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NEW OBSERVATIONS ON NATURAL PYRRHOTITES

Part II. Lamellar Magnetite in Monoclinic Pyrrhotite

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ABSTRACT

Monoclinic pyrrhotite from Norseman, Western Australia, has lamellae of submicrometer thickness, identified by microprobe and electron diffraction as magnetite. The lamella surface is (111) of magnetite parallel to (001) of pyrrhotite, corresponding to a close fit of close-packed planes of the two structures. The perfect lamellar nature of the magnetite in unaltered pyrrhotite indicates origin by exsolution, requiring solid solution of oxygen in earlier pyrrhotite.

It is generally assumed that iron oxides are insoluble in solid iron sulfides, and that all the oxygen present in the sulfide melt will crystallize as magnetite at the solidus (*e.g.*, Rosenqvist and Hynne, 1953). However, Naldrett (1969) observed a solid state reaction between magnetite and pyrrhotite, indicating some oxide solubility; and, as further evidence, we have observed a natural occurrence of extremely fine magnetite lamellae which are oriented parallel to the basal plane of monoclinic pyrrhotite in a drill core from Norseman in Western Australia.

The pyrrhotite was sectioned at a small angle to the basal plane, giving an effective magnification of the width of the lamellae. They are shown in Figure 1. Identification was difficult because of the extremely fine nature of the lamellae. However, one lamella expanded out into an area several micrometers wide (Fig. 1b), and this could be positively identified optically and by microprobe. In addition, a microprobe traverse across a lamella showed a qualitative dip in the sulfur/iron ratio as expected for magnetite. Titanium was not present.

We believe that the perfect lamellar nature of the magnetite in unaltered monoclinic pyrrhotite argues a primary exsolution origin,

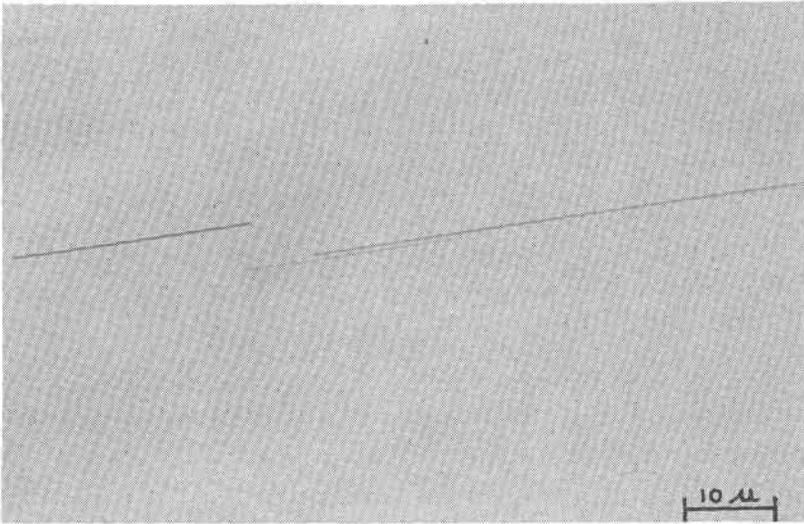


FIG. 1a

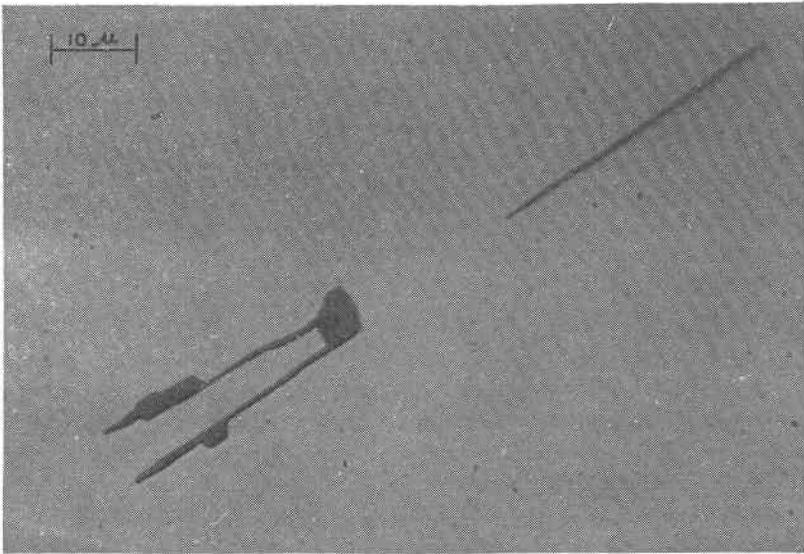


FIG. 1b

FIG. 1. Magnetite lamellae in monoclinic pyrrhotite. (a) Fine lamellae which are abundant throughout the specimen. (b) Broader lamellae which allowed positive identification. Occasional lamellae of intermediate thickness are also observed in this specimen.

although some secondary alteration to smythite is occurring in nearby parts of the sample.

Such lamellae are not commonly observed, probably because in most pyrrhotites they are too fine to be seen. This may be due to the close fit between a (111) magnetite oxygen layer and the (001) pyrrhotite sulfur layer. Thus d_{100} for pyrrhotite = 2.966\AA = d_{220} for magnetite, so that layers of close-packed oxygens will fit if rotated by 30° with respect to the close-packed sulfur lattice. In this orientation, normal metal sites in the pyrrhotite layer coincide in projection with the positions of iron atoms of the tetrahedral interlayer in magnetite (see Fig. 2). There are two kinds of tetrahedrally coordinated iron atoms in the interlayer space in magnetite, one coordinated with three atoms in the layer above, and the other with three atoms in the layer below. A third site is occupied by octahedrally coordinated iron as shown. It can be seen from the diagram that one of the tetrahedral sites (*T*) will remain tetrahedral in a magnetite/pyrrhotite interface while the other will be in an octahedral environment (distorted towards a trigonal prism) similar to that of the octahedral iron atoms (*O*).

The perfect epitaxy would result in a low interfacial energy which would make extremely fine lamellae relatively stable. The Norseman sample is unusually well crystallized (the pyrrhotite grains are ~ 2.5 cm in diameter) and during the recrystallization process, aggregation of the oxygen layers must have occurred, giving visible magnetite.

In order to verify the proposed relationships, a surface with the lamellae nearly vertical was etched for up to 5 minutes with 0.01M HCl saturated with bromine. This etch dissolved the pyrrhotite surface, leaving the magnetite proud of the surface. The glancing angle electron diffraction technique was used to observe diffraction with the beam incident at right angles to the (001) plane of pyrrhotite and the (111) plane of magnetite. Immediately prior to the diffraction experiment, the specimen was washed in 30 percent acetic acid, followed by water and acetone.

The zero layer reflections from pyrrhotite and magnetite are identical in spacing, and if the magnetite has the orientation proposed above, this layer will have a hexagonal diffraction pattern with a spacing of 0.337\AA^{-1} . The magnetite can be recognized in this orientation from the fact that the Ewald sphere cuts the first layer of its reciprocal lattice at some distance from the direct beam, and these first layer magnetite spots should project into the centers of triangles of spots in the zero layer, unlike the superlattice reflections from the first layer of the pyrrhotite. This is exactly what is observed,

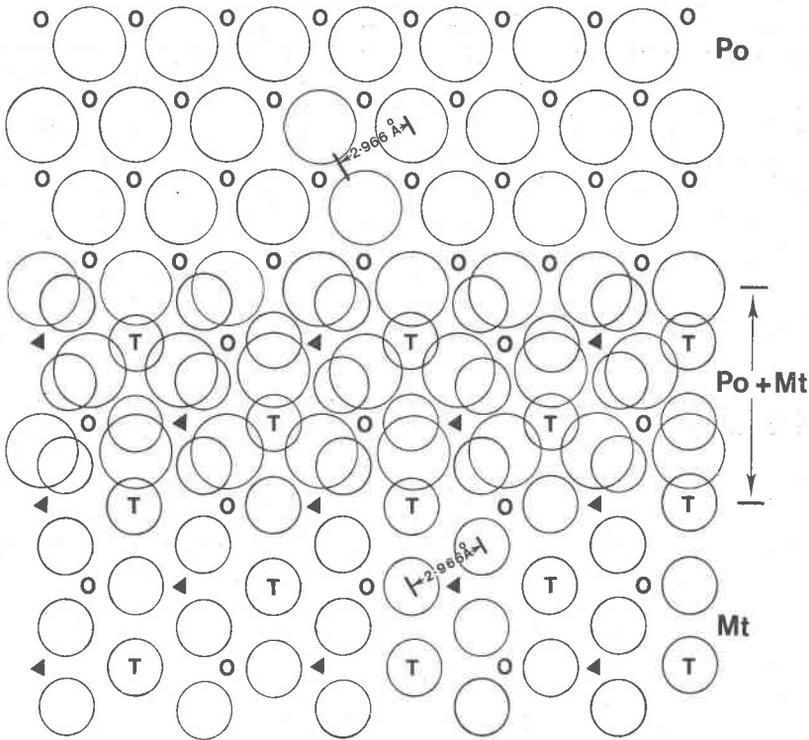


FIG. 2. Projection of one non-metal layer and its adjacent metal layer of atoms on the close packed planes of pyrrhotite (Po) and magnetite (Mt). The layers are overlapped in the center to show the fit between the lattices, and the site symmetry of the metal atoms at an interface between magnetite and pyrrhotite. Large circles are sulfur and smaller circles oxygen. O is an octahedral iron atom and triangles and T's are tetrahedral iron atoms in the individual structures. The equal spacings, d_{100} for pyrrhotite and d_{200} for magnetite, are indicated on the diagram.

but the higher layer magnetite spots are extended perpendicular to (111) suggesting that in addition to the visible magnetite lamellae, there is a reasonable concentration of fine magnetite lamellae with thickness of the order of only tens of angstroms.

We have already pointed out (Bennett, Graham, and Thornber, 1972) that the visible lamellae of magnetite are unlikely to explain fully the anomalous magnetic properties of pyrrhotite, but they should be born in mind in interpreting magnetic susceptibility measurements in this system. The explanation may lie in the fine-scale sub-visible structure suggested in the previous paragraph.

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THE CRYSTAL STRUCTURE OF TILASITE

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ABSTRACT

The crystal structure of the mineral tilasite, $4[\text{CaMg}(\text{AsO}_4)\text{F}]$, has been determined and found to be very similar to that of sphene, as was predicted by Strunz in 1937. The structure refinement shows tilasite to be slightly noncentric, however, and its space group is *Cc*.

INTRODUCTION

Tilasite, $4[\text{CaMg}(\text{AsO}_4)\text{F}]$, was originally described by Sjögren (1895) from an occurrence at Långban, Sweden. Piezoelectric evidence (Smith and Prior, 1911) indicated tilasite to be noncentric. Based on similarity of chemical formulas, morphology, and unit cells, Strunz (1937) proposed the analogy of the structure of tilasite to that of sphene, which had been determined in the centric space group *C2/c* by Zachariassen in 1930. Williams (1970) redescribed tilasite from a new occurrence at Bisbee, Arizona, and commented on its noncentric morphology. The present study was initiated in an attempt to resolve the confusion over the inclusion of apparently noncentric tilasite in the group with centric sphene.