must be at, or very near, $\mathrm{Fe}_{11}\mathrm{S}_{12}$ (47.83 atomic percent iron) on the basis of the following observations.

Reports

Pyrrhotites: Stoichiometric Compounds with Composition $\mathrm{Fe}_{n-1}\mathrm{S}_n$ ($n \geqq 8$)

Abstract. *A new type of natural pyrrhotite, orthorhombic 11*C *type* ($a = 6.892$, $b = 11.952$, $c = 5.744 \times 11$ *angstroms*), *and the hexagonal* 6C *type* ($a = 6.89$, $c = 5.76 \times 6$ *angstroms*) *are described. Their compositions are* $\mathrm{Fe}_{10}\mathrm{S}_{11}$ *and* $\mathrm{Fe}_{11}\mathrm{S}_{12}$, *respectively. Pyrrhotites stable in nature have essentially stoichiometric composition,* $\mathrm{Fe}_{n-1}\mathrm{S}_n$ ($n \geqq 8$), *with the structures of* n/2C *type for* n *even and of* nC *type for* n *odd. The solid solutions between* $\mathrm{Fe}_{11}\mathrm{S}_{12}$ *and* $\mathrm{Fe}_{10}\mathrm{S}_{11}$, *and between* $\mathrm{Fe}_{10}\mathrm{S}_{11}$ *and* $\mathrm{Fe}_9\mathrm{S}_{10}$ *are considered metastable in nature.*

Because of the complexity of solid solution, structure, and magnetic properties, pyrrhotite has been extensively studied, but many important questions remain unanswered. Three different structure types of pyrrhotite were described as stable phases at low temperatures (*1*, *2*), all of which are superstructures of the *NiAs*-type structure with cell dimensions: *A*, about 3.45 Å; *C*, about 5.8 Å. They are hexagonal 2*C* type (troilite, FeS), hexagonal 5*C* type ($\sim\mathrm{Fe}_{11}\mathrm{S}_{12} - \sim\mathrm{Fe}_9\mathrm{S}_{10}$), and monoclinic 4*C* type ($\mathrm{Fe}_7\mathrm{S}_8$). Fleet and MacRae (*3*) have recently described the fourth stable phase at low temperatures, hexagonal 6*C* type. The 1*C* type (*NiAs* type) and the 3*C* type have been confirmed to be stable at high temperatures over wide ranges of composition (*2*, *4*).

The present report describes a new type of pyrrhotite together with the known types, and presents the relationship between the structure type and composition and the stability of possible solid solutions in pyrrhotite.

1) The 2*C* and 6*C* types. Synthetic materials of pyrrhotite with 48.5 and 49.0 atomic percent iron, produced at 600°C and slowly cooled to room temperature, were stored at room temperature for 12 months in a desiccator. The crystals were studied by the x-ray single-crystal method. The photographs show that all crystals consist of the 2*C* and 6*C* types, both of which are hexagonal. The 2*C* type is troilite and has the cell dimensions obtained previously (Table 1) (*5*, *6*). The 6*C* type has the cell dimensions $a = 6.90$ (3.45×2) $\pm$ 0.02, and $c = 34.56$ (5.76×6) $\pm$ 0.08 Å. The *h*0*l* plane of the reciprocal lattice, indicating the superstructure of the 6*C* type, is given schematically in Fig. 1. The composition of the 6*C* type was not precisely determined, but it must be at, or very near, $\mathrm{Fe}_{11}\mathrm{S}_{12}$ (47.83 atomic percent iron) on the basis of the following observations.

The intergrowths of troilite and pyrrhotite were described for the specimen from Merensky Reef, Farm Tweefontein, South Africa (*1*). The values of d(10·2) for troilite and pyrrhotite are 2.0936 Å (50.0 atomic percent iron) and 2.0728 Å (47.9 atomic percent iron), respectively (*1*). The cell dimensions of the subcell for the pyrrhotite (Table 1) are in good agreement with those of the synthetic materials mentioned above. The observed $d_s(101)$ (*7*) and $d_s(102)$ (*7*) of the pyrrhotite were 5.88 and 5.64 Å, respectively (*1*). These values are explained better by the 6*C* type, which gives the calculated values of 5.89 and 5.64 Å for $d_s(101)$ and $d_s(102)$, respectively, than by the 5*C* type, which gives 5.85 and 5.52 Å. Furthermore, the study of natural and fully annealed synthetic intergrowths of troilite and pyrrhotite (*8*) has shown that the iron-rich phase is essentially stoichiometric FeS and the coexisting pyrrhotite contains 47.9 $\pm$ 0.2 atomic percent iron corresponding to $\mathrm{Fe}_{11}\mathrm{S}_{12}$.

2) The 11*C* type. Crystals of pyrrhotite from the East Ongul Island, Antarctica, were studied (*9*, *10*). The value of d(10·2) is 2.0693 $\pm$ 0.0008 Å, indicating 47.60 atomic percent iron by Arnold's curve (*11*). No peak due to monoclinic pyrrhotite was observed in the powder patterns. This pyrrhotite is, therefore, apparently hexagonal, with the composition $\mathrm{Fe}_{10}\mathrm{S}_{11}$ (47.62 atomic percent iron). The cell dimensions of the subcell are $A = 3.446 \pm 0.005$, and $C = 5.744 \pm 0.005$ Å.

Studies on the single crystals of the pyrrhotite indicate that the symmetry is only metrically hexagonal and really

Table 1. Composition, symmetry, and cell dimensions of five structure types of pyrrhotite.

Type	Composition	Atomic percent of iron	Symmetry (space group)	Cell dimensions				Localities and references
				a (Å)	*b* (Å)	*c* (Å)	β (°)	
2*C*	FeS	50.00	Hexagonal (*P*$\bar{6}$2*c*)	5.97 ($3.45 \times \sqrt{3}$)		11.76 (5.88×2)		Synthetic (this study)
				5.958 ($3.440 \times \sqrt{3}$)		11.740 (5.870×2)		Synthetic (*5*)
				5.965 ($3.444 \times \sqrt{3}$)		11.750 (5.875×2)		Del Norte Co., California (*6*)
6*C*	$\mathrm{Fe}_{11}\mathrm{S}_{12}$	47.83	Hexagonal*	6.90 (3.45×2)		34.56 (5.76×6)		Synthetic (this study)
				6.904 (3.452×2)		34.51 (5.752×6)		Merensky Reef, So. Africa (*1*)
11*C*	$\mathrm{Fe}_{10}\mathrm{S}_{11}$	47.62	Orthorhombic (*Cmca* or *C*2*ca*)	6.892 (3.446×2)	11.952	63.184 (5.744×11)†		Ongul, Antarctica (this study)
5*C*	$\mathrm{Fe}_9\mathrm{S}_{10}$	47.37	Hexagonal*	6.88 (3.44×2)		28.70 (5.74×5)†		Outokumpu, Finland (this study)
				6.892 (3.446×2)		28.630 (5.726×5)		Outokumpu, Finland (*1*)
				6.884 (3.442×2)		28.610 (5.722×5)		Mt. Prospect, Connecticut (*1*)
4*C*	$\mathrm{Fe}_7\mathrm{S}_8$	46.67	Monoclinic (*F*2/*d*)‡	6.860 (3.430×2)	11.903	22.788 (5.697×4)	90.5	Kisbanya, Rumania (this study)
				6.872 (3.436×2)	11.903	22.780 (5.695×4)	90.4	Yukon gold district, Alaska (*1*)

* Orthorhombic symmetry is possible as explained in the text. † The *c*-length is not exactly 11*C* or 5*C*, as explained in the text. ‡ To conform to the second setting of this space group, the *a* and *b* axes must be interchanged.

orthorhombic, though apparent hexagonal symmetry was observed for most crystals because of twinning related by 60° or 120° rotation about the pseudohexagonal *c*-axis. The oscillation photographs around the *c*-axis clearly indicate that the crystals are of the 11*C* type (Fig. 2). The cell dimensions of the supercell are, therefore, $a = 2A = 6.892$ (3.446 × 2), $b = 2\sqrt{3}A = 11.952$, and $c = 11C = 63.184$ (5.744 × 11) Å (Table 1). The diffraction aspect is $C{*}ca$ with the possible space groups *Cmca* and *C2ca*. A diagrammatic sketch of the 0*kl* plane of the reciprocal lattice, showing the 11*C* superstructure, is compared with the corresponding ones for the 6*C* and 5*C* types (Fig. 1).

The accurate measurements of the precession photographs, however, revealed slight displacements of the superstructure reflections from the Bragg positions for the 11*C* type along the *c** axis, indicating that the pyrrhotite is of the nonintegral type (*4*) and that the *c*-length of the superstructure is irrationally related to that of the *NiAs* subcell. This implies that the superstructure reflections must be regarded as satellite reflections of the main reflections corresponding to the subcell. The interval between the row lines of the main reflections and their nearest ones of the satellite reflections (*t* in Fig. 1, 11*C*) is 1/(5.54 ± 0.02) of the repeat of the main reflections (*T* in Fig. 1, 11*C*) along the *c** axis. According to the conventional expression for the nonintegral types of structure (*4, 12*), this pyrrhotite belongs to the 5.54*C* type.

Because very few x-ray studies have been made in detail on single crystals of natural pyrrhotite at, or near, the composition $Fe_{10}S_{11}$ and the powder method failed in distinguishing the 11*C* type from the 6*C* or 5*C* type, we have not succeeded in finding the 11*C* type from other localities. However, the 11*C* type is considered to be rather common in nature, as explained later.

3) The 5*C* and 4*C* types. Many crystals consisting of hexagonal and monoclinic pyrrhotites were studied by the single crystal method. All the hexagonal pyrrhotites are of the 5*C* type. The cell dimensions of the subcell of the 5*C* type from Outokumpu, Finland, are nearly the same as those obtained previously (*1*) (Table 1), indicating the composition of Fe_9S_{10} (47.37 atomic percent iron) (*2, 13*).

Slight displacements of the superstructure reflections from the Bragg positions were also observed for the hexagonal pyrrhotite of the Outokumpu specimen, as for the 11*C* type. The interval between the row lines of the main reflections and their nearest ones of the superstructure reflections (*t* in Fig. 1, 5*C*) is not 1/5 of the repeat of the main reflections (*T* in Fig. 1, 5*C*) along the *c** axis, but is 1/(4.94 ± 0.02) of this repeat. Thus the hexagonal pyrrhotite of Outokumpu belongs to the 4.94*C* type of the nonintegral types analogous to the Ongul crystals.

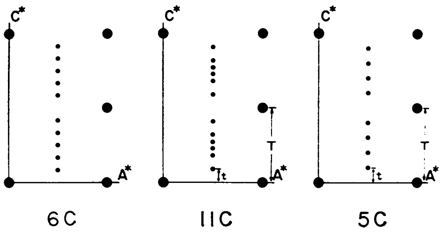

Fig. 1. Diagrammatic sketch of the *A*C** plane of the reciprocal lattice for the 6*C*, 11*C*, and 5*C* types. The interval, *t*, is irrationally related to the repeat of the main reflections, *T*, along the *C** axis, as explained in the text.

Monoclinic pyrrhotites from various localities were also studied. All of them belong to the 4*C* type. Most crystals are twinned aggregates related by 60° or 120° rotation about the pseudohexagonal *c*-axis. A single crystal was obtained among crystals from Kisbanya, Rumania. The cell dimensions, space group (*14*), and composition (*2*) were determined (Table 1). The structure refinement of this crystal is now in progress.

The crystallographic data of natural pyrrhotites so far examined indicate existence of five types of structure (Table 1). All the types have essentially stoichiometric compositions which can be expressed by a general formula, $Fe_{n-1}S_n (n \geqq 8)$. Their structures are of the *n*/2*C* type for *n* even and of the *nC* type for *n* odd, except for the 2*C* type. This type, with the composition of FeS, is an extreme case of $Fe_{n-1}S_n$ with a very large *n*. The correspondence between the stoichiometric composition and the structure type suggests that all the superstructures of pyrrhotite are vacancy controlled. This situation is somewhat analogous to the apparently nonstoichiometric oxides of titanium and vanadium (*15*). Although the 6*C* and 5*C* types always appear with hexagonal symmetry, the close relations among the supercells of the 6*C*, 11*C*, and 5*C* types (Fig. 1) suggest orthorhombic symmetry for the 6*C* and 5*C* types as for the 11*C* type.

Synthetic crystals with the composition from $Fe_{11}S_{12}$ to Fe_9S_{10} were annealed at room temperature for 6 months. They show structures of the nonintegral type, the superstructure reflections displacing continuously from the positions of the 6*C* type to those of the 5*C* type with the change of composition (*16*). Because the Ongul pyrrhotite shows slight displacements of the superstructure reflections from the positions for the 11*C* type toward those for the 6*C* type, its composition is considered to be slightly richer in iron than $Fe_{10}S_{11}$. By similar reasoning, the Outokumpu pyrrhotite is considered to be

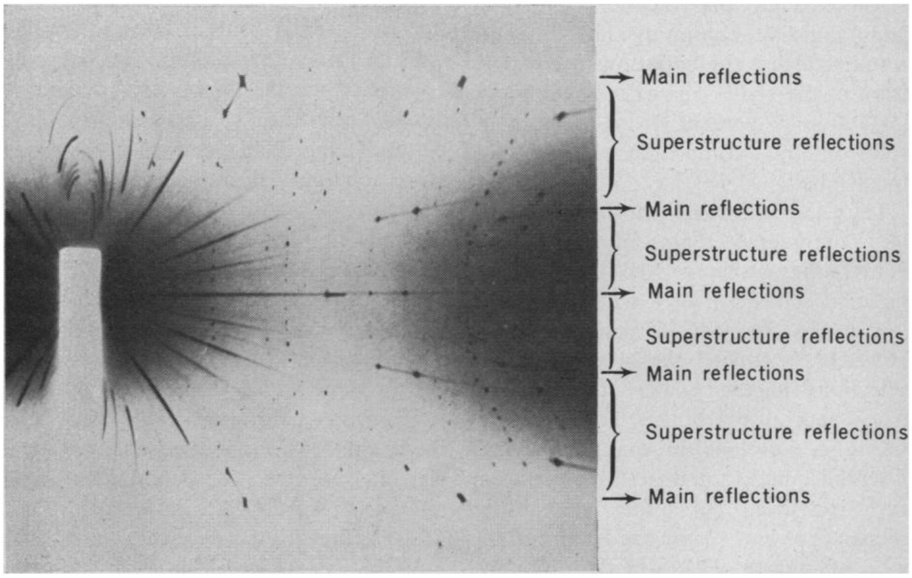

Fig. 2. Oscillation photograph about the *c*-axis of the 11*C* type pyrrhotite from Ongul Island, Antarctica. The main reflections, corresponding to the *NiAs* subcell, and the superstructure reflections are indicated. The diagrammatic sketch of the 0*kl* reciprocal plane is shown in Fig. 1.

slightly poorer in iron than Fe_9S_{10}. If we assume a linear relation between the displacement of superstructure reflections and composition, the deviation from the stoichiometric compositions is 0.02 and 0.03 atomic percent iron for the Ongul and Outokumpu crystals, respectively.

Based on the experimental results on natural and synthetic pyrrhotites mentioned above, it is necessary to examine whether the solid solutions between $Fe_{11}S_{12}$ and $Fe_{10}S_{11}$, and between $Fe_{10}S_{11}$ and Fe_9S_{10} are really stable in nature as is widely accepted (*1, 5, 8*).

Before explaining this question, we shall consider why the displacements of the superstructure reflections take place in natural pyrrhotites. First we must admit the fact that in sulfides a small change of composition in an essentially stoichiometric compound with a superstructure generally results in a continuous change of the cell dimensions, keeping the superstructure reflections at Bragg positions. In such a case, atoms are randomly added on or subtracted from the lattice sites of the original stoichiometric compound. On the other hand, the displacements of the superstructure reflections, observed in essentially stoichiometric pyrrhotites, are considered due to the fact that addition or subtraction of metal atoms takes place by statistical insertion or extraction of completely filled metal layers, retaining the arrangement of the vacant sites in the original structure. In this case, a large deviation from the stoichiometric composition seems difficult, because it must affect the original arrangements of the vacant sites. The Ongul and Outokumpu pyrrhotites seem to indicate that the variation in composition of the stable phases is possible by 0.03 atomic percent iron about the stoichiometric compositions as mentioned above.

Thus the structural consideration of the nonintegral types of pyrrhotite seems unfavorable to the stability of the solid solution over a wide composition range. In fact, Mukaiyama and Izawa (*17*) noticed the broadening of reflections in the powder patterns of many natural pyrrhotites belonging to the solid solutions in question. They observed lamellar and perthite-like textures for these pyrrhotites under the microscope and recognized the existence of phases with slightly different compositions. In addition, the superstructure reflections such as 101 and 102 of the hexagonal natural pyrrhotites (*1*) are not explained by the continuous solid solutions of the nonintegral type observed for the synthetic crystals.

Thus the solid solutions are considered to be metastable and to change to the essentially integral types (*4*) with very narrow ranges about the stoichiometric compositions. This conclusion is also in accordance with the results obtained for the quenched nonintegral types in the Fe-S system (*4, 16*) and for the digenite-type solid solution in the Cu-S system (*12, 18*).

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Australopithecine Endocast (Taung Specimen, 1924): A New Volume Determination

Abstract. *A redetermination of endocranial volume of the original 1924 Taung australopithecine described by Dart indicates a volume of 405 cubic centimeters, rather than the 525 cubic centimeters published earlier. The adult volume is estimated to have been 440 cubic centimeters. This value, plus other redeterminations of australopithecine endocasts, lowers the average to 442 cubic centimeters, and increase the likelihood of statistically significant differences from both robust australopithecines and the Olduvai Gorge hominid No. 7.*

In the course of an investigation of the endocranial remains of the South African australopithecines, it became apparent that the endocranial volumes already published (*1*), particularly that of the Taung child's endocast, required more accurate determinations. The reasons for this are threefold: (i) the actual methods of past volumetric determinations have not been adequately described; (ii) the published value for the Taung endocast, discovered and described by Dart in 1925, is given as 525 cm³, a value which seemed clearly high to me when I examined both casts and the original; (iii) a recent spate of articles (*2*) have appeared debating the significance of the Olduvai specimen No. 7, using the original values of australopithecine endocranial capacity, which are, in my opinion, incorrect. With the kind permission and invitation of Professor Tobias, a full study of the South African fossil endocasts was undertaken, and this report covers the results on the Taung endocast, for which three different reconstructions of a complete hemi-endocast were made.

A mold was first made of the original specimen, and several plaster of paris casts were obtained. These casts were carefully checked against the original, and all measurements were found to be accurate within 0.1 mm. The next step in the reconstruction was to ascertain the midsagittal plane accurately, since it appeared upon close examination that previous casts were faulty in this respect. Since a plane can be defined by a minimum of three points, it was decided to select three points reasonably spaced apart from each other along the median sagittal groove. By setting the cast on its convex side on a flat and level surface, and using three fine-pointed spikes in the same plane as the flat surface, it was possible to orient the casts such that the