RANGE IN COMPOSITION AND STRUCTURE OF 82 NATURAL TERRESTRIAL PYRRHOTITES

R. G. ARNOLD
Saskatchewan Research Council, University Campus
Saskatoon, Saskatchewan

ABSTRACT

The composition and structure of the phases in natural pyrrhotite from 82 different deposits in America, Europe and Africa were investigated. The structure and composition of the phases identified are as follows (atomic % metals): hexagonal FeS – 50.0, hexagonal $Fe_{1-x}S$ – 48.1 to 47.5, monoclinic $Fe_{1-x}S$ – 46.5. From x-ray studies of 28 of the phases it is concluded that all phases probably possess a supercell. Seventy-three per cent of the pyrrhotites examined are two-phase mixtures of hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$, 13 per cent are single-phase hexagonal $Fe_{1-x}S$, 9 per cent are monoclinic $Fe_{1-x}S$ and 5 per cent are two-phase mixtures of hexagonal FeS and hexagonal $Fe_{1-x}S$. In two-phase mixtures of FeS and hexagonal $Fe_{1-x}S$ each phase generally occurs as regularly-shaped lamellae in a matrix of the other. In two-phase mixtures of hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$ either phase can occur as lamellae in a matrix of the other but in a majority of cases, the two phases co-exist as irregularly-shaped grains. These relationships are readily observed on etched, polished surfaces.

The similarity between the compositions and phase relations of low temperature synthetic pyrrhotites and the 82 pyrrhotites studied here indicates that these natural pyrrhotites are low temperature phases. However, this does not necessarily imply that all these natural pyrrhotites originally crystallized at low temperatures. Relatively rapid, low temperature reaction rates, as indicated by experiments, can probably account for the development of the low temperature phases irrespective of original temperature of deposition. A brief summary of some recent low temperature experimental data is given.

INTRODUCTION

Grønvold & Haraldsen (1952) have indicated that the low temperature phase relations of synthetic pyrrhotites involve a two-phase field of hexagonal FeS + hexagonal $Fe_{1-x}S$, and a two-phase field of hexagonal $Fe_{1-x}S$ + monoclinic $Fe_{1-x}S$ separated by a narrow field of hexagonal $Fe_{1-x}S$ solid solutions. The data for the phases described by Grønvold & Haraldsen (1952) are as follows:

Formula	Composition (Atomic % Fe)	Structure
FeS	50.00	Hexagonal (with supercell)
$Fe_{1-x}S$	48.31–47.40	Hexagonal
$Fe_{1-x}S$	$\approx$46.73	Monoclinic

Hexagonal FeS and monoclinic $Fe_{1-x}S$ have a constant composition, whereas, hexagonal $Fe_{1-x}S$ shows a small range of solid solution. Recent low temperature experiments confirm these relationships among the various phases and provide more accurate data on the temperatures of stability of the various assemblages (A. H. Clark, personal communication; Arnold, unpublished). It has been recently pointed out that probably all natural and synthetic pyrrhotites possess supercells (Carpenter & Desborough, 1964). As natural pyrrhotites are examined in more detail it is becoming increasingly evident that they show the low temperature phase relations as outlined by Grønvold & Haraldsen (1952) (Clark, 1964, 1965a, b, d; Carpenter & Desborough, 1964; Desborough & Carpenter, 1965).

Natural two-phase pyrrhotites were recognized many years ago but the identity of the phases involved was uncertain. Schneiderhöhn (1922), Scholtz (1936) and Ramdohr (1960) were among the first workers to describe the appearance of such two-phase, natural pyrrhotites in polished sections. However, Kouvo & Vuorelainen (1962) were the first to confirm that natural two-phase mixtures of FeS and hexagonal $Fe_{1-x}S$ exist by measuring the composition of the two phases in pyrrhotite from Outokumpu, Finland, using the x-ray spacing method. Byström (1945) showed that natural two-phase mixtures of hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$ can occur on the basis of x-ray diffraction studies on Swedish pyrrhotites. Pehrman (1954) was apparently one of the first to describe the appearance of confirmed two-phase mixtures of hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$ from etched, polished surfaces.

The phases mackinawite (tetragonal FeS, Evans, *et al.*, 1964), and the two dimorphs smythite (rhombohedral Fe_3S_4, Erd., *et al.*, 1957) and greigite (cubic Fe_3S_4, Skinner, *et al.*, 1964) are low temperature phases within the FeS-S system; however, the main problem concerning these phases is one of temperature of stability rather than composition and structure, and as they are relatively rare and were not identified in any pyrrhotite examined in the present study, they are not considered here.

In this paper the composition, structure and phase constitution of natural, terrestrial pyrrhotites from 82 different deposits in America, Europe and Africa are compared with published data for both natural and synthetic pyrrhotites. On the basis of this comparison it is concluded that all of these natural pyrrhotites are made up of low temperature phases.

NATURAL PYRRHOTITE COMPOSITIONS

Tables 1 and 2 list the bulk compositions, structures, trace element data and principal admixed impurities for 82 natural pyrrhotite samples from a considerable variety of geological environments. The majority of the 82 pyrrhotite samples are from mines and showings located in

Table 1. Data for Co-existing Natural FeS and Hexagonal $Fe_{1-x}S$

Sample	Wt. fraction of phase*		Composition (At. % metals)				Trace metals in bulk sample (Weight %)				Impurities in samples§
	FeS	$Fe_{1-x}S$	FeS	$Fe_{1-x}S$	FeS + $Fe_{1-x}S$ Meas.†	FeS + $Fe_{1-x}S$ Calc.‡	Cu	Ni	Co	Mn	
Minnesota No. 6	.59	.41	50.0	48.1	49.4	49.2	.015	.186	.032	.005	pn
Insizwa, S.A.	.30	.70	50.0	48.0	48.4	48.6	.150	.911	.090	.021	pn, cp, mg
Kahtadin, Maine	.09	.91	50.0	47.7	47.7	47.9	.022	.168	.138	.015	cp, pn
Broken Hill, Austral.	<.01 (Estimated optically)	>.99	50.0	47.8	47.8	47.8	.080	.012	.052	.136	cp, sp

*Calculated from the relative intensity of the 102 reflections on x-ray diffraction charts.

†Obtained from d_{102} on material homogenized at 350° C for 20 minutes.

‡Calculated from measured composition and weight fraction of each phase.

§pn—pentlandite; cp—chalcopyrite; sp—sphalerite; mg—magnetite.

Source of samples

1. J. D. Mancuso, Bear Creek Mining Company, Salt Lake City, Utah.
2. P. Ramdohr, University of Heidelberg, Germany.
3. L. Pavlides, U.S.G.S., Washington, D.C.
4. R. J. P. Lyons, Department of Geophysics, Stanford University, Calif.

Precambrian areas in Canada. Several samples are from Europe and Africa and a number are younger than Precambrian. For example, 3 samples (6, 9, 34, Table 2) are from deposits in rocks of Ordovician age and 2 samples (13, 25, Table 2) are from deposits in Mesozoic rocks. The list of phases admixed with pyrrhotite gives an approximate indication of the ore mineralogy of the parent deposit. The samples are grab samples, and therefore neither the composition of the pyrrhotites nor the suite of admixed phases are necessarily representative of the whole parent deposit.

The compositions of pyrrhotite were measured with an uncertainty of about ±0.2 atomic % metals* by an *x*-ray spacing method using a Norelco wide-angle recording spectrometer and quartz as internal standard as previously described (Arnold & Reichen, 1962). Toulmin & Barton (1964) have pointed out that 2.0932 Å is a better value for the *d*(102) of FeS (50.0 atomic % metals) than 2.0918 Å which was given by Arnold & Reichen (1962). Accordingly the *d*(102) versus composition relationship used here was that given in Arnold & Reichen (1962) but with the *d*(102) of FeS changed to 2.0932 Å on the graph. An equation for the modified curve was calculated by computer, but the curve of best fit was of too high an order to be useful for hand calculation, and is therefore not given here.

Monoclinic pyrrhotite, mixtures of monoclinic and hexagonal pyrrhotite (Table 2) and two-phase hexagonal pyrrhotites (Table 1) were converted to one-phase hexagonal pyrrhotites before measuring their bulk compositions by heating them in sealed, evacuated silica-glass tubes at 350° C for 20 minutes, then quenching them. The quenched pyrrhotites showed a single, sharp 102 *x*-ray reflection with the exception of several of the most iron-deficient pyrrhotites (inverted monoclinic $Fe_{1-x}S$) which showed essentially single but rather short, stubby reflections, suggesting that a small proportion of the high temperature hexagonal $Fe_{1-x}S$ may have inverted to monoclinic $Fe_{1-x}S$ during quenching. It should be noted that at 350° C the composition of monoclinic $Fe_{1-x}S$ lies within the stability field of pyrrhotite plus pyrite. However, *x*-ray and polished section studies indicate that no appreciable quantity of pyrite is exsolved from inverted monoclinic pyrrhotite in 20 minutes. It was also found that two-phase lumps of hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$ heated at 350° C for 20 minutes were converted to single-phase hexagonal $Fe_{1-x}S$, whereas a mechanical mixture of separate grains of the two phases heated under the same conditions was not completely homogenized but

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* $$\frac{\mathrm{Fe + Ni + Co + Cu + Mn}}{\mathrm{Fe + Ni + Co + Cu + Mn + S}} \times 100$$

TABLE 2. SUMMARY OF DATA FOR 78 PYRRHOTITE SAMPLES

Total metal content and trace elements measured by x-ray diffraction and x-ray fluorescence, respectively. Structural types were determined by x-ray diffraction and optical examination of etched polished surfaces

No.	Samples	Atomic % metals†	Structural types‡	Weight % Cu	Weight % Ni	Weight % Co	Metallic phases co-existing with pyrrhotite§
1	Troilite, Oreg.	50.0	H	.133	.195	.067	cp
2	Brewster, N.Y.	49.8	H	.043	.068	.026	ms, cp, sp
3	Del Norte, Calif.	49.8	H	.400	.321	.098	cp
4	Witwatersrand, S.A.	47.9	H	*.002	.215	.059	py
5	Creston, B.C.	47.8	H	.035	.210	.220	sp, cp
6	Elizabeth Mine, Vt.	47.8	H	.310	.015	.050	sp, cp, py
7	Flat Lake, Y. Terr.	47.7	H	.017	.003	.030	cp
8	Red-A-Ven Mine, Eng.	47.6	H	.075	.013	.091	cp
9	Burra Burra Mine, Tenn.	47.6	H	.310	.002	.034	cp, py
10	Sullivan Mine, B.C.	47.6	H	.056	.011	.012	sp, gn, cp
11	Boliden, Sweden	47.5	H	*.005	.034	.002	py, asp, cp
12	Henderson Mine, B.C.	47.5	H > M	*.001	.071	.035	cp, gn
13	Potosi Mine, Mex.	47.5	H > M	.008	.002	.044	py, sp, cp
14	Finkenberg, Romania	47.5	H > M	.055	.034	.043	py, cp
15	Discovery Mine, N.W.T.	47.5	H > M	.025	.250	.055	cp
16	Long Creek, N.C.	47.5	H > M	.150	.014	.002	py, sp, cp
17	Floyd County, Va.	47.5	H > M	*.002	.170	.052	cp, pn, sp
18	Franklin, N.J.	47.5	H > M	.036	.231	.059	cp, sp
19	Workman Adit, Gila City, Ariz.	47.5	H > M	.327	.251	.198	cp, pn
20	Dinty Lake, Sask.	47.5	H > M	.034	.702	.088	pn, cp
21	Campbell Mine, Que.	47.4	H > M	.052	.133	.054	cp
22	Glen Uranium, Sask.	47.4	H > M	.008	.025	.015	cp
23	Minnesota No. 3	47.2	H > M	.283	.341	.041	cp, mg, cn
24	Hope Adit, Gila City, Ariz.	47.2	H > M	.004	.007	.001	gn
25	Hidden Creek, B.C.	47.2	H > M	.068	.032	.027	py, cp, sp
26	Contwoyto Lake, N.W.T.	47.1	H, M	.020	.003	.011	asp
27	Silberberg, Bavaria	47.1	H, M	.061	.011	.015	cp
28	Black Jack Gulch, B.C.	47.1	H, M	.001	.023	.023	py, cp, gn
29	Smaland, Sweden	47.1	H, M	*.004	.521	.044	pn, cp, mg

TABLE 2—*Continued*

No.	Samples	Atomic % metals†	Structural types‡	Weight %			Metallic phases co-existing with pyrrhotite§
				Cu	Ni	Co	
30	Horne Mine, Que.	47.1	H, M	.114	.007	.054	py, mg, cp
31	Stare Ransko Mine, Czech.	46.9	H, M	.030	.659	.053	pn, mg
32	Warren, B.C.	46.9	H, M	.011	.118	.042	cp
33	Amulet Mine, Que.	46.9	H, M	.240	.004	.015	cp, py, mg
34	Stantrg Mine, Yugosl.	46.9	H, M	.041	.015	.016	gn, cp, sp
35	Obaska Lake, Sask.	46.8	H, M	.007	.032	.037	py, ms
36	Bogus, Sask.	46.8	H, M	.017	.156	.011	cp, py, sp
37	Forbes Lake, Sask.	46.8	H, M	.007	.076	.009	mg
38	Sherritt Gordon, Man.	46.8	H, M	.261	.007	.019	py, cp, sp
39	Brabant Lake, Sask.	46.7	H, M	.076	.007	.065	sp, cp
40	Merrill Island, Que.	46.7	H, M	.174	.023	.072	cp, sp, ms
41	Waddy Lake, Sask.	46.7	H, M	.001	.077	.007	py, cp, sp
42	Last Lake, Sask.	46.7	H, M	.013	.052	.010	cp, sp
43	Central Patricia, Ont.	46.7	H, M	.008	.010	.002	asp, cp
44	Stassfeld, Austria	46.6	H, M	.034	.050	.015	cp, py, asp, st
45	Yxsjoberg, Sweden	46.6	H, M	.005	.004	.033	cp
46	Reforma Mine, Mex.	46.6	H, M	.007	.005	.010	ms, sp, gn
47	Anglo Rouyn, Sask.	46.6	H < M	.007	.383	.119	cp
48	Giant Yellowknife, N.W.T.	46.6	H < M	*.077	.033	.015	cp, asp
49	East Sullivan Mine, Que.	46.6	H < M	.094	.044	.017	py, cp, mg
50	Petsamo, Finland	46.6	H < M	.033	.543	.025	cp, pn
51	Artillary Lake, N.W.T.	46.6	H < M	.050	.058	.027	mg
52	Levack Mine, Ont.	46.6	H < M	.014	.541	.028	pn, cp, mg
53	Neagle Creek, Sask.	46.6	H < M	.002	.073	.033	py, asp, cp, sp
54	Wolverine Bay, Sask.	46.6	H < M	.019	.169	.021	py, cp, sp
55	Faraday Mine, Ont.	46.6	H < M	.013	.056	.005	py, cp
56	Cuprous Mine, Man.	46.6	H < M	.214	.032	.051	cp, sp, py
57	Lancaster, Penn.	46.6	H < M	.014	.651	.079	pn
58	Gwillam, Que.	46.6	H < M	.012	.168	.079	py, cp, sp
59	Pyrrhotite Lake, Sask.	46.6	H < M	.032	.042	.029	sp, cp
60	Kroy, Sask.	46.6	H < M	.001	.034	.012	py

TABLE 2—*Concluded*

No.	Samples	Atomic % metals†	Structural types‡	Weight % Cu	Ni	Co	Metallic phases co-existing with pyrrhotite§
61	Hanson Lake, Sask.	46.6	M	.031	.006	.004	sp, cp
62	Raft Lake, Sask.	46.5	H < M	.002	.187	.248	py, cp
63	Coronation Mine, Sask.	46.5	H < M	.019	.032	.026	py, cp, sp
64	New Calumet Mine, Que.	46.5	H < M	.011	.055	.023	sp, gn, cp
65	Kokko, Que.	46.5	H < M	.005	.083	.108	cp
66	Rottenstone, Sask.	46.5	H < M	.041	.601	.032	py, cp, mg, pn
67	Toad Gabbro, Sask.	46.5	H < M	.009	.008	.031	py, sp, gn
68	Outokumpu, Finland	46.5	H < M	.031	.582	.052	py, cp, pn
69	Algom Mine, Ont.	46.5	H < M	*.003	.130	.039	py
70	Birch Lake Mine, Sask.	46.5	H < M	.018	.007	.382	cp, py, sp
71	Falconbridge Mine, Ont.	46.5	H < M	.019	.552	.030	pn, cp
72	Lynn Lake, Man.	46.5	H < M	.042	.863	.029	pn, cp
73	Vicour Gold Mine, Que.	46.5	M	.015	.028	.019	cp
74	Garson Mine, Ont.	46.5	M	.027	.841	.004	pn, cp
75	Creighton Mine, Ont.	46.4	M	.066	.657	.010	pn, cp
76	Fano, Sask.	46.4	M	.014	.802	.036	pn, cp
77	Frood Mine, Ont.	46.4	M	.028	.860	.052	pn, cp
78	Back River, N.W.T.	46.4	M	.010	.023	.043	cp, sp, ms

*Trace elements determined by spectrophotometer by E. L. Faulkner.

† $\frac{\text{Fe} + \text{Cu} + \text{Ni} + \text{Co} + \text{Mn}}{\text{Fe} + \text{Cu} + \text{Ni} + \text{Co} + \text{Mn} + \text{S}} \times 100$

‡Key to symbols: H—hexagonal; M—monoclinic; asp—arsenopyrite; cp—chalcopyrite; gn—galena; mg—magnetite; ms—marcasite; pn—pentlandite; py—pyrite; sp—sphalerite; st—stibnite.

Source of samples: 1, 2, 68—Professor Edward Sampson, Princeton University, Princeton, N.J.; 3—Smithsonian Institution of Washington, Washington, D.C., No. 94472; 9, 7—C. S. Ross, USGS, Washington, D.C.; 15, 48—L. C. Coleman, University of Saskatchewan, Saskatoon, Sask.; 19, 24—H. C. Granger, USGS, Denver, Colorado; 23—J. D. Mancuso, Bear Creek Mining Company, Salt Lake City, Utah; 26, 51, 78—Dale Pyke, University of Saskatchewan, Saskatoon, Sask.; 55—P. K. Cunningham-Dunlop, Haileybury, Ont. The remaining samples are from the collections of the University of Saskatchewan and the Saskatchewan Research Council.

consisted of two hexagonal pyrrhotites of different composition: one representing the original hexagonal $Fe_{1-x}S$ and the other inverted monoclinic $Fe_{1-x}S$. Therefore, to convert two-phase mixtures of hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$ to one-phase hexagonal $Fe_{1-x}S$, it is advisable to use coarse-grained material consisting of mixed grains rather than finely ground material which may be made up of a large proportion of separate grains of the two phases.

The concentrations of Ni, Co, Cu and Mn in purified pyrrhotite separations are given in Tables 1 and 2. The concentrations of Mn are omitted from Table 2 as the concentration in all samples is less than 0.03 weight %, except in samples 9 and 22, in which the concentrations are 0.41 and 0.19 weight %, respectively. The concentration of each element was measured with a Norelco vacuum-path *x*-ray spectrometer using synthetic pyrrhotite standards as previously described (Arnold & Reichen, 1962). In several samples for which only small amounts of material were available, the concentrations of the elements were measured colourimetrically by E. L. Faulkner as noted (Table 2). The accuracy of the analyses is about 15% of the amount present except near the limit of detection where the accuracy is considerably less. The results of the trace element analyses show that the maximum combined concentration of foreign elements in any sample is 0.940 weight % (77, Table 2). Experiments have indicated that this combined concentration of elements in solid solution has no measurable effect on the compositions of pyrrhotite measured by the *x*-ray method (Arnold & Reichen, 1962). From the examination of polished sections of fractions of the analyzed separations it is evident that relatively high concentrations of Cu are due in part to admixed chalcopyrite. Concentrations of Ni over 0.4 weight % recorded in Tables 1 and 2 represent values corrected for admixed pentlandite. Corrections were estimated from point counts of admixed pentlandite on polished sections by assuming that in pentlandite, Fe/Ni = 1.

X-ray powder photographs of 3 samples of FeS, 6 hexagonal $Fe_{1-x}S$ samples, 15 mixtures of hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$ and 4 monoclinic $Fe_{1-x}S$ samples, taken with a Philips *x*-ray powder camera (57.3 mm dia.; $FeK\alpha/Mn$ filter) all show one or more very weak, low-angle supercell reflections as discussed by Carpenter & Desborough (1964). It is probable that the remaining pyrrhotite phases also possess supercells. The number and position of the extra reflections observed are considerably more erratic than is indicated by Carpenter & Desborough's (1964) work and therefore these reflections will require further investigation. For this reason no new indices based on revised unit cells have been used here, but the indices for normal hexagonal and monoclinic pyrrhotite subcells are used throughout this paper.

Table 1 summarizes the data for 4 two-phase mixtures of FeS and hexagonal $Fe_{1-x}S$. In x-ray diffraction charts these pyrrhotites give two reflections in the 102 reflection position, whose relative intensities are directly proportional to the concentrations of the two phases. The iron-rich phase is assumed to be stoichiometric FeS (50.0 atomic % metals) although the $d(102)$ value in one case is significantly larger than the experimental value of 2.0932 Å. Co-existing hexagonal $Fe_{1-x}S$ varies in composition from 48.1 to 47.7 atomic % metals, and the bulk compositions of the two-phase mixtures measured on homogenized samples range between 47.7 and 49.4 atomic % metals. The bulk compositions of these two-phase mixtures were also calculated from the estimated weight fraction and composition of each phase. The calculated values agree well with the measured values within the limit of error of measurement. The weight fraction of each phase was determined from the intensity ratio of the 102 reflections* on ray diffraction chart records.

Photomicrographs of the 4 two-phase pyrrhotites listed in Table 1 are shown in Fig. 1 as they appear on polished surfaces. The phase with the higher reflectivity is FeS and the other phase is hexagonal $Fe_{1-x}S$. FeS appears to be somewhat softer (polishes low) than hexagonal $Fe_{1-x}S$. In Figs. 1A, 1C and 1D, FeS is the minor phase and occurs in the form of lamellae in a matrix of hexagonal $Fe_{1-x}S$. In Fig. 1B the relationship is reversed, hexagonal $Fe_{1-x}S$ is the minor phase and occurs as lamellae in a matrix of FeS. Reversal of the relative proportions of the two phases can be occasionally observed within a single grain. Kouvo & Vuorelainen (1962) have described similar relationships for a two-phase pyrrhotite from Outokumpu, Finland. The pyrrhotite from Insizwa, South Africa, shown in Fig. 1A, was obtained from Dr. Paul Ramdohr and is apparently the same material described by Scholtz (1936) and Ramdohr (1960). The x-ray data in Table 1 for this pyrrhotite substantiate Dr. Ramdohr's interpretation that the two phases are troilite (FeS) and pyrrhotite (hexagonal $Fe_{1-x}S$). Lyons (1958) had observed the two phases in the Broken Hill pyrrhotite shown in Fig. 1D, but he did not positively identify them. The photomicrograph shown in Fig. 1D is of a local concentration of FeS lamellae. The concentration of FeS in the hand specimen as a whole is very low as indicated in Table 1.

Table 2 summarizes the structures and compositions of 78 natural pyrrhotites. Three of these are single-phase FeS (within the limit of error of measurement), 8 are single-phase hexagonal $Fe_{1-x}S$, 60 are mixtures of hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$ and 7 are monoclinic $Fe_{1-x}S$.

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*For example, weight fraction FeS can be estimated from the intensity of the lower angle 102 reflection divided by the sum of the intensities of both 102 reflections. Intensities are corrected for contribution from the adjacent reflection.

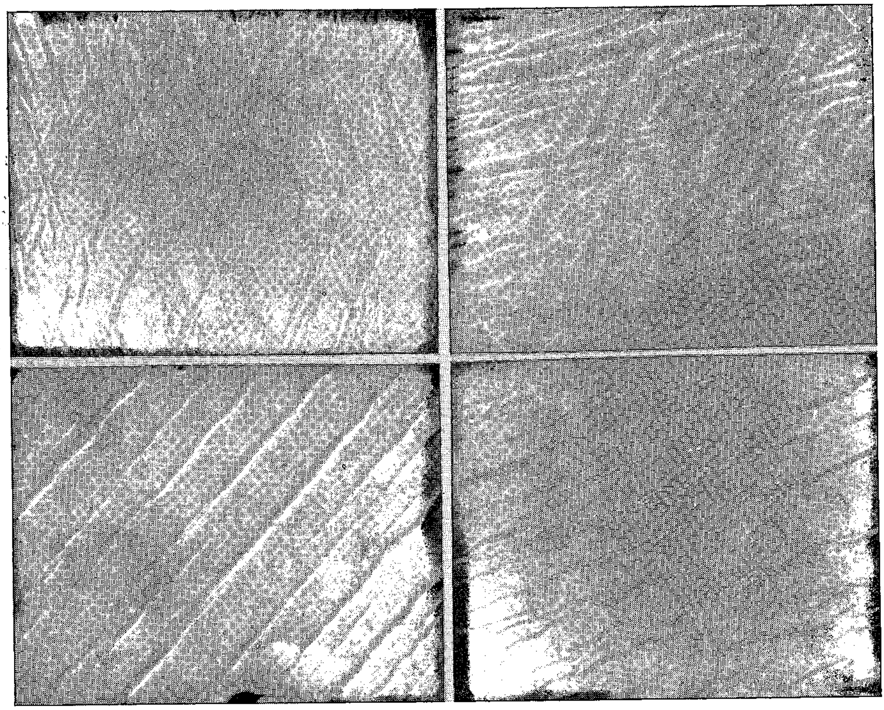

FIG. 1. Photomicrographs of natural co-existing FeS and hexagonal $Fe_{1-x}S$. The phase with the greater reflectivity is FeS.

A. (Upper left). Insizwa, South Africa (120×).
B. (Upper right). Minnesota No. 6 (120×).
C. (Lower left). Kahtadin, Maine (180×).
D. (Lower right). Broken Hill, Australia (100×, lightly etched).

In x-ray diffraction charts a single, sharp, symmetrical 102 reflection is indicative of FeS or hexagonal $Fe_{1-x}S$. Two reflections (202 and $20\bar{2}$) of about equal intensity and about 0.3° 2θ (Cu$K\alpha$) apart* indicate monoclinic $Fe_{1-x}S$ (Byström, 1945). Two reflections about 0.3° 2θ (Cu$K\alpha$) apart* but of unequal intensity indicate a mixture of hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$ (Byström, 1945). For these mixtures the lower angle reflection (superimposed hexagonal 102 and monoclinic 202) is significantly greater in intensity than the other reflection (monoclinic $20\bar{2}$). A rough estimate of the relative proportions of hexagonal $Fe_{1-x}S$ or monoclinic $Fe_{1-x}S$ in a mixture of the two can be obtained from the relative intensities of the two reflections in x-ray diffraction charts (see

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*Byström's (1945) work indicates a separation of about 0.35° 2θ (Cu$K\alpha$). However, an average of a number of measurements on the natural pyrrhotites listed in Table 2 of this paper indicates a separation of about 0.3° 2θ.

Arnold, 1966). However, less than about 10 weight % of the minor phase cannot be detected with a normally equipped x-ray spectrometer using no internal standard. Desborough & Carpenter (1965) indicate that with their x-ray diffraction technique, less than about 20 weight % of the minor phase cannot be detected. The sensitivity of the x-ray diffraction method for small amounts of the second phase is therefore rather poor, and for two-phase pyrrhotites containing small quantities of the minor phase, microscopic examination of etched, polished surfaces of the samples can be used to good advantage to detect the minor phase and to estimate its relative proportion (Arnold, 1966).

Photomicrographs of co-existing hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$ as they appear on etched* polished surfaces are shown in Fig. 2.

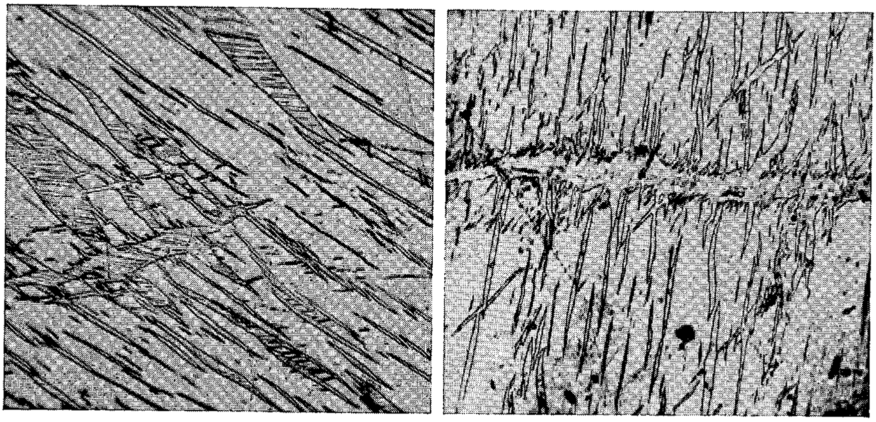

FIG. 2. Photomicrographs of co-existing hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$ (No. 28, Table 2. 165×, etched).

A. (Left) Lamellae and blebs are monoclinic $Fe_{1-x}S$. Matrix is hexagonal $Fe_{1-x}S$. A second set of small, parallel, closely spaced lamellae occur in some of the larger lamellae.

B. (Right) Development of lamellae and blebs appears to be related to veinlet of monoclinic $Fe_{1-x}S$ passing east-west through the photomicrograph.

Monoclinic $Fe_{1-x}S$ etches more strongly (lower reflectivity) than hexagonal $Fe_{1-x}S$ in all samples in which monoclinic $Fe_{1-x}S$ and hexagonal $Fe_{1-x}S$ have been positively identified using an x-ray powder camera. In these photomicrographs, monoclinic $Fe_{1-x}S$ occurs as intersecting and *en echelon* lamellae and blebs in a matrix of hexagonal $Fe_{1-x}S$. These lamellae and blebs are not visible prior to etching. The majority of the lamellae shown have the appearance of an exsolved phase in that they are apparently crystallographically oriented single crystals with smooth,

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*A saturated solution of CrO_3 in water was used.

sharp boundaries. The lamellae terminate or change direction abruptly at grain boundaries of the host (not shown). Several sets of short, narrow, closely spaced lamellae can be seen in Fig. 2A occurring in relatively large lamellae of monoclinic $Fe_{1-x}S$. The identity of these short, closely spaced lamellae is not known and similar lamellae have not been observed in lamellae of hexagonal pyrrhotite. Lamellae of hexagonal $Fe_{1-x}S$ in monoclinic $Fe_{1-x}S$ have been observed, but they are relatively rare. If monoclinic $Fe_{1-x}S$ is the major phase, hexagonal $Fe_{1-x}S$ generally occurs as irregularly-shaped grains in a matrix of monoclinic $Fe_{1-x}S$.

Edwards (1954), Pehrman (1954) and Lyons (1958) show photomicrographs of etched pyrrhotite with structures somewhat similar to those shown here.

In Fig. 2B is a rarely observed veinlet of monoclinic $Fe_{1-x}S$ to which the lamellae of monoclinic $Fe_{1-x}S$ appear to be related. The existence of the veinlet suggests a late development of monoclinic $Fe_{1-x}S$ by alteration of pre-existing hexagonal $Fe_{1-x}S$. In one polished section (Black Jack, Table 2), a small quantity of what appears to be an iron oxide occurs in a veinlet of monoclinic $Fe_{1-x}S$. If the identification of this phase is correct, its presence supports Desborough & Carpenter's (1965) conclusion that some monoclinic $Fe_{1-x}S$ may form by oxidation of hexagonal $Fe_{1-x}S$.

It is evident from Table 2 that there is a clearcut relationship between structural type and composition of pyrrhotite. The most metal-rich phases are hexagonal, the most metal-deficient phases are monoclinic and phases with intermediate bulk compositions are mixtures of hexagonal and monoclinic types. A clear relationship also exists between the relative proportions of hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$ in a mixture and bulk composition. Mixtures relatively rich in hexagonal $Fe_{1-x}S$ have metal-rich bulk compositions and mixtures rich in monoclinic $Fe_{1-x}S$ have more metal-deficient compositions. This relationship indicates a two-phase field of monoclinic $Fe_{1-x}S$ and hexagonal $Fe_{1-x}S$ as suggested by Grønvold & Haraldsen (1952) on the basis of synthetic pyrrhotites. From Table 2 the boundaries of the two-phase field are judged to be located at 47.5 and 46.5 atomic % metals with these values representing the compositions of the co-existing hexagonal and monoclinic phases, respectively.

The compositions of co-existing hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$ given above were confirmed by separating the two phases from 6 different two-phase mixtures listed in Table 2 and measuring their compositions individually by the x-ray diffraction method (see Table 3). The separations were obtained from minus 325 mesh material immersed in acetone using an alternating current magnet. Pyrrhotite fractions with the highest magnetic susceptibility were monclinic $Fe_{1-x}S$ and those with the lowest magnetic susceptibility were hexagonal $Fe_{1-x}S$. Monoclinic

$Fe_{1-x}S$ was inverted to the hexagonal structure before measuring its composition as previously described. The hexagonal $Fe_{1-x}S$ fractions range in composition between 47.5 and 47.3 atomic % metals and average 47.4 atomic % metals and the monoclinic $Fe_{1-x}S$ fractions range in compositions between 46.8 and 46.4 atomic % metals and average 46.5 atomic % metals. The approximate weight percentage of hexagonal $Fe_{1-x}S$ in each mixture was calculated from x-ray line intensities on chart records (see Arnold, 1966). The percentage of hexagonal $Fe_{1-x}S$ in the various mixtures decreases with decreasing metal content of the bulk compositions as one would expect from the "lever law" (Table 3).

TABLE 3. COMPOSITIONS OF CO-EXISTING HEXAGONAL $Fe_{1-x}S$ AND MONOCLINIC $Fe_{1-x}S$

measured on phases separated from 6 mixtures listed in Table 2

Sample	Composition (Atomic % metals) Hexagonal $Fe_{1-x}S$	Monoclinic $Fe_{1-x}S$	Bulk composition*	Weight % hexagonal phase in mixture†
Black Jack Gulch, B.C.	47.5	46.8	47.1	≈55
Bogus, Sask.	47.5	46.6	46.8	≈28
Waddy Lake, Sask.	47.3	46.5	46.7	≈22
Yxsjoberg, Sweden	47.4	46.4	46.6	<10
Levack Mine, Ont.	47.4	46.5	46.6	<10
Pyrrhotite Lake, Sask.	47.3	46.4	46.6	<10
Average Composition	47.4	46.5		

*Bulk composition obtained from data in Table 2.

†Estimated from the relative intensity of reflections on x-ray diffraction chart records (See Arnold 1966).

The bulk compositions of the 4 two-phase hexagonal pyrrhotites from Table 1 and the 78 pyrrhotites from Table 2 are shown in a histogram in Fig. 3A. It is apparent that the bulk compositions of the majority of pyrrhotites are metal-deficient and that bulk compositions in the interval 50 to 48 atomic % metals are relatively rare. Figure 3B shows the frequency distribution of the bulk compositions of 193 natural pyrrhotites from the literature. The sources of these analyses are given in the appendix at the end of this paper. A comparison of the distributions in Fig. 3A and Fig. 3B shows that they are generally similar except that in Fig. 3B, four compositions are considerably more metal-deficient than any of those in Fig. 3A. These low values are probably due to faulty analyses. It is interesting to note that a compilation of pyrrhotite compositions from meteorites by Buddhue (1937) suggests that meteoritic pyrrhotites show approximately the same range of compositions as natural, terrestrial pyrrhotites.

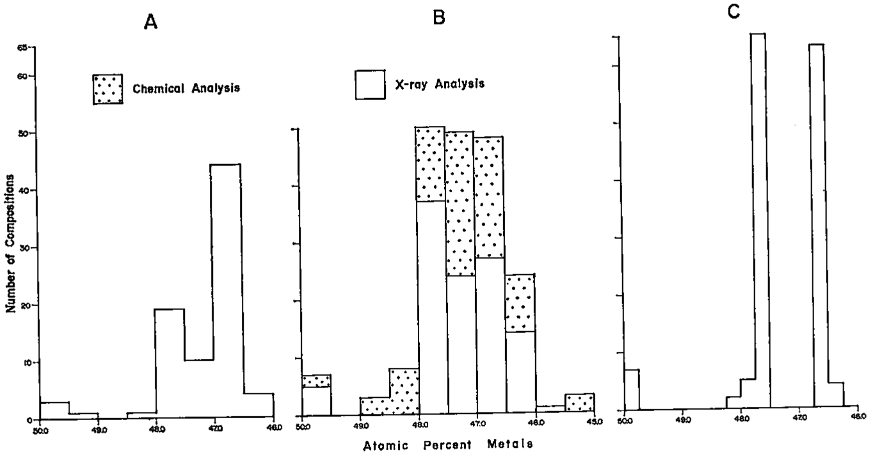

FIG. 3. Frequency distribution of natural, terrestrial pyrrhotite compositions:
A. Bulk compositions of pyrrhotite samples listed in Tables 1 and 2.
B. Bulk composition of 193 pyrrhotites from the literature.
C. Compositions of individual pyrrhotite phases in samples listed in Tables 1 and 2.

If only the compositions of individual hexagonal and monoclinic phases in the samples listed in Tables 1 and 2 are plotted, the phase relations become clear (see Fig. 3C). There are two distinct gaps in the solid solution series. The left hand gap represents the two-phase field of FeS + hexagonal $Fe_{1-x}S$ extending between 49.8 and 48.1 atomic % metals. The right hand gap represents the two-phase region of hexagonal $Fe_{1-x}S$ + monoclinic $Fe_{1-x}S$ extending between 47.5 and 46.5 atomic % metals. Separating the two two-phase regions is a narrow field of hexagonal $Fe_{1-x}S$ solid solutions with variable width. This arrangement of phases and their compositions agrees quite closely with the data given for low temperature synthetic pyrrhotites by Grønvold & Haraldsen (1952).

The principal difference between the compositions of natural and synthetic phases lies in the composition of hexagonal $Fe_{1-x}S$ co-existing with FeS. Grønvold & Haraldsen (1952) give the composition of this phase as 48.31 atomic % Fe, whereas the compositions of the natural phases (Table 1) range between 47.7 and 48.1 atomic % metals. This discrepancy can probably be accounted for by different thermal histories of the natural and synthetic phases. Preliminary experimental work indicates that the composition of hexagonal $Fe_{1-x}S$ co-existing with FeS varies with temperature from approximately 47.8 atomic % metals at 20° C to approximately 48.5 atomic % metals at 100° C (Arnold, unpublished). From these data it can be inferred that Grønvold & Haraldsen's (1952) synthetic, hexagonal $Fe_{1-x}S$ possess a relatively high-temperature composition, whereas the natural phases possess compositions ranging downwards to room temperature values.

In Table 4 are summarized the compositions of various structural types of natural pyrrhotite from the literature. Compositions joined by a hyphen indicate a range of values involving three or more individual compositions. Table 4A lists the compositions of co-existing FeS and hexagonal $Fe_{1-x}S$. In all but one case the compositions agree within the limit of error of measurement with the data given in Table 1. The exception is the low value of 47.2 atomic % metals given for hexagonal $Fe_{1-x}S$ from the Long Island Meteorite (Carpenter & Desborough, 1964).

Table 4B lists the compositions of single-phase, natural, hexagonal $Fe_{1-x}S$ solid solutions from the literature. These values range from 48.1 to 46.8 atomic % metals. The range in composition for this phase determined in the present study is 48.1 (Table 1) to 47.5 atomic % metals (Table 2). Grønvold & Haraldsen (1952) found a range of 48.31 to 47.40 atomic % Fe in synthetic pyrrhotites. In comparison with these data the values 46.8 and 46.9 atomic % metals given in Table 4B are too low. It is probable that these pyrrhotites are undetected mixtures of hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$.

The bulk compositions of mixtures of hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$ from the literature are listed in Table 4C. Within the limit of error of measurement the majority of these values fit within the range 47.5 to 46.5 atomic % metals found in the present study (Table 2) and within the range 47.40 to 46.73 atomic % Fe proposed by Grønvold & Haraldsen (1952) for synthetic pyrrhotites. The only serious disagreement between these data and those in Table 4C is the lower limit of 45.9 atomic % metals placed on the range of bulk compositions by Leonchenkova (1963).

Grønvold & Haraldsen (1952) conclude that synthetic monoclinic $Fe_{1-x}S$ has a constant composition near 46.73 atomic % Fe. The measurements on natural monoclinic $Fe_{1-x}S$ listed in Tables 2 and 3 indicate a constant composition near 46.5 atomic % metals. Considering the limit of error of measurement, these two estimates are probably not significantly different. The majority of the estimated compositions of monoclinic $Fe_{1-x}S$ from the literature (Table 4D) range between 46.7 and 46.5 atomic % metals. However a number of estimates given in Table 4D deviate significantly from this range. The values given by Byström (1945), Kouvo & Vuorelainen (1962) and the upper limit given by Buseck (1962) are too high, whereas the values given by Pehrman (1954) and the metal-deficient limit of the range of compositions given by Leonchenkova (1963) are too low. Compositions significantly richer in metals than 46.7 atomic % metals probably indicate undetected mixtures of hexagonal $Fe_{1-x}S$

TABLE 4. COMPOSITION AND STRUCTURE OF NATURAL PYRRHOTITES FROM THE LITERATURE

A. Co-existing FeS and hexagonal $Fe_{1-x}S$.

Sample	Composition (At. % metals) FeS	Composition (At. % metals) $Fe_{1-x}S$	Reference
Long Island Meteorite, Kan.	50.0	47.2	Carpenter & Desborough (1964)
Merensky Reef, S.A.	50.0	47.9	Carpenter & Desborough (1964)
Ylöjärvi, Finn.	50.0	47.7	Clark (1964)
Cross Gill, England	50.0	47.7	Clark (1965A)
St. John's Mine, England	50.0	47.7	Clark (1965A)
Nigadoo, New Brunswick	50.0	47.7	Clark (1965C)
Panesqueira, Portugal	50.0	47.7	Clark (1965D)
Hanover, New Mexico	50.0	47.8	Desborough & Carpenter (1965)
Outokumpu, Finn.	50.0	47.8	Kouvo & Vuorelainen (1962)
Alexo Mine, Ontario	50.0	47.5	Naldrett (1964)
Dracut, Conn.	50.0	47.7	von Gehlen (1963)

B. Hexagonal $Fe_{1-x}S$ solid solutions.

Composition (At. % metals)	Reference
47.8, 47.7	Arnold (1966)
48.1–46.8	Byström (1945)
47.9–47.2	Carpenter & Desborough (1964)
47.7–46.9	Clark (1965B)
47.8–47.4	Desborough & Carpenter (1965)
48.1, 47.9	Grønvold & Haraldsen (1952)
$\geqslant$47.2	Groves & Ford (1963)
47.8	Kouvo & Vuorelainen (1962)
47.8–46.9	Leonchenkova (1963)
47.4	von Gehlen & Piller (1964)
C. Hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$ mixtures.	
47.6–46.9	Arnold (1966)
47.7–47.3	Byström (1945)
47.0–47.1	Carpenter & Desborough (1964)
47.1–46.7	Clark (1965B)
47.1	Desborough & Carpenter (1965)
47.2	Grønvold & Haraldsen (1952)
47.2–46.8	Groves & Ford (1963)
46.8–45.9	Leonchenkova (1963)
$\leqslant$47.4	Pehrman (1954)
47.1	von Gehlen & Piller (1964)
D. Monoclinic $Fe_{1-x}S$.	
46.7	Arnold (1966)
47.1–46.5	Buseck (1962)
48.3–47.0	Byström (1945)
46.9–46.6	Carpenter & Desborough (1964)
46.7–46.4	Clark (1965B)
46.7	Desborough & Carpenter (1965)
46.7	Erd, Evans, Richter (1957)
46.5	Grønvold & Haraldsen (1952)
$\leqslant$46.8	Groves & Ford (1963)
47.1	Kouvo & Vuorelainen (1962)
46.7–46.5	Kullerud *et al.* (1963)
46.5–45.7	Leonchenkova (1963)
46.0–45.4	Pehrman (1954)
46.6, 46.7	Sawkins *et al.* (1964)
46.7	von Gehlen & Piller (1964)

and monoclinic $Fe_{1-x}S$ and compositions more metal-deficient than 46.5 atomic % metals probably indicate faulty analyses or chemical analyses of impure material.

DISCUSSION

A comparison of the structure, composition and phase relations of synthetic pyrrhotites with data for the 82 natural pyrrhotites (Tables 1, 2, 3) presented in this paper, indicates that these natural pyrrhotites are low temperature phases. However, this does not necessarily mean that all these natural pyrrhotites originally crystallized at low temperatures. Experiments on natural and synthetic pyrrhotites show that the low temperature reaction rates are sufficiently rapid to ensure that slowly cooled natural pyrrhotites would assume the low-temperature phase relations, regardless of the original temperature of crystallization. For example, FeS unmixes from hexagonal $Fe_{1-x}S$ at 100° C in less than 3 months (Arnold, unpublished), and monoclinic $Fe_{1-x}S$ unmixes from hexagonal $Fe_{1-x}S$ within 50 days at 300° C (von Gehlen, 1963). The maximum temperature of stability (<1 atm total pressure) of co-existing FeS and hexagonal $Fe_{1-x}S$ is approximately 125° C and of monoclinic $Fe_{1-x}S$ is 305 ± 5° C (Arnold, unpublished). A. H. Clark (personal communication, 1966)* gives the maximum temperature of stability of monoclinic $Fe_{1-x}S$ as 308 ± 5° C.

Approximately 73 per cent of the 82 pyrrhotites listed in Tables 1 and 2 are mixtures of hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$. These two-phase mixtures are therefore the most common variety of natural pyrrhotite. It is apparent from published compositions of some hexagonal $Fe_{1-x}S$ and monoclinic $Fe_{1-x}S$ phases that a number of these pyrrhotites are actually mixtures of the two-phases. In all probability this is due to the lack of sensitivity of the x-ray diffraction method for small amounts of the second phase. It appears, however, that the bulk compositions of these unrecognized mixtures measured by x-ray diffraction are valid. The bulk compositions of mixtures rich in monoclinic $Fe_{1-x}S$ are probably valid because pyrrhotites showing obviously split reflections are invariably converted to hexagonal $Fe_{1-x}S$ and homogenized by heating before measuring their bulk compositions. The bulk compositions of mixtures rich in hexagonal $Fe_{1-x}S$ also appear to be valid provided the centre of the apparently single reflection (102 and 202 superimposed) is measured below the position of the unresolved or poorly resolved $20\bar{2}$ reflection of monoclinic $Fe_{1-x}S$. The contribution of the $20\bar{2}$ reflection shifts the centre of the superimposed 102 and 202 reflection to higher 2θ values by an amount proportional to the concentration of monoclinic $Fe_{1-x}S$ in the

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*Clark's data has now been published. See *Econ. Geol.* **61**, 780 (1966).

mixture, thereby quantitatively accounting for the concentration of monoclinic $Fe_{1-x}S$ in the mixture. This was demonstrated by measurements on 8 unheated mixtures from Table 2 and was found to be the case for a number of mixtures re-examined by Arnold (1966).

Groves & Ford (1963) have reported that the position of the superimposed 102 and 202 reflection measured above the $20\bar{2}$ position of monoclinic $Fe_{1-x}S$ is indicative of the bulk composition of the mixture. This was not found to be the case on the basis of the measurements on the 8 unheated mixtures from Table 2. For these mixtures the position of the superimposed 102 and 202 reflection is essentially constant regardless of the ratio of the two phases and is indicative of the composition of hexagonal $Fe_{1-x}S$ rather than the bulk composition of the mixture. This result is to be expected as the position of the 102 reflection is related only to the composition of hexagonal $Fe_{1-x}S$ in the mixture, and the composition of this phase is essentially constant when co-existing with monoclinic $Fe_{1-x}S$. The presence of the 202 reflection of monoclinic $Fe_{1-x}S$ does not affect the d_{102}-composition relationship significantly as the position of the 202 reflection is essentially constant and coincides very closely with that of the 102 reflection of hexagonal $Fe_{1-x}S$.

The application of the pyrrhotite-pyrite geothermometer is somewhat problematical at best and the conclusion that natural pyrrhotites are low temperature phases would appear to compound the difficulties. The valid application of this geothermometer will depend upon the development of criteria by which pyrrhotites crystallized above about 305° C can be recognized. Further discussion of this problem should be deferred until the experimental low temperature phase relations and reaction rates are better known.

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APPENDIX

SOURCE OF 193 ANALYSES OF PYRRHOTITE FROM THE LITERATURE PLOTTED IN FIG. 3B

Source	Number of analyses	Analytical method	
		Chemical	*x*-ray
Arnold (1958, Unpublished)	4		x
Arnold (1962)	7		x
Arnold & Reichen (1962)	14	x	x
Buseck (1962)	3		x
Byström (1945)	14	x	
Carpenter & Desborough (1964)	26		x
Clark (1964)	18		x
Doelter & Leitmeier (1926)	55	x	x
Eleesev & Denisov (1957)	26		x
Eleesev (1962)	2		x
Erd, Evans & Richter (1957)	1	x	
Ferris (1961)	1	x	x
Frankel (1948)	2	x	
Grønvold & Haraldsen (1952)	4	x	
Kullerud, *et al.* (1963)	1		x
Mandarino & Mitchell (1960)	1	x	
Mendelssohn (1944)	1	x	
Marmo & Mikkola (1951)	5	x	
Sawkins, *et al.* (1964)	2		x
Skinner (1958)	1	x	x
Tsusue (1962)	3		x
von Gehlen (1963)	2		x

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