MIXTURES OF HEXAGONAL AND MONOCLINIC PYRRHOTITE AND THE MEASUREMENT OF THE METAL CONTENT OF PYRRHOTITE BY X-RAY DIFFRACTION

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In a previous issue of *The American Mineralogist*, Arnold and Reichen (1962) indicated that a d_{102}[1] versus composition relationship, established on the basis of synthetic hexagonal pyrrhotites, can be used to estimate the metal content of natural, hexagonal pyrrhotite, provided that the concentrations of impurities in solid solution are low. This was demonstrated by showing good agreement between the d_{102} versus composition relationship for synthetic, hexagonal pyrrhotite and for 14 chemically analyzed natural pyrrhotites. Thirteen of the natural pyrrhotites used in this comparison were judged to have hexagonal symmetry and one (Tretca) was judged to have monoclinic symmetry by x-ray diffraction. A recent re-examination of eleven of these natural pyrrhotites previously thought to be hexagonal revealed that two are hexagonal, eight are mixtures of hexagonal and monoclinic types and one is monoclinic. In view of this, the d_{102} versus composition relation for those natural pyrrhotites for which suitable material was avialable was re-examined.

The discovery of intergrowths on etched polished surfaces of these pyrrhotites led to their re-examination. Figures 1 and 2 show some typical intergrowths of coexisting monoclinic and hexagonal pyrrhotite produced by etching a polished surface with a saturated solution of chromic acid for about one hour at room temperature. These intergrowths are not visible prior to etching. Powder removed from the polished surfaces and x-rayed, using a large Philips powder camera (114.83 mm diameter), revealed that the strongly etched areas (dark grey) are monoclinic pyrrhotite and the more lightly etched areas (light grey) are hexagonal pyrrhotite. In all cases investigated by the powder camera, monoclinic pyrrhotite is etched more strongly than coexisting hexagonal pyrrhotite. Approximately one weight per cent of the minor phase can be detected optically on a polished surface if it is intergrown with the host.

Figure 1 shows clearcut lamellae and elongated blebs of monoclinic pyrrhotite in a host of hexagonal pyrrhotite. The lamellae are apparently crystallographically orientated and have the appearance of an exsolved phase. They either terminate or change direction abruptly at the grain boundaries of the host. In basal sections of hexagonal pyrrhotite,
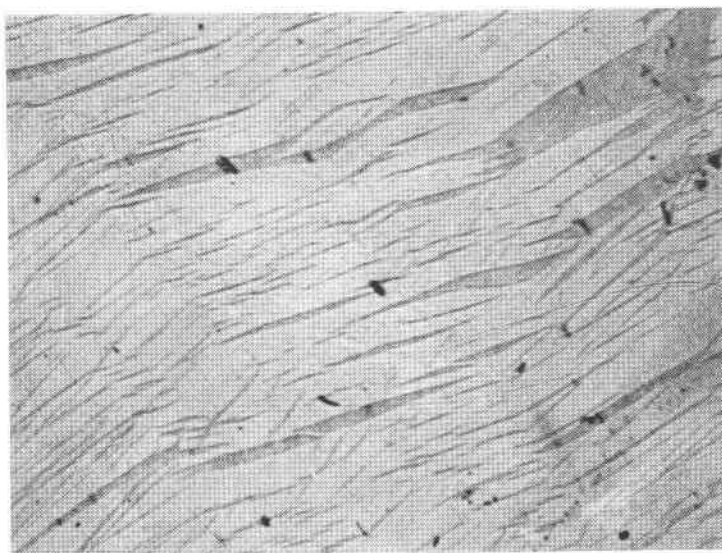
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[1] 102 is abbreviated from 10$\bar{1}$2.

FIG. 1. Lamellae and elongated blebs of monoclinic pyrrhotite (dark gray) in a host of hexagonal pyrrhotite (light gray) (Bluebell, B. C., ×160, etched).
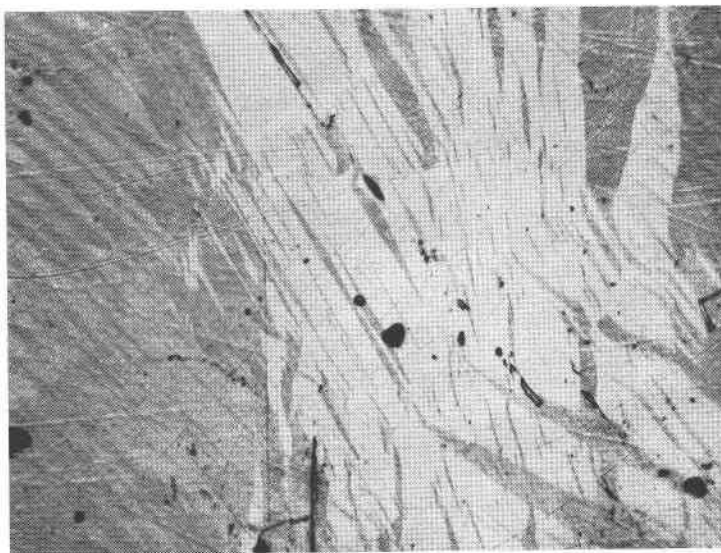

FIG. 2. Lamellae of hexagonal pyrrhotite (light gray) in monoclinic pyrrhotite (dark gray) and vice versa. Left hand third of photomicrograph shows northwest trending lamellae (medium gray) with relatively low reflectivity (Bluebell, B. C., ×160, etched).

lamellae of monoclinic pyrrhotite occur in two sets inclined at angles of 40° to 50° to one another. Figure 2 shows lamellae of hexagonal pyrrhotite in a host of monoclinic pyrrhotite and vice versa. Small, parallel, closely spaced, lamellae of somewhat lower reflectivity are evident in the area of monoclinic pyrrhotite in the left hand portion of Fig. 2. Lamellae of this type also occur in clearcut lamellae of monoclinic pyrrhotite (not shown) and usually meet the lamellae boundaries at an angle of about 70°. The identity of these lamellae with lower reflectivity is not known; they may be polysynthetic twinning. These lamellae have not been observed in hexagonal pyrrhotite.

Pehrman (1954) was one of the first to recognize that etch structures on polished surfaces of pyrrhotite were due to coexisting hexagonal and monoclinic structural types. Lyons (1958), apparently without knowledge of Pehrman's work, detected structures on etched, polished surfaces of pyrrhotite from Australia and suggested that the structures represented monoclinic pyrrhotite exsolved from a hexagonal pyrrhotite host. Desborough and Carpenter (1965) report identifying coexisting monoclinic and hexagonal pyrrhotite under the microscope on unetched polished surfaces, but the reflectivity difference between the two phases was extremely small. It therefore appears that the two phases can be more reliably identified on etched surfaces.

Table 1 summarizes the compositions (by chemical analysis, Arnold and Reichen (1962)), d_{102} values and structural types of the eleven re-examined pyrrhotite samples. X-ray diffraction charts of these pyrrhotites are reproduced in Fig. 3 (upper). A single, sharp, symmetrical 102 x-ray reflection is indicative of hexagonal pyrrhotite, a split reflection consisting of two peaks ($202-20\bar{2}$) of about equal intensity is indicative of monoclinic pyrrhotite (Byström, 1945), and a split reflection, with the high angle reflection ($20\bar{2}$) being significantly lower in intensity than the other (102, 202 superimposed) is indicative of a mixture of hexagonal and monoclinic pyrrhotite (Byström, 1945). These interpretations of a split reflection are valid only for pyrrhotites with bulk compositions more metal-deficient than about 47.5 atomic per cent metals. These pyrrhotites show weak supercell reflections at low angles as found by Carpenter and Desborough (1964). However, the number and position of these reflections are not wholly consistent with those described by Carpenter and Desborough (1964). Therefore their proposed new indices, based on revised hexagonal and monoclinic unit cells, have not been used, but the indices for normal hexagonal and monoclinic pyrrhotite are used here.

The character of the split reflection for various weighed mixtures of hexagonal and monoclinic pyrrhotite is illustrated in Fig. 3 (lower). The vertical scale represents the intensity ratio of the left hand peak (102

TABLE 1. SUMMARY OF CHEMICAL ANALYSES, d_{102} VALUES AND STRUCTURAL TYPES
FOR 11 PYRRHOTITES ORIGINALLY STUDIED BY ARNOLD AND REICHEN (1962)

Three additional pyrrhotites from Arnold and Reichen have been omitted from this table as no material was available for re-examination.

Samples	Arnold and Reichen (1962)		New Data	
	Atomic % metals	d_{102} (Å)	d_{102} (Å)	Structural types‡
McAfee, N. J.	47.80	2.0711	2.0698	H
Bergbau, Austria	47.67	2.0677	2.0666	H
Moise River, Quebec	47.63	2.0701	†	H≫M
Toncray, Virginia	47.53	2.0687	2.0664*	H≫M
Hybla, Ontario	47.50	2.0682	2.0673*	H>M
Bluebell, B. C.	47.28	2.0668	2.0663*	H>M
Highland Surprise, Idaho	47.26	2.0645	†	H≈M
Funter Bay, Alaska	47.19	2.0659	2.0643*	H<M
Riondell, B. C.	46.90	2.0588	2.0575*	H≪M
Clearwater Brook, N. B.	46.90	2.0592	†	H≪M
Kisbanya, Romania	46.70	2.0587	2.0574*	M

* Heated at 350° C. for 30 minutes before measuring.

† No fresh lumps available for heating and re-measuring.

‡ Determined from x-ray charts and by optical examination of etched polished surfaces. H and M represent hexagonal and monoclinic pyrrhotite, respectively.

+202) divided by the sum of the intensities of both peaks. The estimate of background intensity under each peak was compensated for the contribution from the adjacent peak. Ideally this ratio is 1.0 for pure hexagonal pyrrhotite and 0.5 for pure monoclinic pyrrhotite. In practice these ratios are realized in mixtures containing approximately 10 per cent of the minor phase as indicated by the straight line drawn through the points representing the ratios of the various weighed mixtures. It can therefore be concluded that with the x-ray equipment and techniques used here that less than about 10 weight percent of the minor phase cannot be detected in a mixture. Desborough and Carpenter (1965) state that, with their technique, less than 20 weight per cent of the minor phase cannot be detected by x-ray diffraction. The relatively higher sensitivity of the optical method for small amounts of the minor phase should therefore make it a useful adjunct to the x-ray method. The relative proportions of the structural types in the eleven re-examined pyrrhotites (Table 1) were estimated optically on etched polished surfaces and from the curve in Fig. 3.

There is a good correlation between structural type and composition. The two most metal-rich pyrrhotites are wholly hexagonal, the most
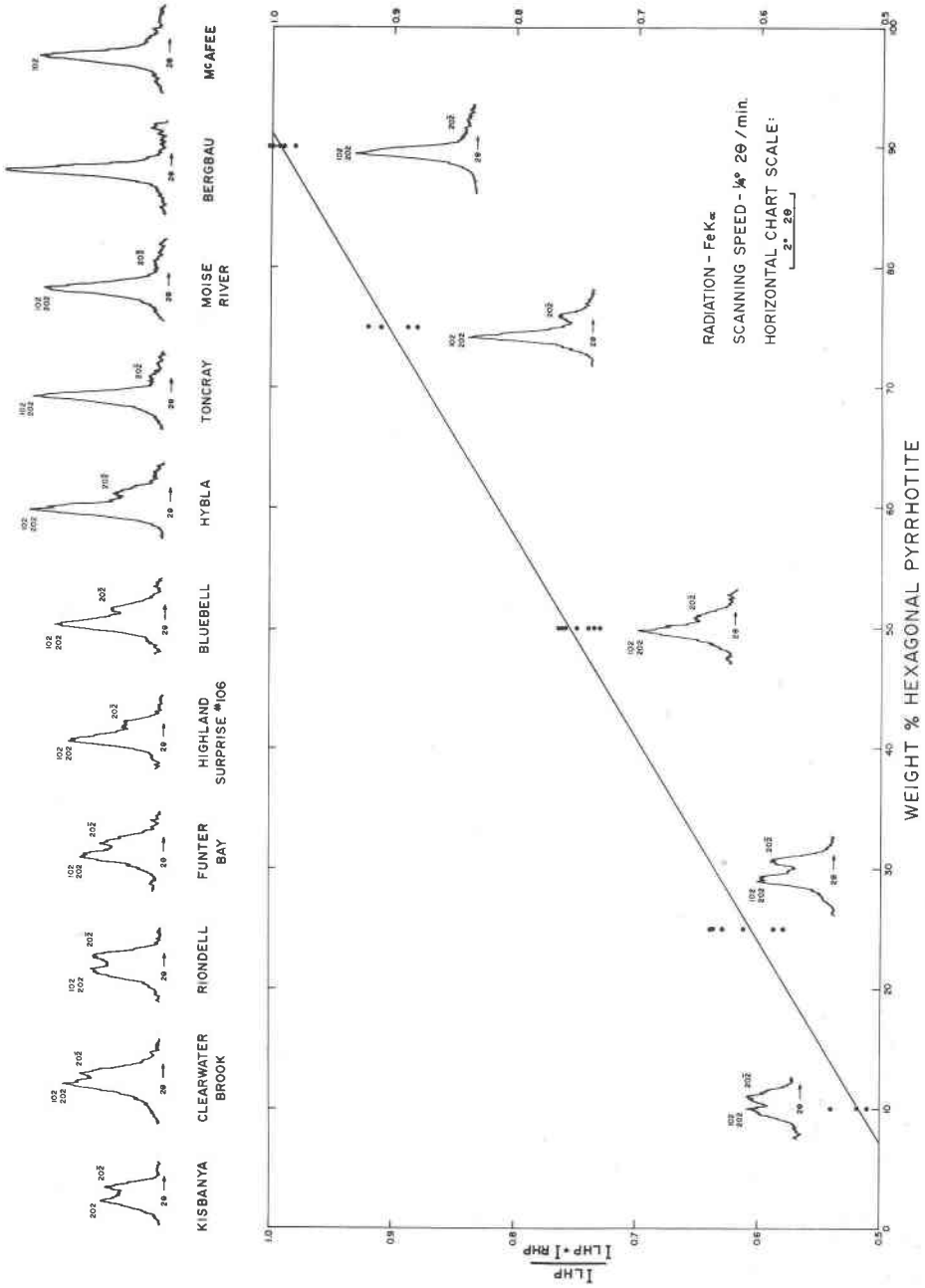
Fig. 3. Upper: X-ray chart records of the 11 re-examined pyrrhotite samples. Lower: X-ray chart records and intensity ratios of various weighed mixtures of hexagonal (McAfee, Bergbau) and monoclinic (Kisbanya) pyrrhotite. I_{LHP} and I_{RHP} represent the intensity of the left-hand and right-hand peaks, respectively.

metal-deficient pyrrhotite is wholly monoclinic and pyrrhotites with intermediate compositions are mixtures of the hexagonal and monoclinic types. A correlation also exists between the bulk composition of two-phase mixtures and the ratio of hexagonal to monoclinic pyrrhotite. Two-phase mixtures high in metals have a high ratio of hexagonal to monoclinic pyrrhotite and two phase mixtures low in metals have a low ratio of hexagonal to monoclinic pyrrhotite. This relationship can be explained by a two-phase field with approximate boundaries at 47.6 and 46.7 atomic per cent metals. This is in approximate agreement with a low temperature two-phase field of hexagonal and monoclinic pyrrhotite with field boundaries at 47.40 and 46.73 atomic per cent Fe, postulated by Grønvold and Haraldsen (1953) on the basis of synthetic pyrrhotites.

The distribution of coexisting hexagonal and monoclinic pyrrhotite in many of the samples is very erratic. Chips from the various parts of a hand specimen can vary from almost pure hexagonal to almost pure monoclinic pyrrhotite. Careful sampling is therefore essential to obtain an accurate estimate of the ratio of the two structural types of pyrrhotite in a hand specimen.

The mis-identification of many of these pyrrhotites as being wholly hexagonal by Arnold and Reichen (1962) appears to be due to the fact that a substantial quantity of quartz, used as internal standard, was added to all samples before x-raying. The resulting dilution of the samples caused a substantial loss of intensity and detail of the reflections. In view of this mis-identification, those pyrrhotites for which coarse-grained, unaltered material was available were inverted to hexagonal symmetry by heating at 350° C. for 30 mintues in sealed, evacuated, silica glass tubes and their d_{102} values remeasured.[1] The d_{102} values for the heated pyrrhotites and for unheated, hexagonal McAfee and Bergbau pyrrhotites are summarized in Table 1 together with the original d_{102} values for these pyrrhotites from Arnold and Reichen (1962).

A comparison of the new d_{102} values with the old shows that they are within the limit or error of measurement of one another, although the new values in each case are somewhat lower than the old. If the new d_{102} values are plotted against the original chemical analysis for each sample (Table 1), all the points lie on the high iron side of the experimental d_{102} versus composition curve. A curve through these points is roughly parallel to the experimental curve but approximately 0.2 atomic per cent richer in iron than the experimental curve at every point. Although this

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[1] Inverted monoclinic pyrrhotites show a single, sharp 102 reflection suggesting hexagonal symmetry. However, the superstructure reflections of the inverted material are similar to those shown by unheated, natural, monoclinic pyrrhotite. This apparent inconsistency has not been resolved.

new curve fits the new d_{102} values more closely than the experimental curve, there are not sufficient data at this time to recommend using a new curve for estimating the compositions of natural hexagonal pyrrhotites.

ACKNOWLEDGEMENT

I would like to thank Dr. A. R. Graham for a translation of Pehrman's paper and for pointing out that etched pyrrhotites can show structures.

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AN UNUSUAL HOURGLASS STRUCTURE IN AUGITE

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Pleochroic hourglass structures are well known in titanaugites from the alkali basic igneous rocks and are easily recognized in thin section. A more obscure hourglass structure, defined by composition and exsolution features, characterizes a common augite from a dolerite pegmatite.

The pegmatite occurs as segregations in an olivine tholeiitic feeder dike—a member of the Tertiary dike swarm of Northwest Ireland. The multiple dike which crosses County Fermanagh is being described in detail (Preston, in prepn.) and the pegmatite samples were collected from its later intrusions, exposed in an old quarry in the Townland of Drogan, near Doraville, northwest of Enniskillen.

In hand specimen, the augites display a fine silvery schiller and a well developed parting on both (001) and (100) surfaces. In thin section, these features may be related to very thin exsolved lamellae. A soft serpentin-