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CRYSTAL CHEMISTRY OF NATURAL PENTLANDITES

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ABSTRACT

The structures of pentlandite from Frood Mine, Ontario ($a = 10.038$Å and composition $Fe_{3.97}Ni_{4.84}Co_{0.07}S_8$) and cobalt pentlandite from Outokumpu, Finland ($a = 9.977$Å and composition $Fe_{1.63}Co_{5.60}Ni_{1.82}S_8$) have been refined anisotropically, using single crystals, to final unweighted *R* values of 2.7% and 1.8%, respectively. The structures of these natural pentlandites were found to be very similar to that of synthetic Co_9S_8. The interatomic distances in these pentlandites including synthetic Co_9S_8 suggest that (a) the octahedral Co in Co_9S_8 is in the divalent low spin state, (b) the octahedral Fe is probably in the divalent high spin state, and (c) all the tetrahedral cations are divalent although valency for the tetrahedral cation is an ambiguous concept because of the delocalization of *d* electrons. Determination of the site populations of Fe and Ni in the two sites of the Frood pentlandite was not successful because of the similarity of the *x*-ray scattering factors of Fe and Ni.

A special aspect of the pentlandite structure is the presence of three metal-metal bonds from each tetrahedral cation, which result in a "cube cluster" of tetrahedral cations. This cube cluster appears to stabilize the pentlandite structure and fixes the total number of *d* electrons in the unit cell to a uniform value as in an electron compound. The structure and chemistry suggest that the structural formula for pentlandite would be $^{VI}[Fe_uNi_v]^{IV}(Fe_xNi_y\Box_z)S_8$. The known physical properties are consistent with the proposed crystal chemistry of pentlandite.

INTRODUCTION

Pentlandite $(Fe,Co,Ni)_9S_8$ is the major ore mineral for Ni and occurs commonly in association with pyrrhotite, pyrite and chalcopyrite. The chemistry of such an important mineral in terms of the solid solution behavior of the major cations is poorly understood because of the lack of crystal chemical data. Knop & Ibrahim (1961) studied the synthetic pentlandite system and found that of the three end members, Fe_9S_8, Co_9S_8 and Ni_9S_8, only Co_9S_8 forms a stable homogeneous phase; the other two end members apparently do not form pentlandite. Recently, however, Nakazawa *et al.* (1973) reported the formation of a cubic iron sulphide as a thin film, with diffraction pattern similar to pentlandite, by flash evaporation and vacuum deposition technique. Knop & Ibrahim also found that the individual substitution of Fe or Ni for Co is limited. However, the solid solution is "complete and the structure is preserved if Fe and Ni are introduced simultaneously." Substitution for Co by Fe and Ni both individually and simultaneously causes an expansion of the unit cell. This observation is puzzling because of the radii of these cations (generally, Fe is larger than Co and would tend to increase the lattice parameter, whereas Ni is smaller than Co and would decrease the lattice parameter) and raises the question, "What are the valencies and spin states of these cations in this structure?" An answer to this question is essential in explaining the solid solution behavior of these cations in pentlandite.

The natural pentlandites were considered by Lindqvist *et al.* (1936) to be isotypic with synthetic Co_9S_8 and to belong to the space group O_h^5-*Fm*3*m* with four formula units, M_9S_8, per unit cell. The 36 metal atoms are distributed over 4 octahedral sites, 4(*b*), and 32 tetrahedral sites, 32(*f*). (These, henceforth, will be referred to as *M*(O) and *M*(*T*) sites, respectively). The 32 sulphur atoms are distributed over 8(*c*) and 24(*e*) equipoints in four-and five-fold coordination by metal atoms, respectively. (These, henceforth, will be referred to as S1 and S2, respectively). The space group and the structure were later confirmed by Pearson & Buerger (1956) and Knop & Ibrahim (1961). Geller (1962) refined the structure of synthetic Co_9S_8 using visually estimated, two-dimensional, single-crystal *x*-ray intensity data. Geller found that the octahedral sites are nearly regular, tetrahedral sites are distorted to give the site symmetry 3*m* and the tetrahedral Co-Co distances are similar to the distance in metallic cobalt indicating considerable metallic bonding.

Previous studies on the crystal chemistry of pentlandite by the Mössbauer technique and magnetic measurements indicate that Fe tends to order in the octahedral sites (Knop *et al.* 1970; Vaughan & Ridout 1971), and that octahedral Fe(II) and Co(III) are in the low-spin state (Vaughan & Burns 1971). It is well known that the interatomic distances in oxide structures are widely used to infer the oxidation and spin states of transition element ions. Such distances are not available for natural pentlandites since structural refinements on single crystals of these minerals have not yet been carried out using modern x-ray diffraction techniques. The octahedral Co-S distance in Co_9S_8 reported by Geller (1962) appears to be too large for low-spin cobalt in sulphides (Rajamani & Prewitt 1972). The aim of our present investigation was to refine the structures of natural Fe-Ni pentlandite and cobalt pentlandite and to compare them with the structure of synthetic Co_9S_8, and to obtain information on the probable cation valencies, spin-states and ordering parameters using interatomic distances. An attempt has also been made to explain the mineral chemistry of pentlandite by combining the structural data with chemical data obtained from microprobe analyses of natural pentlandites. The known physical properties have been discussed in the light of the mineral chemistry of pentlandites.

Experimental

Since pentlandite usually occurs in intimate association with pyrrhotite, care was taken to select a "single-crystal" by taking precession pictures of several pentlandites. One good, approximately equant, crystal of Fe-Ni pentlandite from Frood Mine, Sudbury, Ontario, of dimension 0.05 mm was mounted on the [110] axis. The space group conditions and unit cell dimension were checked using precession photographs. In addition, a crystal of cobalt-pentlandite, from Outokumpu, Finland, was selected and precession photographs were taken by mounting a crystal of dimension 0.04 mm along the [110] axis. The diffraction patterns were extremely sharp indicating good crystals for collecting intensity data. The cell dimensions of these crystals are calculated from 2θ values measured on the single-crystal diffractometer. The chemical compositions of these pentlandites as well as a few other pentlandites from different localities were determined using the ARL electron probe microanalyzer. Homogeneous, stoichiometric single crystals of FeS_2, CoS_2, and NiS_2 were used as standards for Fe, Co, Ni and S. The analytical data are listed in Table 1. The cell parameters, the chemical formulas assuming no anion vacancies in the structure and the calculated densities of the Frood and Outokumpu pentlandites are shown in Table 2.

Integrated intensities of 420 reflections were collected for each crystal (within the range of $\sin \theta/\lambda = 0.06 - 0.70$) automatically on a PDP-15/35 controlled Picker diffractometer at room temperature using a graphite monochromator and Mo$K\alpha$ radiation. A scan speed of 2°/min. was used and background counts were accumulated for 5 seconds on both sides of the peaks. A standard reflection was measured for every 20 reflections. The intensity data thus obtained were converted into observed structure factors after applying Lorentz and polarization corrections. The observed structure factors of the symmetry-equivalent reflections were averaged and 98 reflections were used for the refinement of the structures. The two strongest reflections, 440 and 800, were rejected during the refinement because they appear to suffer from secondary extinction. The absorption correction was not made because although the linear absorption coefficients were 160 and 165 cm^{-1} for the Frood and Outokumpu pentlandites, respectively, the transmission factors varied only between 0.28 and 0.25 for Frood pentlandite and between 0.31 and 0.27 for Outokumpu cobalt pentlandite.

TABLE 1. MICROPROBE ANALYSES OF SOME PENTLANDITES.

Sample	Fe		Ni		Co		S		Total	Metal/Sulfur
	wt %	At %	wt %	At %	wt %	At %	wt %	At %	wt %	(Atomic)
Frood	28.82	23.50	36.92	28.67	0.59	0.45	33.35	47.38	99.68	1.110
Outokumpu	11.64	9.59	13.64	10.69	42.2	32.95	32.60	46.78	100.08	1.131
Outokumpu	28.80	23.37	37.40	28.87	0.62	0.48	33.46	47.30	100.28	1.114
Creighton	29.6	24.51	35.06	27.6	0.41	0.32	33.00	47.60	98.07	1.101
117073	34.38	28.08	31.04	24.12	0.88	0.68	33.13	47.13	99.43	1.122
11522	34.80	28.5	29.00	22.70	1.92	1.50	33.00	47.30	98.72	1.114
R11297	34.70	28.19	29.67	22.93	2.28	1.76	33.30	47.12	99.95	1.122
R618	24.79	20.52	28.80	22.70	12.60	9.86	32.53	46.91	98.72	1.131
Minn.	32.81	26.98	31.10	24.32	2.04	1.59	32.90	47.11	98.85	1.123
M4-3	29.60	24.47	35.50	28.00	0.22	0.17	32.90	47.41	98.22	1.110
#3-8	25.10	20.67	40.30	31.62	0.55	0.43	32.90	47.30	98.85	1.114
#3-18	28.30	23.19	37.00	28.84	0.18	0.14	33.50	47.82	98.98	1.091

Samples 117073, 11522, R11297, R618 were obtained from U.S. National Museum.
Samples M4-3, #3-8, and #3-18 are from Marbridge Mine, Quebec, Canada.
Minn: Sample from Duluth Complex, Northern Minnesota.

Refinement

The probable space groups on the basis of the diffraction symmetry are O_h^5-$Fm3m$, T_d^2-$F\bar{4}3m$ or O^3-$F432$. Since the generally accepted space group is the centrosymmetric one (Knop & Ibrahim 1961; Pearson & Buerger 1956; Geller 1962) the structures were refined in the space group $Fm3m$. L. W. Finger's RFINE least-squares program was used to refine the structure. The four octahedral cations are assumed to be in 4(*b*) at (½,½,½), *etc.* The starting positional parameters for 32(*f*) and 24(*e*) positions were taken from the refinement of Co_9S_8, as given by Geller. Doyle & Turner's (1968) atomic scattering factors for neutral atoms were used along with correction factors for anomalous dispersion. The first three cycles of refinement using unit weights and individual isotropic temperature factors ($B = 0.5$ for cations and $B = 1.0$ for anions) resulted in an unweighted R of 10.1% for the Frood pentlandite. The isotropic temperature factor for the tetrahedral cations was considerably higher than for the octahedral ones. Microprobe analysis of several grains of Frood pentlandite from the same sample indicated a metal/sulphur ratio of approximately 1.11 which is significantly less than 1.125 required for the stoichiometric composition (even after allowing for the precision of our microprobe analysis). It was assumed that the structure could be cation deficient with some tetrahedral vacancies as was indicated in the refinement in the form of relatively large temperature factors. Six more cycles of refinement with complete occupancy of octahedral sites and approximately 1.5% vacancies in the tetrahedral sites resulted in an R of 3.5%. The temperature factor for the cations in the two sites improved considerably. Attempts to refine the structure on the basis of octahedral vacancies resulted in a high R factor and abnormal temperature factors for the tetrahedral cations. Six additional cycles were run to refine the occupancies of Fe and Ni in the octahedral and tetrahedral sites, with the constraints of chemistry. Three different models of cation distribution which include (1) enrichment of Fe in the octahedral site over a random distribution [$M(O) = 0.7\,\mathrm{Fe} + 0.3\,\mathrm{Ni}$; $M(T) = 0.41\,\mathrm{Fe} + 0.58\,\mathrm{Ni}$] (2) enrichment of Ni in the octahedral site [$M(O) = 0.3\,\mathrm{Fe} + 0.7\,\mathrm{Ni}$; $M(T) = 0.46\,\mathrm{Fe} + 0.51\,\mathrm{Ni}$] and (3) random distribution of Fe and Ni in the two sites [$M(O) = 0.445\,\mathrm{Fe} + 0.555\,\mathrm{Ni}$; $M(T) = 0.44\,\mathrm{Fe} + 0.55\,\mathrm{Ni}$] were tried during the occupancy refinement. However, the R factors and refined parameters were almost identical in all three models and thus it was not possible to determine the distributions of Fe and Ni through site occupancy refinement. Refinement of the structure using weights based on counting statistics (Prewitt & Sleight 1968) reduced the R factor to 2.9% without changing the positional parameters and

TABLE 2. COMPOSITIONS, CELL PARAMETERS AND CALCULATED DENSITIES OF FROOD AND OUTOKUMPU PENTLANDITES

	Frood Pentlandite	Outokumpu Pentlandite
Composition	$Fe_{3.97}Ni_{4.84}Co_{0.07}S_8$	$Fe_{1.63}Ni_{1.82}Co_{5.60}S_8$
Total Metal	8.88	9.05
Cell Parameter	a=10.038(1)Å	a=9.977(1)Å
Calculated Density	5.03 gm/cc	5.25 gm/cc

TABLE 3. POSITIONAL AND THERMAL PARAMETERS IN FROOD PENTLANDITE AND OUTOKUMPU Co-PENTLANDITE (STANDARD DEVIATIONS IN BRACKETS).

Atoms		Positional Parameter			Temperature Factors (Å²)						
					Isotropic	Anisotropic					
		x	y	z	B	$\beta_{11}\times10^2$	$\beta_{22}\times10^2$	$\beta_{33}\times10^2$	$\beta_{12}\times10^2$	$\beta_{13}\times10^2$	$\beta_{23}\times10^2$
4(*b*) *M*(*O*)	Frood	1/2	1/2	1/2	0.55(4)	---	---	---	---	---	---
	Outokumpu	1/2	1/2	1/2	0.55(3)	---	---	---	---	---	---
32(*f*) *M*(*T*)	Frood	0.12608(4)	0.12608(4)	0.12608(4)	0.42(3)	0.106(9)	0.106(9)	0.106(9)	0.008(4)	0.008(4)	0.008(4)
	Outokumpu	0.12617(2)	0.12617(2)	0.12617(2)	0.49(2)	0.124(4)	0.124(4)	0.124(4)	0.006(2)	0.006(2)	0.006(2)
8(*a*) S1	Frood	1/4	1/4	1/4	0.58(4)	---	---	---	---	---	---
	Outokumpu	1/4	1/4	1/4	0.621(3)	---	---	---	---	---	---
24(*e*) S2	Frood	0.2632(1)	0	0	0.42(3)	0.09(1)	0.11(1)	0.11(1)	0	0	0
	Outokumpu	0.2623(1)	0	0	0.49(2)	0.093(8)	0.138(6)	0.138(6)	0	0	0

Frood: $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.027$. Secondary extinction correction factor $C=5\times10^{-7}$.

Outokumpu: $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.018$. Secondary extinction correction factor $C=4\times10^{-7}$.

TABLE 4. MAGNITUDE AND ORIENTATION OF THERMAL ELLIPSOIDS. (STANDARD DEVIATIONS IN PARENTHESES)

		Frood Pentlandite				Outokumpu Co-Pentlandite			
Atom	Ellipsoid Axis	r.m.s. Amplitude (Å)	Angles (°) w.r.t. *a*	*b*	*c*	r.m.s. Amplitude (Å)	Angles (°) w.r.t. *a*	*b*	*c*
M(*T*)	r_1	0.070(2)	114.05	114.05	35.19(10)	0.077(1)	113.69	113.69	34.63(30)
	r_2	0.070(2)	65.86	65.86	144.66(10)	0.077(1)	65.48	65.48	144.07(30)
	r_3	0.079(2)	54.74	54.74	54.74	0.082(1)	54.72(1)	54.72(1)	54.76(2)
S2	r_1	0.067(5)	0.0	90.0	90.0	0.069(3)	0.0	90.0	90.0
	r_2	0.075(2)	90.0	90.0	180.0	0.083(2)	90.0	90.0	180.0
	r_3	0.075(2)	90.0	90.0	180.0	0.083(2)	90.0	90.0	180.0

temperature factors of the atoms. The final two cycles of anisotropic refinement resulted in an unweighted *R* factor of 2.7% for the 94 unrejected reflections.

We also tried to refine the structure on the basis of Eliseev's structural model (quoted in Knop & Ibrahim, 1961; see Knop *et al.* 1965) for natural pentlandites—complete ordering of Fe and Ni in the 32(*f*) positions with excess cations located in 4(*a*) at (0,0,0). Refinement of the structure in the above model resulted in poor agreement of the observed and calculated structure factors. One cycle of refinement in the noncentrosymmetric $F\bar{4}3m$ space group also resulted in a very large *R* factor. Attempts were also made to refine the structure on the basis of ordering of Fe and Ni in the tetrahedral sites, with the octahedral site located at the equipoint 4(*b*). Neither the temperature factor nor the *R* factor was changed with this ordered model.

The same procedure was repeated to refine the structure of cobalt pentlandite. Since the composition of this mineral is close to its stoichiometric composition, there should not be any tetrahedral vacancies. Refinement was initialized with the coordinates and temperature factors obtained for Fe-Ni pentlandites and with chemistry-constrained cation distributions in the two sites. The first three cycles of refinement resulted in an *R* factor of 3.1%. The next few cycles to refine the occupancy of cations in the two different sites were not successful because of the close similarity of the *x*-ray scattering factors of Fe, Co, and Ni. The final cycles of anisotropic refinement included a secondary extinction factor, positional, and thermal parameters. The refinement converged giving a final unweighted *R* factor of 1.8% for the 95 unrejected reflections. The refined atomic coordinates, temperature factors and thermal ellipsoids of *M*(*T*) and S2 atoms for the two pentlandites are listed in Tables 3 and 4. The final (averaged) structure factors of the independent reflections for the two pentlandites are listed in Table 5.

DISCUSSION

The structure of natural pentlandite is essentially similar to that of synthetic Co_9S_8. The positional parameter *x* for the tetrahedral sites, *M*(*T*), is very close to that obtained by Geller (1962) for Co_9S_8. However, a slight change in the *x* parameter for the S2 site has been observed (the present values are 0.263 and 0.262 for the two pentlandites as compared to 0.259 reported by Geller for Co_9S_8). Values of selected interatomic distances and angles are listed in Tables 6 and 7. The sulphur, S2, octahedron surrounding

TABLE 5. OBSERVED AND CALCULATED STRUCTURE FACTORS

Frood Pentlandite						Outokumpu Pentlandite					
hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
200	98	90	12.22	13	15	200	85	90	12.22	19	19
400	269	234*	442	51	56	400	228	231	442	59	57
600	109	100	642	61	63	600	99	100	642	64	63
800	708	660*	842	41	42	800	634	663*	842	44	45
10.00	36	37	10.42	50	50	10.00	32	32	10.42	48	48
12.00	111	107	12.42	10	12	12.00	94	98	12.42	17	15
220	95	95	662	157	159	220	95	96	662	157	157
420	86	86	862	37	37	420	86	88	862	38	39
620	73	74	10.62	119	119	620	71	73	10.62	117	117
820	41	38	12.62	20	17	820	43	40	12.62	20	20
10.20	60	59	882	21	17	10.20	55	56	882	21	21
12.20	26	22	10.82	37	35	12.20	23	26	10.82	37	35
440	748	763*	333	226	241	440	767	792*	333	248	243
640	45	46	533	228	242	640	42	43	533	239	240
840	157	150	733	175	177	840	144	141	733	173	169
10.40	76	77	933	71	71	10.40	74	75	933	70	67
12.40	436	441	11.33	97	98	12.40	413	430	11.33	98	99
660	67	66	13.33	125	129	660	65	64	13.33	123	125
860	57	56	553	238	246	860	58	57	553	244	240
10.60	50	51	753	116	118	10.60	49	49	753	114	113
12.60	5	10	953	27	28	12.60	13	11	953	24	27
880	482	499	11.53	109	111	880	483	491	11.53	109	109
10.80	22	21	773	114	114	10.80	20	18	773	118	116
111	137	147	973	135	137	111	152	147	973	135	134
311	320	318	11.73	135	137	311	326	318	11.73	127	127
511	318	311	993	157	161	511	308	306	993	152	153
711	152	143	444	191	193	711	138	139	444	195	185
911	40	35	644	71	74	911	33	34	644	76	74
11.11	131	129	844	557	576	11.11	126	127	844	566	566
13.11	157	158	10.44	28	28	13.11	146	151	10.44	24	24
331	187	189	12.44	93	97	331	189	185	12.44	89	88
531	93	107	664	52	54	531	106	104	664	52	53
731	189	187	864	20	22	731	187	188	864	24	22
931	202	201	10.64	52	50	931	194	196	10.64	50	47
11.31	128	127	884	104	107	11.31	119	120	884	99	98
13.31	23	24	10.84	53	52	13.31	24	21	10.84	52	52
551	46	44	555	249	252	551	45	44	555	248	242
751	193	195	755	69	68	751	191	192	755	68	65
951	211	212	955	4	10	951	202	203	955	17	9
11.51	69	84	11.55	122	124	11.51	78	80	11.55	120	120
771	146	149	775	128	127	771	142	141	775	126	126
971	57	59	975	151	150	971	55	56	975	145	144
11.71	84	86	995	176	173	11.71	85	86	666	145	135
991	18	8	666	141	137	991	3	8	866	41	38
222	256	277	866	40	37	222	284	274	10.66	101	101
422	69	74	10.66	105	103	422	75	75	886	39	36
622	188	190	886	36	34	622	190	188	777	148	145
822	43	41	777	160	156	822	45	44	977	72	73
10.22	138	138	977	78	78	10.22	136	136			

*denotes reflections that were rejected in the refinement

TABLE 6. INTERATOMIC DISTANCES (Å) IN PENTLANDITES.

(STANDARD DEVIATIONS IN PARENTHESES)

Atom	Frood Pentlandite	Outokumpu Pentlandite	Synthetic Co_9S_8 (after Geller, 1962)
M(*O*)-S2(x6)	2.377(2)	2.373(1)	2.392(11)
M(*T*)-S1	2.154(1)	2.140(1)	2.132(5)
-S2(x3)	2.258(1)	2.239(1)	2.208(8)
-*M*(*T*)(x3)	2.531(1)	2.518(1)	2.501(6)
-*M*(*T*)(x3)	3.518(1)	3.494(1)	3.481(8)
S1 -*M*(*T*)(x4)	2.154(1)	2.140(1)	2.132(5)
S2 -*M*(*O*)	2.377(2)	2.373(1)	2.392(11)
-*M*(*T*)(x4)	2.258(1)	2.239(1)	2.208(8)
-S2(x4)	3.362(2)	3.355(2)	3.382(15)

TABLE 7. IMPORTANT BOND ANGLES IN PENTLANDITE
(STANDARD DEVIATIONS IN PARENTHESES)

Atoms	Frood (°)	Outokumpu(°)
S2-*M*(*O*)-S2	90.0	90.0
S1-*M*(*T*)-S2	107.18(4)	107.42(3)
S2-*M*(*T*)-S2	111.66(4)	111.45(2)
M(*T*)-*M*(*T*)-*M*(*T*)	90.0	90.0
M(*T*)-S1-*M*(*T*)	109.47	109.47
M(*T*)-S2-*M*(*T*)	68.19(4)	68.44(3)
M(*T*)-S2-*M*(*O*)	127.55(4)	127.32(3)

the cations in M(O) is very regular (the calculated octahedral Co-S distance in Co_9S_8 using x(S2) = 0.263 is 2.35Å as against 2.39Å reported by Geller). The tetrahedral sites are trigonally ($3m$) distorted, one distance (M-S1) being considerably shorter than the other three. All three basal edges of each distorted tetrahedron are shared by adjacent tetrahedran and short metal-metal distances occur across the shared edges. The metal-metal distances in all these structures are similar to the distances found in metallic Fe, Co, and Ni. These distances can be considered as representing metallic-bonding (Cotton 1966; Hulliger 1968). Thus, each tetrahedral cation is coordinated to three other tetrahedral cations, in addition to four sulphur atoms. Each S1 is surrounded by four $M(T)$ atoms in the form of a regular tetrahedron. Each S2 atom is coordinated to one M(O) and four $M(T)$ atoms which occur at the corners of a square pyramid. The isotropic temperature factor of the M(O) cation is slightly greater than that of $M(T)$ cation, consistent with the general relationship between the cation coordination number and temperature factors observed for pyroxene structures (Cameron *et al.* 1973). Also, the S1 atom has a higher temperature factor than the S2 atom, again consistent with the relation between the coordination number and temperature factors of anions (the higher the coordination number of the anion, the smaller the temperature factor). The point symmetries of atomic positions in the structure indicate that only $M(T)$ and S2 atoms could be anisotropic. The r.m.s. amplitudes, listed in Table 4, show that these atoms are slightly anisotropic.

TABLE 8. INTERATOMIC DISTANCES IN IMPORTANT SULPHIDE STRUCTURES

Structure Type	Minerals	Octahedral Bond Distance	Tetrahedral Bond Distance
Pyrite	Pyrite FeS_2	2.26Å	---Å
	Cattierite CoS_2	2.32	---
	Vaesite NiS_2	2.40	---
Spinel	Greigite Fe_3S_4	2.466	2.14
	Linnaeite Co_3S_4	2.25	2.19
	Polydymite Ni_3S_4	2.28	2.22
NiAs	Troilite	2.447	---
	Jaipurite	2.338	---
	β-NiS	2.394	---
Pentlandite	Synthetic Co_9S_8	2.35(?)	2.190
	Outokumpu Pn	2.373	2.209
	Frood Pn	2.377	2.228
Heazlewoodite	Ni_3S_2	---	2.28
Mackinawite	$(Fe)_{1+x}S$	---	2.244

Cation valencies, spin states and ordering

Interatomic distances in sulphide minerals can be used to predict probable cation valencies and spin states for a given coordination number and also, to some extent, cation ordering. Table 8 shows interatomic distances in several isostructural sulphide minerals including pentlandite. The octahedral Co-S distances in synthetic Co_9S_8 is slightly larger than the distances in CoS_2 (pyrite type) and CoS (jaipurite) where octahedral Co is probably in the divalent low spin state (Burns & Vaughan 1971). The octahedral Co in pentlandite could be divalent, low-spin. The absence of Jahn-Teller distortion, expected for the divalent low spin Co, may be attributed to the delocalization of electrons in the conduction (σ^*) band (Jellinek 1969).

As mentioned earlier, Knop *et al.* (1970) and Vaughan & Ridout (1971) studied the Mössbauer spectra of natural pentlandites and observed an enrichment of Fe in the octahedral site.

$$K_D = [X^{\mathrm{Fe}}_{M(O)}/(1 - X^{\mathrm{Fe}}_{M(O)})]^*[(1 - X^{\mathrm{Fe}}_{M(T)})/X^{\mathrm{Fe}}_{M(T)} = 3.86].$$

However, a comparison of octahedral M-S distances in pyrite (${}^{\mathrm{VI}}Fe^{2+}(L\cdot S) - S = 2.26$Å), troilite (${}^{\mathrm{VI}}Fe^{2+}(H\cdot S) - S = 2.45$Å) and Frood pentlandite (2.377Å) indicates that the octahedral Fe^{2+} probably is not in the low-spin state, particularly if there is any enrichment of Fe in the octahedral site. This distance can be interpreted as indicating either a random distribution of divalent, high-spin Fe in the two sites or an enrichment of Ni in the octahedral site which also contains a small amount of divalent, low-spin Fe. The latter possibility is not consistent with the fact that the divalent low-spin Fe will have a much greater octahedral site preference energy than Ni^{2+} and hence would be enriched in the octahedral site. In both Frood and Outokumpu pentlandites, the octahedral M-S distances are approximately equal, thereby suggesting that the octahedral site in the Outokumpu pentlandite is not completely filled with Co.

The tetrahedral Co-S distance in synthetic Co_9S_8 is identical to the Co-S distance in Co_3S_4 which is a normal thiospinel and suggests that tetrahedral Co could be divalent. Similarly, the tetrahedral M-S distances in natural pentlandites are consistent with divalent cations in tetrahedral coordination. However, assignment of formal valency to the tetrahedral cations becomes difficult and has no meaning in the chemical sense because of the complexity of bonding. As pointed out earlier, the presence of three metal-metal bonds for each tetrahedral cation leads to the formation cluster of 8 metal atoms at the corners of a cube. This is shown in Figure 1, which represents part of the pentlandite structure. Qualitative aspects of bonding in pentlandite have been discussed by Vaughan (1971) who suggested ordering of Fe and Ni in the alternate corners of the cube cluster in Fe-Ni pentlandite. As indicated elsewhere, the structure was refined on the basis of an ordered model by splitting the tetrahedral sites into two sets [$M(T1) = xxx, \bar{x}x\bar{x}, \bar{x}\bar{x}x, x\bar{x}\bar{x}$ and $M(T2) = \bar{x}\bar{x}\bar{x}, xx\bar{x}, x\bar{x}x, \bar{x}xx$], occupying the alternate corners of a cube, and filling the individual set completely with either Fe or Ni. Such an ordered model did not change either the R factor or the temperature factors. Thus, evidence for ordering of Fe and Ni in the tetrahedral sites of natural pentlandites is inconclusive. If ordering of Fe and Ni within the tetrahedral sites were real, then ordering of cations in the octahedral sites would be required depending on the Fe:Ni ratios; for example, Fe might be ordered in the octahedral sites for Fe-rich compositions. Such a simple explanation of ordering, as proposed for many electron compounds, does not appear to hold for pentlandites since it was shown by Knop *et al.* (1970) and Vaughan & Ridout (1971) by Mössbauer techniques that Fe is ordered in the octahedral sites even when Fe:Ni ratio is close to unity. However, it is not possible to determine unequivocally any ordering by *x*-ray techniques though our interatomic distances would suggest no such ordering of Fe in Fe-Ni pentlandite.

Mineral chemistry

The refinement of the structure of Frood pentlandite (composition $Fe_{3.97}Ni_{4.84}Co_{0.07}S_8$) on the basis of a cation-deficient model needs some explanation. Studies on the composition of natural pentlandites by Knop *et al.* (1965), Graterol & Naldrett (1971), and Harris & Nickel (1972) indicate (a) a wide range of M:S ratios, (b) a wide range of Ni:Fe ratios which increases in a general way with increasing Ni content of the bulk composition of the sulphide assemblage and, (c) no correlation between the sulphur content of pentlandite and the mineral assemblage containing pentlandite. Further, Knop & Ibrahim (1961) outlined the compositional limits within which pentlandite, $(Fe,Ni,Co)_9S_8$, occurs in the M_9S_8 section of the system Fe-Co-Ni-S (see Fig. 2). It should be mentioned here that the compositional limits of pentlandite in the synthetic system were, in fact, just estimated from the bulk compositions of the starting materials and from the observed lattice parameter variations. The actual compositions of pentlandites within the stability region are not known because they were not directly determined and, also, at least some of the run products contained other admixed phases. Figure 2 also shows the compositions of some natural pentlandites, most of which fall close to a line for which Fe:Ni = 1:1 or on the Ni-rich side of the line. Perhaps it would be appropriate to consider the possibility suggested by Rosenqvist (1954) that the pentlandite structure could be stabilized by an electron/atom ratio. In spite of large variations in the composition, the total number of "3*d*" electrons in the unit cell of pentlandite appears to be uniform, thereby supporting Rosenqvist's suggestion. Thus, if the pentlandite structure is stabilized by a particular electron/atom ratio (within a small allowable range) no stoichiometry can be expected in this phase. Since Co_9S_8 and $Fe_{4.5}Ni_{4.5}S_8$ are the most stable phases with complete solid solution, it can be assumed that the structure is stabilized by seven *d* electrons per cation. It should be emphasized here that this requirement arises because of the formation of the cube cluster of the tetrahedral cations which are numerically eight times more abundant than the octahedral sites. Increasing the Ni content in pentlandite over 4.5 atoms in the formula unit would cause cation vacancies in the tetrahedral sites if the number of *d* electrons in the cube cluster were kept constant. In general, the structural formula for Fe-Ni pentlandite can be written as $^{VI}[Fe_uNi_v]^{IV}(Fe_xNi_y\square_z)_8S_8$, where x = mole fraction of Fe in the tetrahedral sites, y = mole fraction of Ni in the tetrahedral sites, z = tetrahedral vacancy for Ni-rich compositions or excess cations for Fe-rich compositions:

$$z = [(x \times 6) + (y \times 8) - 7] \div 7.$$

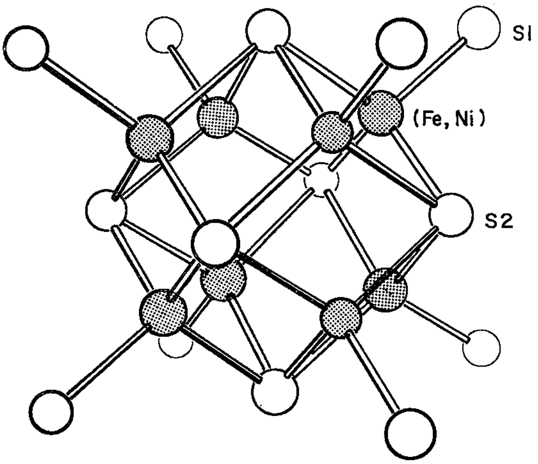

FIG. 1. Part of the Pentlandite structure showing the "cube cluster" of tetrahedral cations which are coordinated to one S1 and three S2 atoms.

Then the metal/sulphur ratio in pentlandite will be given by:

$$M/S = (9 - 8z) \div 8 = 1.125 - z.$$

The above equation predicts a relation between the M/S ratios and Ni/Fe ratios in pentlandite. Figure 3 shows such a relation between M/S ratios and Ni content in natural pentlandites—the plot being based on the electron microprobe data given by Harris & Nickel (1972) and on some of our own data given in Table 1. The M/S ratios decrease with increasing Ni content

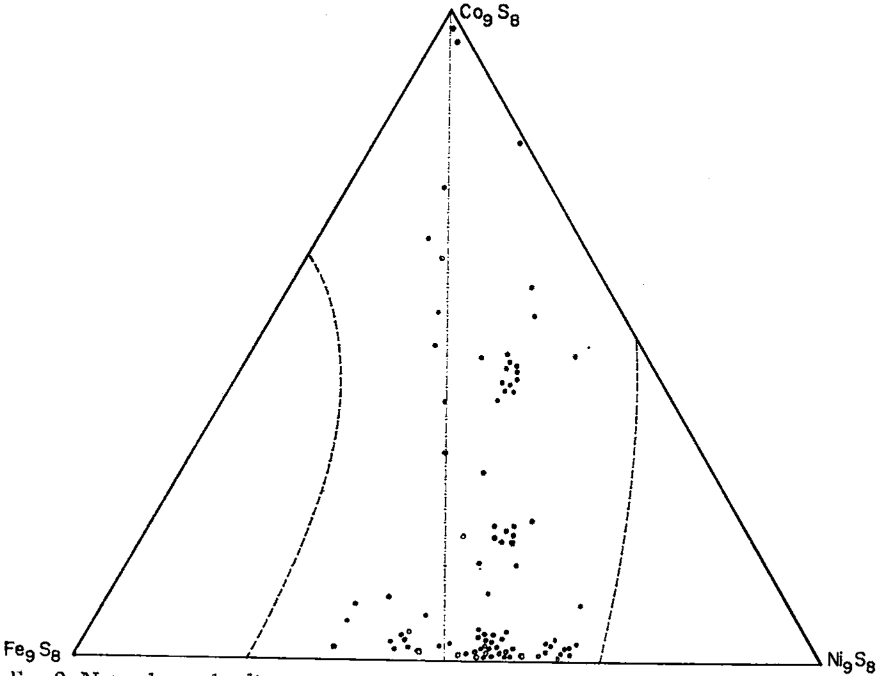

FIG. 2. Natural pentlandite compositions (after Harris & Nickel 1972). Dashed lines represent the estimated solid solution limits outlined by Knop & Ibrahim (1961) in the M_9S_8 section of the system Fe-Co-Ni-S. Dashed-dot line represents the compositions for which Fe:Ni = 1:1. Open circles represent the compositions reported in this work.

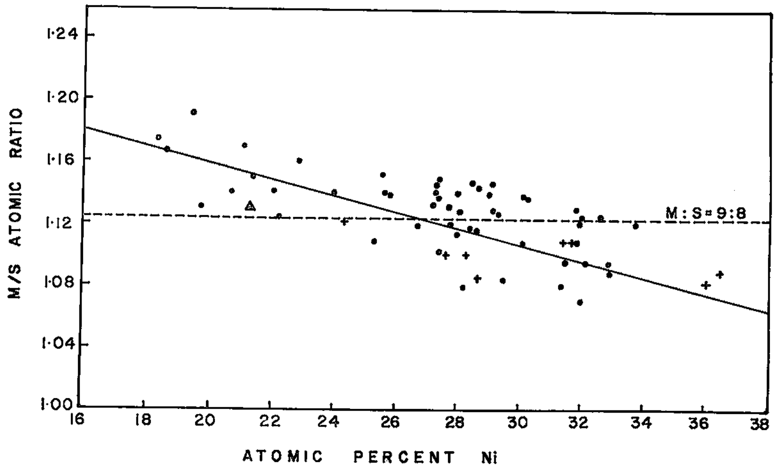

FIG. 3. Variation of metal/sulphur atomic ratios with Ni content in natural pentlandite. The solid line represents the equation $M/S = 1.125 - Z/8$. Full circles are from pentlandite compositions after Harris & Nickel (1972). Crosses are from the present study. The full triangle is from argentian pentlandite after Vuorelainen *et al.* (1972).

in natural pentlandites as required by the above equation. The observed slope agrees with the theoretical one shown in Figure 3. The scattering in the data points is probably due to the low precision involved in the analysis of sulphur by the microprobe. This observation indicates that the pentlandite structure could be stabilized by *d* electrons like an electron compound or Hume-Rothery phase. Since the octahedral sites can be completely filled with either Fe, Co or Ni, the total number of *d* electrons in the unit cell will not be constant but will be fairly uniform (260 ± 4 per unit cell). The excess cations that are required for Fe-rich compositions may be located in the normally unoccupied tetrahedral sites.

Physical properties

The foregoing interpretation of structure and chemistry of pentlandites with the predicted probable cation valencies, spin states and ordering accounts for the various physical properties of pentlandites and Co pentlandites observed by various investigators (Knop & Ibrahim 1961; Knop *et al.* 1965; Kouvo *et al.* 1959; Petruk 1969; and Burns & Vaughan, 1971). In natural pentlandites, the cell parameter, *a*, decreases with increasing Co content. Microhardness of pentlandite increases with increasing Co content. Further, the phase Co_9S_8 is found to be stable up to 835°C (Rosenqvist 1954); however, the synthetic $Fe_{4.5}Ni_{4.5}S_8$ is reported to be stable only up to 610°C (Kullerud 1963). These variations of physical properties with increasing Co content could be explained by the presence of low spin divalent Co in the octahedral sites and the greater (ligand field) stabilization energy gained by divalent Co in the tetrahedral sites compared to Fe^{2+} and Ni^{2+} ($\Delta_{Co_t} > \Delta_{Ni_t} > \Delta_{Fe_t}$).

Though the cell parameter, microhardness and thermal stability varies with Co content in pentlandite, reflectivity does not appear to vary significantly with composition (Burns & Vaughan 1970; Vaughan 1971). This could be, perhaps, the manifestation of a uniform number of *d* electrons in the unit cell. A small increase in reflectivity for Co-pentlandite ($R = 55\%$ as against 49.6 to 52% for $Fe_{4.5}Ni_{4.5}S_8$, Vaughan 1971) could be due to the presence of low spin Co(II) in the octahedral sites. Recently, Vuorelainen *et al.* (1972) reported the occurrence of argentian pentlandite ($Ag_{.81}Ni_{2.84}Fe_{5.4}S_8$) in some Finnish sulphide deposits. Even here, the total number of *d* electrons in the cubic cluster is nearly the same. Substitution of Ag in pentlandite is reported to have drastically reduced the reflectivity and microhardness and increased the lattice parameter. Assuming Ag is monovalent (indicated by the lattice parameter 10.50Å as against 10.07Å for normal pentlandite) a consideration of the size of the Ag ion and the three metal-metal bonds required for a tetrahedral cation would lead us to predict ordering of Ag in the octahedral sites. It should be noted here that there is only 0.8 Ag in the formula unit, thereby suggesting that such an ordering of Ag is not impossible from structural consideration. Refinement of the structure of argentian pentlandite by Hall & Stewart (1973) indicates such an ordering of Ag in the octahedral site.

The variation of cell parameter with composition in Fe-Ni pentlandite is rather interesting. Knop & Ibrahim showed that the cell parameter decreases with increasing Ni content in pentlandite. However, the variation is not linear as indicated by their Fig. 7 (Knop *et al.* 1965, p. 307) which shows that "*a*" decreases at first rapidly in the Fe-rich region, relatively less rapidly in the region where Fe:Ni ratio is close to unity, and flattening out with increasing Ni. This variation is difficult to explain by radii considerations alone. The variation might mean that the type of solid solution could be similar to the metal addition for Fe-rich compositions and metal omission for Ni-rich compositions to maintain uniformity of electron concentration. Donnay & Shewman (1971) observed that the cell volume of synthetic pentlandite [$(Fe_{1-n}Ni_n)_9S_8$; $n = 1/2$] decreases with increasing sulphur content and attributed this to metal omission and addition solid solution. Increasing Ni content alone in pentlandites causes a simultaneous decrease in the cell volume with an increase in sulphur content, thereby suggesting that the metal addition and omission solid solution exists in this structure to maintain a uniform number of *d* electrons in the unit cell. Recently, Nakazawa *et al.* (1973) reported the formation of cubic ion sulphide as a thin film (≈500Å) by flash evaporation and vacuum deposition technique. Though the diffraction pattern of this cubic iron sulphide appears to be similar to that of pentlandite, the lattice parameter is significantly higher than that expected through simple substitution of Co by Fe. Unfortunately, the exact chemical composition of this new phase is not known. It is predicted that the phase could be extremely cation rich ($Fe_{9+x}S_8$) if the structure is similar to natural pentlandite.

Conclusions

1. The structure of natural pentlandite is essentially similar to the synthetic Co_9S_8. A slight change only in the *x* parameter of S(*e*) atoms was observed.

2. The structure appears to be stabilized by metal-metal bonding. Three such bondings around each tetrahedral cation results in the formation of a metallic cube cluster. Because of the metal-metal bonding and cluster formation, the total number of *d* electrons in the unit cell remains uniform, as in an electron compound, in spite of large variations in compositions.

3. Metal addition and omission solid solutions and ordering of cations in the two different sites appear to be controlled by the cube cluster formation.

4. The structural formula for Ni-rich pentlandites would be $M_{9-x}S_8$ and for Fe-rich ones, $M_{9+x}S_8$.

5. Interatomic distances in natural pentlandite suggest that the octahedral Co could be divalent low spin; and the octahedral Fe may be divalent high spin. Complete delocalization of *d* electrons in the structure because of the metal-metal bonding makes the assignment of formal valency (in the chemical sense) for the tetrahedral cations meaningless though our interatomic distances are consistent with the presence of divalent species. Because of uncertainties about Geller's (1962) two dimensional refinement results, the structure of synthetic Co_9S_8 is now being refined to provide more information about the spin state of octahedral Co in the pentlandite structure.

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