THERMAL STABILITY OF PENTLANDITE

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ABSTRACT

The thermal stability of pentlandite was studied by quenching, differential thermal analysis, and high-temperature *x*-ray diffraction experiments. Rigid silica tubes were employed as reaction vessels, and vapor, therefore, is an inherent phase in all three types of experiments.

Synthetic pentlandite of $Fe_{4.5}Ni_{4.5}S_8$ composition was found to decompose at 610°±2° C. to $(Fe,Ni)_{1-x}S$ with hexagonal pyrrhotite structure and to a high-temperature nonquenchable phase, equivalent to $Ni_{3\pm x}S_2$ of the pure Ni-S system, but containing some iron. Of these phases $(Fe,Ni)_{1-x}S$ has low Ni content and a metal-to-sulphur ratio of 9:10 or possibly slightly higher, and the $Ni_{3\pm x}S_2$ phase has a metal-to-sulphur ratio of 3:2 or slightly less.

The first appearance of liquid was recorded at 862° C. in differential thermal analysis experiments on synthetic material of $Fe_{4.5}Ni_{4.5}S_8$ composition. This temperature corresponds to that given in the literature as the "melting point" for pentlandite. Experiments on pentlandite from Frood Mine, Sudbury, show breakdown of pentlandite at 613° C. and melting effects in the temperature region 864° to 881° C.

These experimental results have important bearing on the geological interpretation of pentlandite-pyrrhotite assemblages in ores such as those of the Sudbury area.

In the pure Fe-Ni-S system a field containing homogeneous liquid of composition pertinent to the formation of pentlandite-pyrrhotite or pentlandite-heazlewoodite assemblages exists above approximately 1000–1100° C. On cooling $(Fe,Ni)_{1-x}S$ first crystallizes from the liquid. This phase coexists down to 862° C. with a metal-rich iron-nickel-sulphur liquid. Below 862° C., but above 610° C., the $(Fe,Ni)_{1-x}S$ phase coexists with $(Ni,Fe)_{3\pm x}S_2$. At 610° C. pentlandite appears and the $(Fe,Ni)_{1-x}S$-$(Ni,Fe)_{3\pm x}S_2$ assemblage is no longer stable. At lower temperatures, depending upon bulk composition, the pyrrhotite-pentlandite or pentlandite-$(Ni,Fe)_{3\pm x}S_2$ pairs are stable. The $(Ni,Fe)_{3\pm x}S_2$ phase breaks down on cooling below about 550° C., and, depending upon the metal-to-sulphur ratio, heazlewoodite and pentlandite, or heazlewoodite, awaruite, and pentlandite, or heazlewoodite, millerite (or Ni_7S_6), and pentlandite will form stable assemblages.

INTRODUCTION

Pentlandite is the major source of nickel. It usually occurs in intimate association with pyrrhotite and often with chalcopyrite. It is as a rule found in basic rocks such as norites, and the primary sulphides in such localities may well represent a derivation from the host rocks by magmatic segregation. Also in basic rocks, but much less commonly, pentlandite is found in association with heazlewoodite (Ni_3S_2), awaruite (Ni_3Fe), or both.

Previous experimental studies on the stability of pentlandite and on the pyrrhotite-pentlandite relations almost without exception have been confined to the quenching method. In this procedure it is assumed that the phase relations existing at the temperature of the experiment can be effectively quenched. It has become apparent that this often is not a valid assumption. Quenching experiments indicated the appearance of liquid at about 880° C. when pure $Fe_{4.5}Ni_{4.5}S_8$ was studied and as low as 845° C. when mixtures of $Fe_{4.5}Ni_{4.5}S_8$ and $(Fe,Ni)_{1-x}S$ with $Fe/Ni = 1/1$ were investigated (Kullerud, 1956). Additional D.T.A. and high-temperature x-ray diffraction experiments that now have been performed reveal nonquenchable phenomena also in the Fe-Ni-S system.

The purpose of the present paper is to present new experimental data on the thermal stability of pentlandite and to discuss briefly the geological significance of these findings.

METHODS OF INVESTIGATION

Starting Materials

Nickel was obtained from Dr. E. M. Wise of the International Nickel Company, Inc. The material was received as a powder, produced by the carbonyl process, and contained 0.09 per cent carbon. The analysis of this material after reduction in a stream of hydrogen at 600° C. for 1 hour showed it to consist of 99.977 per cent Ni and only 0.01 per cent carbon. The other principal contaminants were 0.001 S, 0.001 Co, 0.01 Fe, and <0.001 Cu (all in wt. per cent).

Iron was obtained from the American Smelting and Refining Company. The material was received as a powder and contained 99.999+ per cent Fe according to the producer's analysis. This powder was also reduced in a stream of hydrogen at 600° C. for 1 hour.

Sulphur was obtained from Dr. W. N. Tuller, Superintendent of Laboratory, Freeport Sulphur Co., Port Sulphur, Louisiana, and has only 0.007 per cent impurities, all of which is carbonaceous material.

Pentlandite from Frood Mine, Sudbury, was obtained from Professor J. E. Hawley, Queen's University, Kingston, Ontario. This material, which is exceptionally pure, was used in some of the present experiments. Chemical analysis of pentlandite from Frood Mine was performed by Dickson (1904). It gave 34.98 Ni, 0.85 Co, 30.04 Fe, and 33.30 S (all in wt. per cent).

Techniques

The basic methods employed in this study were (1) quenching experiments, (2) differential thermal analysis, and (3) high-temperature x-ray powder diffraction. Rigid silica-glass tubes were used as reaction vessels in all three types of experiments, and vapor, therefore, is an inherent phase in all these experiments.

Identification of Phases

The products of the experiments were identified at room temperature by their macroscopic physical properties, optical properties in reflected light, and *x*-ray powder diffraction patterns. In addition, identifications were made at elevated temperature by means of high-temperature *x*-ray diffraction.

EXPERIMENTAL RESULTS

Quenching Experiments

Iron, nickel, and sulphur were heated together, in the ratio $Fe_{4.5}$:$Ni_{4.5}$:S_8, in evacuated silica tubes with minimum vapor space at 500°, 600°, 700°, and 800° C. for periods of time ranging from 7 to 35 days. The tubes heated at 500°, 600°, and 700° C. were opened after all visible sulphur had reacted with the metals. The material was ground under acetone, inserted in a new tube, and reheated. Such grinding homogenizes the sample and shortens the additional time period needed to achieve equilibrium. The loss of material during the process of opening the tubes, grinding their contents, and loading new tubes amounted to less than 1 mg of a total of more than 500 mg. It was assumed that this small loss coincided in composition with that of the bulk. At 800° C. reaction rates were high so it was not necessary to open the tubes and grind their contents. After the completion of each experiment the tubes were plunged rapidly into cold water where they cooled to room temperature in a few seconds. *X*-ray diffraction powder patterns as well as polished sections were made of the products of all experiments. The *x*-ray patterns were the same, within the limits of error of the measuring method, whether the experiment took place at 500°, 600°, 700°, or 800° C. The diffractometer patterns obtained all agreed closely with that given for natural pentlandite by Berry & Thompson (1962), with no additional or missing reflections. The polished sections of materials synthesized at 500° and 600° C. showed homogeneous pentlandite with typical (111) cleavage and with reflectivity almost as high as that of pyrite. The materials synthesized at 700° and 800° C., however, appeared inhomogeneous in polished sections.

Homogeneous pentlandite synthesized at 500° and 600° C. also becomes inhomogeneous when reheated at 700° C. for various periods of time followed by rapid chilling. This inhomogeneity, which is shown in Fig. 1, is not readily observed in air but becomes distinct when oil immersion is used.

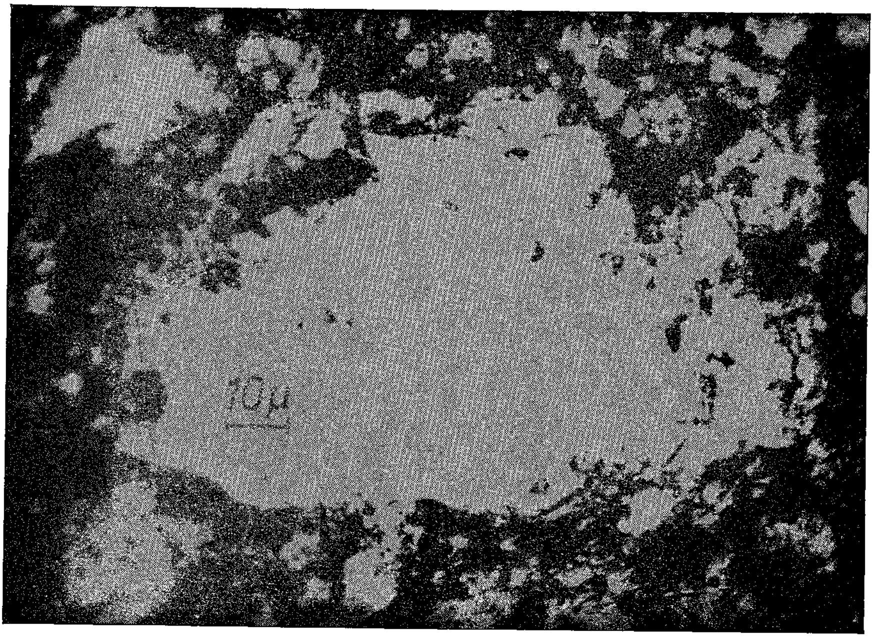

FIG. 1. Photomicrograph showing textures in material of $Fe_{4.5}Ni_{4.5}S_8$ composition after heating at 700° C. for 21 days followed by rapid cooling. The x-ray powder diffraction pattern of this material at room temperature is that of pentlandite (Table 1). Oil immersion.

It appears in polished sections and in the photomicrograph of Fig. 1 as if two distinct phases are present, one white and one medium grey. The white phase appears anisotropic and the medium grey phase, isotropic. However, these observations are cited with some reservation because high magnification, at which depolarization effects are strong, is required for satisfactory observation of the texture. X-ray powder diffraction patterns made from smear mounts of this material show only pentlandite. The peaks are sharp and there are no missing or additional reflections. Since amounts of both the white and medium grey materials sufficient to produce x-ray reflections are present, it is concluded that both are pentlandite and that the colour difference observed in polished sections is due to a difference in composition. The texture shown in Fig 1 is, then, the result of disequilibrium, because under equilibrium conditions pentlandite of only one composition can exist in one and the same experiment.

The results of the studies of the products from quenching experiments indicate that synthetic pentlandite is stable at and below 600° C. but breaks down under the outlined experimental conditions at some temperature between 600° and 700° C. On cooling from temperatures above the breakdown point the high-temperature phases react to form pentlandite, and if the cooling rate is slow homogeneous pentlandite is obtained. A different situation arises, however, if the cooling rate is rapid, such as in quench-type experiments. Here pentlandite during the cooling process rapidly forms where the breakdown phases are in physical contact with each other, and creates a shell around each grain of each phase. The thickness of this shell depends upon the cooling rate. The shielding effect of the shell slows down the reactions between isolated grains. Because of the ability of pentlandite to form solid solution towards the Fe side as well as the Ni side of stoichiometric composition (Lundqvist, 1947; Kullerud, 1956), the pentlandite shell will react with the remaining parts of the enclosed grains. The compositions of the resulting pentlandites depend on the compositions of these grains. As seen from Fig. 1 two distinctly different pentlandites occur. In the light of the above considerations this would indicate that pentlandite breaks down to two condensed phases.

Differential Thermal Analysis Experiments

These experiments were undertaken to determine the exact temperature of pentlandite breakdown in the presence of vapor. Pentlandites synthesized in quenching type experiments at 500°, 600°, 700°, and 800° C. were investigated. The closed, evacuated D.T.A. silica tubes were heated and cooled at a constant rate of 4° C. per minute. A few milligrams of Lake Toxaway quartz was used as internal standard in each experiment. The high-low quartz inversion appeared at 573° C. both on heating and cooling as shown in Fig. 2.

The curves obtained on all materials, whether synthesized at 500°, 600°, 700°, or 800° C., were identical. On the left side of Fig. 2 are given the heating curve (bottom) and cooling curve (top) of pentlandite synthesized at 600° C. A very strong thermal effect appears at 610° C. on heating and at 609° C. on cooling. On further heating a second peak appears at 862° C. Although each experiment was run to 1000° C., additional peaks were not recorded. On cooling the second peak appeared at 863° C. The temperature of this peak coincides more or less with the melting point of about 880° C. given in the literature for pentlandite (for instance, Kullerud, 1956). Comparison of the two peaks shown on the left side of Fig. 2 indicates that the lower temperature peak is at least as strong as that produced, presumably by melting, at 862° C. The peak at 610° C. must, because of its relative magnitude, be interpreted as the result of breakdown of pentlandite and not of a polymorphic inversion.

D.T.A. experiments were also performed on natural pentlandite from

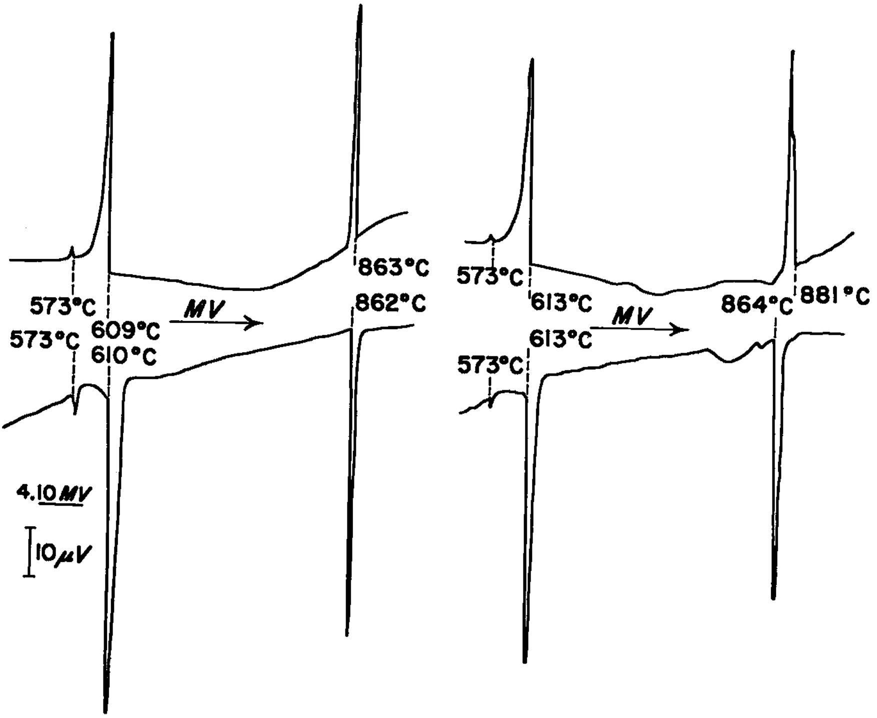

FIG. 2. Differential thermal analysis curves on synthetic $Fe_{4.5}Ni_{4.5}S_8$ (left) and natural pentlandite (right).

Frood Mine, Sudbury. The results of one such experiment are shown on the right side of Fig. 2, where the heating curve is on the bottom and the cooling curve on the top. Lake Toxaway quartz was again used as internal standard. The heating and cooling rates of 4° C. per minute and all other experimental conditions were the same as those used for the synthetic materials. The first heat effect, aside from that due to the internal standard, is recorded at 613° C. both on heating and on cooling of the natural pentlandite. The second strong heat effect appears at 864° C. on heating and at 881° C. on cooling. Thus, melting and solidification of the natural material occur over a temperature interval of about 17° C., whereas the synthetic material melted and solidified rather abruptly (see left side of Fig. 2). The small disturbances recorded both on heating and on cooling of the natural material consistently appear in each of six repeated D.T.A. experiments on the same material. For this reason these small effects are real and are not due to mechanical effects such as slumping of the material in the D.T.A. tube. This natural pentlandite is not entirely pure but is intergrown with small amounts of pyrrhotite and chalcopyrite, and also contains some cobalt in solid solution. The minor thermal effects appearing in the 750°–850° C. temperature region in D.T.A. experiments on natural pentlandite may be related to the accessory minerals or conceivably even to the cobalt content of the pentlandite.

High-temperature X-ray Diffraction Experiments

The synthetic products were also investigated by means of a high-temperature *x*-ray diffraction technique. To avoid oxidation, during these experiments the samples were kept in sealed silica tubes with wall thickness of 0.01 mm. and outside diameter of 0.3 mm.

The first film exposure was made at room temperature on $Fe_{4.5}Ni_{4.5}S_8$ synthesized at 700° C. and rapidly cooled. The results of this experiment are given in Table 1, where the data of Berry & Thompson (1962) on natural pentlandite are also listed for comparison. The reflections of the synthetic material all correspond closely with the reflections of natural pentlandite, leaving no doubt that the experimental product is pentlandite. A few reflections with intensities of 1 or less, given by Berry &

TABLE 1. COMPARISON OF THE *x*-RAY POWDER DIFFRACTION PATTERN OF $Fe_{4.5}Ni_{4.5}S_8$ OF WHICH A PHOTOMICROGRAPH IS GIVEN IN FIGURE 1 AND THAT OF NATURAL PENTLANDITE BY BERRY & THOMPSON (1962). BOTH PATTERNS WERE MADE AT ROOM TEMPERATURE.

$Fe_{4.5}Ni_{4.5}S_8$		Natural pentlandite*		
I	*d* in Å	*I*	*d* in Å	Indices
w	5.75	2	5.84	111
		1/2	5.05	002
		1	3.58	022
s	3.02	6	3.04	113
m	2.90	2	2.92	222
		1	2.52	004
w	2.31	3	2.31	133
m	1.940	4	1.940	115 333
vs	1.781	10	1.781	044
vw	1.701	1/2	1.704	135
w	1.535	1	1.538	335
w	1.521	1	1.518	226
		1/2	1.453	444
		1/2	1.412	117 155
m	1.313	3	1.310	137 355
m	1.260	3	1.259	008

*Some of the weak reflections given by Berry & Thompson (1962) in the diffractometer pattern of natural pentlandite do not appear in the pattern of the synthetic material because the latter was kept inside a silica tube during the exposure.

Thompson, did not appear in the pattern of synthetic pentlandite when the material was sealed in silica tubes and when Cu radiation was employed; they were present, however, on diffractometer tracings made from smear mounts and with Fe radiation.

A second exposure was made at 600° C. Again the pentlandite pattern was obtained, but with considerable displacements of the reflections, indicating a large increase in the cell edge with temperature. This increase, which presently is being determined accurately, far exceeds that of any other investigated sulphide.

A third exposure was made at 670° C. The results of this experiment are given in Table 2. This pattern shows no similarity to that of pentlandite. The *x*-ray data for natural pyrrhotite (Berry & Thompson, 1962), as well as for high-temperature nonquenchable Ni_3S_2 and $Ni_{3-x}S_2$ (Kullerud & Yund, 1962), are also given in Table 2. Comparison of these with the new pattern shows that five of the new reflections closely coincide with those of hexagonal pyrrhotite and the remaining four apparently belong to the nonquenchable $Ni_{3\pm x}S_2$ phase. Since the extent of solid solution of iron in $Ni_{3\pm x}S_2$ is not known, it is not possible to estimate accurately its composition from the *x*-ray data alone, but the *d* values do indicate a metal-to-sulphur ratio slightly less than 3:2. To account for the $Fe_{4.5}Ni_{4.5}S_8$ bulk composition the pyrrhotite resulting from the breakdown must have a metal-to-sulphur ratio slightly higher than 9/10.

Table 2. *X*-ray Powder Diffraction Data at 670° C. on Synthetic Material of $Fe_{4.5}Ni_{4.5}S_8$ Composition Compared with the Room-Temperature Pattern of Natural Hexagonal Pyrrhotite (Berry & Thompson, 1962) and with Those Obtained at 650° C. on Synthetic Ni_3S_2 and $Ni_{3-x}S_2$ (Kullerud & Yund, 1962)

$Fe_{4.5}Ni_{4.5}S_8$ 670° C.			Hexagonal pyrrhotite Room temperature			Ni_3S_2 650° C.		$Ni_{3-x}S_2$ 650° C	
I	2θ	*d* in Å	*I*	*d* in Å	Indices	*I*	*d* in Å	*I*	*d* in Å
							n.o.*	50	4.13
w	29.369	3.038	4	3.00	$10\bar{1}0$				
m	29.850	2.950				50	3.01	100	2.96
w	33.634	2.662	6	2.65	$10\bar{1}1$				
m	43.543	2.078	10	2.08	$10\bar{1}2$				
s	49.670	1.835				100	1.850	100	1.823
w	52.012	1.758	5	1.728	$11\bar{2}0$				
vw	58.919	1.567				100	1.576	50	1.511
vw	69.970	1.345	4	1.328	$20\bar{2}0$				
vw	72.913	1.297					n.o.	20	1.289

*n.o., not observed.

A fourth exposure was made after the sample was cooled to room temperature. The pattern obtained was again that of pentlandite; no other reflections appeared.

PENTLANDITE STABILITY RELATIONS IN THE FE-NI-S SYSTEM

In the Fe-Ni-S system pentlandite of $Fe_{4.5}Ni_{4.5}S_8$ composition is situated as shown in Fig. 3 by the dark circle marked 1. Breakdown of this pentlandite at 610° ± 2° C. to pyrrhotite and the $(Ni,Fe)_{3\pm x}S_2$ phase is indicated by a fully drawn tie line. Because of the variable metal-to-sulphur and Fe-Ni ratios of both the $(Fe,Ni)_{1-x}S$ and $(Ni,Fe)_{3\pm x}S_2$ solid solutions, the $(Fe,Ni)_{1-x}S$ – $(Ni,Fe)_{3\pm x}S_2$ join is ternary. However, the $T - X$ relations in an area including $Fe_{4.5}Ni_{4.5}S_8$ composition can be projected on a plane. This has been done in Fig. 4, in which breakdown of pentlandite is shown schematically. Solid solutions among the phases are not shown. Pyrrhotite with some nickel in solid solution and with the above estimated metal-to-sulphur ratio of 9/10 or a little higher appears on the left side. Pentlandite and this pyrrhotite are stable together below 610° ± 2° C.

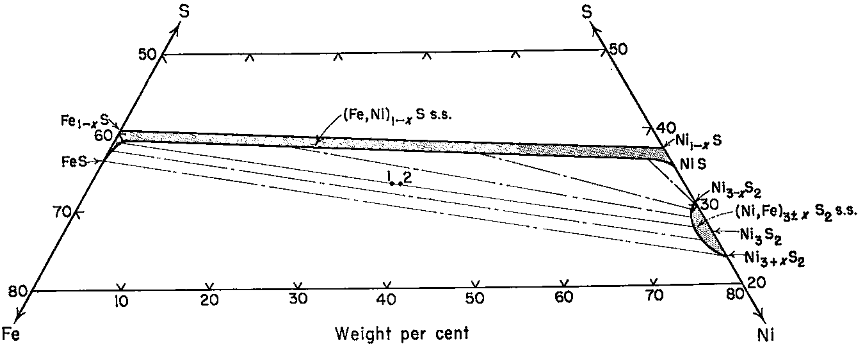

FIG. 3. Relations between $(Fe,Ni)_{1-x}S$ and $(Ni,Fe)_{3\pm x}S_2$ solid solutions at a temperature slightly above 610° C. Synthetic (1) as well as natural (2) pentlandites have broken down to $(Fe,Ni)_9S_{10}$ with <2 per cent Ni and $(Ni,Fe)_{3-x}S_2$ with $x \sim 0$ and with a few per cent Fe.

On the right side in Fig. 4 the $Ni_{3\pm x}S_2$ phase appears. In the pure Ni-S system the x in the $Ni_{3\pm x}S_2$ formula equals zero at low temperatures; the compound then is stoichiometric, has Ni_3S_2 composition, and corresponds to the mineral heazlewoodite (Kullerud & Yund, 1962). Pentlandite and heazlewoodite form a stable mineral pair below approximately 550° C. Stoichiometric Ni_3S_2 in the pure Ni-S system inverts to the high-temperature nonquenchable $Ni_{3\pm x}S_2$ modification at 556° C. (Kullerud & Yund, 1962). This high-temperature phase forms considerable solid solution on the Ni side as well as on the S side of the 3:2 stoichiometric ratio. Because of the eutectoid relations described by Kullerud & Yund

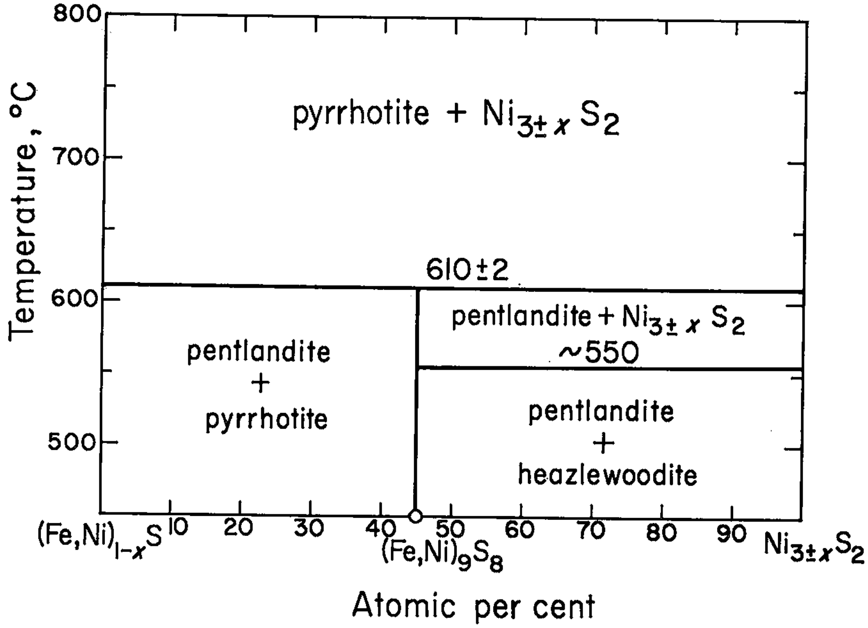

FIG. 4. Schematic illustration of phase relations along the $Fe_{1-x}S$-$Ni_{3\pm x}S_2$ join, showing pentlandite ($Fe_{4.5}Ni_{4.5}S_8$ composition) breakdown at 610° C. Solid solutions among the phases are not shown.

(1962), this phase is stable as low as 533° C. if it coexists with metallic Ni, and 524° C. if it coexists with the Ni_7S_6 phase (Kullerud & Yund, 1962). Since the metal-to-sulphur ratio of the $Ni_{3\pm x}S_2$-type phase resulting from pentlandite breakdown apparently is slightly less than 3:2, its inversion temperature, disregarding the possible effect of iron, must lie below 556° C. In Fig. 4 this temperature of inversion is given as approximately 550° C. Above this temperature but below 610° ± 2° C. pentlandite is stable with the nonquenchable $Ni_{3\pm x}S_2$ phase, which melts to liquid + $\alpha Ni_{1-x}S$. The incongruent melting point of this phase in the pure Ni–S system is at 806° C. and 30.25 ± 0.25 wt. per cent S (Kullerud & Yund, 1962). However, in the D.T.A. experiments no heat effect was recorded at 806° C. The strong heat effect at 862° C. probably indicates that iron goes into solid solution in the $Ni_{3\pm x}S_2$ phase and increases the melting temperature from 806° to 862° C.

Information on the compositions of coexisting pyrrhotites and pentlandites from ores is available in the published analyses performed on each mineral after separation from assemblages containing both.

Hawley (1962) indicates that the over-all average of the Ni content of pyrrhotites occurring with pentlandite in the Sudbury district is about

1.6 wt. per cent. The Co content averages 0.064 wt. per cent and is disregarded in the following discussion. The average metal-to-sulphur ratio of hexagonal nonmagnetic Sudbury pyrrhotite occurring with pentlandite is 0.9:1.0 as determined by the *x*-ray method by Arnold & Reichen (1962). Pentlandite occurring with pyrrhotite has the formula $(Fe,Ni)_9S_8$, or close to it, where the Ni-to-Fe ratio is close to 11/10 (Hawley, 1962). The Co content of Sudbury pentlandite is decidedly higher than that of the pyrrhotite and may average about 1.0 wt. per cent.

In Fig. 3 the positions of Sudbury pentlandite and pyrrhotite in the Fe-Ni-S system, disregarding their Co contents, are given by the number 2 respectively by the intersection of the fully drawn tie line with the boundary of the $(Fe,Ni)_{1-x}S$ solid solution.

Assuming that these mineral compositions pertain at the invariant point where pentlandite breaks down and assuming rather limited Fe solubility in $Ni_{3\pm x}S_2$ at this temperature, it is seen from Fig. 3 that the metal-to-sulphur ratio of the $(Ni,Fe)_{3\pm x}S_2$ phase produced by pentlandite decomposition is 3:2 or close to this ratio. This is in accordance with the *x*-ray *d* values given in Table 2, which indicate that the metal-to-sulphur ratio of this phase in the synthetic system is slightly less than 3:2, $(Ni,Fe)_{3-x}S_2$.

GEOLOGICAL IMPLICATIONS

The thermal stability of both synthetic pentlandite, of composition $Fe_{4.5}Ni_{4.5}S_8$, and natural pentlandite was determined in the presence of vapor. The experimental information is, for this reason, applicable in the strictest sense only when vapor occurs as a phase. This may not always be the case during ore deposition, and the *P–T* regions where vapor is not present, therefore, should be considered as well. The effect of rock pressure and of partial pressures $P_S < P_{total}$ on the phase relations of sulphide systems have been discussed by Kullerud (1959) and Kullerud & Yoder (1959).

The iron-nickel sulphides under discussion in natural occurrences commonly contain small amounts of cobalt and are usually associated with copper-iron sulphides such as chalcopyrite. Although small concentrations of cobalt in solid solution in pentlandite apparently do not influence the breakdown temperature significantly, as demonstrated in Fig. 2, the presence of copper may affect the solidus and liquidus relations. It may lower the temperatures of liquification considerably but, even more significantly, may widen the region of existence of the two-liquid immiscibility field (Kullerud & Yund, 1962; Kullerud, 1962).

The extent of sulphide liquid immiscibility in the Fe-Ni-Cu-S system has as yet not been determined experimentally and cannot be discussed fully. It appears from present knowledge of phase relations, however, that, if a sulphide liquid existed from which the minerals in question were derived, it must have been more metal rich than any originating through liquid immiscibility in the pure Fe-Ni-S system. Therefore, if sulphide liquid immiscibility is an important factor in the formation of pentlandite-pyrrhotite ores, copper must play a very significant role in the establishment of a sufficiently metal-rich liquid.

Although the liquidus relations in the Fe-Ni-S system are not completely known, the data in existence on the $(Fe,Ni)_{1-x}S$ – $(Ni,Fe)_{3\pm x}S_2$ join elucidate the processes of deposition of the minerals on this join. Jensen (1942), Kullerud & Yund (1962), and Kullerud (1962) determined the melting relations of the $Fe_{1-x}S$, $Ni_{1-x}S$, $Ni_{3\pm x}S_2$, and $(Fe,Ni)_{1-x}S$ solid solution series. The present study supplies data on the temperature at which liquid appears when the bulk composition is $Fe_{4.5}Ni_{4.5}S_8$. In the pure Fe-Ni-S system compositions that on cooling ultimately result in mixtures of pentlandite and pyrrhotite will persist as a homogeneous liquid down to perhaps 1100° or even 1000° C. The higher the Fe:Ni ratio is, the higher the temperature (maximum 1192° C.) that is required to produce a homogeneous liquid. Compositions that on cooling will produce pentlandite-heazlewoodite assemblages, also depending on the Fe-to-Ni ratio, may remain as a homogeneous liquid possibly down to 900° C.

Cooling of a homogeneous liquid of a composition lying on the fully drawn tie line but on the left of the point marked 1 in Fig. 3 leads to crystallization at about 1100° C. of $(Fe,Ni)_{1-x}S$ solid solution in which the Ni content is considerable and may equal the Fe content for Ni-rich bulk compositions. These mix-crystals coexist with a metal-rich iron-nickel-sulphur liquid ($\sim$ 20 wt. per cent S).

At 862° C. the $(Ni,Fe)_{3\pm x}S_2$ phase appears. The tie lines between the iron-nickel-sulphur liquid phase and the Ni-rich $(Fe,Ni)_{1-x}S$ solid solution apparently are broken, and through a series of reactions taking place over a narrow temperature range tie lines are established between the $(Ni,Fe)_{3\pm x}S_2$ phase and nickel-poor $(Fe,Ni)_{1-x}S$ solid solution (pyrrhotite). The latter tie lines are shown in Fig. 3. The $(Ni,Fe)_{3\pm x}S_2$-pyrrhotite assemblage remains until the cooling process reaches 610° C., at which temperature pentlandite becomes stable. Pentlandite forms through reaction between $(Ni,Fe)_{3\pm x}S_2$ and pyrrhotite. When the bulk composition lies between pyrrhotite and pentlandite, the $(Ni,Fe)_{3\pm x}S_2$ phase is consumed and a mixture of pentlandite and pyrrhotite remains (see Fig. 4).

Cooling of a homogeneous liquid of a composition also lying on the fully drawn tie line but on the right of the point marked 1 in Fig. 3 at some temperature between 900° and 1000° C. leads to crystallization of

$(Fe,Ni)_{1-x}S$ solid solution. This phase, which now contains significantly more Ni than Fe, coexists with iron-nickel-sulphur liquid, which probably contains > 20 wt. per cent S. At 862° C. $(Ni,Fe)_{3\pm x}S_2$ appears and the $(Fe,Ni)_{1-x}S - (Ni,Fe)_{3\pm x}S_2$ tie line is established as discussed above. When in the cooling process 610° C. is reached, pentlandite becomes stable and forms through reaction between $(Ni,Fe)_{3\pm x}S_2$ and pyrrhotite. When the bulk composition lies between pentlandite and $(Ni,Fe)_{3\pm x}S_2$, the pyrrhotite is consumed and a mixture of pentlandite and $(Ni,Fe)_{3\pm x}S_2$ remains (see Fig. 4). This assemblage is only stable down to about 550° C. (see above) where the $(Ni,Fe)_{3\pm x}S_2$ phase breaks down. Depending upon the metal-to-sulphur ratio of the $(Ni,Fe)_{3\pm x}S_2$ phase, the breakdown product in addition to heazlewoodite (Ni_3S_2) may also consist of awaruite (Ni_3Fe), which results when $M/S > 3$, or Ni_7S_6 (or millerite), which results when $M/S < 3$.

Below about 550° C., therefore, the two minerals pentlandite-heazlewoodite alone will occur only if $M/S = 3$; the pentlandite-heazlewoodite-awaruite assemblage occurs if $M/S > 3$; and the pentlandite-heazlewoodite-Ni_7S_6 (or millerite) assemblage forms if $M/S < 3$ in the high-temperature $(Ni,Fe)_{3\pm x}S_2$ phase.

Iron is much more abundant in ores than is nickel; therefore, pentlandite-pyrrhotite assemblages are far more common than assemblages of pentlandite and heazlewoodite or of pentlandite and the products formed by breakdown of the high-temperature $(Ni,Fe)_{3\pm x}S_2$ phase.

In high-temperature ore deposits containing pentlandite in association with pyrrhotite pentlandite is the later mineral to form. Because of the shape of its solvus towards pentlandite, pyrrhotite coexisting with pentlandite will exsolve additional pentlandite during cooling (Kullerud, 1956). Phase relations of this kind have been described from many localities and were recently described in detail from Sudbury by Hawley (1962).

Pentlandite with very few exceptions occurs in ores that are associated with basic rocks such as norite and gabbro and is usually found in coexistence with pyrrhotite. Recently pentlandite also in association with troilite or pyrrhotite has been observed in numerous stony meteorites (Ramdohr & Kullerud, 1961). Provided pentlandite was deposited in the presence of vapor, the temperature pertaining at the time of its formation must have been below 610° C.

Because of the previously discussed large thermal expansion of the pentlandite unit cell edge, the stability of pentlandite is believed to be considerably influenced by pressure. At high pressures and in the absence of a vapor phase pentlandite may have been deposited at temperatures significantly higher than 610° C.

The pentlandite-pyrrhotite solvus when accurately determined may serve as a valuable geological thermometer. However, pressure may also influence the position of this solvus, and it therefore should be determined in the presence of vapor at the pressure of the system as well as at high pressures in the absence of vapor.

ACKNOWLEDGMENTS

The writer is indebted to Dr. H. S. Yoder, Jr., for stimulating discussions during preparation of the manuscript, to Dr. N. Morimoto for help with the high-temperature x-ray diffraction studies, to Dr. G. Moh for making the photomicrograph, to Professor J. E. Hawley for an exceptionally pure sample of Sudbury pentlandite, to Dr. W. N. Tuller for the high purity sulphur, and to Dr. E. M. Wise for the high purity nickel.

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Manuscript received September, 1962