RANGE IN SOLID SOLUTION AND STRUCTURE OF NATURALLY OCCURRING TROILITE AND PYRRHOTITE

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ABSTRACT

Natural iron-deficient iron sulfide, pyrrhotite, is dimensionally hexagonal or monoclinic. A new hexagonal supercell is described in which a and c are two and five times A and C respectively, of the NiAs type substructure. This type of supercell is observed in pyrrhotites ranging in composition from about 48.0 ± 0.2 to 47.0 ± 0.2 atomic per cent metals. It has been identified in specimens from 13 localities of wide geographic distribution.

The monoclinic supercell described herein has A and B doubled, and C quadrupled. This cell is identical to the one previously proposed for monoclinic pyrrhotite. This supercell was identified in specimens from 18 localities. Thus all natural pyrrhotites studied are superstructure types.

Troilite (FeS) from two meteoritic and two terrestrial occurrences has a cell in which $a = \sqrt{3} A = B$, and $c = 2C$, corresponding to that generally attributed to troilite in the literature. The simple NiAs cell (B−8 structure) was not identified for naturally occurring members of the pyrrhotite group.

Pyrrhotite ranges from 46.5 to 48.0 atomic per cent metals in the specimens studied. Intergrowths of troilite and pyrrhotite were identified in one terrestrial and one meteoritic occurrence.

The restricted range in composition of natural pyrrhotite limits the temperature range of the pyrite-pyrrhotite solvus from approximately 325° to 520° C. The structural stability of natural pyrrhotite, rather than the temperature of crystallization, prohibits the existence of natural pyrrhotite with less than 46.5 atomic per cent metals.

INTRODUCTION

The complexity of the solid solution, structure, and magnetic properties of pyrrhotite ($Fe_{1-x}S$) and troilite (FeS) is attested by the voluminous literature which has appeared in the last 50 years. Recently, emphasis has been placed on the solid solution of pyrrhotite because the composition of pyrrhotite coexisting in equilibrium with pyrite in natural assemblages is reported by Arnold (1961) to be indicative of the minimum temperature of formation of this assemblage.

The present paper presents the composition range and structural types determined for naturally occurring troilite and pyrrhotite. It is believed that, in general, the material studied is representative of the variation in composition and structure of naturally occurring phases. It is shown that in natural specimens studied in this investigation, solid solution is not continuous from troilite to pyrrhotite. In addition, all hexagonal and monoclinic pyrrhotites studied exhibit a superlattice. These superlattices have not been reported for synthetic compounds of comparable compositions. In view of these findings, several comments are made regarding the pyrrhotite geothermometer.

The behavior of hexagonal and monoclinic pyrrhotites on heating is currently being investigated by the authors in order to discover what factors might control the superstructure and monoclinicity. For further information see Kullerud *et al.* (1963).

In this paper the term pyrrhotite group will be used to include any iron sulfide phase with the NiAs substructure. The mineral name pyrrhotite will be restricted to hexagonal or monoclinic iron deficient phases, and the name troilite will be used for the hexagonal phase of a composition at, or near, stoichiometric FeS.
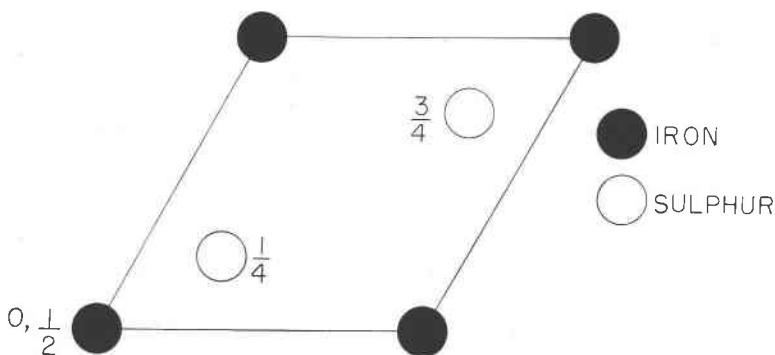

Fɪɢ. 1. Diagram of the simple NiAs cell (B−8 structure) proposed by Alsén (1925) projected on (0001).

Previous Work

Alsén (1925) was the first investigator to assign pyrrhotite to the NiAs structure. This structure is shown in Fig. 1. Hägg and Sucksdorff (1933) demonstrated that the variation in metal content is the result of omissions of metal atoms in the structure. They also reported that in synthetic compounds ranging in composition from 50.0 to 48.3 atomic per cent iron, the simple cell is distorted to a supercell. This supercell has been confirmed by Bertaut (1956) and Andreson (1960). The dimensions of this cell are $a = \sqrt{3} A = B$, and $c = 2C$.[1]

Grønvold and Haraldsen (1952) reported that the simple NiAs cell predominates at room temperature for synthetic compounds from 48.2 to 46.73 atomic per cent metals, whereas more iron-deficient synthetic com-

[1] The convention of Wuensch (1963, p. 157) will be followed. . . . "Normal lower case symbols are used to denote the crystallographic axes of the super-structures based on the NiAs arrangement since these are true unit cell translations. The NiAs type substructure will be denoted by the hexagonal A_1, A_2, C, or where convenient, by the orthohexagonal axes, A, B, C, with $[A] = A_1$, $B = \sqrt{3} A_1$."

pounds ranging from 46.73 to 45.44 atomic per cent iron are monoclinic. This monoclinic cell was reported to correspond to a cell proposed by Byström (1945) for naturally occurring Swedish pyrrhotites. The parameters cited for this cell are $a = 5.94$ Å $= B$, $b = 3.43$ Å $= A$, $c = 5.68$ Å $= C$, and $\beta = 90.37°$.

Buerger (1947) observed that pyrrhotite crystals from Morro Velho, Brazil, and Schneeberg, Saxony exhibit a superlattice in which $a = 2A$ and $c = 4C$. Although the composition of the crystals was not known, they were assumed to be iron deficient by virtue of their ferromagnetism. Buerger (1947) stated that this cell is probably hexagonal, but the presence of non-space group extinctions suggested that the crystals are twinned and that the true symmetry of pyrrhotite might be monoclinic or orthorhombic.

Subsequent study of the same sample from Morro Velho by Wuensch (1963) indicates that this pyrrhotite is monoclinic, or possibly triclinic. Wuensch's findings confirm earlier work by Bertaut (1953) who proposed a monoclinic superlattice for a pyrrhotite whose composition and occurrence is unspecified. For both cells $a = 2B$, $c = 4C$.

Solid Solution in Naturally Occurring Members of the Pyrrhotite Group

The composition of 65 monoclinic and hexagonal pyrrhotites were determined by the d(102) method described by Arnold and Reichen (1962) and Arnold (1962). Monoclinic pyrrhotites were heated in evacuated tubes at 350° C. for 10 minutes in the manner described by Kullerud and others (1963) for their conversion to hexagonal symmetry. The spacing was measured on a Norelco diffractometer with quartz as an internal standard (FeKα radiation). The chart speed was $\frac{1}{2}°$ per minute. Measurements were also taken from powder photographs in which quartz was used as an internal standard. Powder photographs were taken with FeKα radiation in 114.59 mm. cameras.

The composition range indicated by x-ray analyses is presented in Fig. 2, which shows two distinct composition groups. One group corresponds to stoichiometric FeS (troilite) and the other ranges in composition from 47.8 to 46.5 atomic per cent iron (pyrrhotite).

These results confirm earlier work by Lindroth (1946) who found that natural iron-deficient pyrrhotites occur between 48.27 and 46.54 atomic per cent iron. More recently, Arnold (1958) (1962), Arnold and Reichen (1962), Arnold, *et al.* (1962), Tsusue (1962), and others utilizing the d(102) method have obtained compositions within the range shown in Fig. 2. It is significant that none of these investigators have found compositions outside the range given above.

The proposal that phases between $\sim$50.0 and $\sim$48.0 atomic per cent iron do not occur in natural assemblages is supported by the existence of microscopic lamellar intergrowths of troilite and pyrrhotite in which the pyrrhotite composition is less than 48.0 atomic per cent iron. These intergrowths were observed in polished sections taken from the Long Island meteorite, a specimen from the Merensky Reef, Farm Tweefontein, South Africa, and a specimen from Hanover, New Mexico.

When viewed under crossed polars intergrown troilite and pyrrhotite go to extinction together, indicating that the *c* axes lie in a parallel plane.

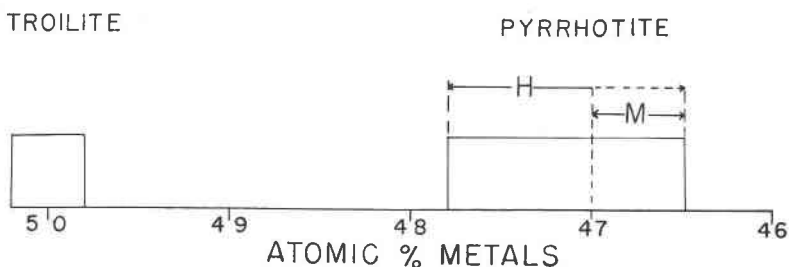TROILITE   PYRRHOTITE

FIG. 2. Diagram showing composition range observed for troilite and pyrrhotite. Also shown are the composition ranges determined for monoclinic (M) and hexagonal (H) pyrrhotite (solid line). Compositions of hexagonal pyrrhotite (H) below 47.0 atomic per cent iron (dashed line) are reported in the literature, but were not found in this investigation.

In powder photographs of the intergrowths, the d(102)[1] line is doubled. Thus for the Merensky Reef sample, d(102) troilite = 2.0936 Å ($\sim$50.0 atomic per cent iron), and the d(102) pyrrhotite = 2.0728 Å (47.9 atomic per cent iron); and, for the Long Island meteorite, d(102) troilite = 2.0952 Å ($\sim$50.0 atomic per cent iron), and d(102) pyrrhotite = 2.0650 Å (47.2 atomic per cent iron). Comparable relations are described by Kuovo, Vuorelainen, and Long (1963) for pyrrhotite and troilite intergrowths from Outokumpu, Finland.

Von Gehlen observed these intergrowths in pyrrhotite from Dracut, Connecticut and determined the two phases to be pyrrhotite (47.69 atomic per cent iron) and troilite. In heating experiments of synthetic pyrrhotite with a composition of 49.18 atomic per cent iron, von Gehlen reports that the homogenous phase separated into troilite and pyrrhotite (48.26 atomic per cent iron) when heated to 94° C. for 56 days.

Scholtz (1936) described intergrowths of two iron sulphide phases which he termed *alpha* and *beta* pyrrhotite. Ramdohr (1960, p. 551) sug-

[1] For the troilite cell the (10$\bar{1}$2) reflection of the NiAs cell is actually the (11$\bar{2}$4) of the troilite supercell.

gested that the two phases correspond to troilite and pyrrhotite but gave no quantitative evidence pertaining to their compositions. In light of this study, Ramdohr's conclusion is deemed justified. The softer component is troilite. When the intergrowth is examined immediately after polishing or buffing, troilite is the brighter phase, but upon oxidation it becomes noticeably darker in a period of about 2 hours.

Structural Types of Naturally Occurring Members of the Pyrrhotite Group

General. Two structural types of pyrrhotite have been found in the investigation of natural specimens, including one meteorite in which troilite also occurs. The natural pyrrhotites are comprised of monoclinic and hexagonal types; both structures are based on the NiAs type structure but exhibit a superstructure.

Precession photographs (MoKα radiation), powder photographs (114.59 mm diam. camera, FeKα radiation), and diffractometer (FeKα radiation) methods were utilized in the examination of the structural types of pyrrhotite. Due to the limited quantity of troilite available, only precession photographs and powder photographs were prepared. Twenty-nine of the 32 powder photograph mounts were prepared from optically singular grains in polished surfaces. The d-spacings for all possible reflections for the monoclinic and hexagonal supercells were computed with the U.W. CDC 1604 computer.

As indicated previously, the convention of Wuensch (1963, p. 157) will be followed in which superlattice dimensions are referred to the hexagonal A and C (or for convenience, orthogonal axes, A, B, C, where B $= \sqrt{3}$ A of the NiAs cell).

The hexagonal and monoclinic superlattice types found in natural specimens during this investigation include the following:

Hexagonal (troilite) Hägg and Sucksdorff (1933)	Hexagonal (pyrrhotite)	Monoclinic (pyrrhotite) Bertaut, 1953
$a = \sqrt{3} A = B = 5.9$ Å $c = 2C = 11.7$ Å	$a_1 = a_2 = 2A = 6.88$ Å $c = 5C = 28.7$ Å	$a = 2A\sqrt{3} = 2B = 11.9$ Å $b = 2A = 6.7$ Å $c = 4C = 22.8$ Å $\beta = 90.40°$

Superlattice reflections of these three types are present on both powder and precession photographs. Reflections in the low 2θ region on powder photographs provide a convenient method of recognizing the three types found in the present investigation.

Natural hexagonal troilite. Troilite from two terrestrial and two meteoritic occurrences was examined by powder photographs. One of the meteoritic

and one of the terrestrial specimens were examined by precession photographs. Powder photographs were also prepared from synthetic FeS which was kindly provided by Gunnar Kullerud of the Geophysical Laboratory, Washington, D. C. All 5 specimens show the lines in powder photographs described by Berry and Thompson (1962) in which $a = \sqrt{3}$ A $= B$, $c = 2C$. The spacing corresponding to the (102) reflection was measured from powder photographs with quartz as an internal standard. The d-values are as follows:

Locality	d ($11\bar{2}4$) ± 0.0008 Å
Merensky Reef, Bushveld Complex, Farm Tweefontein, South Africa	2.0936
[1]Sulfide deposit (locality cannot be given), Eastern Transvaal, South Africa	2.0936
[1]Aztec (Holbrook) meteorite, Navajo Co., Arizona	2.0918
Long Island meteorite, Kansas	2.0952
FeS, synthetic	2.0918

[1] Examined by precession photographs.

Troilite can be recognized in powder photographs by the presence of a 5.18 Å line, and the absence of lines with larger spacings.

Natural hexagonal pyrrhotite. Powder photographs of pyrrhotite from 13 localities, including one meteorite, and precession photographs of crystals from 5 localities have been studied (Table 1). Single crystals studied by

TABLE 1. SELECTED PARAMETERS OF NATURAL HEXAGONAL PYRRHOTITES

Locality	d($2\cdot0\cdot\bar{2}\cdot10$) ± 0.0008 Å	d($10\bar{1}1$) ± 0.03 Å	d($10\bar{1}2$) ± 0.03 Å	c calc. from d($0\cdot0\cdot0\cdot20$)
Ducktown, Tennessee	2.0671	5.86	5.52	28.71
Betty Baker Mine; (Gossan Lead), Virginia	2.0676	5.87	5.53	28.72
Savannah Mine, North Carolina	2.0675	5.89	5.55	28.72
Silver Creek, British Columbia	2.0701	5.84	diffuse	28.68
Blackwell Mine; Riondel, British Columbia	2.0670	5.86	5.50	28.68
Outokumpu, Finland	2.0659	5.84	diffuse	28.63
Merensky Reef; Farm Tweefontein, South Africa	2.0728	5.88	5.64	28.76
Troldal Mine; Trondjem, Norway	2.0701	5.90	5.50	28.70
Morro Velho, Brazil	2.0677	5.84	5.50	28.68
Mt. Prospect, Connecticut	2.0642	5.80	5.52	28.61
Kimberly, British Columbia	2.0701	5.84	5.55	28.66
Ore Knob Mine, North Carolina	2.0690	5.84	5.54	28.68
Long Island Meteorite, Kansas	2.0650	5.82	5.48	too weak

the precession method show that $a = 2A$ and $c = 5C$ (Fig. 3). In powder photographs hexagonal pyrrhotite shows a 5.86 ± 0.04 Å line and a 5.57 ± 0.07 Å line, corresponding to the $d(10\bar{1}1)$ and the $d(10\bar{1}2)$. These two lines serve to distinguish this structural type.
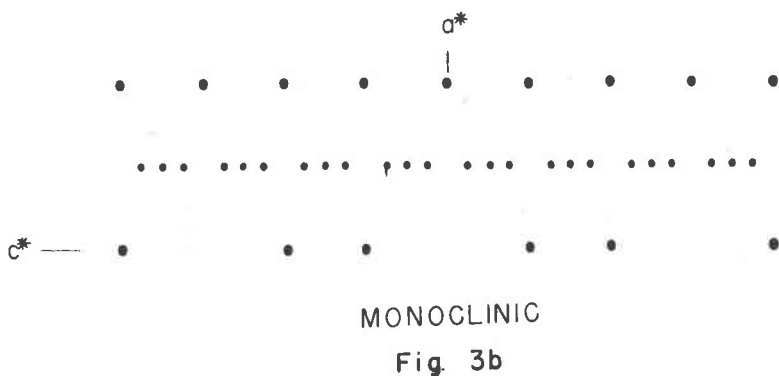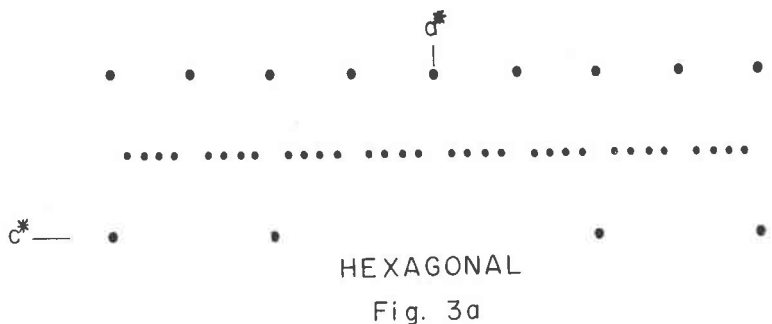

HEXAGONAL

Fig. 3a

MONOCLINIC

Fig. 3b

FIG. 3a and 3b. Diagrammatic sketches of a^*-c^* precession photographs (MoKα) illustrating differences between naturally occurring hexagonal and monoclinic pyrrhotites. Large circles represent substructure reflections and small circles correspond to superstructure reflections. The diagram does not show true intensity relationships.

Parameters of a and c were obtained for a sample from Ore Knob, North Carolina by scanning the $(20\bar{2}0)$ and the $(2 \cdot 0 \cdot \bar{2} \cdot 10)$ peaks on a diffractometer. The diffractometer was calibrated to $\pm 0.005\ 2\theta$ with an external silicon standard. The dimensions obtained are $a = 6.881 \pm .002$ Å and $c = 28.68 \pm .01$ Å. A powder photograph of the same material was measured and the indices and spacings are given in Table 2. Diffractometer traces of hexagonal pyrrhotite with more than 47.2 atomic per cent

iron show that all strong reflections are not doubled and that pyrrhotite from these localities is dimensionally hexagonal.

The presence of this supercell in all natural hexagonal pyrrhotites studied from a variety of geological occurrences, as well as one meteoritic occurrence, is inferred to indicate that all natural hexagonal pyrrhotites have the supercell in which $a = 2A$, $c = 5C$. A list of these occurrences is given in Table 1 along with the spacings of the $(2 \cdot 0 \cdot \bar{2} \cdot 10)$ reflection which

TABLE 2. POWDER DATA FOR PYRRHOTITE SAMPLE FROM ORE KNOB, NORTH CAROLINA. ($a = 6.881$ Å, $c = 28.68$ Å), FeKα

hkil	d (obs.) Å	d (calc.) Å	Intensity
10$\bar{1}$1	5.85	5.83	mw
10$\bar{1}$2	5.54	5.50	vw
20$\bar{2}$0	2.98	2.98	ms
0·0·$\bar{0}$·10	2.87	2.87	vw
20$\bar{2}$5	2.65	2.64	s
2·0·$\bar{2}$·10 (Kβ)	2.27	2.066	vw
2·0·$\bar{2}$·10	2.066	2.066	vs
30$\bar{3}$1	1.983	1.982	vw
22$\bar{4}$0 (Kβ)	1.901	1.721	vw
22$\bar{4}$0	1.720	1.721	ms
2·0·$\bar{2}$·15	1.609	1.609	w
40$\bar{4}$0	1.492	1.491	w
40$\bar{4}$5	1.445	1.444	w
0·0·0·20	1.434	1.434	m
4·0·$\bar{4}$·10	1.320	1.322	m
2·0·$\bar{2}$·20	1.291	1.292	w
4·0·$\bar{4}$·15	1.176	1.175	w
2·2·$\bar{4}$·20	1.103	1.102	m

corresponds to the d(102) of Arnold (1962). Judging from this spacing all hexagonal pyrrhotites examined contain more than 47.0 atomic per cent iron (Fig. 2). Arnold (1962), Arnold and Reichen (1962), and Arnold *et al.* (1962) have reported numerous occurrences of hexagonal pyrrhotite with less than 47.0 atomic per cent iron.

Natural monoclinic pyrrhotites. Powder photographs of 20 specimens of pyrrhotite from 18 localities and precession photographs of crystals from two of these 18 localities have been studied. The superlattice observed on precession photographs containing a^* and c^* is the same as that described by Buerger (1947), Bertaut (1953), and Wuensch (1963). This superlattice is distinguishable in powder photographs by the presence of a 5.75 ±0.06 Å line, a 5.27±0.04 Å line, and a 4.67±0.04 Å line (Table 3). The

two latter lines cannot be indexed on the basis of the troilite cell, the simple NiAs cell, or the hexagonal superlattice cell ($a = 2A$, $c = 5C$) previously described herein.

Diffractometer scanning ($\frac{1}{2}°$ and $\frac{1}{4}°$ per minute) indicates that 00l and

TABLE 3. SELECTED PARAMETERS OF NATURAL MONOCLINIC PYRRHOTITES

Locality	Centers of Monoclinic peaks				c calc. from d(0·0·16) ±0.025 Å
	d(408–408) ±0.0008 Å	d(111–111) ±0.03 Å	d(112–112) ±0.025 Å	d(113–113 ±0.025 Å	
Gabbro, Ironton quad., Missouri	2.0575	5.73	5.27	4.69	22.78
Gabbro, Ironton quad., Missouri	2.0575	5.73	5.24	4.70	22.83
Norite, Calais quad., Maine	2.0558	5.72	5.28	4.69	22.81
Helen Mine; Michipicotin, Ontario	2.0575	5.69	5.32	4.70	22.78
Sudbury, Ontario	2.0565	5.72	5.30	4.70	22.78
San Bartola, Chihuahua, Mexico	2.0573	5.72	5.26	4.68	22.79
Mt. Crillon, Alaska	2.0565	5.71	5.24	4.70	22.79
Hanover District; Grant Co., New Mexico	2.0565	5.73	5.23	4.67	22.80
Sheritt-Gordon, Manitoba	2.0599	5.78	5.29	4.69	22.75
Worthington, Ontario	2.0575	5.72	5.27	4.68	22.80
Mt. Prospect, Conn.	2.0599	5.73	5.24	4.71	22.80
Marmora, Ontario	2.0592	5.73	5.28	4.69	22.79
Hecla Mine; Burke, Idaho	2.0599	5.73	5.27	4.70	22.79
Yukon Gold District, Alaska	2.0575	5.74	5.27	4.71	22.78
Hakansboda, Sweden	2.0565	5.71	5.24	4.68	22.77
Blind River, Ontario	2.0565	5.72	5.25	4.72	22.80
Homestake, South Dakota	2.0601	5.81	5.29	4.70	22.94
Santa Eulalia, Chihuahua, Mexico	2.0575	5.71	5.27	4.68	22.77

0kl are single and sharp, whereas h0l and hkl are multiple. This proves the cell is dimensionally monoclinic.

Bertaut (1953) and Wuensch (1963) have proposed that $c = 4C$ is inclined to $a = 2B$. This supercell can also be ascribed to a smaller cell in which $a = 2B$, $b = 2A$, $c = 12.82$ Å, and $\beta = 118°$ (Bertaut, 1952). Measurements taken from precession photographs of the three pseudohexagonal $a^*–c^*$, and the three pseudohexagonal $b^*–c^*$ orientations indicate that 4C is inclined to 2B by $0.3° \pm 0.1°$. Splitting of the (102) hexagonal reflection into 4 peaks was observed on a diffractogram tracing ($\frac{1}{8}°$ per minute). The

four peaks have true indices (408), ($\overline{4}$08) and, (228), ($\overline{2}$28) with multiplicities of 2, 2, 4 and 4, respectively.

Diffractometer scanning across the single peaks using variable time, fixed count, and an external silicon standard for calibration to $\pm 0.005°$ 2θ provided sufficiently accurate parameters for calculation of the cell dimensions. Two specimens, one from Sudbury, Ontario, and one from the Yukon District, Alaska, were examined and showed identical cell dimensions, based on measurement of the (400), (040) and ($0 \cdot 0 \cdot 16$) reflections.

The β-angle was determined by a best fit method in which calculations of all d-values were obtained by means of a computer program for β-angles of 90.32°, 90.40°, 90.45°, 90.50° and 90.60°, respectively. A closer correspondence of observed with calculated d-values was found when $\beta = 90.40°$ (Table 4). This determination for the β-angle is in good agreement with those of Byström (1945), Grønvold and Haraldsen (1952), and Bertaut (1953), but in disagreement with Wuensch (1963) who proposed that the β-angle is 91.79° for a monoclinic crystal from Morro Velho, Brazil.

Powder photograph data for the Yukon, Alaska specimen are presented in Table 4.

In this investigation, the range of composition of monoclinic pyrrhotite after being converted to the hexagonal form by heating is 46.6–46.9 atomic per cent iron. Kullerud and others (1963) report compositions between 46.45 and 46.70 atomic per cent iron for monoclinic pyrrhotite from four widely separated localities.

Mixtures of hexagonal and monoclinic pyrrhotite. From the appearance of the peaks corresponding to the (102) NiAs cell reflection obtained for material from Mt. Prospect, Conn., and Homestake, S. D., these samples could not readily be interpreted as either monoclinic or hexagonal. The intensity of the first peak (55.98° 2θ) was 5 to 10 times greater than that of the second peak (56.35° 2θ) which was barely perceptible, but the separation was the same as that for typical monoclinic pyrrhotites which yield peaks of equal intensity. For the Mt. Prospect specimen, a precession photograph and 3 powder photographs from single grains displayed the hexagonal supercell ($a = 2A$, $c = 5C$). One grain showed the monoclinic supercell ($a = 2B$, $c = 4C$). Four powder photographs of grains of the Homestake material showed the monoclinic supercell: however, one grain exhibited the hexagonal superstructure. The appearance of the peaks for both samples was virtually identical on the diffractograms.

The compositions indicated by the d(102) method for Mt. Prospect and Homestake (heated to 600° C.) are very similar; e.g., Mt. Prospect

TABLE 4. POWDER DATA FOR NATURAL MONOCLINIC PYRRHOTITE, YUKON GOLD DISTRICT, ALASKA. $a = 11.903$ Å, $b = 6.872$ Å, $c = 22.78$ Å, $\beta = 90.4°$

d(obs.) Å	Intensity	hkl	calc.) Å
5.74	mw*	111 $\bar{1}11$	5.76 5.75
5.27	w*	112 $\bar{1}12$	5.28 5.27
4.71	w*	113 $\bar{1}13$	4.69 4.68
4.43	vvw*	211 $\bar{2}11$	4.42 4.41
3.61	w*	106 115 $\bar{1}15$ $\bar{1}06$	3.62 3.62 3.61 3.61
3.43	w	020, 310	3.44
3.28	vw	400, 220 (Kβ)	
3.22	vw*	206 116 $\bar{1}16$ $\bar{2}06$	3.21 3.21 3.20 3.19
3.13	m*	313 023 $\bar{3}13$	3.14 3.13 3.12
2.975	s	400, 220	2.976
2.916	vw	404, 224 (Kβ)	
2.849	vw	008	2.847
2.634	vs*	404 224 $\bar{2}24$ $\bar{4}04$	2.645 2.641 2.634 2.630
2.547	vw*	316 026 $\bar{3}16$	2.555 2.548 2.540

* Broad line.

TABLE 4—(*continued*)

d(obs.) Å	Intensity	hkl	d(calc.) Å
2.374	vvw	019	2.375
2.274	vw	408, 228 (Kβ)	
2.205	vw*	422 132 1̄32 4̄22	2.209 2.207 2.206 2.205
2.159	vw*	133 1̄33	2.158 2.156
2.057	vvs*	408 228 2̄28 4̄08	2.065 2.061 2.054 2.050
1.982	vvw*	331 3̄31	1.977 1.976
1.892	vw	040, 620 (Kβ)	
1.766	w*	428 4̄28	1.770 1.761
1.718	s	040, 620	1.718
1.633	w*	242 2̄42	1.634 1.633
1.488	vw	800, 440	1.488
1.439	w*	804 444 4̄44 8̄04	1.442 1.441 1.438 1.437
1.425	w	0·0·16	1.424
1.323	mw*	808 448	1.323 1.327
1.315	mw*	4̄48 8̄08	1.317 1.315
1.288	vw*	4·0·16 2·2·16	1.288 1.286

TABLE 4—(continued)

d(obs.) Å	Intensity	hkl	d(calc.) Å
1.281	vw*	$\bar{2}\cdot2\cdot16$ $\bar{4}\cdot0\cdot16$	1.283 1.281
1.174	m*	$8\cdot0\cdot12$ $4\cdot4\cdot12$	1.175 1.173
1.167	m*	$\bar{4}\cdot4\cdot12$ $\bar{8}\cdot0\cdot12$	1.169 1.167
1.125	vw	840	1.125
1.102	m	$8\bar{4}4$	1.102
1.097	mw*	$6\cdot2\cdot16$ $0\cdot4\cdot16$	1.099 1.096
1.093	mw	$\bar{6}\cdot2\cdot16$	1.093
1.044	m	$\bar{8}48$	1.044
.99155	m	$12\cdot0\cdot0\ (\alpha_1)$	.99189
.99158	m	$12\cdot0\cdot0\ (\alpha_2)$	.99189

=47.03 atomic per cent iron, and Homestake=47.06 atomic per cent iron.

These relations are due to mixtures of both hexagonal and monoclinic types of the same, or very similar compositions. The first strong peak represents the $(2\cdot0\cdot\bar{2}\cdot10)$ reflection of the hexagonal phase and the (408) and (228) reflections of the monoclinic phase. The much less intense second peak corresponds to the $(\bar{4}08)$ and $(\bar{2}28)$ reflections of the monoclinic phase. It is significant that such mixtures occur when the gross composition is very close to the monoclinic-hexagonal transition; e.g., ~47.0 atomic per cent metals. Mixtures of monoclinic and hexagonal phases are reported by Grønvold and Haraldsen (1952) and Groves and Ford (1962). However, von Gehlen (1963) failed to find such mixtures.

THE PYRRHOTITE GEOTHERMOMETER

Since the work of Arnold (1962) and Arnold and Reichen (1962) many investigators have utilized the d(102) method of determining the composition of pyrrhotites. The composition of pyrrhotite from numerous ore deposits has been determined by this method and the range of composi-

tion shown for natural pyrrhotite may now be evaluated. It is significant that a single hexagonal pyrrhotite phase has been synthesized over a composition range from about 50.0 to 45.8 atomic per cent iron (Arnold, 1962). However, natural pyrrhotites apparently have a more restricted composition range, judging from the numerous composition determinations made for this mineral by other investigators and the present writers. Furthermore, natural pyrrhotites in this composition range generally show a relationship between symmetry and composition; specifically, monoclinic pyrrhotites are restricted to a composition of less than 47.0 ± 0.1 atomic per cent metals.

The application of the pyrrhotite-pyrite solvus is questionable above about 600° C. because Kullerud and Yoder (1959) and Arnold (1962) showed that pyrrhotite compositions on the pyrrhotite-pyrite solvus could not be quenched from temperatures above this temperature. Furthermore, the existence of limitations on iron-deficiency of natural pyrrhotite precludes use of the high temperature end of the pyrrhotite-pyrite solvus in geothermometry. Consequently, the range of temperature over which the geothermometer is useful is very small. The $\pm 50°$ uncertainty of the temperature estimates utilizing the x-ray spacing method for determining the composition of natural pyrrhotite further limits the usefulness of the pyrrhotite geothermometer.

The pyrrhotite-pyrite solvus determined by Arnold (1962) applies to natural assemblages containing pyrrhotite with a composition between 44.8 and 47.3 atomic per cent iron, which corresponds to 735° C. and 325° C., respectively, assuming equilibration between pyrite and pyrrhotite is maintained. Considering the maximum amount of iron deficiency (46.5 atomic per cent iron) found in the determination of the composition of numerous natural specimens of wide geographic distribution and varied geologic environments, the range of the pyrrhotite geothermometer at present is limited to a temperature range from about 325° C. to 520° C., at best. In other words, the pyrrhotite geothermometer has a useful range of about 200° C.

The limitation of natural pyrrhotite to compositions more iron-rich than about 46.5 atomic per cent suggests that a more iron-deficient pyrrhotite is not stable when cooled under geologic conditions. Many of the most iron-deficient natural pyrrhotites occur in specimens which contain no pyrite. This indicates that the *structural stability* of pyrrhotite, and not the temperature of formation, is the major factor which prohibits the existence in nature of pyrrhotite with less than 46.5 atomic per cent iron.

Arnold (1962) failed to observe a superstructure for pyrrhotite synthesized above 325° C. and quenched to room temperature. In a forthcoming paper (Desborough and Carpenter, in preparation) it will be shown

that pyrrhotites synthesized at 580° C. and quenched to room tempera-
ture exhibit the same superlattice as natural pyrrhotite quenched from
the same temperature. It is noteworthy that a superlattice has not previ-
ously been noted for synthetic pyrrhotite. It is believed that Arnold's
d(102) vs. composition curve is valid; however, it is probable that both
the natural and synthetic phases studied by Arnold (1962) and Arnold
and Reichen (1962) were superstructure types.

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