

NEW OBSERVATIONS ON NATURAL PYRRHOTITES PART I. MINERAGRAPHIC TECHNIQUES

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ABSTRACT

A detailed study of several natural monoclinic pyrrhotites, some from areas of nickel mineralization, has shown ubiquitous fine-scale twinning which is associated with a magnetic domain structure. A sulphur-rich phase (smythite at room temperature) may be exsolving as a submicroscopic intergrowth, perhaps by a spinodal mechanism, to give the observed optical and magnetic domain structures and to account for the magnetic reversal phenomenon. The inter-laminated monoclinic pyrrhotite/smythite assemblage may be stabilized by a large coherent energy term. The twin or magnetic domain boundaries can then be places of coherent nucleation of phases such as pentlandite and violarite during both exsolution and alteration processes.

INTRODUCTION

Two recent reviews of the iron-sulphur system (Taylor, 1970a; Ward, 1970) have shown the vast amount of effort that has been put into the study of pyrrhotite, and the large number of questions which still remain to be answered.

This paper is an attempt to clarify the mutual relationships between hexagonal and monoclinic pyrrhotite, and the closely related mineral smythite. In this way we try to correlate and explain the following unusual properties of natural "monoclinic" pyrrhotite:

- (a) The fine-scale lamellar twinning commented on by Arnold (1967) which we have found to be ubiquitous.
- (b) The lamellar arrangement of magnetic domains first reported by Besnus (1959).
- (c) The magnetic reversal phenomena described by Bhimasankaram and Lewis (1966), whereby certain pyrrhotites may become magnetized in the opposite direction to the magnetizing field.
- (d) The lamellar or flame-like exsolution or intergrowth of various phases with pyrrhotite.
- (e) The exsolution of pyrite in the phase field of Fe_7S_8 pyrrhotite by the application of stress (Graf and Skinner, 1970), which with other evidence (Arnold, 1969; and Yund and Hall, 1969) suggests that monoclinic pyrrhotite may be metastable over a wide temperature range.

The samples to be discussed have mainly come from a limited area in the Eastern Goldfields of Western Australia. All have been characterized by X-ray powder diffraction using a Hagg-Guinier focussing camera, and the monoclinic phase is always the $4C$ type with cell dimensions equal within experimental error to those quoted by Corlett (1968) ($a = \sqrt{3}A = 11.880 \text{ \AA}$; $b = 2A = 6.852 \text{ \AA}$; $c = 4C = 22.738 \text{ \AA}$, and $\beta = 90^\circ 38'$). The details of the supercell are not important to the argument, but the nickel arsenide type subcell, with its slight monoclinic distortion, is a basic consideration.

OBSERVATIONS

Oriental Variations

There are six equivalent directions in which the monoclinic distortion can occur. This is shown schematically in Figure 1, where (a) shows the undistorted structure with the c axis normal to the ab planes. In (b) the ab planes are still parallel to each other but the monoclinic distortion has taken place in a number of directions. As a result, the lattice above the plane u is misoriented with respect to that between planes u

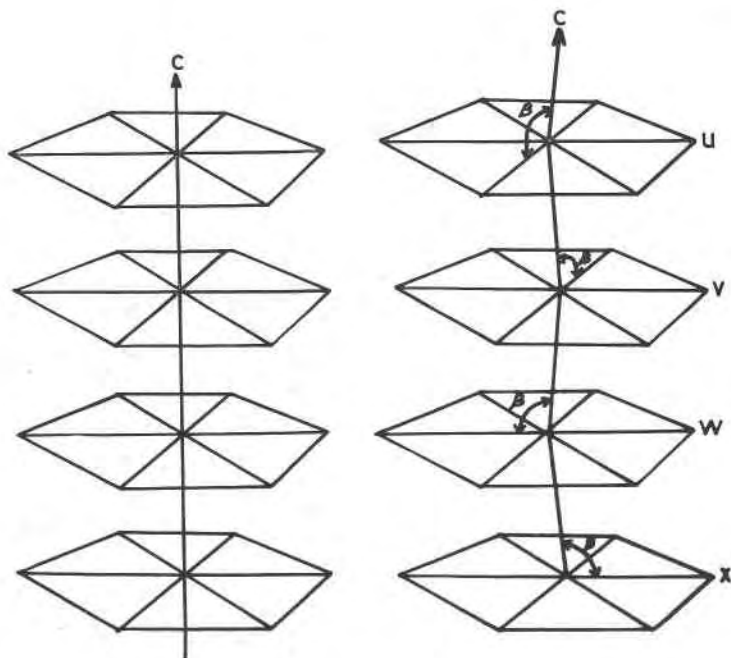


FIG. 1. (a) Schematic representation of the axis in a hexagonal structure, (b) the monoclinic distortion giving rise to lamellar twinning.

and v , etc. We believe this to be the major explanation for the finely laminated appearance of the monoclinic pyrrhotite crystals, and it will be referred to as "lamellar twinning". The simple twin law described by Wuensch (1963) would allow only two orientations to be present. Although we have observed many crystals with two orientations predominating, many others have at least four, and probably all six orientations present (Corlett, 1968). These observations require single crystal X-ray techniques. Fragments examined by the Weissenberg technique show that lamellar twinning is approximately parallel with the ab crystallographic plane. Since the ab planes are all parallel, the c^* axes of all lamellae are collinear, and the $00l$ reflections will appear as a single reflection while the other sublattice reflections will have degenerated into anything up to four spots, depending on the number of the six possible orientations that are present.

Other types of misorientation are often present, in which the ab planes are no longer parallel so that the $00l$ reflections show several spots. These will be referred to as "macro misorientations", and no doubt include the $(10\bar{1}1)$ twins referred to in Palache, Berman, and Frondel (1944, p. 231-234).

Figure 2 shows the 004 and 100 subcell reflections for a crystal fragment which has only lamellar twinning, (a), and for a fragment which also includes other misorientations, (b). In the latter case the 004 reflection shows a line of spots, each elongated parallel to the rotation axis. This indicates that in each subcrystal there is a range of crystal orientations over 1 or 2° in accord with the subparallel and slightly curved appearance of the lamellae. There is some optical evidence that the curvature may be due to a second set of lamellar twinning on another plane.

The lamellar microstructure can be observed after very careful polishing of pyrrhotite surfaces, especially under crossed nicols in oil immersion (Figure 3a). It can be developed by etching at 60°C for three minutes with a solution of 25 HCl, 7 thiourea, and 68 weight percent water (Fig. 3c), or with the usual chromate etch which is used for distinguishing hexagonal pyrrhotite. Although the lamellae undergo differential etching by this treatment, not all the "macro misorientation" boundaries have etched.

Magnetic Domains

Regions of high magnetic intensity, or domain boundaries, can be observed by placing a suspension of colloidal magnetite in water on the surface (Fig. 3b). This is the Bitter technique (Bitter, 1932); the colloidal magnetite can be prepared by the method of Gustard (1967),

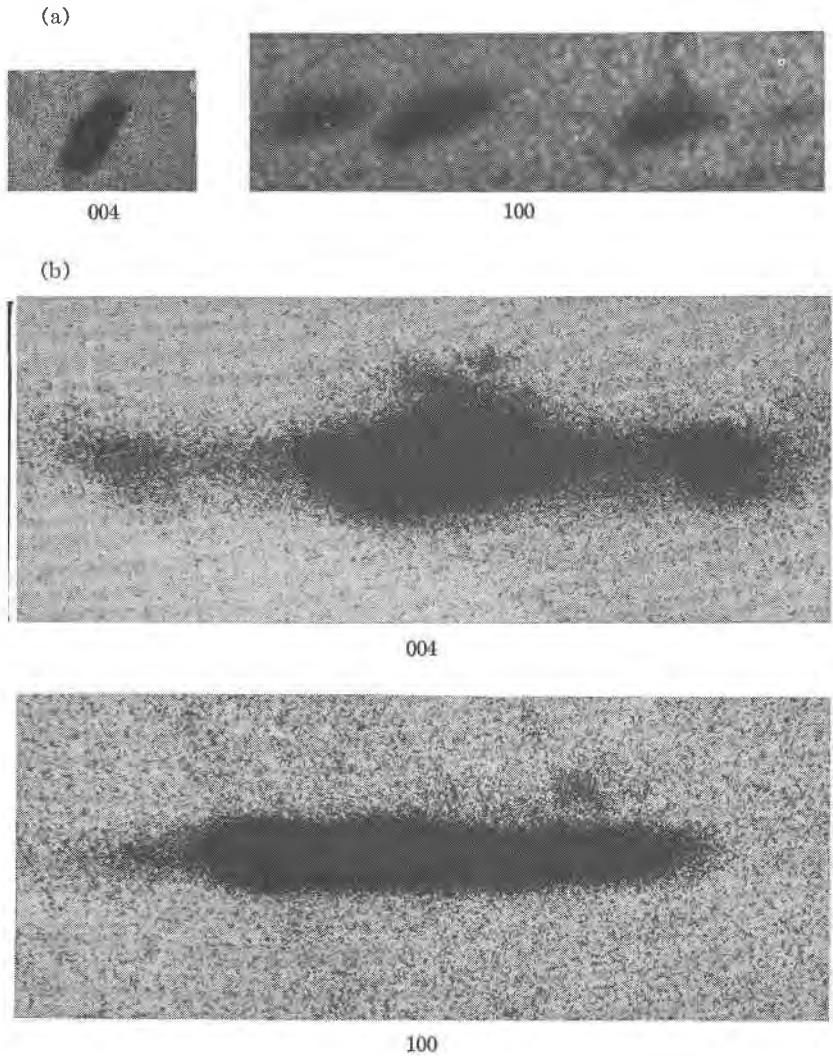


FIG. 2. (004) and (100) Weissenberg reflections from the subcell of fragments of monoclinic pyrrhotite, (a) lamellar twinning, (b) other misorientations.

except that the colloid is suspended in water plus detergent. The magnetic boundaries also are usually lamellar, and can often be correlated with the boundaries of the monoclinic lamellae. The "macro" boundaries are not delineated by the colloidal magnetite, and magnetic discontinuities generally pass through them. This is consistent with the fact that the (00 l) plane is the easy magnetic direction (Hihara, 1960).

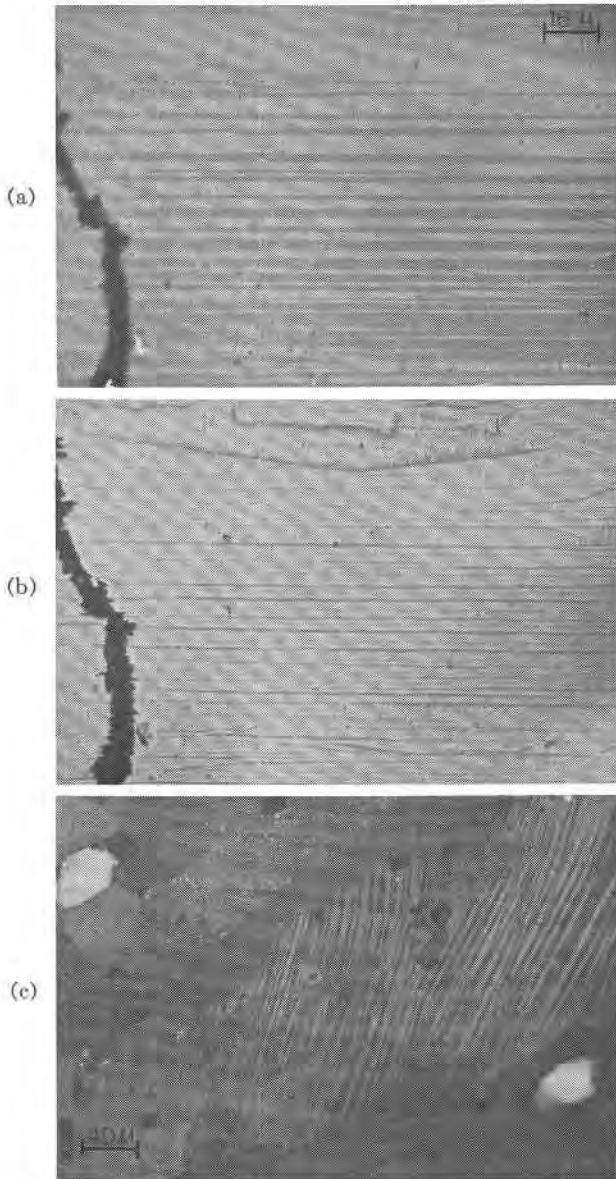


FIG. 3. Typical appearance of lamellar twinning in monoclinic pyrrhotite from Kambalda, Western Australia, (a) unetched, crossed nicols, (b) magnetic colloid on unetched surfaces, (c) another specimen etched with thiourea etch.

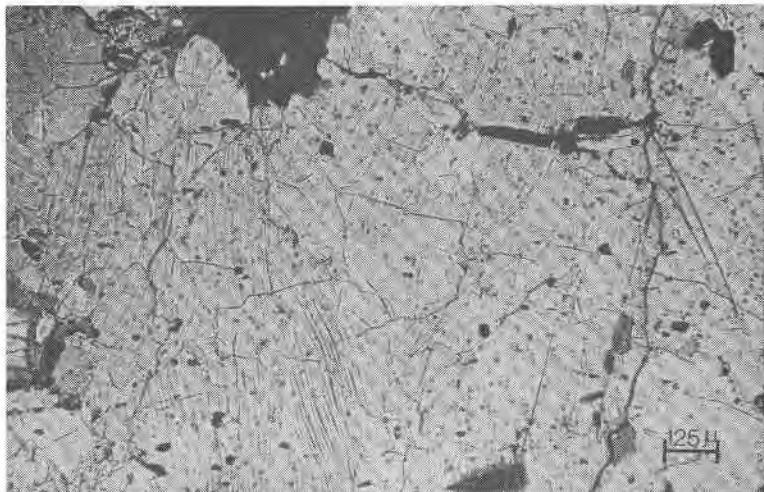


FIG. 4. Lamellar twinning brought out by heating to 300°C in air.

Figure 4 shows laminar domains emphasized by surface oxidation. The same structure is made visible by colloidal magnetite suspension, suggesting that the magnetic boundaries are associated with some structural feature which shows differential resistance to oxidation.

Magnetic Reversal in Intergrown Phases

First mentioned by Lotgering (1956), this property has been best described by Bhimasankaram and Lewis, 1966. On cooling a pyrrhotite specimen from 600°C in a weak magnetic field, two Curie temperatures are observed at about 560°C and about 310°C (there is slight disagreement on the exact values). If the external field is removed or reduced at a temperature just above the lower Curie temperature (say, 330°C), a reversal of magnetic direction will take place on further cooling, and the specimen will become magnetized in a direction opposite to the original field.

This phenomenon can be explained if the pyrrhotite is a lamellar intergrowth of two phases. It is generally agreed that the low temperature Curie point is a property of the monoclinic pyrrhotite phase, but the origin of the Curie point at 560°C is in dispute. It must be a strongly magnetic phase, and magnetite has been suggested (Schwarz, 1965). However, 1 percent of this phase is needed to explain the anomaly (Bhimasankaram and Lewis, 1966), and this has never been observed in polished section. We shall return to this point again.

Further evidence from Bhimasankaram and Lewis (1966) relevant to the identity of the second phase follows:

- (a) Heating the specimen in air causes an increase in the amount of the phase with the higher Curie temperature. (Is this connected with the "thermal etching" shown in Figure 4?)
- (b) The higher Curie temperature phase can be removed by severe leaching of the sample with 50 percent HCl, but reappears on heating at 590°C in a vacuum.
- (c) It is not clear whether these measurements are characteristic of all monoclinic pyrrhotites, as the samples seem to have been carefully selected. Synthetic pyrrhotite gave the same results, but as there was oxygen in the iron used, the samples could contain iron oxide, or be sulphur rich.

An alternative explanation might be sought in terms of the magnetic exchange coupling between the iron atoms in the pyrrhotite structure, but this suffers from the disadvantage that it seems to depend too critically on vacancy ordering at temperatures where such ordering is unlikely.

Controls of Exsolution Phases

The cooling sequence in a magmatic ore body is usually discussed in terms of the equilibrium assemblages as determined, for example, by Kullerud and others, and documented in the Year Books of the Carnegie Institution. However, in interpreting the mineragraphy of an ore body, mechanisms and rates of exsolution come into consideration (Naldrett and Kullerud, 1967). Yund and McCallister (1970) have recently applied exsolution theory to mineral systems, and point out the importance of the strain energy that is built up because of the difference in structure and volume between a nucleating phase and the matrix. The precipitating phase will tend to exsolve in an orientation which minimizes the strain energy, and this is especially important where coherence is possible between the phases. Where the structure of the equilibrium precipitate phase has a high energy interface with the matrix, coherence between an intermediate nucleating phase and the matrix may result in a low enough strain energy to stabilize the intermediate phase, which can then exist metastably over a wide range of conditions.

In the present context, precipitation from the high temperature monosulphide solid solution (mss) is of prime interest. This is a NiAs-type phase, which can tolerate considerable variation in the metal to sulphur ratio, as well as a variety of cations such as Zn, Ni, Cu, Cr, and Co, some of which can replace iron in all proportions. At lower temperatures, the composition range is much narrower, and

various other metal sulphides are stable. Those of major interest in an ore body would be chalcopyrite, pyrite, pentlandite and the various pyrrhotites. Although magnetite is said to separate from the liquid sulphides above 934°C (Naldrett, 1969), we will consider this also as a possible exsolution phase.

Coherency is likely between sulphides whose structures are based on close packing of sulphur atoms, and the close-packed (111) planes of cubic structures are likely to be parallel to the basal planes of hexagonal structures. The limit of coherency will be a function of the misfit between these two close-packed planes. Table 1 compares idealized S-S distances within the close-packed planes of selected minerals that are likely to exsolve from the mss. Violarite is included, although the occurrences we have studied are more likely to be due to supergene alteration of pentlandite and pyrrhotite. The figures are taken from the Powder Data File (1970) and the data of Morimoto *et al.* (1970).

The lamellae may be very thin; for example, if the magnetic reversal results were due to 1 percent of magnetite precipitated at twin boundaries in the pyrrhotite $\sim 6\mu\text{m}$ apart, the magnetite would be

TABLE 1

Idealised S-S distances within the close-packed planes, and interplanar distances, of minerals which may have a coherent interface with monoclinic pyrrhotite.

	Mineral	S-S distance	Interplanar Spacing
FeS	Troilite	3.44 Å	2.94
Fe ₁₁ S ₁₂	"Hexagonal Pyrrhotite"	3.45 Å	2.88
Fe ₁₀ S ₁₁		3.45 Å	2.87
Fe ₉ S ₁₀		3.44	2.87
Fe ₇ S ₈	Monoclinic Pyrrhotite	3.43 Å	2.85
Fe ₉ S ₁₁	"Smythite"	3.46 Å	2.86
Fe ₃ S ₄		3.46 Å	2.87
Fe ₃ O ₄	Magnetite	(3.42) Å *	
(Fe,Ni) ₉ S ₈	Pentlandite	3.55 Å	2.90
(Fe,Ni) ₃ S ₄	Violarite	3.35 Å	2.73

* Equivalent repeat distance for oxide: O-O distance $\times \frac{\sqrt{3}}{2}$

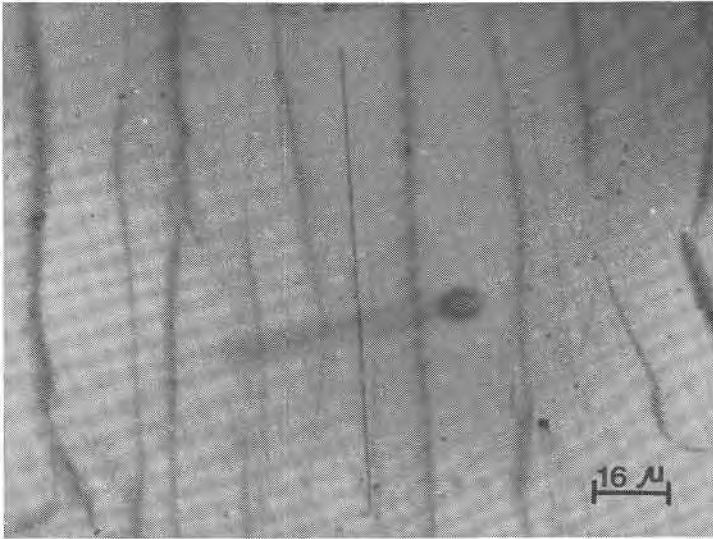


FIG. 5. Pyrrhotite from Norseman, with the c axis nearly vertical and magnetic colloid added, showing a magnetic lamina as a straight line compared with the more irregular magnetic domain boundaries.

$\sim .06\mu\text{m}$ wide. This will affect both the breadth and the intensity of X-ray reflections from the phase in question.

Magnetite Intergrowths. A magnetite lamella $.06\mu\text{m}$ thick would be beyond optical resolution unless it was sectioned obliquely. Although we have observed lamellar magnetite, we believe that subvisible magnetic cannot be associated with the majority of the magnetic domain boundaries in pyrrhotite, because of its strictly planar habit. As shown in Figure 5, (which is an oblique section), the magnetic boundaries tend to be wavy, and there is no apparent relation between the magnetic domain boundaries and the visible magnetite.

Pentlandite Intergrowths. Lamellae of pentlandite within a pyrrhotite matrix are commonly reported (Naldrett and Kullerud, 1967; and Fleet and Macrae, 1969). The flame-like growth tends to be along the pyrrhotite basal plane.

Violarite Intergrowths. Craig (1967) and Bird (1969) have reported violarite lamellae within a pyrrhotite matrix. During supergene alteration, violaritization occurs along the pyrrhotite basal planes. Evi-

dence for a very fine intergrowth of violarite and pyrrhotite is provided by single crystal diffraction as in Figure 6.

Smythite Intergrowths. Erd *et al.* (1957) in their comprehensive report on smythite (Fe_3S_4) make the point that it is practically indistinguishable from pyrrhotite. It is similar morphologically and structurally, and is also subject to microtwinning on the basal plane. Taylor (1970b) has described a material of composition approximately Fe_9S_{11} , which is more typical of most occurrences, and the optical properties have been described by Nickel and Harris (1970). All the structures are based on the NiAs-structure with different distributions of iron vacancies in planes parallel to (00*l*), and all would be expected to interlami-

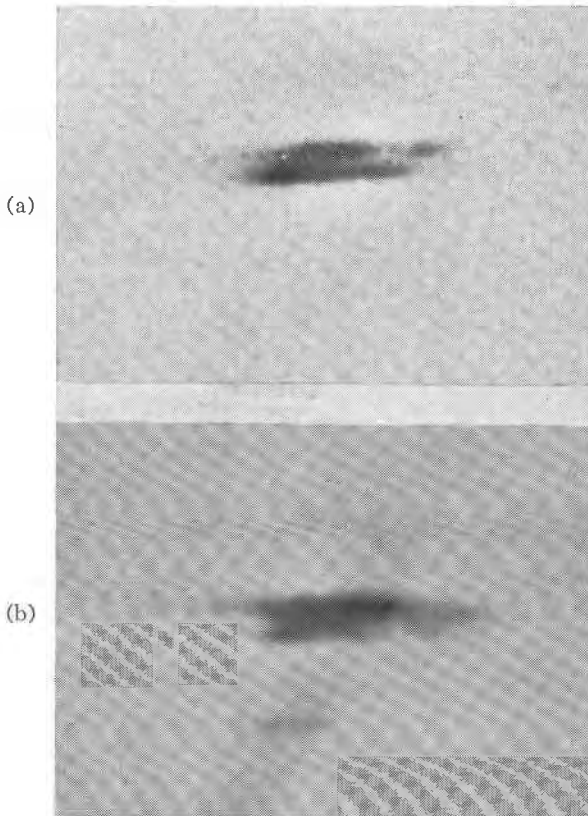


FIG. 6. (110) Weissenberg reflections from crystals with intimate intergrowth of pyrrhotite and smythite as shown by the splitting. The diffuse smear above is probably due to violarite. (a) is from Norseman, (b) from Kambalda.

nate freely. We have observed smythite of Taylor's composition, verified by microprobe analysis, in the Norseman drill core sample (Figure 7) and in numerous supergene ores from Kambalda, and are currently working on methods to differentiate the various NiAs-related phases. The fine lamellae of smythite shown in Figure 7 appear to be an alteration product of pyrrhotite. Smythite also appears as an intermediate phase during the violaritisiation of pyrrhotite. We assume that the main features of the diffraction pattern of Taylor's smythite do not differ greatly from those of Erd *et al.*, and use the 110 subcell reflection as a diagnostic line for smythite in powder patterns. It is well resolved from the main pyrrhotite reflections and should not interfere with the 606 superstructure reflection at 1.747Å. Care must be taken to establish that there is no siderite present as a contaminant as this has a strong reflection with a "d" spacing the same as the 110 smythite spacing. Figure 6 shows the 110 Weissenberg reflections of crystals from (a) Norseman, and (b) Kambalda. Both show the main spot slightly split, as expected from an intimate intergrowth of smythite and pyrrhotite (the $\alpha_1 - \alpha_2$ splitting is not visible at this diffraction angle). The 100 and 200 reflections are not split, but the 300 and 110 are, because of the pseudorhombohedral symmetry of smythite. Diffuse 1.0.10, 1.0.13, 0.1.11, and 0.1.14 reflections are also observed, which accounts for most of the intense smythite reflections. Smythite ap-

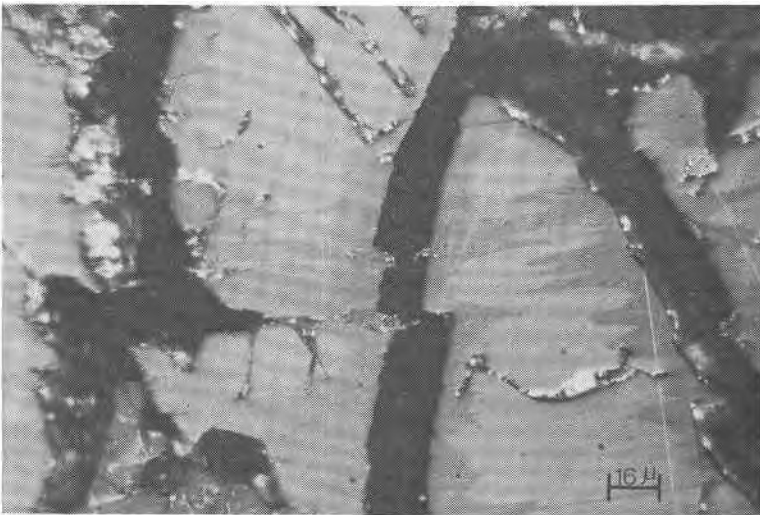


FIG. 7. Fine interlaminations of smythite in monoclinic pyrrhotite. Unetched with crossed nicols and oil immersion.

pears lighter in colour than pyrrhotite in ordinary light, and when etched for 8 minutes at 50°C with a saturated CrO₃ solution it becomes isotropic and easily differentiated from the pyrrhotite.

A small piece of smythite prised from a crack in this region gave rotation and Weissenberg patterns having a hexagonal pseudo-cell with a_0 approximately 3.47Å and c_0 approximately 34Å, corresponding to the smythite cell. The superlattice reflections, however, could be divided into two groups having different shapes, suggesting two crystals or a twin, so the true cell is in doubt. In spite of apparent rhombohedral absences, the true symmetry seems to be hexagonal or lower, in agreement with Taylor (1970b).

DISCUSSION

Magnetic Reversals

One of the phases described above is a strong contender as an interlamination with pyrrhotite to explain the magnetic reversal results. It should have a magnetic ordering temperature of about 570°C. On cooling through this temperature in a magnetic field, this phase will become magnetized parallel to the field. If the external field is now switched off, the reverse field from this component will pass through the pyrrhotite phase, as shown in Figure 8a, magnetizing it when the temperature reaches the pyrrhotite Curie temperature. The efficiency of this magnetic reversal process will be greatly impaired, as shown in Figure 8b, if the lamellae are not more or less continuous throughout the pyrrhotite. This rules out magnetite as the magnetic phase, and in the pure Fe-S system only smythite is left to fulfill this role. A small nickel impurity would perhaps be enough to provide thin lamellae of violarite, but this could not explain Bhimasankaram and Lewis's (1966) results on synthetic samples.

Pyrrhotite containing 2 percent of smythite would have a composition corresponding to the formula Fe_{6.99}S₈, extremely difficult to distinguish from Fe₇S₈. It may be significant that the majority of our microprobe analysis of Kambalda pyrrhotites are slightly sulphur-rich compared to Fe₇S₈.

It is observed that heating to 350°C, cooling, and re-polishing does not change the position of the magnetic domain boundaries. This would be expected if the boundaries are associated with compositional variations, but would not be expected for pure domain boundaries controlled by the pyrrhotite Curie temperature of 310°C. In addition, the domain boundaries are observed microscopically to remain fixed when the sample is magnetised.

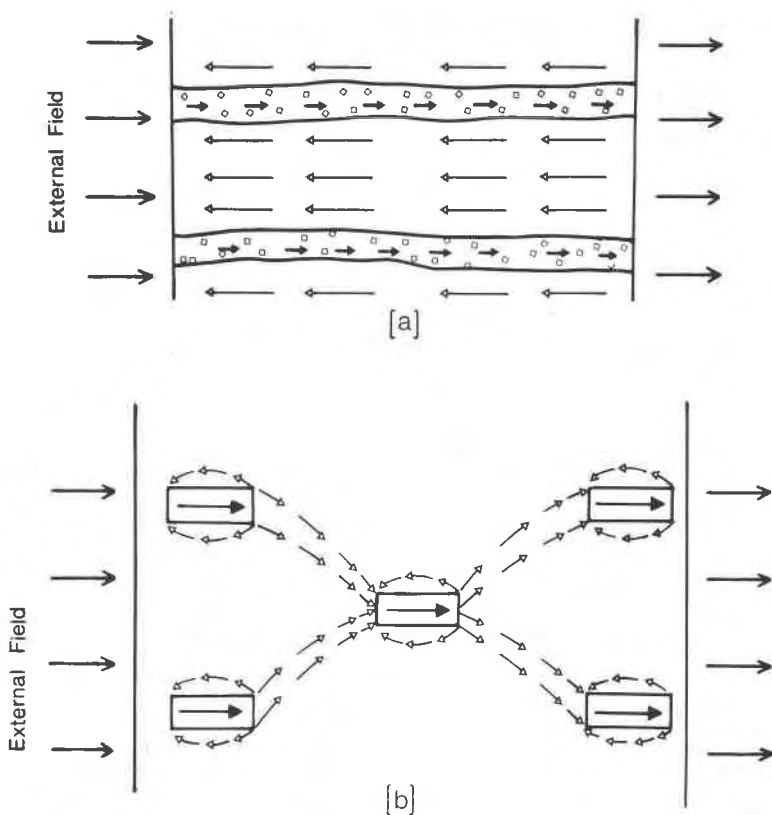


FIG. 8. Magnetic fields due to laminar intergrowths. (a) Continuous interlamination results in magnetic reversal, because the low curie temperature phase (white) is cooled in the back field of the previously magnetised high temperature phase (stippled). (b) Discontinuous lamellae cannot reverse the field.

Understandably, the Curie temperature of the strongly magnetic smythite is not known, as this mineral is normally unstable above 75°C with respect to pyrrhotite and pyrite. However, it is probable that the coherent energy term between pyrrhotite and smythite would be large enough to stabilize the very narrow lamellae proposed. (Table 1 gives an indication of the closeness of fit of the two lattices). Because of the close structural similarity between the two minerals, there is a possibility that the vacancy layers of iron atoms can be dislocated, allowing the phase boundaries to be only sub-parallel to the (001) plane.

The ordering temperature for vacancies in pyrrhotite and smythite is likely to be of the order of 300°C , as for the β transition in hexa-

gonal pyrrhotite, so that at temperatures higher than this the structure should revert to disordered iron-rich and iron-deficient pyrrhotite. The high-temperature magnetic transition may then correspond to the appearance and disappearance of the segregated structure rather than to a true Curie temperature. It would vary with overall composition, probably paralleling the pyrrhotite-pyrite solvus, accounting for the difference of 18° between Bhimasankaram and Lewis's (1966) results and those of Schwarz (1965).

Pyrrhotite Stability

Two unresolved problems in the literature may be correlated with a theory of genesis for the kind of structure proposed.

- (a) Graf and Skinner (1970) showed that application of shear stress at 200°C and above to quenched material of Fe_7S_8 composition caused pyrite to exsolve from the hexagonal pyrrhotite.
- (b) The stability of monoclinic pyrrhotite has also been questioned on other grounds. Arnold (1969) reviews this matter, and Yund and Hall (1969) have added some further comments. Basically, the evidence is that monoclinic and hexagonal pyrrhotite and pyrite (plus vapor) develop experimentally at a range of compositions; there is a sharp decrease in the amount of monoclinic pyrrhotite as pyrite first appears, allegedly showing that monoclinic pyrrhotite is metastable, at least at temperatures above about 200°C .

In view of the structural difference between pyrite and pyrrhotite, it is reasonable to assume that some supersaturation could occur on cooling through Arnold's (1962) solvus. This supercooling could well be sufficient to bring a metastable solid solution within a spinodal region where it would become unstable with respect to compositional fluctuations, and alternating iron- and sulphur-rich volumes with the defect NiAs structure would result.¹ The iron-rich regions could favour nucleation of hexagonal pyrrhotite at low temperatures, and the sulphur-rich regions could favour nucleation of smythite or pyrite depending on the conditions. Monoclinic pyrrhotite could nucleate from either phase, according to composition, lowering the free energy available to reach final equilibrium. The phases could be intergrown on any scale, the limit being a single unit cell thickness as observed

¹Such a spinodal would be formed within a solid solution having the NiAs structure, which extends metastably at least to the FeS_2 composition (*cf.* $\text{Cd}(\text{OH})_2$ structure). The full range of this solid solution is not seen in the equilibrium diagram because of the interference of the stable stoichiometric compound pyrite.

in some oxide systems (*e.g.* Allpress and Wadsley, 1969), and the limits of stability of individual minerals could be greatly affected. However, in the case of Fe_7S_8 compositions, we believe it is the assemblage which is metastable, rather than the monoclinic pyrrhotite itself, and this could explain the results of Arnold (1968) and Yund and Hall (1969). In both cases, starting materials were quenched from the homogeneous hexagonal pyrrhotite region before annealing. If this thermal treatment results in some compositional segregation, pyrite will precipitate from the most sulphur-rich regions, leaving an iron-rich pyrrhotite which is hexagonal. In addition, the application of shear stress would cause loss of coherency between metal-rich and metal-deficient regions, causing precipitation of pyrite, as observed by Graf and Skinner (1970).

CONCLUSIONS AND GEOLOGICAL IMPLICATIONS

If the amount and distribution of these magnetic domains can be easily and unambiguously determined, they may provide a useful tool in determining the geological sequence of events in a particular sample. We assume that spinodal compositional variations are introduced when a pyrrhotite assemblage is cooled from temperatures of about 600°C or more through the pyrrhotite/pyrite solvus, and that lamellar twinning is caused by cooling below the upper stability limit of monoclinic pyrrhotite—about 295°C —as described in Figure 1. During the hexagonal to monoclinic transition, a new “*c*” direction (*i.e.*, a twin boundary) may be introduced when a sulphur-rich lamella is encountered by the transforming phase, or when the stress has built up to unacceptable proportions. The former is likely to result in multi-component twinning, since the deformation is not limited by stress, whereas the latter may result in two twin orientations only. According to this model, sulphur-rich pyrrhotite which had cooled from a high temperature would have a smythite-like phase associated with the twin boundaries, which would provide a structural control for the magnetic domain boundaries. This material would show magnetic reversal phenomena. If the excess sulphur had been introduced below the pyrrhotite/pyrite solvus, entirely different properties would result. At this stage one can only conjecture whether a similar argument may hold for pyrrhotite of overall composition exactly corresponding to the formula Fe_7S_8 ; in the absence of compositional variations one would expect relatively mobile magnetic domains (Kittel, 1966), although the twin boundaries would still exert some control. Thermomagnetic behaviour would be normal. Thus the microstructure arising from sulphurization, sedimentation or other processes

that occur below either of the Curie points, may differ from that due to cooling of a melt. Its influence could extend not only to exsolution phenomena, but also to supergene alteration mechanisms and to other post-depositional processes such as the uptake of nickel during serpentinization of surrounding rocks (Ewers, 1971). For example, the origin of banding in the massive ore zones of the nickel ore body at Kambalda (Travis and Woodall, 1968) is not known, but it is usual to find that all the minerals are similarly banded. In some other samples there is little trace of the macroscopic banding; the pyrrhotite appears to be massive and the pentlandite forms transverse veins similar to the veins of silicate/carbonate gangue that are also present. However, within the pyrrhotite, the lamellae are still aligned parallel to the ore contact. Is there a suggestion of a secondary origin for the pentlandite in the latter sample, or has this some other significance?

It is apparent that much more work needs to be done, both in characterizing the lamellae and in interpreting their meaning. We are continuing to work in these directions. In particular, the magnetic reversal work is being tackled with a view to correlating it with the microstructure and phases present, and it will be published as Part II of the present paper. Further work is also projected on the relationship of the phases pentlandite-violarite-smythite.

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REFERENCES

- ALLPRESS, J. G., AND A. D. WADSLEY (1969) Multiple phase formation in the binary system $Nb_2O_5-WO_3$. VII. Intergrowth of $H-Nb_2O_5$ and $WNb_{12}O_{38}$. *J. Solid State Chem.* **1**, 28-38.
- ARNOLD, R. G. (1962) Equilibrium relations between pyrrhotite and pyrite from 325° to 743°C. *Econ. Geol.* **57**, 72-90.
- (1967) Range in composition and structure of 82 natural terrestrial pyrrhotites. *Can. Mineral.* **9**, 31-50.
- (1969) Pyrrhotite phase relations below $304 \pm 6^\circ\text{C}$ at < 1 atm total pressure. *Econ. Geol.* **64**, 405-419.
- BESNUS, M. J. (1959) Structure magnétique de la pyrrhotine. *C. R. Acad. Sci. Paris.* **248**, 1634-1637.
- BHIMASANKARAM, V. L. S., AND M. LEWIS (1966) Magnetic reversal phenomena in pyrrhotite. *Geophys. J. Roy. Astr. Soc.* **11**, 485-497.

- BIRD, W. H. (1969) A note on the occurrence of violarite, Copper King mine, Boulder Country, Colorado. *Econ. Geol.* **64**, 91-94.
- BITTER, F. (1932) Experiments on the nature of ferromagnetism. *Phys. Rev.* **41**, 507-515.
- CORLETT, M. (1968) Low-iron polymorphs in the pyrrhotite groups. *Z. Kristallogr.* **126**, 124-142.
- CRAIG, J. R. (1967) The Fe-Ni-S System, violarite stability relations. *Carnegie Inst. Wash. Year Book*, **66**, 434-436.
- ERD, R. C., H. J. EVANS JR., AND D. H. RICHTER (1957) Smythite, a new iron sulphide and associated pyrrhotite from Indiana. *Amer. Mineral.* **42**, 309-333.
- EWERS, W. E. (1972) Nickel-iron exchange in pyrrhotite. *Aust. Inst. Mining Met. Proc.*
- FLEET, M. E., AND N. MACRAE (1969) Two-phase hexagonal pyrrhotite. *Can. Mineral.* **9**, 699-705.
- GRAF, J. L. JR., AND B. J. SKINNER (1970) Strength and deformation of pyrite and pyrrhotite. *Econ. Geol.* **65**, 206-215.
- GUSTARD, B. (1967) The ferromagnetic domain structure in hematite. *Proc. Roy. Soc. (London) Ser. A*, **297**, 269-274.
- HIHARA, T. (1960) Magnetic and electrical properties of iron sulphide single crystals. *J. Sci. Hiroshima Univ. Ser. A*, **24**, 31-53.
- KITTEL, C. (1966) *Introduction to Solid State Physics*, 3rd ed., Ch. 15. John Wiley and Sons, New York.
- LOTGERING, F. K. (1956) On the ferrimagnetism of some sulphides and oxides. *Philips Res. Rep.* **11**, 190-249.
- MORIMOTO, N., H. NAKAZAWA, K. NISHIGUCHI, AND M. TOKONAMI (1970) Pyrrhotites: Stoichiometric compounds with composition $Fe_{n-1}S_n$ (>8) *Science*, **168**, 964-966.
- NALDRETT, A. J. (1969) The system Fe-S-O. *J. Petrology*, **10**, 171-201.
- NALDRETT, A. J., AND G. KULLERUD (1967) A study of the Strathcona Mine and its bearing on the origin of the nickel-copper-ores of the Sudbury district. *J. Petrology*, **8**, 453-531.
- NICKEL, E. H., AND D. C. HARRIS (1971) Reflectance and microhardness of smythite ($Fe_{2.2}S_3$). *Amer. Mineral.* **56**, 1464-1469.
- PALACHE, C., H. BERMAN, AND C. FRONDEL (1944) *System of Mineralogy of . . . Dana, 7th Ed.*, **1**, John Wiley and Sons, New York.
- SCHWARZ, E. J. (1965) Thermomagnetic properties of sulphide ore from the Noranda area, Canada, measured with a magnetic balance. *Can. J. Phys.* **43**, 220-226.
- TAYLOR, L. A. (1970a) Low temperature phase relations in the Fe-S system. *Carnegie Inst. Wash. Year Book*, **69**, 259-270.
- (1970b) Smythite and associated minerals from the Silverfields mine, Cobalt, Ontario. *Amer. Mineral.* **55**, 1650-1658.
- WARD, J. C. (1970) The structure and properties of some iron sulphides. *Rev. Pure Appl. Chem.* **20**, 175-206.
- WOODALL, R., AND G. A. TRAVIS (1969) The Kambalda nickel deposits, Western Australia. *Ninth Commonwealth Mining Met. Congr., Mining Petrol. Sect.*, Paper 26.
- WUENSCH, B. J. (1963) On the superstructure and twinning in pyrrhotite. *Mineral Soc. Amer. Spec. Pap.* **1**, 157-163.

- YUND, R. A., AND H. T. HALL (1969) Hexagonal and monoclinic pyrrhotites.
Econ. Geol. 64, 420-423.
- , AND R. H. MCCALLISTER (1970) Kinetics and mechanism of exsolution.
Chem. Geol. 6, 5-30.

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