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PENTLANDITE COMPOSITIONS AND ASSOCIATIONS IN SOME MINERAL DEPOSITS *

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ABSTRACT

Some forty-five new electron-probe analyses have been made of pentlandites and cobalt pentlandite from a variety of different sulphide assemblages mainly from Canadian deposits. Variations from 9.8 to 34.2 at. % Ni, 1.3 to 31.8 at. % Fe, and 0 to 41.7 at. % Co were found. The Ni : Fe ratios were found to be characteristic of the particular sulphide assemblages containing the pentlandites. Evidence for appreciable deviation of pentlandite compositions from a 9 : 8 metal : sulphur ratio is not strong. The nickel contents of monoclinic pyrrhotites in assemblages containing pentlandite exhibit a weak correlation with the nickel contents of co-existing pentlandites. A ternary Fe-Ni-S composition diagram that explains most of the mineral compositions and associations found in this work has been constructed, and some minor discrepancies with the results of studies in the synthetic systems have come to light.

INTRODUCTION

Technologically, pentlandite is of great importance, as it is one of the most important ore minerals of nickel. The mineral is also of considerable mineralogical interest since it lies in the central portion of the Fe-Ni-S system, and exists as a stable component in a variety of different sulphide assemblages. Its composition exhibits wide variations in intimate response to its chemical environment. The purpose of this paper is to present new compositional data on pentlandites from a variety of occurrences, mostly Canadian, and, together with previously published data, to develop a comprehensive picture of pentlandite compositions and associations.

PREVIOUS WORK

There is a voluminous literature on pentlandite, and it is not the authors' intention to provide a complete literature survey. Rather, we will

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introduce here only those works of a comprehensive nature that are directly relevant to our investigation.

Reviews of the compositional variations exhibited by pentlandite have been undertaken by Eliseev (1955) and, more recently, by Knop *et al.* (1965). Both compilations were based largely on chemical analyses made on pentlandite concentrates and are thus open to question because of the possibility of the concentrates containing foreign minerals. Both authors, of course, recognized this danger, and Eliseev sought to deal with this problem by rejecting all analyses with $Ni < Fe$; as pointed out by Knop *et al.* (1965) and as will be shown later in this paper, this is not a correct assumption. Knop *et al.* (1965) compiled a list of 79 analyses, discarding only those with metal : sulphur ratios below 0.90 and those with a large excess of iron over nickel. They were able to demonstrate large compositional variations, particularly with respect to iron, nickel, and cobalt, but they did not concern themselves with the sulphide assemblages co-existing with pentlandite.

Laboratory experiments aimed at determining compositional limits of pentlandite in the Fe-Ni-S system were recently undertaken by Shewman & Clark (1970) and by Craig & Naldrett (1971). These studies showed clearly, apparently for the first time, that the composition of pentlandite is closely related to the sulphide mineral assemblage in which it occurs. Electron-probe analyses of pentlandites from different sulphide assemblages in the Marbridge ore deposits, Quebec (Graterol & Naldrett 1971) showed that the pentlandite in natural assemblages shows similar compositional relationships to those exhibited by synthetic systems.

SAMPLES

The samples investigated in this work were derived in various ways : most had been submitted over a period of years by mining companies in connection with mineral processing investigations at the Mines Branch, some were collected by the authors on visits to the deposits, and some were sent by individuals in response to written requests. No attempt was made to obtain a systematic sampling of pentlandites across the country, as this would have been beyond the scope of this investigation, nor do the numerous analyses shown in the tables bear any consistent relationship to the size or importance of the different deposits.

The origins of the samples are given in Table 1 together with brief remarks about the geological environments of the deposits.

PROCEDURE

Pentlandite-bearing assemblages, from 21 Canadian deposits that represent a wide range of geological environments, were collected as part of a broader program aimed at investigating the distribution of nickel in low-grade nickel deposits. Quantitative electron-probe analyses were made of the pentlandite and associated minerals in the polished sections made

TABLE 1. SAMPLES INVESTIGATED

Deposit	Location	Geological Environment	Reference
Atikokan	Hutchinson Twp., Ont.	Altered gabbro	Hawley (1930)
Bird River	Lac du Bonnet, Man.	Fault zone of ultra-basic sill	D.T. Anderson (pers. comm.)
Cassiar	McDame Lake, B.C.	Serpentinized ultramafic	Gabrielse (1963)
Creighton	Sudbury, Ont.	Norite irruptive	Souch & Podolsky (1969)
Del Norté Co.	California	Serpentinite	Eakle (1922)
Dumbarton	Lac du Bonnet, Man.	Granite-andesite contact	Karup-Møller & Brummer (1970)
Dumont	Val d'Or, Que.	Serpentinized ultrabasic	Eckstrand (1971)
Expo Ungava	Wakeham Bay, Ungava, Que.	Shears within serpentinite	Gold (1962)
Falconbridge	Sudbury, Ont.	Contact of andesite and greenstone	Davidson (1948)
Helen	McDame Creek, B.C.	Serpentine	O'Grady (1950)
Long Lac	Rainy River, Ont.	Serpentinite	Shklanka (1969)
Lorraine	Gaboury Twp., Que.	Contact of andesite and gabbro	Kish (1965)
Marbridge No. 2	Malartic, Que.	Contact of metasedimentary gneiss and meta-ultrabasics	Buchan & Blowes (1968)
Marbridge Nos. 3 and 4	Malartic, Que.	Ultramafic rock	Graterol & Naldrett (1971)
McKim	Sudbury, Ont.	Basal contact of norite, and in granite footwall	Clarke & Potapoff (1959)
McWatters	Langmuir Twp., Ont.	Peridotite sill	Pyke & Middleton (1970)
Mooihoek	South Africa	Serpentinized ultrabasic	Wagner (1929)
Muskox	Northwest Territories	Serpentinized ultrabasic	Chamberlain (1967)
Nicopor	Schreiber, Ont.	Amphibolite-granite contact	Thomson (1957)
Old Nick	Bridesville, B.C.	Brecciated greywacke in serpentine	McKechnie (1966)
Pefkos	Cyprus	Serpentinized ultrabasic	Antun *et al.* (1966)
Strathcona	Sudbury, Ont.	Basal contact of norite	Cowan (1968)
Texmont	Bartlett and Geikie Twp., Ont.	In peridotite, near contact with mafic volcanics	Pyke & Middleton (1970)

from the collected samples, using an Materials Analysis Company electron probe. Analyses were made for nickel, iron, cobalt and sulphur using synthetic $NiS_{1.07}$, synthetic pyrite, and cobalt metal as standards. Corrections were made using Rucklidge's (1967) computer program, revised and up-dated.

Only the relatively coarse pentlandite grains ($\geqq$ 50 microns) were analyzed to reduce the possibility of spurious counts from the associated minerals. Each analysis shown in this paper represents an average of a number of spot analyses (usually from five to ten) made on different pentlandite grains in the same polished section.

PENTLANDITE COMPOSITIONS

The pentlandite analyses, shown in the Tables 2 to 10, are grouped according to the type of sulphide assemblage in which the mineral was

TABLE 2. ANALYSES OF PENTLANDITES FROM PENTLANDITE-TROILITE ASSEMBLAGES (see figure 2a)

Sample	Ni		Fe		Co		S		Total
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%
Pefkos	23.6	18.3	38.0	30.9	6.3	4.8	32.4	46.0	100.3
Mooihoek	23.7	18.6	38.4	31.8	4.3	3.4	32.0	46.2	98.4
Muskox E 18322	25.2	19.5	37.9	30.9	5.1	4.0	32.1	45.6	100.3
Del Norté Co.	25.4	19.7	34.7	28.4	6.4	4.9	33.0	47.0	99.5
Muskox E 22418	26.5	20.7	38.6	31.7	1.1	0.8	32.7	46.8	98.9
Muskox E 18328	28.1	21.6	37.7	30.4	2.6	2.0	32.8	46.0	101.2

TABLE 3. ANALYSES OF PENTLANDITES FROM PENTLANDITE-AWARUITE ASSOCIATIONS (see figure 2h)

Sample	Ni		Fe		Co		S		Total
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%
Dumont	27.8	21.4	37.7	30.6	1.9	1.5	33.0	46.5	100.4
Dumont	27.5	21.5	35.4	29.1	2.5	2.0	33.0	47.4	98.4
Dumont	28.4	22.2	32.9	27.1	4.6	3.6	32.9	47.1	98.8
Dumont	28.8	22.2	37.4	30.3	0.9	0.7	33.2	46.8	100.3
Dumont	29.4	22.9	36.7	30.0	1.0	0.8	32.4	46.3	99.5
Dumont *	24.6	18.8	41.0	33.1	1.3	1.0	33.5	47.1	100.4

* No awaruite.

found. The tables are arranged in approximate order of increasing nickel content, and the analyses within each table are also arranged in the order of increasing nickel content, in terms of atomic percent nickel. Violarite, which appears to be almost always secondary, generally occurs in veinlets and particles too intimately intergrown with other minerals to enable reliable analyses to be obtained and for this study, no particular attention was paid to the presence or absence of this mineral. The problems concerning the origin of violarite under different P-T conditions is worthy of further study.

In addition to our own analyses, Tables 4 to 9 also contain some recent analyses taken from the literature in which the mineral assemblages were given.

The compositions of the pentlandites for the various assemblages are shown in the general Fe-Ni-S composition diagram (Fig. 1), and the

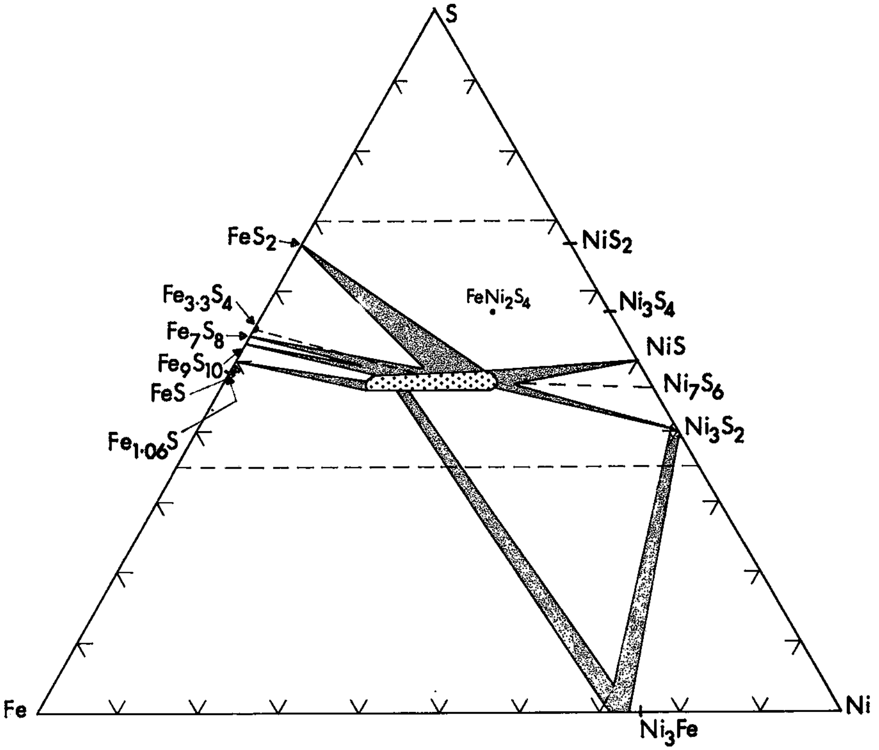

FIG. 1. Composite diagram of the Fe-Ni-S system showing pentlandite compositions (plotted as atomic percent) in relation to the associated sulphide phases. The mackinawite composition ($Fe_{1.06}S$) is as determined by Taylor & Finger (1970), and the smythite composition ($Fe_{3.3}S_4$ is as reported by Nickel (1971).

TABLE 4. ANALYSES OF PENTLANDITES FROM PENTLANDITE-PYRRHOTITE ASSEMBLAGES (see figure 2b)

Sample	Ni		Fe		Co		S		Total
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%
Muskox S-20	31.0	24.0	33.5	27.2	2.6	2.0	33.1	46.8	100.2
Dumbarton No. 5	32.6	25.3	27.3	22.2	6.5	5.0	33.5	47.5	99.9
Old Nick	32.6	25.6	32.8	27.1	1.2	0.9	32.2	46.4	98.8
Dumbarton No. 1	33.3	25.6	28.2	22.8	6.2	4.8	33.3	46.8	101.0
Dumbarton No. 4	33.0	25.8	27.5	22.6	6.3	4.8	32.7	46.8	99.5
Expo Ungava	35.8	27.6	32.9	26.6	0.0	0.0	32.5	45.8	101.2
Strathcona * STR-18	34.5	27.2	29.9	24.8	1.3	1.1	32.2	46.9	97.9
Strathcona * STR-7	35.2	27.3	29.8	24.2	2.5	1.9	32.8	46.6	100.3
Strathcona * STR-4	35.4	27.3	29.8	24.2	2.2	1.7	33.1	46.8	100.5
Strathcona * STR-23	35.0	27.4	30.5	25.1	1.4	1.1	32.5	46.4	99.4
Strathcona * STR-14	35.1	27.7	29.7	24.6	1.0	0.8	32.4	46.9	98.2
Creighton	35.7	27.7	30.1	24.5	0.8	0.6	33.3	47.2	99.9
Strathcona M.	35.9	27.9	29.2	23.9	1.2	0.9	33.2	47.3	99.5
McKim Mine	35.2	28.0	28.1	23.5	2.3	1.8	32.1	46.7	97.8
Dumbarton No. 3	35.9	28.4	27.8	23.1	1.7	1.3	32.6	47.2	98.0
Dumbarton No. 8	37.0	28.5	28.8	23.3	1.3	1.0	33.6	47.2	100.7
Falconbridge	36.4	28.7	28.2	23.5	1.5	1.2	32.2	46.6	98.3
Dumbarton No. 9	37.1	29.0	27.8	22.9	1.7	1.3	32.7	46.8	99.3
Strathcona * STR-1	37.9	29.1	29.6	23.9	0.8	0.6	33.0	46.4	101.3
Dumbarton No. 2	37.7	29.2	28.1	22.8	1.5	1.1	33.1	46.9	100.4

* From Vaughan *et al.* (1971).

TABLE 5. ANALYSES OF PENTLANDITES FROM PENTLANDITE-PYRITE-PYRRHOTITE ASSEMBLAGES (see figure 2c)

Sample	Ni		Fe		Co		S		Total
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%
Strathcona ** STR-8	34.5	26.7	29.3	24.0	2.6	2.1	33.2	47.2	99.7
Texmont D	34.7	27.3	30.8	25.5	0.7	0.6	32.3	46.6	98.6
Marbridge * 3-27	35.2	27.4	30.2	24.8	0.3	0.2	33.3	47.6	99.0
Long Lac Rainy River	35.8	28.1	28.0	23.1	2.4	1.8	32.7	47.0	98.9
Marbridge * 3-31	36.2	28.2	28.4	23.2	0.6	0.4	33.8	48.2	99.0
Strathcona STR-11	37.0	28.6	30.2	24.6	0.4	0.3	32.8	46.5	100.4

* From Graterol & Naldrett (1971).
** From Vaughan *et al.* (1971).

TABLE 6. ANALYSES OF PENTLANDITES FROM PENTLANDITE-PYRRHOTITE-SMYTHITE ASSEMBLAGES (see figure 2d)

Sample	Ni		Fe		Co		S		Total
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%
Bird River Mine	37.2	28.9	26.8	21.9	2.8	2.2	33.0	47.0	99.8
Lorraine Mine	37.9	29.5	27.4	22.5	0.9	0.7	33.6	48.0	99.8
Nicopor	38.3	29.8	28.5	23.3	0.7	0.5	32.6	46.4	100.1
Atikokan	38.2	30.2	27.8	23.1	n.d.	n.d.	32.3	46.7	98.3

TABLE 7. ANALYSES OF PENTLANDITES FROM PENTLANDITE-PYRITE ASSEMBLAGES (see figure 2e)

Sample	Ni		Fe		Co		S		Total
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%
Texmont A	37.9	29.3	28.7	23.3	0.5	0.4	33.1	47.0	100.2
Texmont C	38.6	30.1	27.4	22.4	1.0	0.8	32.8	46.7	99.8
Marbridge 4-22 *	38.8	30.1	27.3	22.3	0.2	0.2	33.3	47.4	99.6
Marbridge 4-24 *	40.9	32.0	24.9	20.4	0.7	0.5	32.9	47.1	99.4
Marbridge 4-26 *	40.9	31.8	25.2	20.6	1.0	0.7	32.9	46.9	100.0
Marbridge 4-27 *	41.2	32.4	23.4	19.3	2.3	1.8	32.3	46.5	99.2

* From Graterol & Naldrett (1971).

TABLE 8. ANALYSES OF PENTLANDITES FROM PENTLANDITE-MILLERITE (± PYRITE) ASSEMBLAGES (see figure 2f)

Sample	Ni		Fe		Co		S		Total
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%
Marbridge 4-23 *	39.7	30.3	25.0	20.0	0.4	0.3	35.4	49.4	100.5
Marbridge 3-41 *	40.0	31.5	24.1	20.0	1.0	0.8	33.1	47.7	98.2
Strathcona	40.5	31.9	24.3	20.1	1.4	1.1	32.5	46.9	98.7
Marbridge 3-40 *	40.8	31.9	24.1	19.8	1.0	0.8	33.1	47.4	99.0
Marbridge 3-33 *	42.1	32.0	25.0	20.0	1.3	1.0	33.7	47.0	102.1
Marbridge 3-37 *	42.6	32.0	24.2	19.1	0.8	0.6	35.1	48.3	102.7
Marbridge 4-25 *	41.7	32.6	24.1	19.8	0.7	0.6	32.8	47.0	99.3
Marbridge 3-35 *	41.4	32.9	24.9	20.8	0.4	0.3	31.6	46.0	98.3
Marbridge 3-43 *	41.8	32.9	24.2	20.0	0.9	0.7	32.2	46.4	99.1
Marbridge 3-32 *	42.0	32.9	23.1	19.1	0.3	0.3	33.2	47.7	98.6
Marbridge 3-34 *	42.6	32.9	23.0	18.7	0.7	0.5	33.9	47.9	100.1
Marbridge No. 2 **	42.6	33.3	25.0	20.6	0.2	0.2	32.2	46.0	100.0
McWatters 6B	43.3	33.8	24.1	19.8	0.1	0.1	32.5	46.4	100.0

* From Graterol & Naldrett (1971).
** From Buchan & Blowes (1968).

TABLE 9. ANALYSES OF PENTLANDITES FROM PENTLANDITE-HEAZLEWOODITE (± MILLERITE AND GODLEVSKITE) ASSEMBLAGES (see figure 2g)

Sample	Ni		Fe		Co		S		Total
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%
Helen A	41.2	32.1	19.5	16.0	5.3	4.2	33.5	47.7	99.5
Texmont B	42.0	33.7	21.8	18.0	1.6	1.2	32.8	47.1	99.2
Marbridge 3-45 *	43.4	33.8	22.6	18.5	1.5	1.2	32.7	46.6	100.2
Texmont *	44.2	34.2	22.8	18.5	0.9	0.7	32.9	46.6	100.8

* From Graterol & Naldrett (1971).

individual assemblages are shown in Figure 2 with a tie-line connecting each composition to that of the co-existing sulphides. In constructing these diagrams, the cobalt content of pentlandite, if below approximately 6 wt. %, was apportioned equally between the iron and the nickel.

DISCUSSION

Assemblages in the Fe-Ni-S system

This work has confirmed other recent observations (Shewman & Clark 1970, Graterol & Naldrett 1971, Craig & Naldrett 1971) that the composition of pentlandite is intimately related to the sulphide assemblage in which it occurs. When Fig. 1 is compared with diagrams derived from studies in synthetic systems (Shewman & Clark 1970, Craig & Naldrett 1971), one major difference is immediately apparent : the complete solid-solution between $Fe_{1-x}S$ and $Ni_{1-x}S$, generally referred to as *Mss* and which exists above 400°C, is completely missing in our diagram ; even the partial solid-solution (Mss_2) stable at 250°C (Craig & Naldrett 1971) is absent. This implies that the temperature of final equilibrium of all the investigated pentlandite assemblages that contain pyrite or millerite was

TABLE 10. ANALYSES OF COBALT PENTLANDITES FROM PENTLANDITE-HEAZLEWOODITE (± AWARUITE *) ASSEMBLAGES

Sample	Ni		Fe		Co		S		Total
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%
					Cobaltian Pentlandites				
Dumont	31.0	24.3	24.3	20.0	11.9	9.3	32.4	46.4	99.6
Dumont	31.8	24.9	22.2	18.2	13.3	10.4	32.6	46.5	99.9
Univex	32.7	26.7	18.7	16.0	14.0	11.4	30.7	45.9	96.1
					Cobalt Pentlandites				
Univex	12.3	9.8	1.6	1.3	52.8	41.7	32.5	47.2	99.2
Dumont **	21.3	16.8	9.0	7.4	37.4	29.3	32.2	46.5	99.9
Dumont **	22.8	17.9	10.2	8.4	34.5	26.9	32.5	46.8	100.9
Dumont **	23.6	18.7	13.9	11.6	29.7	23.4	31.9	46.3	99.1
Dumont **	24.2	19.1	16.3	13.5	26.3	20.7	32.5	46.7	99.3
Univex	25.3	19.5	14.1	11.4	29.2	22.4	33.2	46.7	101.8
Cassiar N-4	29.0	22.8	8.7	7.2	30.5	23.9	32.0	46.1	100.2

* From samples only.
** Associated with awaruite, no heazlewoodite.

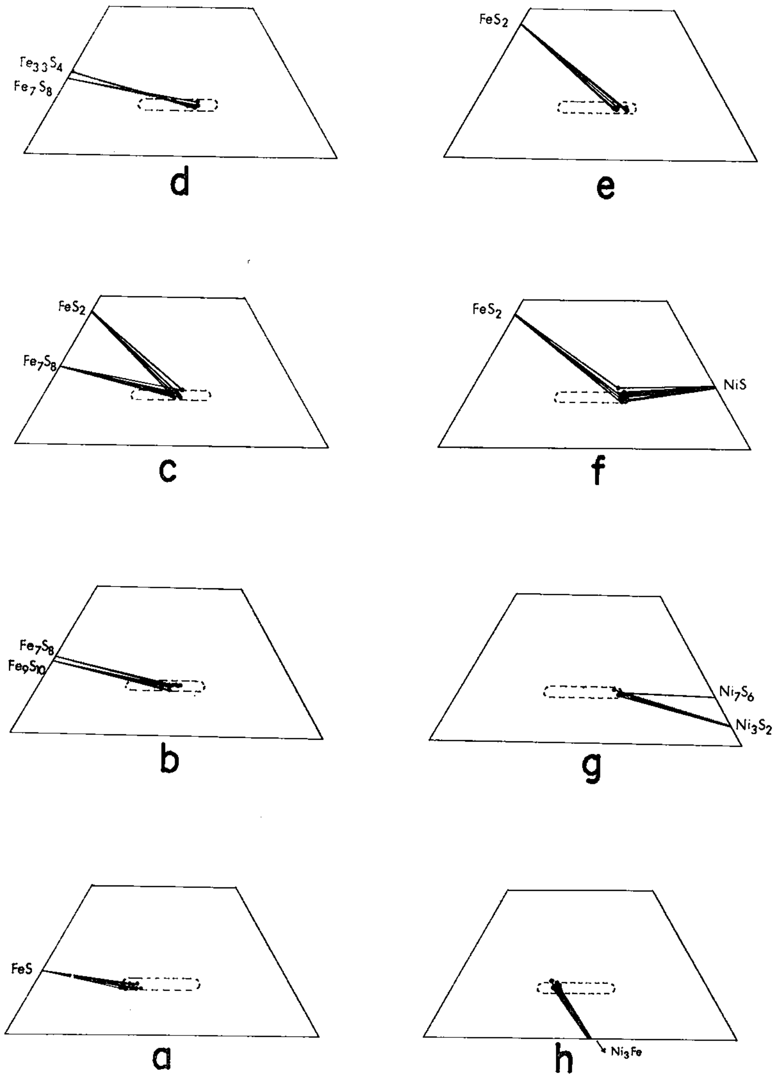

FIG. 2. Individual diagrams representing the central area (see dashed lines Fig. 1) of the Fe-Ni-S system showing the pentlandite compositions listed in Tables 2-9 for the different sulphide assemblages. The compositions are plotted as atomic percent.

below 250°C. The tentative diagram for part of the Fe-Ni-S system proposed by Graterol & Naldrett (1971) for temperatures below 135°C comes closest to our observations.

Starting with troilite-pentlandite assemblages and working around the composition diagram in a clockwise direction, the following observations can be made :

1. Table 2 and Fig. 2a give the composition of pentlandites found in pentlandite-troilite assemblages. The pentlandite composition is characterized by the lowest Ni : Fe ratio which allows it to be distinguished from the pentlandite-pyrrhotite assemblages.

2. Table 4 and Fig. 2b give the compositions of pentlandites found in pentlandite-pyrrhotite assemblages. It appears that a distinction can be made between pentlandite compositions in assemblages containing both hexagonal and monoclinic pyrrhotites and those containing only the monoclinic variety. The pentlandites in assemblages containing hexagonal pyrrhotite have a lower Ni : Fe ratio than the others ; the samples in which hexagonal pyrrhotite was recognized include the Old Nick, Expo Ungava and the Strathcona sample nos. STR. 18, 7, 4, 23 and 14. These pentlandites all contain $\leqq$ 27.7 atomic percent nickel (28.2 at. % if half the cobalt content is added to the nickel). The apparent exceptions among the low-nickel pentlandites are the Dumbarton nos. 5, 1 and 4. These three samples all have high cobalt contents. If the nickel content of the Dumbarton pentlandites is augmented by one-half of the cobalt, then they have "adjusted" nickel contents in excess of 28 atomic percent, and are not, in fact, exceptions.

3. The pentlandites in assemblages containing pyrite and monoclinic pyrrhotite (Table 5 and Fig. 2c) and those containing smythite and monoclinic pyrrhotite (Table 6 and Fig. 2d) fall within the same compositional range as those containing pyrrhotite alone, although the pentlandites with smythite have a lower Ni : Fe ratio than those with pyrite. The occurrence of pentlandite together with smythite from several localities having a restricted compositional range seems to suggest this mineral pair represents an equilibrium assemblage. The fact that the tie-line (smythite-pentlandite) crosses the pyrite-pyrrhotite-pentlandite tie-lines may mean that there are two different sets of P-T equilibrium conditions. For this reason, the smythite-pentlandite tie-line is given in Fig. 1 as a dashed rather than a solid line.

4. Pentlandite from pentlandite-pyrite associations (Table 7 and Fig. 2e) and from pentlandite-millerite assemblages, generally with some pyrite, (Table 8 and Fig. 2f) contains a higher Ni : Fe ratio than that co-existing with pyrrhotite, establishing rather conclusively that millerite

and pyrrhotite cannot co-exist under these conditions. The apparent tie-line connecting pyrite and millerite indicates that pentlandite cannot co-exist with vaesite (NiS_2). The position of violarite ($FeNi_2S_4$) on the pyrite-millerite join poses some phase problems, but these are disregarded here because of insufficient data on compositions of violarite co-existing with pentlandite : it can be assumed, however, that at very low temperatures the pyrite-millerite tie-line probably breaks down to give pyrite-violarite-pentlandite and millerite-violarite-pentlandite assemblages.

5. Heazlewoodite-pentlandite assemblages (Table 9 and Fig. 2g) contain pentlandites with the highest Ni : Fe ratios. When millerite occurs in this assemblage, godlevskite (Ni_7S_6) always seems to be present. In all the occurrences of godlevskite noted to date, the godlevskite appears to be secondary ; its most frequent occurrence is a fine-grained intergrowths with millerite, apparently replacing primary heazlewoodite. This indicates that godlevskite is stable at very low temperatures, perhaps under conditions similar to those favouring the development of smythite and violarite.

6. The association pentlandite-heazlewoodite-awaruite was not found during this study, and the authors are not aware of this three-phase assemblage having been reported, in spite of the fact that the assemblage is a stable one in the synthetic system (Shewman & Clark 1970, Craig & Naldrett 1971). The apparent absence or at least the scarcity of this assemblage is rather surprising in view of the large area occupied by this three-phase assemblage on the Fe-Ni-S ternary diagram and since the heazlewoodite-awaruite association is not an uncommon one (Ramdohr 1967).

7. Equally surprising is the composition of the pentlandite associated with awaruite (Table 3 and Fig. 2h). In the synthetic system awaruite co-exists with a broad range of pentlandite compositions toward the nickel-rich end of the pentlandite solid solution (Craig & Naldrett 1971). In contrast to this, the pentlandite described in this study has a composition at the iron-rich end of the solid solution.

Cobalt content

A number of cobalt pentlandites and pentlandites with cobalt contents greater than 6 wt. % were analyzed (Table 10). These pentlandite compositions, together with those listed in Tables 2 to 9, are plotted in Fig. 3 as atomic percentages of the end-members Co_9S_8, Fe_9S_8 and Ni_9S_8. These compositions cover a fairly wide area on the diagram but they all fall within the solid-solution field of synthetic pentlandite found by Knop & Ibrahim (1961). The position of the solid-solution field in the ternary diagram indicates that the 3*d*-electron content remains relatively unchanged and supports the suggestion, apparently first made by Rosenqvist (1954), that the pentlandite phase might be electron stabilized.

Metal-sulphur ratios

$(Ni,Fe,Co)_9S_8$ contains 47.06 atomic percent sulphur, and if pentlandites were strictly stoichiometric they should all have this sulphur content. The sulphur contents of all the pentlandites listed in Tables 2 to 10 are shown in a frequency distribution diagram (Fig. 4). The analyses show a clustering slightly to the metal-rich side of the ideal composition, although the range extends almost from $M_{8.5}S_{8.0}$ (48.5 at. %S) to $M_{9.5}S_{8.0}$ (45.7 at. %S) (one analysis lies beyond this range, — Marbridge 4-23 — reported by Graterol & Naldrett, and the analysis could therefore not be checked; perhaps this is an erroneous determination). The questions as to whether

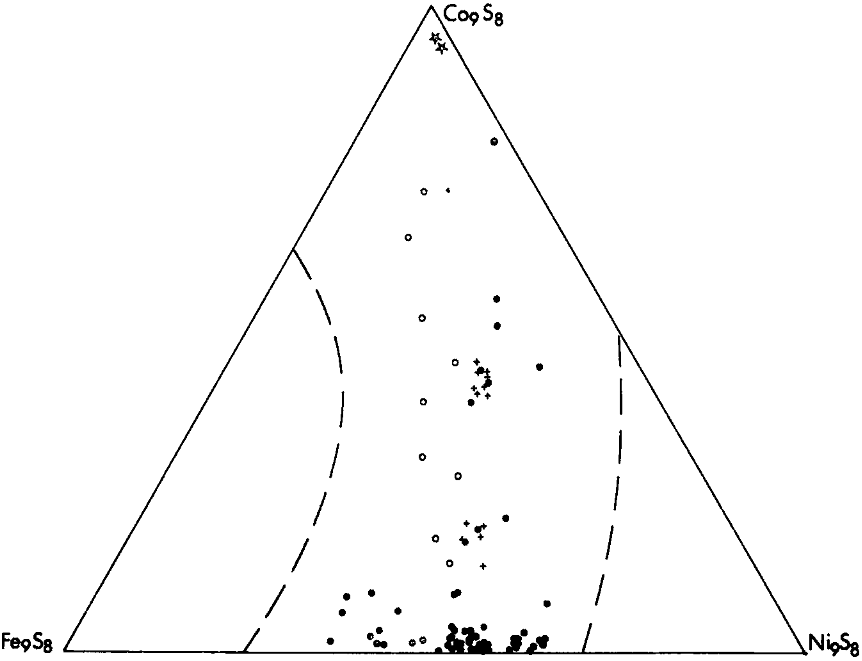

FIG. 3. Pentlandite compositions plotted as atomic percent with respect to cobalt, iron and nickel contents. Dashed lines represent the solid-solution limits defined by Knop & Ibrahim (1961). Open circles represent cobalt pentlandites from Outokumpu (Kouvo *et al.* 1959, Huhma 1970). Crosses represent additional unpublished compositions obtained in this study. Stars represent re-analyzed cobalt pentlandite from Cobalt, Ontario (Petruk *et al.* 1969).

the pentlandite compositions are actually spread over this range or whether this effect is due to analytical error remain open. Data (Shewman & Clark 1970) on synthetic pentlandite compositions quenched from 600°C with Fe : Ni = 1 : 1 gave sulphur solubility limits of 46.2 to 47.9 atomic percent, a narrower range than observed in this study. If the spread is due to analytical error, then the extreme compositions represent an error of ± 1.2 wt. %S ; this seems rather large but is nevertheless possible.

The centre of gravity of the analyses shown in Figure 4 is slightly toward the sulphur-poor side of M_9S_8 ; this supports the conclusions of Knop *et al.* (1965), based on their compilation of earlier pentlandite analyses, that the average pentlandite composition is slightly metal-rich. On the other hand, if the non-stoichiometry of pentlandite were real, then one could expect a correlation between sulphur and the mineral assemblage containing the pentlandite ; assemblages characterized by low-sulphur minerals such as heazlewoodite or awaruite would presumably have sulphur-poor pentlandite, whereas the reverse might be expected in pentlandites from a sulphur-rich assemblage containing pyrite. Such a correlation is not possible from the data presented here because the sulphur analyses are not considered sufficiently accurate and because of the narrow limits of sulphur solubility determined by Shewman & Clark (1970) for pentlandite.

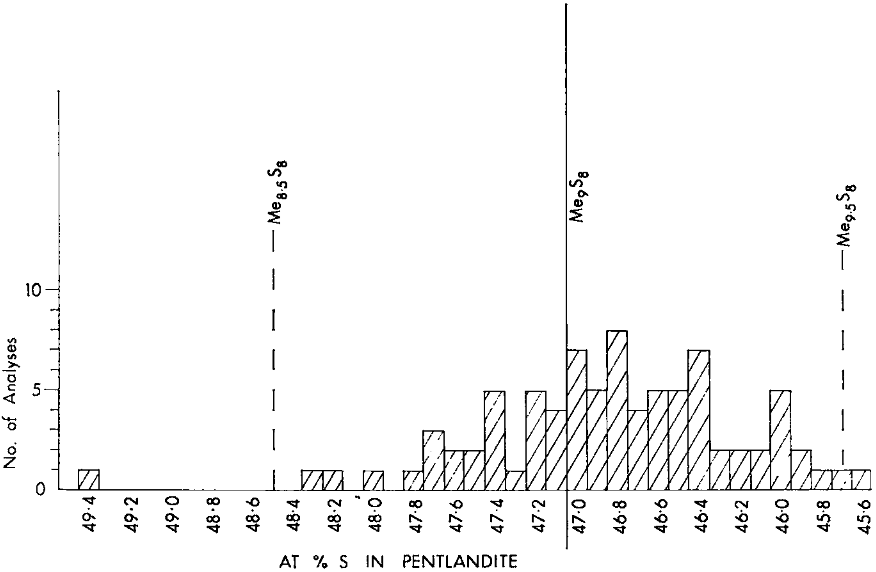

FIG. 4. Frequency distribution of sulphur content of pentlandite.

Composition of pyrrhotite co-existing with pentlandite

When the nickel contents of monoclinic pyrrhotite co-existing with pentlandite are plotted against the nickel content of the pentlandite, a trend toward positive correlation between the nickel contents of the two phases is discernible (Fig. 5). However, there is a pronounced scatter of points. This scatter is, perhaps, not unexpected because of the rather wide variation of nickel content within even one polished section. A typical variation is in the neighbourhood of ± 0.15% Ni, which would be enough to account for the scatter. This variation of Ni contents within one polished section seems to suggest that deposits have not managed to attain a stable equilibrium.

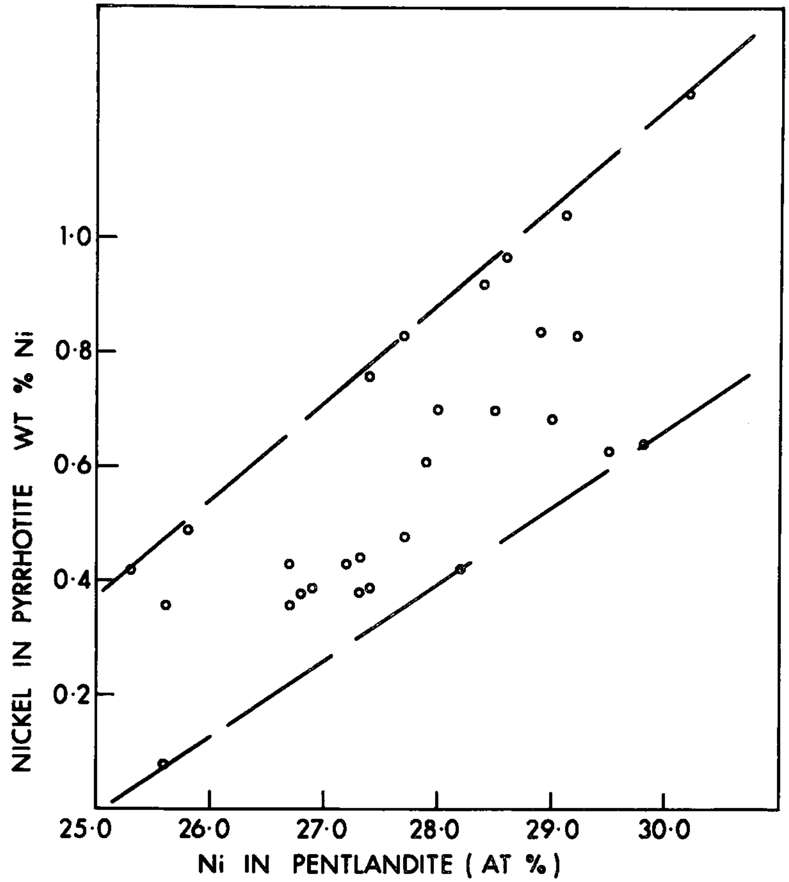

Fig. 5. Nickel in co-existing pentlandite and pyrrhotite.

SUMMARY

This study shows that the composition of natural pentlandites is intimately related to the sulphide assemblage in which it occurs. Based on the synthetic work of Graterol & Naldrett (1971), it appears that the temperature of final equilibrium of all the pentlandite assemblages was below 135°C. The metal : sulphur ratios in the natural pentlandites show a greater spread than that observed by Shewman & Clark (1970) on synthetic pentlandites but this could be due to analytical error. Although the evidence for deviation of pentlandite compositions from a 9 : 8 metal : sulphur ratio is not strong, the analyses show a clustering slightly to the metal-rich side. The presence of violarite ($FeNi_2S_4$) on the pyrite-millerite join, of smythite ($Fe_{3.3}S_4$) on the pyrite-pyrrhotite tie-line, and of godlevskite (Ni_7S_6) on the millerite-heazlewoodite tie-line poses some phase problems. In all the natural occurrences, these minerals which appear to be secondary are stable at very low temperatures. The apparent absence of the association pentlandite-heazlewoodite-awaruite is surprising as is the narrow range of pentlandite compositions associated with awaruite nearer the iron-rich end of the solid solution.

The cobalt pentlandites examined in this study cover a fairly wide area on the ternary diagram and trend more towards the iron-poor side. In comparison, cobalt pentlandites from the Outokumpu region, Finland, indicate equal distribution of cobalt between iron and nickel.

The results of this study have further very important economic and geological implications when applied to orebodies, in particular to the low-grade nickel-bearing serpentinites. These bodies represent large-tonnage low-grade (0.25-0.5 wt. % Ni) ore deposits in which pentlandite is usually the major nickel-bearing sulphide. Pentlandite in the commonly-found pentlandite-heazlewoodite assemblage contains higher than average nickel contents of approximately 44 wt. % Ni whereas pentlandite in the pentlandite-awaruite assemblage contains approximately 28 wt. % Ni. Not only must the assemblage be taken into consideration, but equally important are the cobalt contents. This relationship is clearly illustrated in Figure 3 which shows that the pentlandites containing higher cobalt contain lower nickel. With increasing interest in the development of low-grade nickel deposits as a potential source of nickel in the future, these factors could be important in determining whether or not an economic concentrate can be obtained.

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