

## Superstructure and Nonstoichiometry of Intermediate Pyrrhotite

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### Abstract

To elucidate the relationship between the superstructure and chemical composition of the pyrrhotite group, natural crystals of pyrrhotite, ranging between approximately  $\text{Fe}_9\text{S}_{10}$  and  $\text{Fe}_{11}\text{S}_{12}$ , have been extensively studied by X-ray single crystal methods.

Pyrrhotite crystals from the Kishu mine are mixtures of three 4C, 4.88C, and 5C types. The 5C type is orthorhombic and has the cell dimensions  $a = 6.8848(14)$ ,  $b = 11.936(6)$ ,  $c = 28.6760(15)$ , and diffraction aspect  $C^*ca$ . In the Kohmori mine, various orthorhombic pyrrhotites of nonintegral type—the  $nC$  pyrrhotites—occur together with the 2C type. The observed  $n$  values range between 5.36 and 5.80. The 6C type from the Makimine Mine is metrically orthorhombic with  $a = 6.8950(2)$ ,  $b = 11.9536(4)$  and  $c = 34.518(2)$  but is really monoclinic with diffraction aspect  $F^*/d$ .

The relationship between the cell dimensions and the  $n$  value for the  $nC$  pyrrhotites, including the 5C and 6C types, from various localities indicates that the change of the  $n$  values depends mainly on the chemical composition. The relationship between the composition and the mean  $d$  value of 112 and 022, which correspond to 102 by the hexagonal subcell, for the  $nC$  pyrrhotite has been obtained by the least squares method assuming a linear equation as follows:

$$d_{\text{mean}} = 1.5929 + 0.01002x$$

where  $d_{\text{mean}}$  represents the mean  $d$  value of 112 and 022 in Å, and  $x$ , the chemical composition of iron in atom percent. The 5C and 6C types are considered as special cases of the  $nC$  pyrrhotites, which are equivalent to the intermediate pyrrhotites.

### Introduction

The pyrrhotite group includes monoclinic pyrrhotites, hexagonal or intermediate pyrrhotites, and troilites (Carpenter and Desborough, 1964). Each is a superstructure of the NiAs type with subcell dimensions:  $A$ , about 3.45 Å, and  $C$ , about 5.8 Å. Their compositions are approximately 46.67, 47.20–47.80, and 50.0 atomic percent iron, respectively (Desborough and Carpenter, 1965).

Five natural pyrrhotites—essentially corresponding to stoichiometric compositions  $\text{Fe}_7\text{S}_8$ ,  $\text{Fe}_9\text{S}_{10}$ ,  $\text{Fe}_{10}\text{S}_{11}$ ,  $\text{Fe}_{11}\text{S}_{12}$ , and  $\text{FeS}$ —were designated by Morimoto *et al* (1970) as 4C, 5C, 11C, 6C, and 2C on the basis of the number of units along the  $c$  axis. Here 4C corresponds to monoclinic pyrrhotite, 5C, 11C, 6C to hexagonal or intermediate pyrrhotite, and 2C to troilite. However, orthorhombic symmetry of 11C was described independently by Morimoto *et al* (1970) and by Vorma (1970). Morimoto *et al* (1970) considered that the composition of pyrrhotite was essentially stoichiometric and could be expressed by a general formula,  $\text{Fe}_{n-1}\text{S}_n$  ( $n \geq 8$ ), with the structure of  $(n/2)C$  type for  $n$  even and of  $nC$  type for  $n$  odd.

Among these five types, 11C from East Ongul Island, Antarctica, shows slight displacements of the superstructure reflections from the Bragg positions along the  $c^*$  axis. The reciprocal lattice patterns of the 11C type are shown schematically by the  $A_1^*C^*$  and  $A_2^*C^*$  planes (Fig. 1 a and b), where  $A_1^*$ ,  $A_2^*$ , and  $C^*$  represent the reciprocal axes of the NiAs subcell. When the 11C type consists of small domains related by  $120^\circ$  and/or  $180^\circ$  rotation about the  $c$  axis, the reciprocal lattice becomes apparently hexagonal by superposition of the  $A_1^*$  and  $A_2^*$  (Fig. 1 c). Along the  $c^*$  axis, the repeat distance for the main reflections ( $= T$  in Fig. 1c) is 5.54(2) times as large as  $t$ , the distance of the nearest superstructure reflection from the  $A_1^*$  or  $A_2^*$  axis. Accordingly, this pyrrhotite was called the 5.54 C type, following the convention used by Morimoto and Koto (1969) and Morimoto *et al* (1970) for such nonintegral types of structures. Another nonintegral type of pyrrhotite with 4.94C occurred at the Outokumpu mine, Finland (Morimoto *et al*, 1970). Extensive studies on natural crystals of pyrrhotite from various localities (Carpenter and Desborough, 1964; Mukaiyama and Izawa, 1966) strongly suggest the existence of a solid solution with

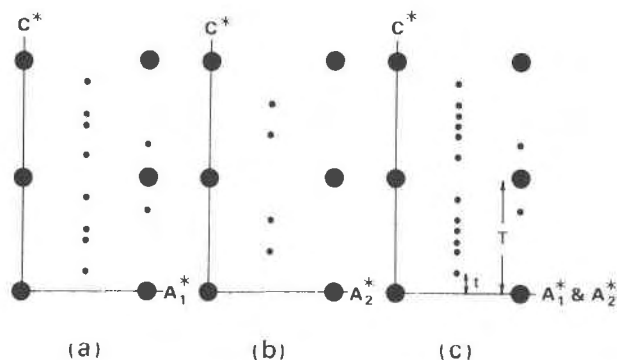


FIG. 1. The reciprocal planes of the 11C type. Vertical axes  $C^*$ , horizontal axes: (a)  $A_1^* = [1\bar{1}0]$ , (b)  $A_2^* = a^*$ , and (c)  $A_1^*$  and  $A_2^*$  superposed by twinning. Large circles represent main reflections and small circles correspond to superstructure reflections. The interval  $t$  is irrationally related to the repeat of the main reflections  $T$  along the  $C^*$  axis, as explained in the text.

the nonintegral-type structures in the composition range approximately between  $Fe_9S_{10}$  and  $Fe_{11}S_{12}$ .

In the study of the phase relations of the system  $FeS-Fe_7S_8$ , Nakazawa and Morimoto (1971) indicated that a continuous stability field of the nonintegral types extends in the composition range from  $Fe_9S_{10}$  to somewhat more Fe-rich than  $Fe_{11}S_{12}$  at temperatures higher than  $150^\circ C$ , the  $n$  value changing continuously with composition and temperature. However, no information was obtained in the study on the stability of the nonintegral types at low temperatures.

Although some nonintegral digenite of  $5.5a$  type was described from the Magma mine, Superior, Arizona (Morimoto and Gyobu, 1971), only very few nonintegral types have been described for sulfide minerals in general, and our knowledge of the stability and crystal structure of the nonintegral types is extremely limited.

In this investigation, intermediate pyrrhotites of compositions between approximately  $Fe_9S_{10}$  and  $Fe_{11}S_{12}$ , were selected from various localities according to their  $d$  values for  $102$  as indexed by the fundamental hexagonal cell (called hereafter hexagonal  $102$ ). Detailed single-crystal X-ray studies were made on them in order to describe the crystallography of intermediate pyrrhotites and to elucidate the relationship between superstructure and nonstoichiometry of the pyrrhotites. As explained in this paper, the existence of intermediate pyrrhotites belonging to the nonintegral type has been confirmed in natural specimens. They are expressed as  $nC$ , or  $nC$  pyrrhotites as a whole, where  $n$  is a nonintegral number between 4.88 and 6.00.

The superstructure reflections in intermediate pyrrhotite behave like the  $e$ -type reflections in intermediate plagioclase. Precise description and structural understanding of their behavior hence constitute an important problem in modern mineralogy.

### Experimental

Many crystals of pyrrhotite from various localities were studied by X-ray single crystal and powder methods (Morimoto, Gyobu, Izawa, and Mukaiyama, in preparation). The main effort has been concentrated on elucidating the crystallography of the  $5C$ ,  $6C$ , and other types belonging to the composition range of intermediate pyrrhotite. If crystals consisted of three or more different types, as from the Kishu and Kohmori mines, they were thoroughly studied by X-ray single crystal methods.

The structure types were first determined by accurately measuring the positions of superstructure reflections in precession patterns. The cell dimensions of the subcells were precisely determined by the back-reflection Weissenberg method with  $FeK\alpha_1$ ,  $FeK\alpha_2$ ,  $CoK\alpha_1$ , and  $CoK\alpha_2$  radiations based on  $330$ ,  $224$ ,  $115$ ,  $223$ ,  $060$ ,  $044$ ,  $025$ , and  $043$  reflections of the orthorhombic subcell with  $A \sim 3.44 \text{ \AA}$ ,  $B \sim 5.97 \text{ \AA}$ , and  $C \sim 5.75 \text{ \AA}$ . Silicon powder was used as an internal standard. Least squares refinements of the dimensions were made by the UNICS (Sakurai, 1969) on NEAC-700 at the Data Processing Center, Osaka University.

The compositions of the  $nC$  pyrrhotites were determined by assuming  $Fe_9S_{10}$  and  $Fe_{11}S_{12}$  compositions for  $5C$  and  $6C$ , respectively, and by interpolating the volumes of the subcells of the  $nC$  pyrrhotites into the curves between those of  $5C$  and  $6C$ . These intermediate pyrrhotites range in composition from  $Fe_9S_{10}$  to  $Fe_{11}S_{12}$ ; this corresponds to 47.20 to 47.80 atomic percent iron and therefore a total range of only 0.57 wt percent iron. Although it is difficult to support the indicated composition of the pyrrhotites in such a narrow composition range by independent chemical data, the self-consistent results obtained in this study support the method mentioned above. It must be noted, however, that the inference of very precise compositional data may not be warranted, because minor elements—for example, Ni, Co, and Cu, which are mostly less than 0.2 atomic percent (Arnold and Reichen, 1962)—were here included in the atomic percent iron.

### 4.88C and 5C Type Pyrrhotites

Pyrrhotite occurs in aggregates of very thin hexagonal crystals up to 10 mm in diameter in the druses

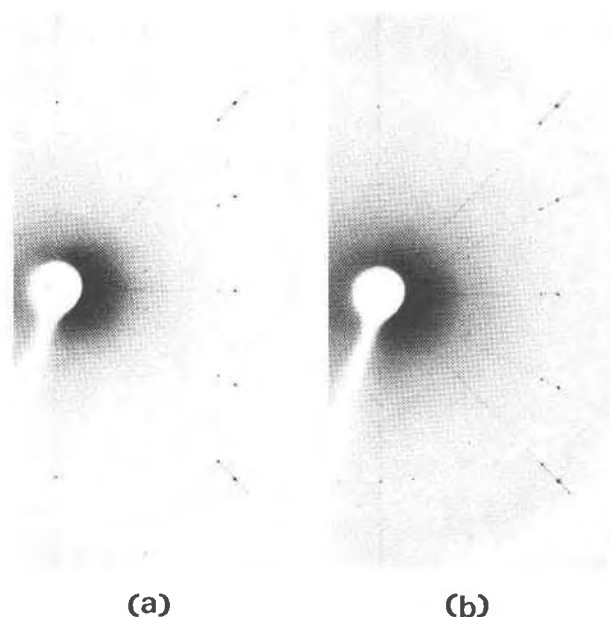


FIG. 2. Precession photographs of the 4.88C type from Kishu mine. Vertical axes  $C^*$ , horizontal axes: (a)  $A_1^* = [110]$ , (b)  $A_2^* = a^*$ . Only first and third order superstructure reflections are observed in (a), and only second ones in (b), besides the main reflections. Refer to Figure 1.  $FeK\alpha$ , 32 kV, 48mA, and 10 hours.

of the deposits at the Kishu mine (Nakamura and Hunahashi, 1970). Grains of about 0.1 mm in diameter were obtained for single crystal studies by crushing a few morphologically beautiful crystals of

about 2 to 5 mm diameter. Strongly magnetic grains were confirmed to be the 4C type and were omitted before further study. About thirty grains were examined by oscillation and precession methods. Interpretation of the X-ray patterns of some grains was often hampered by the presence of twinning or of aggregates. Altogether twenty-two grains were well oriented, and the structure types of their component crystals were identified. Three types of pyrrhotites—4C, and the two intermediate pyrrhotites, 5C and 4.88C—occurred in combinations (and with frequencies) as follows: 4C, 1 grain; 4C and 4.88C, 1 grain; 4C and 5C, 2 grains; 4.88C, 3 grains; and 5C, 15 grains.

The 4C type is the usual monoclinic pyrrhotite described previously (Tokonami, Nishiguchi, and Morimoto, 1972). Because of the twinning by a rotation of  $60^\circ$  around the pseudo-hexagonal  $c$  axis, most intermediate crystals show pseudo-hexagonal symmetry. Among the fifteen 5C crystals, however, a few were untwinned. The intensity distribution of their X-ray reflections, including the superstructure reflections, indicated orthorhombic symmetry. The diffraction aspect is  $C^*ca$ . The cell dimensions are  $a = 6.8848(14)$ ,  $b = 11.9436(6)$  and  $c = 28.6760(15)$  Å.

The third type of pyrrhotite from the Kishu mine is of the  $nC$  type and shows slight displacement of the superstructure reflections from the positions corresponding to 5C. Accurate measurements of the

TABLE 1. Crystallographic Constants of Intermediate Pyrrhotites with Different  $n$  Values and Their Compositions Obtained from the Volume of the Subcell (Fig. 5)

Specimen Number	$n$ Value	Dimensions of Subcell			Subcell Volume	$d$ Value of Hexagonal 102			Composition**
		$a/2$	$b/2$	$c'$		$d_{112}$	$d_{022}$	$d_{mean}$	
Kishu Mine, Japan									
KI-1	4.88(2)	3.4422(4)	5.9705(5)	5.7313(8)	117.788(23)	2.0663(3)	2.0673(3)	2.0666(3)	47.29
KI-2	5.00(1)	3.4424(7)	5.9718(3)	5.7352(3)	117.900(9)	2.0671(3)	2.0683(1)	2.0675(2)	47.37
Suetake, Kohmori Mine, Japan									
K-1	5.38(2)	3.4457(5)	5.9737(6)	5.7455(3)	118.263(13)	2.0698(2)	2.0683(1)	2.0700(2)	47.63
K-2	5.54(2)	3.4455(6)	5.9751(8)	5.7478(5)	118.331(34)	2.0703(3)	2.0712(3)	2.0706(3)	47.68
K-3	5.64(2)	3.4467(5)	5.9749(7)	5.7487(9)	118.387(45)	2.0707(4)	2.0713(4)	2.0709(4)	47.72
K-4	5.75(2)	3.4465(4)	5.9759(8)	5.7503(5)	118.433(23)	2.0710(2)	2.0718(3)	2.0712(3)	47.75
Chigusa, Makimine Mine, Japan									
M	6.00(1)	3.4475(1)	5.9768(2)	5.7530(5)	118.541(11)	2.0717(1)	2.0724(1)	2.0720(1)	47.83
East Ongul Island, Antarctica									
O	5.54(2)	3.4455(4)	5.9725(8)	5.7453(5)	118.230(23)	2.0697(2)	2.0703(3)	2.0699(3)	47.60
Luikonlahti Mine, Finland									
L	5.53(2)	3.4470(6)	5.9715(10)	5.7501(7)	118.359(60)	2.0709(4)	2.0710(5)	2.0709(5)	47.70

\* standard deviations in parentheses.

\*\* in atomic weight percent.

positions of the superstructure reflections indicate a nonintegral  $n$  value of 4.88(2) (Fig. 2). The symmetry is the same as that of 5C. The superstructure reflections are sharp (Fig. 2). The subcell dimension of 4.88C was measured by the back-reflection Weissenberg method (Table 1).

The abundance of the 5C:4.88C:4C types in the Kishu specimens, if we include those 4C grains omitted prior to X-ray work, was 55:15:30. Crystals of the 5C and 4.88C types, whose compositional relationships will be explained later, never occurred together in grains of the size (0.1 mm<sup>3</sup>) used for the single crystal methods in this investigation. However, they do occur together as intergrowths with 4C, with the  $b$  and  $c$  axes in common.

Morimoto *et al* (1970) found pyrrhotite from the Outokumpu mine to consist of 4C and 4.94C. Thus the nonintegral types from 4.88C to 5C with the composition range near Fe<sub>9</sub>S<sub>10</sub> are not considered rare in nature.

### $n$ C Pyrrhotites

Pyrrhotite crystals from mesothermal copper-pyrrhotite veins in serpentinite at the Kohmori mine are mostly intermediate pyrrhotites that contain from 47.2 to 47.8 atomic percent iron, as determined from the  $d$  value of the hexagonal 102. Minor amounts of 4C occur in the upper part of the veins (Mukaiyama, Yui, Takakura, and Izawa, 1964).

The bulk composition of pyrrhotite from the Suetake vein in the Kohmori mine was determined to be 47.57 atomic percent iron from the  $d$  value of the hexagonal 102. After magnetic separation of 4C, the specimens consisted mainly of the intermediate pyrrhotites of 47.65–47.73 atomic percent iron with a  $d$  value of 2.0701–2.0708 Å for the hexagonal 102. A minor amount of 4C, possibly less than five wt

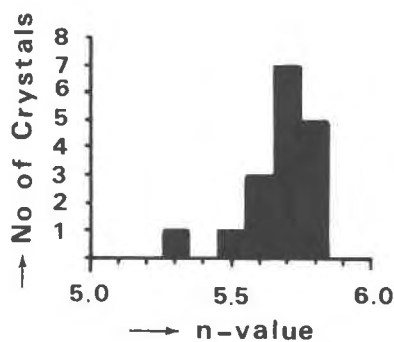


FIG. 3. The frequency histogram of observed  $n$  values for intermediate pyrrhotites from the Kohmori mine.

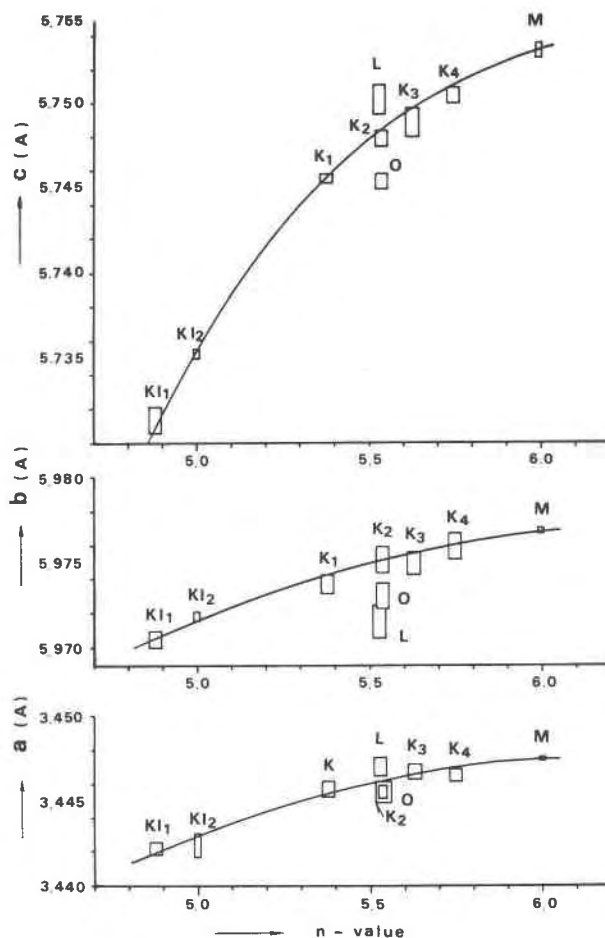


FIG. 4. Relationship between the dimensions of the subcell and the  $n$  value for intermediate pyrrhotites. The specimen numbers are taken from Table 1, and the same numbers are used for the following figures. Possible errors in measurements are represented by squares in this and the following figures.

percent of the total amount, was still present (Mukaiyama and Izawa, 1966).

For seventeen Suetake grains, the  $n$  values were precisely determined by the precession method and, for seven others, by the oscillation method. Surprisingly, the displacements of the superstructure reflections from the Bragg positions along the  $c^*$  axis vary from grain to grain even though the crystals were obtained from one small specimen. Among the twenty-four grains, twenty-one are homogeneous with the nonintegral type structure in which the  $n$  value changes from 5.55 to 5.80, except one grain of 5.38C. Three grains with 5.72C or 5.75C show intergrowth with 2C. The symmetry of the  $n$ C pyrrhotites is orthorhombic as is 5.54C from the East Ongul Island, Antarctica (Morimoto *et al*, 1970). The frequency histogram of the observed  $n$  values for the

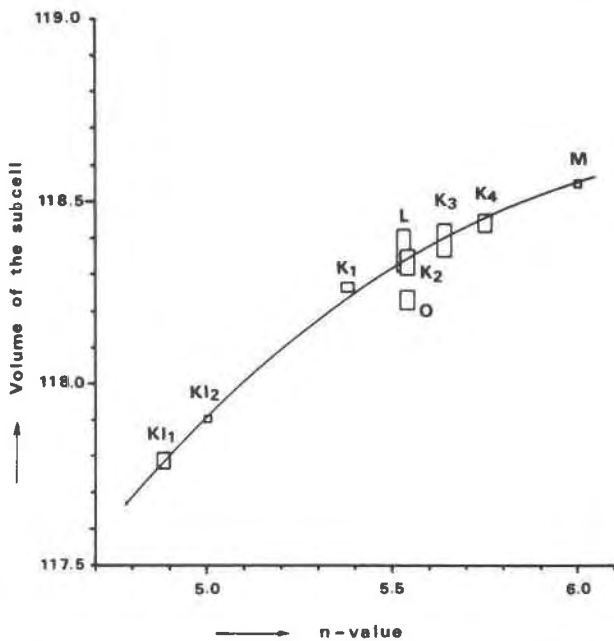


FIG. 5. Relationship between the volume of the subcell and the  $n$  value for intermediate pyrrhotites.

crystals from the Kohmori mine is given in Figure 3. The maximum peak of the histogram is at about 5.7 of the  $n$  value.

The dimensions of the subcells for the selected specimens of the  $nC$  pyrrhotites of the Kohmori mine were obtained (Table 1). As described later in more detail, the  $n$  values of pyrrhotite are rather simply related to the dimensions of the subcell for all the intermediate pyrrhotites.

Crystals from the Luikonlahti mine, Finland, are 5.53C with orthorhombic symmetry. Some are intergrown with 2C, as described by Vormo (1970).

Using only X-ray powder patterns, it is very difficult to distinguish the mixtures of integral and nonintegral types from the homogeneous nonintegral type, but ore microscopy seems to distinguish them effectively in some cases (Carpenter and Bailey, 1973). The X-ray single crystal methods here used to characterize pyrrhotite crystals of intermediate compositions yielded the following observations on  $nC$  pyrrhotites:

(a) Many  $nC$  pyrrhotites of different  $n$  values occur together with 4C and 2C. In many specimens one kind of  $nC$  pyrrhotite has been found in one locality together with 4C or 2C, such as 5.54C in the East Ongul Island (Morimoto *et al.*, 1970), 4.94C in the Outokumpu mine (Morimoto *et al.*, 1970), and 4.88C in the Kishu mine (this study).

(b) Intergrowth between two or more  $nC$

pyrrhotites has never been observed in the grains used for the single crystal method, the average size of which is about 0.1 mm<sup>3</sup>.

### 6C and 2C Type Pyrrhotites

A pyrrhotite specimen collected at Chigusa in the Makimine mine consisted of 6C with exsolved 2C under the ore microscope (Morimoto, Gyobu, Izawa, and Mukaiyama, in preparation). About ten grains were examined. The ratio of 6C and 2C is about 4:1 in most grains, but one grain was found to contain only 6C. The cell dimensions of 6C are  $a = 6.8950(2)$ ,  $b = 11.9536(4)$  and  $c = 34.518(3)$  Å, representing metrically orthorhombic symmetry. However, the intensities of the superstructure reflections clearly indicate monoclinic symmetry. The diffraction aspect is  $F^*/d$ .

The 2C type or troilite is hexagonal and has the cell dimensions described earlier (Evans, 1970).

### Relationship between the $n$ Value and Composition

The dimensions of the subcells are plotted against  $n$  value for  $nC$  pyrrhotites from the Kohmori mine and other localities (Fig. 4). The dimensions of the sub-

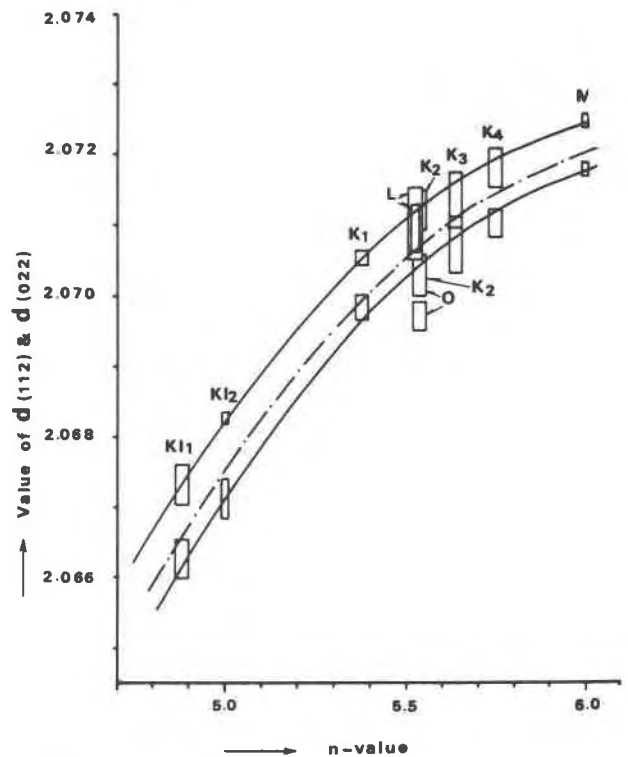


FIG. 6. Values of  $d_{112}$  and  $d_{022}$  of the orthorhombic cell against the  $n$  value for intermediate pyrrhotites. The mean  $d$  values are shown by the central curve.

cells of 5.53C from the Luikonlahti mine, Finland, and 5.54C from the East Ongul Island, Antarctica, are also measured and refined (Table 1). Interestingly, the cell dimensions of these two *nC* pyrrhotites do not fit with the curves obtained from the values for the *nC* pyrrhotites from the Kohmori mine and those for 5C and 6C (Fig. 4).

The volumes of the subcells, calculated from the dimensions of the subcells (Table 1), are plotted against the *n* values (Fig. 5). Because the crystals deviate from hexagonal symmetry,  $d_{102}$  of the pseudo-hexagonal cell corresponds to the crystallographically different  $d_{112}$  and  $d_{022}$  of the orthorhombic or metrically orthorhombic cells. The values of  $d_{112}$  and  $d_{022}$  were calculated from the dimensions of the subcells (Table 1), and are plotted against the *n* values (Fig. 6). The weighted mean of  $d_{112}$  and  $d_{022}$  based on their multiplicity was also given as a mean  $d$  value (Fig. 6) and is used in the further discussion.

To determine the chemical compositions of the *nC* pyrrhotites, we assumed that 5C and 6C have stoichiometric compositions of  $\text{Fe}_9\text{S}_{10}$  and  $\text{Fe}_{11}\text{S}_{12}$ , corresponding to 47.37 and 47.83 atomic percent iron, respectively, and that the subcell volume changes linearly with composition in the range of the *nC* pyrrhotites. The straight line of the subcell volume for the chemical composition is expressed as follows:

$$x = -36.817 + 0.71404V \quad (1)$$

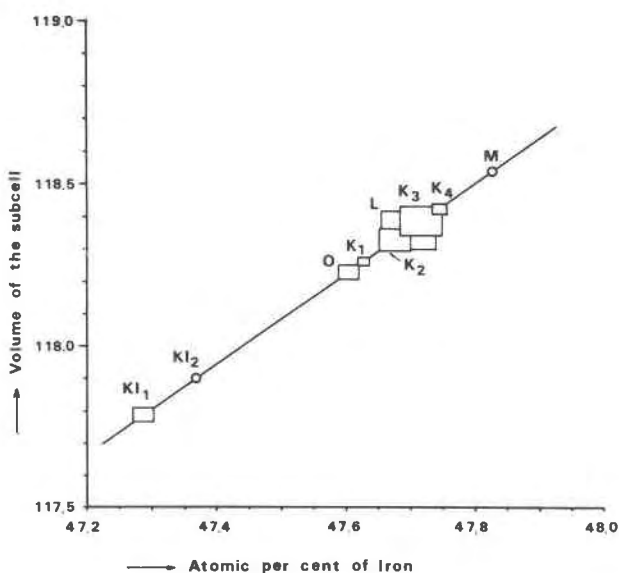


FIG. 7. Estimated compositions of intermediate pyrrhotites based on the volume of the subcells. The compositions of 5C and 6C are assumed to be  $\text{Fe}_9\text{S}_{10}$  and  $\text{Fe}_{11}\text{S}_{12}$ , respectively.

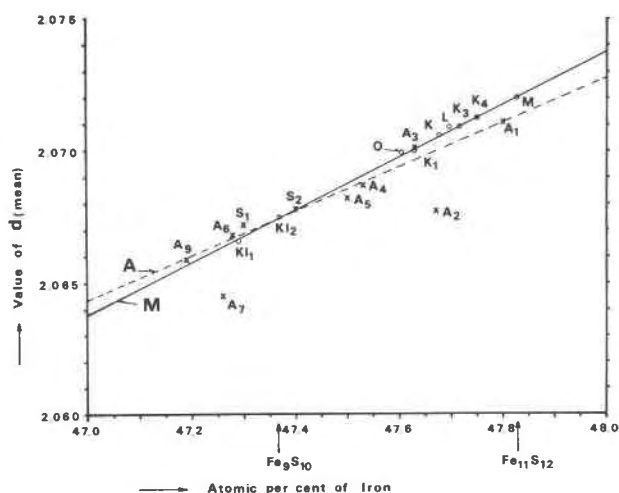


FIG. 8. Relationship between composition and mean  $d$  value for intermediate pyrrhotites. Specimen numbers are taken from Tables 1 and 2. The full and broken lines represent Eqs. 3 and 5, respectively.

where  $x$  represents atomic percent iron and  $V$  is the subcell volume in  $\text{\AA}^3$ . The compositions of the *nC* pyrrhotites were obtained by interpolating or extrapolating their volumes into the straight line (Fig. 7). Although the Luikonlahti and the East Ongul Island specimens have the same *n* value, within the range of error (Table 1), they are different, with 47.70 and 47.60 atomic percent iron, or  $\text{Fe}_{10.03}\text{S}_{11}$  and  $\text{Fe}_{10.00}\text{S}_{11}$ , respectively.

The mean  $d$  values for the *nC* pyrrhotites are plotted against the chemical compositions obtained by the subcell volumes, as mentioned above (Fig. 8). The relationship between the mean  $d$  values and compositions for the *nC* pyrrhotites has been obtained by applying the least squares method to the data of Table 1 for quadratic and linear equations. They are, respectively,

$$d_{\text{mean}} = -1.8459 + 0.15469x - 0.001522x^2 \quad (2)$$

and,

$$d_{\text{mean}} = 1.5929 + 0.01002x \quad (3)$$

where  $d_{\text{mean}}$  represents the mean  $d$  value in  $\text{\AA}$ , and  $x$  the chemical composition in atomic percent iron. For both equations, the standard deviation of the mean  $d$  values is less than  $0.0001 \text{\AA}$ . Equation (2) can be compared with that obtained by Arnold (1962) from synthetic pyrrhotites, namely:

$$d = -0.0182 + 0.0767x - 0.00069x^2 \quad (4)$$

Though his equation generally agrees over the entire composition range of pyrrhotite with the results for

natural pyrrhotites (Arnold and Reichen, 1962), a small deviation is observed in the composition range between  $\text{Fe}_9\text{S}_{10}$  and  $\text{Fe}_{11}\text{S}_{12}$ . To obtain better agreement with the experimental data of this composition range, a new equation has been obtained by applying the least squares method on the data by Arnold and Reichen (1962) and by Skinner (1958) shown in Table 2. The resultant equation is:

$$d = 1.6685 + 0.00842x \quad (5)$$

where the standard deviation is less than 0.0002 Å. This is in good agreement with Eq. 3, the maximum difference in  $d$  values being only 0.0006 Å in the composition range of the intermediate pyrrhotite. The curves in Figure 8 represent Equations (3) and (5).

Similar continuous displacement of the superstructure reflections, with compositional change, was observed for the synthetic digenite-type solid solution in the Cu-S system (Morimoto and Koto, 1969; Morimoto and Gyobu, 1971).

To indicate the deviation from hexagonal symmetry, the difference between  $d_{112}$  and  $d_{022}$  values is defined as non-hexagonality and was plotted for different crystals (Fig. 9). Among  $nC$  pyrrhotites from various localities, those from the Luikonlahti mine and from East Ongul Island show metrically close relation with hexagonal symmetry compared with other crystals which have almost similar values of hexagonality.

Relationships between the  $n$  value and the composition (Fig. 10) show those from the nonintegral types of the Kohmori mine to be slightly different

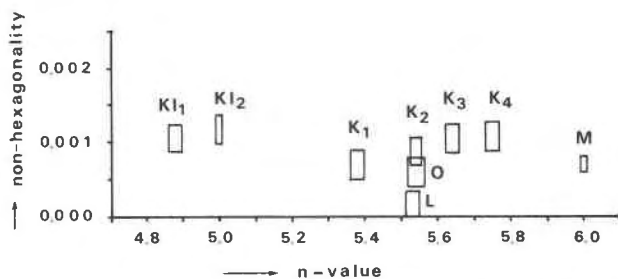


FIG. 9. Non-hexagonality, the difference between  $d_{112}$  and  $d_{022}$  for the intermediate pyrrhotites.

from those of other localities, though the general relationship is similar. Such relationship between  $n$  and  $x$  is probably modified by the modes of occurrence of the intermediate pyrrhotites through the state of ordering of vacancies in the crystal structures and the amount of minor components. Further study is necessary to elucidate the relationship more precisely.

#### Composition and Symmetry of the Intermediate Pyrrhotites

Intermediate pyrrhotites were long believed to have hexagonal symmetry and, therefore, were often called hexagonal pyrrhotites. They were considered to constitute a continuous solid solution from about 47.20 to 47.80 atomic percent iron in nature (Desborough and Carpenter, 1965; Mukaiyama and Izawa, 1970). However, on the basis of studies of single crystals of intermediate pyrrhotites, especially of the 5.54C type, Morimoto *et al* (1970) proposed that intermediate pyrrhotites actually consist of a few approximately stoichiometric compounds such as the 5C ( $\text{Fe}_9\text{S}_{10}$ ), 11C ( $\text{Fe}_{10}\text{S}_{11}$ ), and 6C ( $\text{Fe}_{11}\text{S}_{12}$ ) types.

As shown by specimens from the Kohmori mine and other localities, the present investigation confirms that intermediate pyrrhotites can take any non-stoichiometric composition in the composition range from about 47.28 to 47.83 atomic percent iron. The integral types 5C and 6C with compositions  $\text{Fe}_9\text{S}_{10}$  (47.37 atomic percent iron) and  $\text{Fe}_{11}\text{S}_{12}$  (47.83 atomic percent iron) respectively, are considered as special cases of the nonintegral types, though they are very close to the end compositions of intermediate pyrrhotites.

Kase (1974) and Miyazaki, Mukaiyama, and Izawa (1974) independently studied the change in composition of pyrrhotites with geological conditions in the Bessi mine. They determined with X-ray powder patterns the composition of pyrrhotites using Arnold's (1962) curve. Their results indicate that the

TABLE 2. Compositions and  $d$  Values of the Hexagonal 102 of Intermediate Pyrrhotites\*

Specimen Number*	Composition (atomic percent iron)	$d$ Value of Hexagonal 102
A1	47.80	2.0711
A2**	47.67	2.0677
A3	47.63	2.0701
A4	47.53	2.0687
A5	47.50	2.0682
A6	47.28	2.0668
A7**	47.26	2.0645
A9	47.19	2.0659
S1	47.3	2.0672
S2	47.4	2.0678

\* A and S represent specimens taken from Arnold and Reichen (1962) and Skinner (1958), respectively.

\*\* these specimens omitted from the least squares refinement for Eq.5.

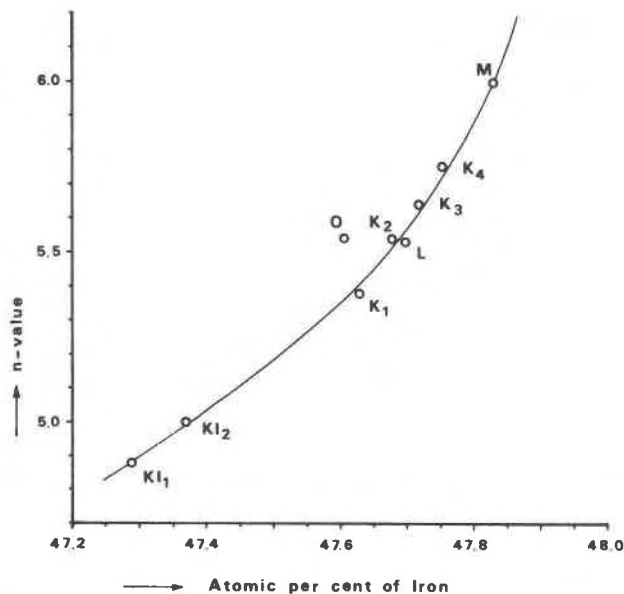


FIG. 10. Relationship between  $n$  value and composition for the intermediate pyrrhotites.

composition of intermediate pyrrhotites is continuous in the composition range from about 47.20 to about 47.80 atomic percent iron and that the most abundant compositions of intermediate pyrrhotite are controlled by geological conditions or by depth of the ore deposit in the Bessi mine.

The present study also indicates that all the intermediate pyrrhotites are only pseudohexagonal. They are apparently orthorhombic ( $5C$  and  $nC$ ) or even pseudoorthorhombic ( $6C$ ). Koto, Morimoto, and Gyobu (1974) indicate that the  $6C$  type is only metrically orthorhombic, actually being structurally monoclinic with space group  $F2/d$ . The orthorhombic symmetry of intermediate pyrrhotite seems to result from enhancement of symmetry by some statistical arrangement of iron vacancy (Nakazawa, Morimoto and Watanabe, 1974).

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