

whose essential crystal structure is *known*, an alternate procedure presents itself, which was not considered by Hey: *the use of the total number of atomic sites per cell*, as found in the structure determination, divided by *Z*, the number of formula units per cell, if desired. This procedure carries the assumption that both omission and addition solid solutions are absent. It has been found advantageous for minerals such as tourmalines, where substitution is so abundant that one should not assume any one crystallographic position to be free of it. The assumption made is, of course, checked in the end, when the observed density is compared with the calculated density, which is based on the derived formula and the cell dimensions. Hey's recommended procedure does not permit this comparison of densities, and although in theory it is just as good to compare the calculated number of atoms per cell with the number required by the structure, in practice this is less satisfactory. The density comparison has become so standard that data compilations such as *Crystal Data* (Donnay, 1963) devote a column to each density. In addition, and more important, the errors inherent in density and cell-dimension determinations, as discussed by Hey (1939, p. 403), are kept out of the formula.

The advantages that this procedure may have for many minerals over the procedures that assume a constant number of certain cations or anions are the following. There is no need to decide each time which elements should be used as the basis of computation. No assumption concerning the formula is "built in" when the formula is derived. The percent error in the conversion factor is minimized by the proposed procedure.

I wish to thank the many scientists who have kindly discussed this problem with me, especially Drs. M. Hey, Brian Mason, E. G. Zies and J. Zussman for their constructive remarks.

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THE AMERICAN MINERALOGIST, VOL. 49, SEPTEMBER-OCTOBER, 1964

DISCUSSION OF "PYRRHOTITE MEASUREMENT" BY GROVES AND
 FORD, *AM. MINERAL.* 48, 911-913

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Much interest has been shown in the use of pyrrhotite (Fe_{1-x}S) for geothermometry as described by Arnold (1962) and Arnold and Reichen

(1962). However, their curve for determining the composition of pyrrhotite from x -ray measurements is useful only for hexagonal samples, whereas much natural material consists of either monoclinic or a mixture of hexagonal and monoclinic pyrrhotite.

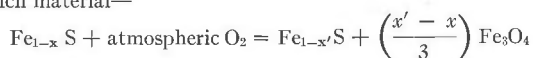
Groves and Ford (1963) comment on methods by which monoclinic pyrrhotite must be processed in order to make it hexagonal, and certain of their points need clarification. Before doing this, it should be emphasized that no matter how manipulated, monoclinic pyrrhotite may be of little or no value for thermometry because it may not exhibit the same extended range of composition as does the hexagonal form.

Two points mentioned by Groves and Ford will be discussed:

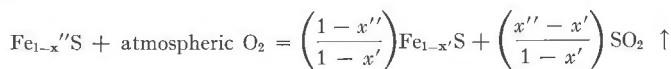
- 1) the degree of oxidation of pyrrhotite when exposed to the atmosphere, and
- 2) the use of diffraction patterns of material containing both monoclinic and hexagonal pyrrhotite for determining the composition of the hexagonal form.

In connection with grinding pyrrhotite in air, Groves and Ford mention that "the effects of oxidation are negligible over a short period" (p. 911). Although this may be substantially correct, a warning should be added that finely ground pyrrhotite should not be left exposed to the air for many days. Neglecting the effect of trace elements, possible reactions when pyrrhotite is not properly protected from the atmosphere are:

- 1) For Fe-rich material—



- 2) For S-rich material—



where $x < x' < x''$. Thus, pyrrhotite tends to oxidize and so change toward an intermediate equilibrium composition (Buseck, 1962a). Grønvd and Haraldsen (1952) indicate that pyrrhotite examined by them showed, upon oxidizing, a decrease in unit cell dimensions produced by a relative increase in sulfur content. When compared to static pyrrhotite grains, the rate at which oxidation occurs will be greatly accelerated by the pressure developed during crushing and grinding. Such pressure produces large stresses on the individual grains, activating their surfaces and generating heat, which further facilitates the reaction. Therefore it seems that oxidation would be most pronounced during grinding; the results below show that it occurs even under static exposure to the atmosphere.

Ten samples of hexagonal pyrrhotite were examined for compositional changes as a result of oxidation that may have occurred during the three

years that they were stored at room temperature. In each case the original mounts were examined both before and after the storage period. Unfiltered Fe x -radiation was used for the measurement, with Si as an internal standard. The samples were oscillated eight or more times using a scanning speed of $\frac{1}{2}^\circ$ per minute and a chart speed of 1" per minute.

The range in the value of d_{102} of the unoxidized samples was 2.0472 to $2.0689 \pm .0010$ Å, corresponding to a range in atomic per cent of Fe of 45.80 to 47.55 (Arnold, 1962). The maximum compositional change encountered as a result of oxidation in three years was an apparent decrease of 0.35 atomic per cent Fe. This occurred in the most Fe-rich sample of the group. Samples containing slightly less than 47.0 atomic per cent Fe showed no change in the d_{102} , whereas those containing still smaller amounts of Fe showed a slight increase in the d_{102} , suggesting that in these samples oxidation produces a decrease in the S content. The measured changes were thus in the direction indicated by equations (1) and (2).

The effect of oxidation was determined for one specimen nine days after the initial measurement of the d_{102} was made—it indicated a loss of 0.2 atomic per cent Fe from its original composition of 47.2 atomic per cent Fe. No further change was indicated when the same mount was again x -rayed after three years, suggesting that the rate of oxidation is most rapid upon initial exposure to the air, as might be expected. From their results, it seems likely that the samples of Groves and Ford were in the compositional range where oxidation would not be pronounced; however, it is certainly necessary to use caution when dealing with pyrrhotites of unknown composition.

When x -rayed, many specimens examined by Groves and Ford showed two peaks about $0.35^\circ 2\theta$ apart, occurring at roughly $56^\circ 2\theta$ with FeK_α radiation. As the relative intensity of the peaks varied for the several specimens, the authors concluded that there was hexagonal pyrrhotite mixed with the monoclinic pyrrhotite, in agreement with the conclusions of Byström (1945). It is presumably not known whether this hexagonal pyrrhotite is the original high temperature form or the low temperature inversion product described by Grønvold and Haraldsen (1952). Groves and Ford found that when the sample is annealed at 600°C . for 18 hours, the single reflection produced by the hexagonal (102) peak coincides with "the reflection having the lower value of 2θ when both structural types (hexagonal and monoclinic) are present." They therefore conclude that measurement of the peak with the lower 2θ in the unannealed sample is adequate for determining the composition of the hexagonal pyrrhotite. This is not a generally valid conclusion. Moreover, if the sample is truly a mixture of monoclinic plus hexagonal pyrrhotite at low temperatures, then the measurement of only the "hexagonal" peak of the unhomog-

enized sample would not provide information on the original composition of the entire sample.

Recent work (Buseck, 1962b; Kullerud *et al.*, 1963) has shown that the position of the (102) reflection, and thus the composition of hexagonal pyrrhotite formed by annealing monoclinic material, is a function of the annealing procedure. The compositional changes during heating depend

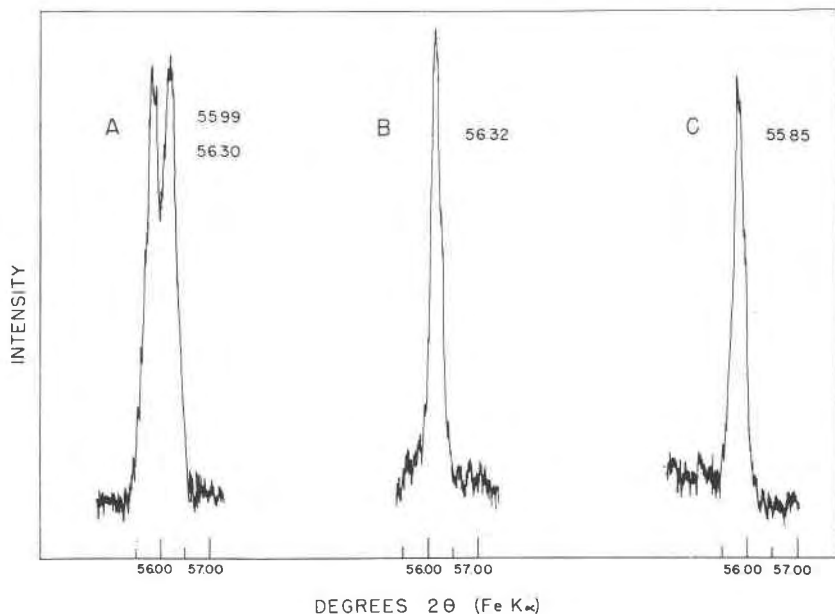


FIG. 1. X-ray diffraction patterns of the (102) reflections of hexagonal pyrrhotite ("B," "C") and the (202) and (202) reflections of monoclinic pyrrhotite ("A"). Sample "A" was annealed in an evacuated tube for 0.1 hours at 555° C. to produce "B" and for 100 hours at 346° C. to produce "C."

either on exsolution of pyrite from the pyrrhotite or on reaction with minor pyrite which may remain in the sample even after repeated magnetic separations. Which reaction does in fact occur is a function of the original pyrrhotite composition as well as the heating temperature and time. In order to minimize the effects of re-equilibration during annealing, it is best not to heat the samples above 470° C. or for periods longer than several minutes.

Since the d_{102} of hexagonal pyrrhotite obtained by heating can have varying values, depending on the heating history, and since it is probable that pyrrhotite heated at 600° C. for 18 hours will have partially re-equilibrated (Kullerud *et al.*, 1963), it is not generally valid to use such

material for determining the composition of the original pyrrhotite. Indeed, the single hexagonal peak produced by annealing monoclinic pyrrhotite may be made to approximate either of the original monoclinic peaks (Fig. 1), depending only on the annealing history of the pyrrhotite. If the lower monoclinic peak was considered coincidental with one produced by coexisting hexagonal pyrrhotite, as suggested by Groves and Ford, and so plotted on the curve of Arnold (1962), it would indicate a temperature of approximately 400° C., whereas the hexagonal pyrrhotite peaks produced by annealing would, in this instance, indicate temperatures ranging from below 350° C. up to 570° C. Thus the exact superposition that Groves and Ford found between one of the monoclinic pyrrhotite peaks and the hexagonal peak produced by annealing is probably fortuitous.

At the present time it appears as if the determination of the original composition of samples now containing monoclinic pyrrhotite presents serious difficulties, if *x*-ray methods are to be used; these may possibly be avoided if the samples are heat treated. However, even in this instance problems are likely to arise if, for example, there is incomplete homogenization, incomplete inversion of low temperature phases, or if there is re-equilibration with extraneous pyrite during heating. Until further work clearly defines the low temperature forms of pyrrhotite and their relation to the high temperature hexagonal variety, samples containing monoclinic pyrrhotite should be used for geothermometry only with the utmost caution if at all.

The writer is grateful to Drs. Gunnar Kullerud and Carleton Moore for reviewing the manuscript and making helpful suggestions.

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