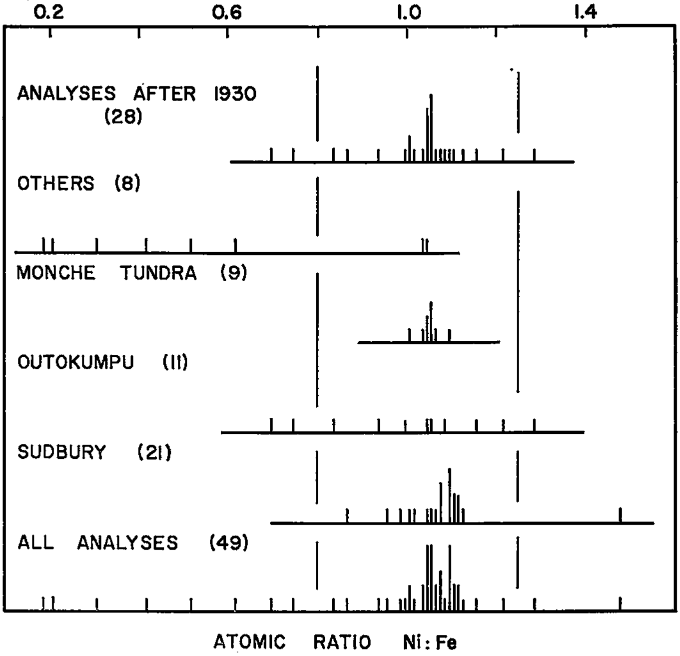

FIG. 2. Analyses of natural pentlandite grouped according to their atomic Ni:Fe ratios. The two vertical lines refer to the Ni:Fe limits permitted by Eliseev's formula. The number of analyses in a particular distribution is indicated in brackets.

Inspection of the distributions shows that all the analyses reported before 1959, and a few more recent ones as well, fall within a very small region of the composition triangle Fe-Co-Ni (Fig. 3). They can in fact be accommodated by a formula $Fe_xCo_yNi_z$ with $4.1 < x < 4.7$, $0 \leqq y < 0.4$, and $4.0 < z < 4.8$. If three doubtful points are discarded the range of $x$ and $z$ can be narrowed down even more. In these "classical", low-cobalt pentlandites the Ni:Fe ratio does not exceed 1.15 and is never, with the exception of four analyses (three of which are doubtful), lower than unity. As may be seen in Fig. 1 the Fe:Co:Ni ratios of these classical pentlandites are all amply provided for by Eliseev's formula.

On the other hand, the high-cobalt pentlandites reported in 1959 by Kouvo, Huhma & Vuorelainen are entirely within the existence limits of synthetic $\pi$(Fe, Co, Ni, S) but far outside the composition range permitted by Eliseev's formula (Fig. 1). To corroborate Kouvo's results, and to remove any possible objection to his chemical analysis

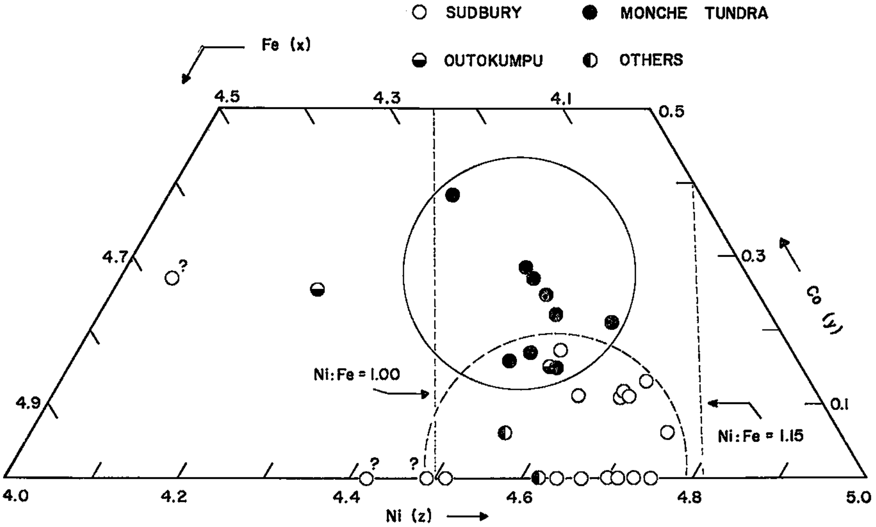

FIG. 3. Fe:Co:Ni ratios in classical pentlandites (Table 1). The Monche Tundra (solid-line circle) and the Sudbury (broken-line circle) pentlandites show regional constancy within relatively narrow limits.

on grounds of insufficient quantities of sample and incomplete separation, microprobe analyses of three high-cobalt specimens from Outokumpu (Nos 26, 28 and 29) were obtained. When plotted together these nine analyses fall within an elongated composition region along the Ni:Fe = 1 line. It is interesting to note that the Ni-Fe ratios of the high-cobalt specimens are all within 0.70—1.29, in spite of the strong variation in their cobalt content, and most of them are much closer to unity.

From these observations it is concluded that (a) the formula proposed by Eliseev does not account for the composition of the pentlandite species, but it does accommodate the Fe:Co:Ni ratios of the classical pentlandites; (b) pentlandite is to be considered an iron-cobalt-nickel sulphide rather than an iron-nickel sulphide; and (c) no general significance should be attached to particular values of the Ni:Fe ratio, as any value consistent with the homogeneity range of $\pi$(Fe,Co,Ni,S) may occur. It may, however, be meaningful to consider special values, or ranges of values, of the ratio as regionally dependent and characteristic of particular ore bodies, as appears to be the case for the classical pentlandites of the Sudbury basin and Kola Peninsula (Figs. 2 and 3).[5]

This is equally true of the ratios (Co + Ni): Fe and Ni:Co. Naldrett's

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[5] Note added in proof: Andronopoulos (1961) examined a pentlandite from Akrini near Veria, W. Macedonia, by microprobe and found the Ni:Fe ratio to be approximately 2:1.

numerous determinations (1961) of the weight ratio Ni:Co in Sudbury pentlandites (Nos. 55-79; see also Hawley, 1962) may be of great importance for the topography and genetic studies of the Sudbury ore, but they do not throw additional light on the general problem of the cobalt content of the mineral. This is shown in Fig. 4, where the logarithms of all the Ni:Co weight ratios referred to in Table 1 (plus the averages for Sudbury quoted in Hawley's Table 6) are plotted against the logarithms of weight per cent Co. Although the logarithmic representation strongly distorts the Fe-Co-Ni composition triangle, there is no doubt that all the points fall within the homogeneity region of synthetic π(Fe,Co,Ni,S), the majority being quite close to the Ni:

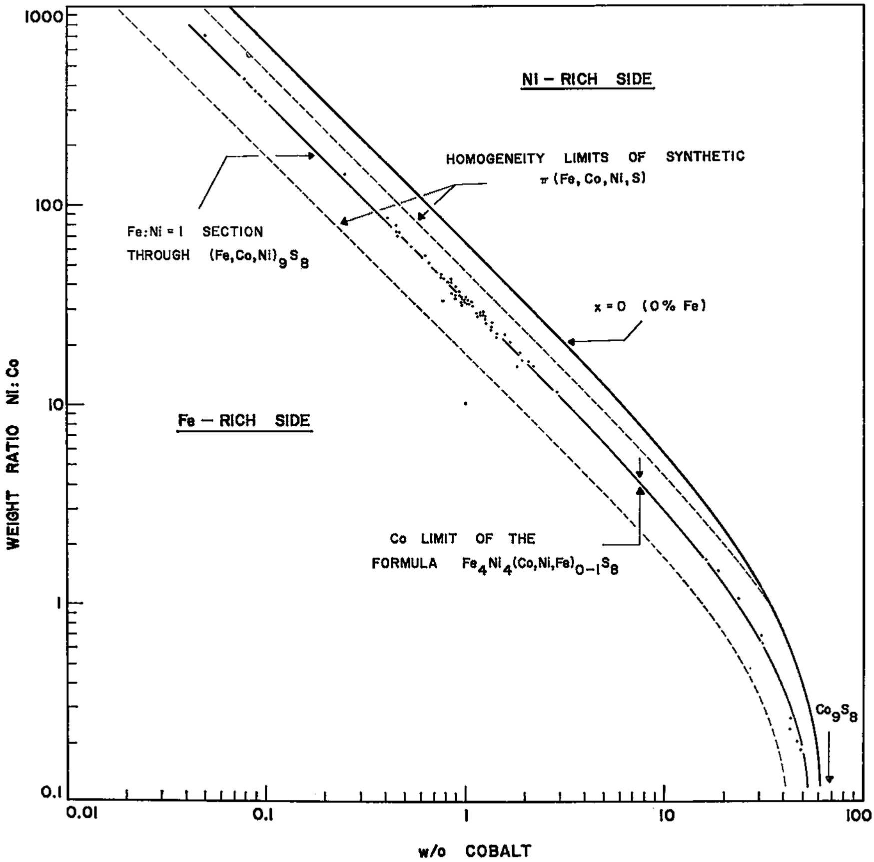

FIG. 4. Logarithmic plot of the Ni:Co weight ratio against weight per cent of cobalt. Included are all specimens of Table 1 for which the ratio is known or estimated as well as the averages quoted by Hawley (1962) for Sudbury pentlandite.

Fe = 1 line.[6] In fact, Fig. 4 can be conveniently used for checking the correctness of cobalt and nickel determinations. The apparent constancy of the weight ratio Ni:Co, in the vicinity of 34, for Sudbury pentlandite (Hawley, 1962) is thus only of regional significance.

Attention is drawn here to the very low cobalt and nickel contents of the pyrrhotite and chalcopyrite associated and in contact with pentlandite in specimen No. 29, below 0.2 weight per cent each. Considering that this specimen contained 31.2 weight per cent Co, this disproportionation is significant for cobalt distribution studies in sulphide assemblies and agrees well with the observations made by Naldrett on Sudbury material.

## The $M$:S Ratio

The crystal structure of the $\pi$ phase ideally requires an $M$:S ratio of 9:8 = 1.125. In so far as one can rely on the $M$:S ratios that have been reported for the mineral it is seen (Fig. 5) that most values are

TABLE 2. UNIT-CELL DIMENSIONS OF UNTREATED PENTLANDITE (literature values)

| No.[1] | Origin | Level, ft. | $a$, Å[2] | |
|---|---|---|---|---|
| | Beiern, Norway (Alsén, 1925) | | 10.02 | ±7 |
| | Klevagruva, Småland, Sweden (Byström, 1946) | | 10.035 | 3[3] |
| | Lavergruvan, Västerbotten, Sweden (Byström, 1946) | | 10.046 | 3[3] |
| | Monche Tundra, Kola Peninsula, No. 220 (Eliseev, 1955) | | 10.043 | 4[4] |
| | Monche Tundra, Kola Peninsula, No. 221 (Eliseev, 1955) | | 10.058 | 3 |
| 20 | Varislahti, Finland (Kouvo, Huhma & Vuorelainen, 1959) | | $9.969_7$ | 1 |
| 22 | Outokumpu, Finland (Kouvo, Huhma & Vuorelainen, 1959) | | $9.999_8$ | 1 |
| 25 | Outokumpu, Finland (Kouvo, Huhma & Vuorelainen, 1959) | | $10.067_5$ | 1 |
| | Sudbury, Ont. (LLW) | | 10.02 | |
| | Worthington mine, Sudbury, Ont. (Robinson & Brooker, 1952) | | 10.042 | 5 |
| 39 | Frood mine, Sudbury, Ont. (Michener, 1940)[5] | lower levels | 9.55 | |
| 60 | Falconbridge mine, Sudbury, Ont., SF2 (Naldrett) | 575 | 10.036 | 3 |
| 61 | Falconbridge mine, Sudbury, Ont., SF4 (Naldrett) | 1400 | 10.043 | 3 |
| 62 | Falconbridge mine, Sudbury, Ont., SF5 (Naldrett) | 1925 | 10.040 | 3 |
| 65 | Falconbridge mine, Sudbury, Ont., SF10 (Naldrett) | 4025 | 10.036 | 3 |
| 66 | Hardy mine, Sudbury, Ont., SH47 (Naldrett) | 250 | 10.051 | 3 |
| 68 | Hardy mine, Sudbury, Ont., SH51 (Naldrett) | 375 | 10.051 | 3 |
| 71 | Hardy mine, Sudbury, Ont., SH55 (Naldrett) | 500 | 10.054 | 3 |
| 72 | Hardy mine, Sudbury, Ont., SH58 (Naldrett) | 625 | 10.044 | 3 |
| 75 | Hardy mine, Sudbury, Ont., SH62 (Naldrett) | 750 | 10.050 | 3 |
| 78 | Hardy mine, Sudbury, Ont., SH65 (Naldrett) | 875 | 10.041 | 3 |
| 79 | Hardy mine, Sudbury, Ont., SH67 (Naldrett) | 1125 | 10.041 | 3 |

[1]See Table 1. — [2]Uncertainty refers to the last decimal (third decimal for Nos. 20, 22 and 25). — [3]The original values, 10.015 and 10.026, although stated to be in Å, were really in kX (*cf.* also Struct. Repts **10**, 91). — [4]Averaged from $a(\alpha) = 10.041 \pm 3$ Å and $a(\beta) = 10.046 \pm 4$ Å. — [5]Argentiferous pentlandite, see text.

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[6] The only exception is No. 4, but this is a very old analysis and not much confidence can be placed in the cobalt determination.

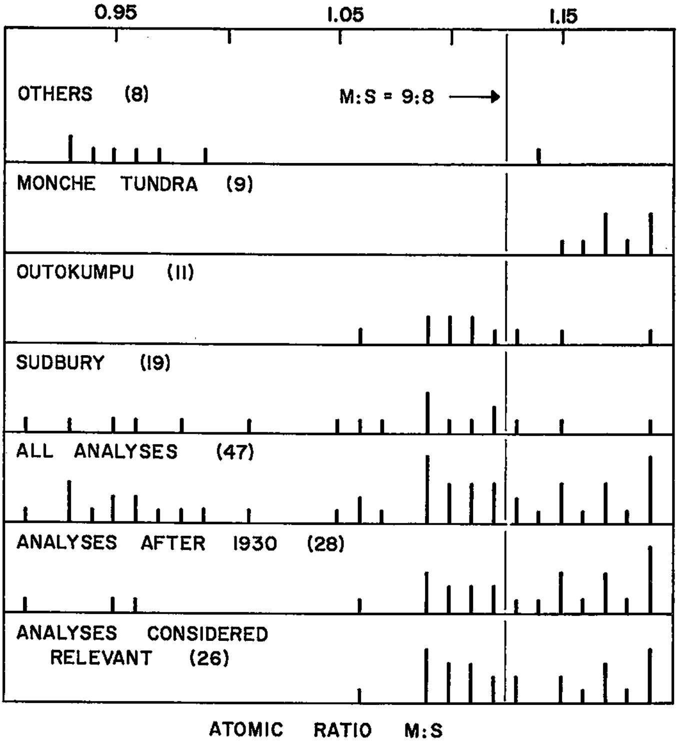

FIG. 5. Analyses of natural pentlandites grouped according to their M:S ratios in the interval 0.90 - 1.20. The number of analyses in a particular distribution is indicated in brackets.

greater than unity, the arithmetic average of the 47 ratios of Table 1 being 1.08 ± 0.09. When only values greater than unity (35 in all) are used the ratio increases to 1.124 ± 0.05, which is remarkably close to the ideal value. With "relevant" values, i.e., those that we consider reliable in the present context (Nos. 9-17, 19-29, 38, 43, 45, 46 and 54; 26 in all), a ratio of 1.133 ± 0.04 is obtained.

The meaning of these averages is uncertain. Rejection of $M$:S ratios smaller than unity is probably justified, but the closeness of the mean, 1.124, to the ideal ratio may well be fortuitous. Strangely enough Eliseev's formula does not accommodate the Monche Tundra analyses, even though they are expressly dealt with in his paper; and it is these ratios that are responsible for raising the average from 1.124 to 1.133 when only the "relevant" analyses are included.

While $M$:S ratios lower than 9:8 might be caused by admixture of species richer in sulphur than pentlandite, ratios higher than 1.125

can only originate in admixtures of heazlewoodite or one or two relatively rare sulphides, though of course oxides, arsenides and other species not contributing to the overall sulphur content would have the same effect. Assuming that the analysed specimens were all carefully handpicked and fractionated, which is not very likely,[7] it would seem that the composition of the homogeneous natural pentlandite phase does not correspond exactly with the formula $M_9S_8$ but is slightly higher in metal.

It seems unlikely that the problem of the $M$:S ratio in the mineral can ever be settled unless an accurate method of sulphur analysis *in situ* is available. As for assistance from synthetic studies, Lundqvist could not detect any variation in the sulphur content of quenched $\pi$(Fe,Ni,S) samples, and a similar observation was made with quenched $\pi$(Co,S) samples (Lundqvist & Westgren, 1938). Kullerud (1963) observed, in powder photographs of synthetic $Fe_{4.5}Ni_{4.5}S_8$ taken at 600° C, a large increase in the lattice parameter of the $\pi$ phase which he says far exceeded that of any other investigated sulphide. Since he reports to have obtained completely homogeneous $\pi$ at temperatures below the break-up temperature of $\pi(Fe_{4.5}Ni_{4.5}S_8)$, 610 ± 2° C, the increase in $a$ would seem to be due solely to thermal expansion rather than to a change in the $M$:S ratio. The appearance of faint pyrrhotite lines in the powder patterns of synthetic $(Fe,Ni)_9S_8$ samples at room temperature (LLW; Knop & Ibrahim), which has been interpreted as originating in an $M$:S ratio of the equilibrium $\pi$(Fe,Ni,S) somewhat higher than 9:8, may, in view of Kullerud's finding, have been caused by incomplete equilibration, but this point requires further work.

Our own preliminary experiments (Knop & Sutarno) show a slight dependence of the room-temperature $a(\pi)$ on the sulphur content in samples $(Fe,Ni)_9S_{8-x}$ ($0 \leqq x \leqq 0.2$) that were carefully prepared, homogenized, annealed at 580-600° C for several days and slowly cooled. The homogeneity range is quite small, but it is wider than the corresponding range for $\pi$(Co,S), which has been found to be very narrow, approximately $1.123 \leqq$ Co:S $\leqq 1.126$ (Stubbles, 1957; Knop & Ibrahim).

## PENTLANDITES BASED ON SYSTEMS OTHER THAN Fe-Co-Ni-S

The only example is the argentiferous pentlandite (No. 39) reported by Michener (1940) (see also Hawley, 1962) from the lower levels of

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[7] Even in Kullerud's recent study (1963) the "exceptionally pure" material from Frood mine supplied by Hawley was not entirely pure but was intergrown with small amounts of pyrrhotite and chalcopyrite.

the Frood mine, Sudbury. This material is said to have contained possibly as much as 3.8 weight per cent Ag and some bismuth. Its lattice parameter, 9.55 Å, was far below the range of $a$ values for natural pentlandite. This is odd, since the lowest $a(\pi)$ value found in the system $(Fe,Co,Ni)_9S_8$ was 9.928 Å (for pure $Co_9S_8$), and silver, with its much larger atomic radius than the radii of the 3$d$-elements, would be expected to increase, or at least not decrease, the size of the unit cell of the $\pi$ phase. As shown in Fig. 6, examination of synthetic samples $Co_8MS_8$ (not necessarily one-phase), where $M$ = Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ru, Rh, Pd, Ag, Sn, Os, Ir and Pt, has demonstrated that none of these elements lower the cell size of $\pi$(Co,S), although Fe, Ni, Ru, Rh and Pd increase it noticeably (Knop, 1962). With the exception of the five last-named the metals do not seem to enter the $\pi$ structure to any appreciable extent. Similarly, the spectrographic analyses of Sudbury pentlandite quoted by Hawley (1962) show a conspicuous absence of elements other than Fe, Co, Ni and S,[8] although the apparent reluctance to enter pentlandite might also be explained by an overall paucity of such elements in the ore body or by unfavourable distribution equilibria.

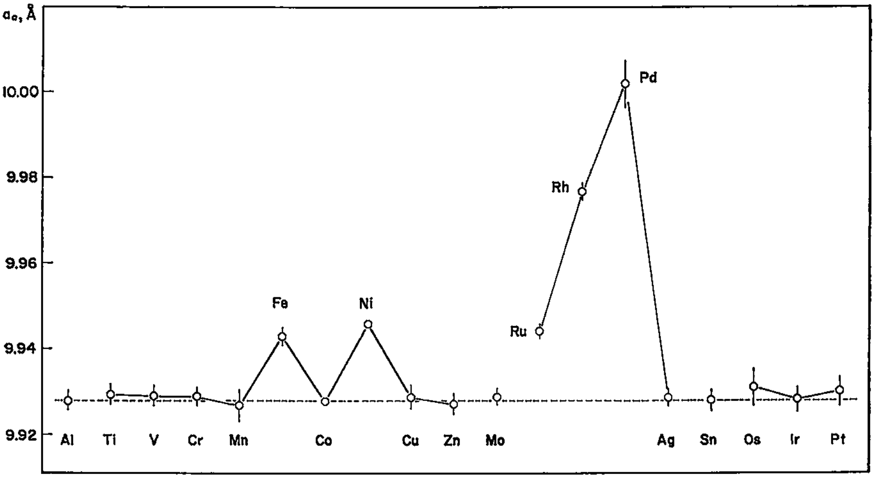

FIG. 6. Effect of substitution on the unit-cell dimensions of $\pi(Co_8MS_8)$. Only Fe, Ni, Ru, Rh and Pd expand the lattice. The $a$ value of $Co_9S_8$ is indicated by the broken line.

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[8] Cr, V. Ti, Mo and Sn are often below the limits of detection; Pb may be present in amounts up to 0.1 weight per cent. Ag is often associated with lead but varies from less than 1 ppm to 14 ppm. Even Se is found to average no more than 90 ppm.

In spite of careful search Hawley, in his extensive work on the Sudbury ores, did not encounter argentiferous pentlandite. Micheners' polished sections have unfortunately not been kept, and the original material is virtually impossible to duplicate, since the section of the Frood mine from which it came is now inactive (Michener, 1963).

Since no information bearing on the identity of Michener's material could be found in the literature, synthetic samples of gross compositions $Co_8AgS_8$ and $Fe_4Ni_4AgS_8$ were prepared by dry synthesis from high-purity elements in vacuo.[9] The cobalt sample was found to consist of a $\pi$ phase ($a$ = 9.928 ± 0.001 Å) and argentite. A few faint lines could not be identified with certainty. The high-angle lines of the Fe-Ni sample lacked in sharpness even on repeated annealing, so that the accuracy of the lattice parameter determination was low. But there was no doubt that the pattern was composite, consisting of a $\pi$ phase pattern ($a$ = 10.119 ± 0.003 Å; Mo used as a calibration substance) and a pattern of another face-centered cubic phase with $a$ = 10.499 ± 0.003 Å, whose composition is as yet unknown. The latter pattern seemed to be stronger relative to that of the $\pi$ phase.

Recalling that $a$ of pure $Co_9S_8$ is 9.9279 ± 0.0005 Å (Knop & Ibrahim; Fig. 6), the cobalt $\pi$ phase in contact with argentite cannot have contained an appreciable amount of silver. Comparison of $a$ of $\pi(Fe_4Ni_4AgS_8)$ with the lattice parameter of $\pi(Fe_{4.5}Ni_{4.5}S_8)$ shows an increase of 0.004 Å, which is too small and uncertain to be considered as meaningful information. It is thus seen that in neither case was the lattice parameter of the "parent" compound lowered by the presence of silver.

The evidence is only circumstantial, but it seems reasonable to conclude from it that the mineral is unlikely to have been a $\pi$ phase. In view of the smallness of the samples the analytical figures must be viewed with caution, and in fact the method which was used to extract minute amounts of the mineral from the matrix does not exclude the possibility that silver may have been introduced as a contamination from the surrounding material (Michener, 1963). Any suggestion as to the identity of the mineral must thus be only tentative.

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[9] The samples were prepared in the usual way (see Knop & Ibrahim). The grinding and annealing was repeated until there was no further improvement in the powder photographs. $Co_8AgS_8$ (1st sample): reacted at 750° C.; 750° C./13 days, cooled with furnace; heated briefly to 970° C., cooled in furnace; 700° C./8 days, cooled with furnace over 3 days. $Co_8AgS_8$ (2nd sample); reacted at 800° C.; 750° C./6 days; heated briefly to 1000° C., cooled in furnace (well sintered, silvery in appearance); 600° C./10 days, cooled with furnace over two days. $Fe_4Ni_4AgS_8$: reacted at 800° C.; 730° C./41 hrs.; heated briefly to 1000° C., cooled in furnace (sample had partially melted); 650° C./5 days; 600° C./7 days, cooled with furnace over a week.

## UNIT CELL DIMENSIONS OF SYNTHETIC $\pi$(Fe,Ni,S)

These are shown in Fig. 7 which is essentially based on previous results (Knop & Ibrahim). The extreme values are 10.211 ± 0.002 Å, for $\pi(\mathrm{Fe}_{6.75}\mathrm{Ni}_{2.25}\mathrm{S}_8)$, and 10.086 ± 0.002 Å, for $\pi(\mathrm{Fe}_{2.25}\mathrm{Ni}_{6.75}\mathrm{S}_8)$. The homogeneity limits are now being determined more accurately, but there is no doubt that they are wider than previously stated by Lundqvist. For comparison the corresponding curve for $\pi[(\mathrm{Fe,Ni})_8\mathrm{CoS}_8]$ is included. The decrease in *a* due to the *ca* 7.6 weight per cent Co is no greater than 0.055 Å, i.e., about 0.5 per cent. The sensitivity of the lattice parameter to variations in the cobalt content is thus low, and the two calibration curves are not well suited for estimating the composition of pentlandite from powder photography, except perhaps at the steep slope toward the iron-rich side.

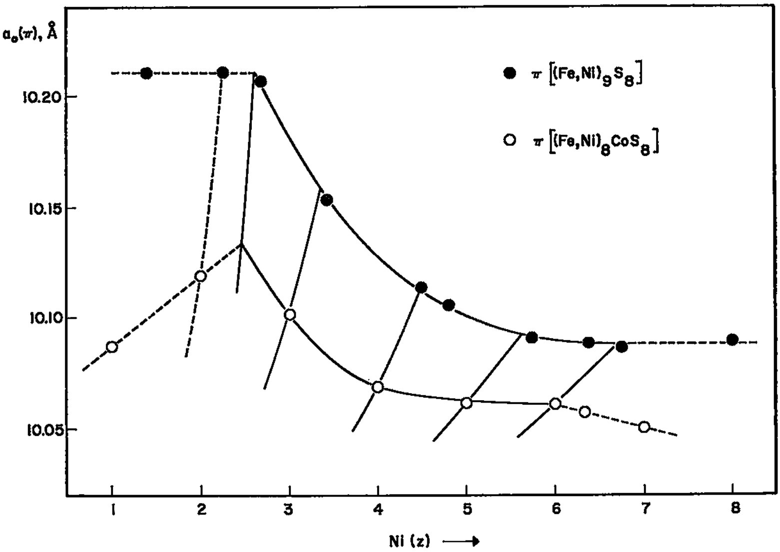

FIG. 7. Variation of *a* of $(\mathrm{Fe,Ni})_9\mathrm{S}_8$ and $(\mathrm{Fe,Ni})_8\mathrm{CoS}_8$ with composition (Knop & Ibrahim, 1961; slightly revised).

## UNIT CELL DIMENSIONS OF NATURAL PENTLANDITE

In the lower half of Fig. 8 *a* values for untreated classical pentlandite (max. 2 weight per cent Co) are shown, both literature values and our own (for details see Tables 2 and 3). The lattice parameters of all the pentlandites are lower than the values obtained with synthetic samples of

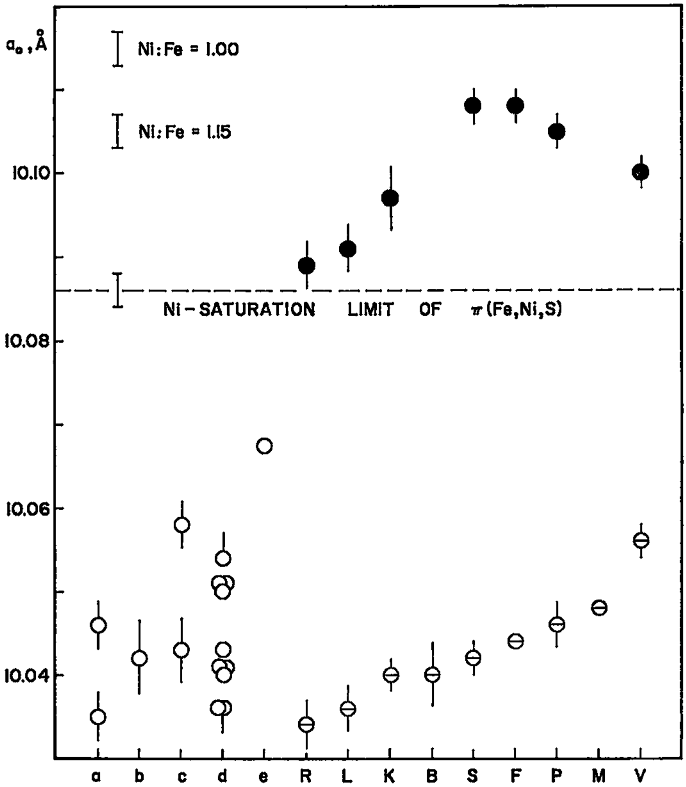

FIG. 8. Unit-cell dimensions of natural pentlandite before (crossed circles) and after (full circles) annealing *in vacuo* (see Table 3). Literature values for untreated pentlandite (open circles): a, Byström (2); b, Robinson & Brooker; c, Eliseev (2); d, Naldrett (11); e, Kouvo, Huhma & Vuorelainen (No. 25).

Ni:Fe between 1 and 1.15, and indeed with any composition $(Fe,Ni)_9S_8$. The highest *a* reported for the mineral, 10.067 Å (No. 25), is still below the lower limit of *a* for synthetic π(Fe,Ni,S) at the nickel saturation boundary, and typical values are appreciably lower. The difference between the average *a*, 10.045 ± .008 Å, for the natural pentlandites and *a* for the synthetic phase of Ni:Fe = 1.15 is 0.06 Å, i.e., about 0.6%.

On the other hand, the *a* values of the two Co-rich specimens (Nos. 20 and 22) are, as far as can be estimated, quite close to those of the corresponding synthetic compositions (Fig. 9). When allowance is made for the deviation of the Ni:Fe ratio from unity the two points are brought even closer to the curve.

The discrepancy for the classical pentlandites cannot be explained by allowing for the cobalt content of the mineral. The decrease in *a* from $\pi(Fe_{4.5}Ni_{4.5}S_8)$ to $\pi(Fe_4CoNi_4S_8)$ amounts to 0.046 Å per 7.6 weight per cent Co, and the difference becomes smaller with the decreasing Ni:Fe ratio. Thus for 2 weight per cent Co it would be 0.012 Å or less, which is insufficient to bring the synthetic values down into the *a* range of the mineral.

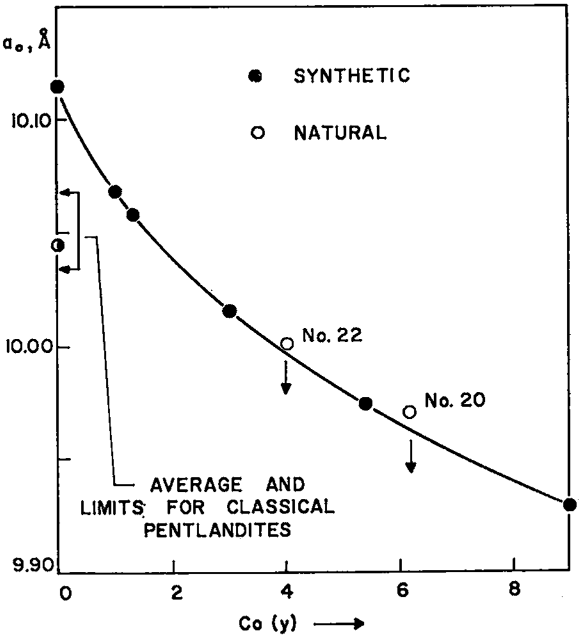

FIG. 9. Comparison of the unit-cell dimensions of two Co-rich pentlandites (Nos. 20 and 22) with *a* of synthetic $\pi(Fe_xCo_yNi_zS_8)$ ($M$:S = 9:8, Ni:Fe = 1).

## INCREASE OF *a* ON HEAT TREATMENT

When carefully separated natural pentlandite (−100 mesh) was annealed in vacuo at temperatures between 360 and 390° C, its lattice parameter increased and was now in the range of values obtained with the synthetic π phase (Fig. 8, upper half; Table 3) (Ibrahim). The increase was of the order of ½%. Although there was no sustained trend, specimens with initially low *a* tended to have low *a* values after annealing.

TABLE 3. UNIT-CELL DIMENSIONS OF PENTLANDITE BEFORE AND AFTER HEAT TREATMENT

| Sample[1] | untreated[2] | heat-treated[2] | Remarks[3] |
|---|---|---|---|
| P II | 10.046 ± 3 Å | 10.105 ± 2 Å | Essentially Pe; 375° C/66 hrs. in vacuo |
| V II | 10.056 2 | 10.100 2 | Essentially Pe; 375° C/66 hrs. in vacuo |
| R | 10.034 3 | 10.089 3 | 375° C/66 hrs. in vacuo |
| L | 10.036 3 | 10.091 3 | Mostly Pe; 375°/66 hrs. in vacuo |
| M | 10.048 1 | | |
| S | 10.042 2 | 10.108 2 | Essentially Pe; No. 45 of Table 1; 355-390° C/36 hrs. in vacuo |
| F | 10.044 1 | 10.108 2 | Pure Pe; 355-390° C/38 hrs. in vacuo |
| K | 10.040 2 | 10.097 4 | 375° C/66 hrs. in vacuo |
| B | 10.040 4 | | |
| | | *Creighton mine, Sudbury, Ont.* | |
| SL | 10.0426 ± 18 | 10.043 ± 2 | 117° C/64 hrs. in vacuo |
| | | 10.0472 14 | 151° C/64 hrs. in vacuo |
| | | 10.100 3 | 200° C/63 hrs. in vacuo |
| SL | 10.0423 ± 17 | 10.1024 15 | 300° C/63 hrs. in argon at 1000 atm. |
| | | 10.1008 18 | 390° C/63 hrs. in argon at 1000 atm. |
| | | 10.1022 23 | 390° C/63 hrs. in argon at 2000 atm. |
| SH | 10.0432 ± 17 | 10.1033 ± 18 | 200° C/63 hrs. in vacuo |
| | | 10.1022 22 | 365° C/63 hrs. in vacuo |
| | | 10.1011 25 | 300° C/63 hrs. in argon at 1000 atm. |
| | | 10.1034 32 | 390° C/63 hrs. in argon at 1000 atm. |
| | | 10.1010 26 | 390° C/63 hrs. in argon at 2000 atm. |

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[1] See Table 1 for origin of samples. SL and SH, hand-picked and magnetically fractionated: L least magnetic, H more magnetic of the two final fractions.

[2] Uncertainties refer to the third or to the third and fourth decimal places.

[3] Essentially Pe: a few very faint foreign lines, mostly of pyrrhotite. Mostly Pe: weak pyrrhotite lines present.

A more detailed investigation of Creighton mine pentlandite has shown that the lattice expansion is irreversible and takes place somewhere between 150 and 200° C. (Table 3). It has not yet been established whether the expansion occurs at a definite temperature or over a temperature range. Once it has taken place a further increase of temperature (up to 390° C.) does not produce additional increase in the room-temperature values of $a$.

## WHY DOES PENTLANDITE EXPAND ON ANNEALING?

Two things must be considered before an attempt is made to explain the expansion. First, with the exception of F all the heat-treated specimens contained some pyrrhotite prior to annealing. Secondly, the synthetic $(Fe,Ni)_9S_8$ samples were not completely homogeneous $\pi$. Consequently the compositions for which $a(\pi)$ were determined, though close, were not identical with the overall sample compositions (see above under $M$:S ratio).

As for the admixed pyrrhotite, it may be argued that heating increases the equilibrium saturation with iron of the π phase in contact with the pyrrhotite, which in turn leads to an expansion of the π lattice. However, the amounts of pyrrhotite present in S/H and S/L must have been very small, to judge from heavily exposed powder photographs and, to some extent, the magnetic behaviour, and in none of the specimens except L could the pyrrhotite content be described as significant.[10] The iron content of synthetic π at Ni:Fe = 1 would have to be increased by about 30% in order to produce an increment of 0.05 Å in *a*, and by more if the Ni:Fe ratio is greater than unity. Even if the entire amount of pyrrhotite dissolved in the π phase on heating, which is not very likely at the temperatures in question, and assuming that the pyrrhotite is a pure iron sulphide, the initial ratio of pentlandite to pyrrhotite required to increase *a* by 0.05 Å would have to be about 8:7. It is thus very unlikely that the explanation can be found in the uptake of iron by the pentlandite.

The second point cannot be very significant if one considers the rate of change of *a* with composition, and in any case the presence of small amounts of pyrrhotite in the synthetic samples would make comparison with the impure natural specimens, if anything, more favourable.

Oxidation and insufficient annealing of the synthetic samples may be ruled out as possible causes of the difference in *a*. The powders for heat treatment were sealed under $10^{-5} - 10^{-6}$ torr air pressure in quartz tubes with free volumes not exceeding 2-3 ml. The annealing temperatures were too low to produce significant changes in the $M$:S ratio, and available evidence shows that changes in $M$:S do not affect $a(\pi)$ appreciably (see above, and Knop & Sutarno). While recent results show that the synthetic samples were probably not sufficiently annealed, the internal consistency of $a(\pi)$ is good (Fig. 7 and 9).

Two possible explanations then come to mind. Assuming that there is no change of composition on annealing, the smaller unit-cell volume corresponds to a higher density, which in turn may have been produced by the action of high pressure during the formation of the mineral or during subsequent compaction. It could also be the result of geometrical ordering in the metal sublattices, which again would depend on very slow cooling or very long annealing times.

If the smaller unit-cell volume of natural pentlandite is the result of slow cooling, or annealing, at high pressure, it seems reasonable to expect that the lattice expansion on laboratory annealing could be

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[10] F especially was a very pure pentlandite, probably as pure as one can ever hope to obtain (see footnote no. 7).

prevented by maintaining comparable pressure during the heat treatment.

To test this hypothesis carefully separated Creighton mine pentlandite was annealed at 300 and 390° C. in purified argon under pressure. Gold liners charged with pentlandite powder (−100 mesh) were placed in high-pressure bombs and flushed with argon. About half the final pressure of argon was applied before heating, and as the temperature increased the pressure was gradually adjusted to its final value.

Comparison with specimens of the same material annealed *in vacuo* shows that the pressure did not prevent the lattice expansion from taking place (Table 3). In fact, once the temperature was high enough for the expansion to occur it did not seem to matter, up to 390° C., whether or not the temperature was subsequently raised. The increased *a* values were again in the synthetic range and showed very little spread. There seemed to be no difference between the L and H magnetic fractions.

Even when allowance is made for the initially lower gas pressure the pressure during passage through the transformation temperature must have been at least 500 atm in the first group of runs, and at least 1000 atm in the second, and likely higher in both cases. This would correspond to a vertical overburden of siliceous rock of at least 10,000 ft., which is well in excess of the recent depth of the mined ore body.

Naldrett, in an attempt to test the same point, examined located specimens of untreated pentlandite from different depths of the Hardy and Falconbridge mines. He arrived at a similar conclusion, namely that the depth was in no relationship to the lattice parameter of the mineral (corrected for the effect of cobalt) beyond a random spread (Table 2). Although his finding depends, *per se*, on the uncertainties in the estimates of the local rock-pressure conditions, when considered together with the results of the pressure annealing it appears to support the contention that pressures up to 1500-2000 atm do not suppress the lattice expansion.

The second possibility, *viz.*, order in the 32(*f*) sublattice (and possibly also in the 4(*b*) sublattice) in the untreated state and statistical distribution in the annealed state, is difficult to test by diffraction experiments, *x*-ray or neutron, and so far no evidence in support of either arrangement has been available. At present nothing can be said about the state of order in the mineral. A useful hint indicating a possible experimental approach may be contained in Michener's observation (1940) that the Sudbury "cobalt pentlandite" (No. 42) was weakly magnetic, in contrast with the non-magnetic very low cobalt species. If this difference in properties is real a detailed magnetic investigation might throw light on the problem of order. Unfortunately the Ni:Fe and $M$:S ratios of No. 42 are low, thus suggesting that pyrrhotite may have been responsible for the weak magnetism.

As for the first, compaction, hypothesis, in the absence of reasonably reliable estimates of pressures prevailing at, and subsequent to, the time of formation of pentlandite at any given locality the results of the pressure-annealing experiments are inconclusive. It may be that still higher pressures *would* counteract the lattice expansion. On the other hand, compaction may have been brought about by the action of pressure alone, without the necessity of simultaneous exposure to temperatures higher than those resulting from normal geothermal conditions; and if the phenomenon is due to ordering, geological time alone may have been responsible for the establishment of an ordered state, in spite of the presumably very low diffusion rates in the solid at ordinary temperatures, as apparently is the case with pyrrhotite (Smith, 1963).

The observed behaviour of pentlandite on heat treatment seems to suggest that those pentlandites in which lattice expansion occurs either cannot have been exposed *in situ* to temperatures in excess of 150° C once they have formed, as otherwise the lattice would have expanded; or if they had been, the time elapsed since the heating must have been sufficiently long for the unit-cell volume to decrease by some kind of ordering process. It should be borne in mind, however, that pentlandites from widely separated localities show similar behaviour, though it is unlikely that their geological histories are closely similar, and the same holds even for different sections of a large ore body.

Because of the geological implications as well as intrinsic interest it seems worth while to investigate the lattice expansion in more detail. Such a study by a variety of physical methods is now under way.

## Conclusions

1. Pentlandite is a natural $\pi$(Fe,Co,Ni,S) phase. There is nothing to suggest that its composition range is in any way different from that of the corresponding synthetic phase. Consequently the Fe:Co:Ni ratio may vary within wide limits (Fig. 1).

2. The crystal structure proposed for pentlandite by Lindqvist, Lundqvist & Westgren has been confirmed (Knop & Ibrahim; Pearson & Buerger; Geller). The model proposed for the structure by Eliseev is inconsistent with observed facts. Nothing is known at present about the degree of order in the metal sublattices.

3. The crystal structure does not require a fixed ideal value of the

Ni:Fe ratio. The "true" value of this ratio, or for that matter of the Ni:Co or Co:Fe ratios, is therefore meaningless, except when it refers to a centroid for a particular ore body or geological area. However, the mean of 28 selected analyses is 1.05 with a spread that is surprisingly narrow relative to the possible range of 0.33 −3.

4. The ideal $M$:S ratio is 9:8, but there are indications that the actual ratio may be slightly higher and dependent on the cobalt content. The composition of the mineral is probably best represented by the formula $(\mathrm{Fe,Co,Ni})_{9+x}\mathrm{S}_8$, $x \geqq 0$. The range of $x$, though very small, is uncertain.

5. The "classical," i.e., low-cobalt, pentlandites reported in the literature have Fe:Co:Ni ratios that are accommodated by the formula $\mathrm{Fe}_x\mathrm{Co}_y\mathrm{Ni}_z$, where $4.1 < x < 4.7$, $0 \leqq y < 0.4$, and $4.0 < z < 4.8$.

6. The formula $\mathrm{Fe_4Ni_4(Co,Ni,Fe)_{0\text{-}1}S_8}$ proposed by Eliseev is not sufficiently general and is in some respects invalid, although it does represent the compositions of many of the classical pentlandites.

7. It is doubtful whether the "argentiferous pentlandite" reported by Michener (1940) was a homogeneous $\pi$(Fe,Ni,Ag,S) phase. The identity of the mineral must be considered as not established.

8. Homogeneous $\pi$ phases of the type $\pi$(Fe,Co,Ni,$M$,S), where $M$ = Ru, Rh or Pd, can conceivably exist as minerals.

9. The unit-cell dimensions of the classical pentlandites are relatively constant. The reported values are all between 10.034 and 10.067 Å.

10. On annealing at temperatures above 150° C. *in vacuo* classical pentlandite undergoes a lattice expansion. The expansion is not prevented from taking place by argon pressures up to 2000 atm.

11. Although the nature of the expansion process is not known at present, its existence has certain geological implications.

## ACKNOWLEDGMENTS

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