

New observations on natural pyrrhotites. Part III. Thermomagnetic experiments

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Abstract

A sensitive magnetic thermobalance has been constructed and used to study "hexagonal" and monoclinic pyrrhotites. Confusion about magnetism of the former has been cleared up by using different thermal cycles, and hexagonal pyrrhotites may be made magnetic at will. The breakdown temperature of monoclinic pyrrhotite is still uncertain and probably varies with content of impurities, as there seems to be a difference between dry and hydrothermal systems.

Vacancy diffusion in pyrrhotite proceeds rapidly at 200°C, negating the value of structural information as an indicator of temperature or pressure of formation. Reaction occurs with adsorbed water or oxygen at temperatures from less than 350° to 500°C or more.

Experimental evidence has been obtained for solid state exsolution of magnetite, postulated in Part II [*Am. Mineral.*, 57, 1876-1880 (1972)].

Introduction

In parts I and II of this series (Bennett *et al.*, 1972) evidence was presented that fine magnetite lamellae are present in many pyrrhotites, and that they may be an exsolution feature. Experimental confirmation of the latter suggestion is described in an appendix.

To investigate these lamellae more thoroughly, and to provide an easier means of detecting and perhaps even measuring their presence, a magnetic balance with a 10cm electromagnet was constructed.

Apparatus

The magnet pole-pieces are shaped to give a constant force [$H(dH/dx)$] over a region about 1cm long, and a double-wound silica furnace, insulated by a vacuum and reflecting gold mirror, surrounds the specimen in the 3.8cm pole-piece gap. Fields up to 8kgauss and temperatures up to 650°C can be routinely attained.

The balance is horizontal, with quintuple filamentary suspension, and uses a feedback loop with restoring coil driven by an LVDT position sensor to operate at null displacement. We are indebted to F. Chama-laun of Flinders University, Adelaide, for the general features of the design and for his initial encouragement.

The specimen consists usually of 10-250 mg of material sealed in a small silica capsule at a vacuum

of better than 10^{-4} torr. The capsule is attached to a thin silica extension which can be clipped into a groove in the balance arm. The specimen position within the capsule may be fixed with a wad of silica wool if required. The magnet and furnace are wheeled into position and an axial thermocouple arranged to be almost touching the specimen capsule. The fact that short-term fluctuations of temperature are reflected reproducibly in changes of magnetic force indicates that the thermocouple accurately follows the specimen temperature. We believe dynamic temperature can be measured to better than $\pm 5^\circ\text{C}$ at 200°C/hr.

Data can be obtained manually, or a thermomagnetic run can be pre-programmed using an Ether-Wheelco cam-operated temperature controller. To eliminate errors due to drift of the baseline at the higher sensitivities, the magnet current can be turned off automatically at intervals of 2 or 5 minutes, thus providing a "zero" field calibration. The magnetic force is recorded as a function of specimen temperature on a Hewlett-Packard X-Y recorder. Standard heating and cooling rates were 50°, 200°, and 400°C/hr.

Pyrrhotite compositions and structures

The general features of the magnetic properties of materials in the Fe-S system are well known (Hor-

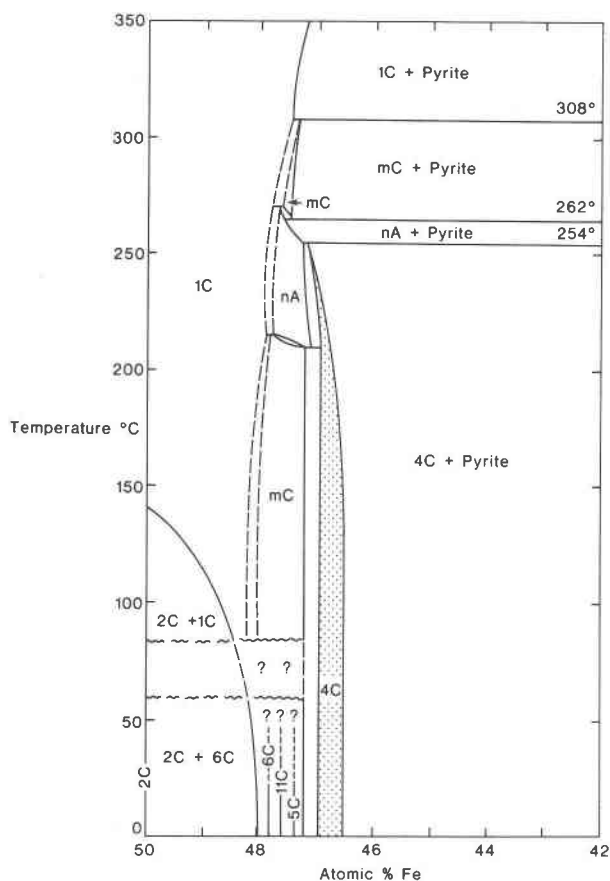


Fig. 1. Equilibrium phase diagram (hydrothermal) of the pyrrhotite region of the Fe-S system (after Kissin, 1974).

wood *et al.*, 1976; Schwarz and Vaughan, 1972) although there are still some misconceptions about the magnetism of "hexagonal pyrrhotites" (Schwarz and Harris, 1970; Gorbunova *et al.*, 1973).

Phases having a structure related to nickel arsenide, based on hexagonal close-packing of sulfur atoms with iron atoms in some of the octahedral interstices, have been reported between the compositions FeS and Fe₃S₄. At room temperature, however, the most common of these phases lie between troilite, FeS, and smythite, Fe₉S₁₁. At high temperatures the disordered nickel arsenide structure also persists to a sulfur-rich limit of approximately Fe₉S₁₁. Recent work using hydrothermal transport and recrystallization methods (Kissin, 1974) has sought to delineate regions of stability of ordered phases between room temperature and 320°C (Fig. 1).

All of these phases are either ferrimagnetic or antiferromagnetic when the vacancies are ordered, and paramagnetic at high temperatures. In general one has tended to speak of "hexagonal" phases in the

composition range FeS to Fe₉S₁₀, "monoclinic" for the Fe₇S₈ phase, and "rhombohedral" for Fe₉S₁₁, but the situation is more complicated than this. The "hexagonal" phases are normally antiferromagnetic ("non-magnetic"), and the monoclinic and rhombohedral phases ferrimagnetic.

The magnetic properties of pyrrhotite arise to a great extent from the manner in which the vacant iron sites are ordered (the general formula for all these phases is Fe_{1-x}S). In a vacancy-ordered structure, some of the close-packed iron layers (sandwiched between close-packed sulfur layers) contain all the vacancies, while others contain none. Because the iron spins within a layer are all arranged parallel with one another, and spins in adjacent layers are opposed, there may be an excess of spins in one direction. The simplest structure in which this occurs is that of the monoclinic "4C" structure, in which every second layer is a complete iron layer with spins in one direction, and the alternate "vacancy" layer has one site in four vacant (Fig. 2). Of the seven iron atoms in a formula unit, therefore, one has its spin unpaired. In a vacancy-disordered structure, there are equal numbers of vacancies on all adjacent layers, and therefore all spins are paired.

If there are no vacancies (as in troilite), or if the vacancy layers are adjacent or equally divided between odd and even positions, all spins are paired and there is no net moment. There is still, however, the possibility of a magnetic transition, because the spin direction may be parallel to the close-packed layer or perpendicular to it. Such a transition occurs at 180°C for compositions near FeS, in which the high-temperature structure has the spins oriented parallel to the plane of iron atoms. It is interesting that this transition is not closely related to a structural transition which occurs at 147°C. The two were

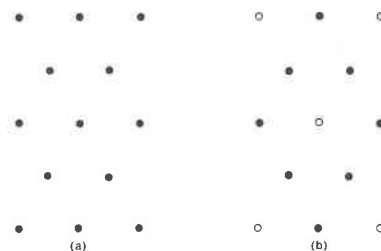


Fig. 2. Filled layers (a) and "vacancy" layers (b) of iron atoms in pyrrhotites. Open circles in (b) represent the vacancies caused by the removal of one atom in four. The layers are separated by approximately close-packed sulfur atoms. Magnetic properties of the pyrrhotites depend on the sequence of (a) and (b) layers, and on the spin ordering within the layers. At low temperatures spins in adjacent iron layers are usually opposed.

confused for many years, because both transition temperatures depend on composition and do coincide for a particular composition (Horwood *et al.*, 1976).

Observations

We were attempting to use the apparatus as a "magnetic spectrometer" in a manner described independently by Townsend *et al.* (1979) to determine relative amounts of hexagonal and monoclinic pyrrhotite and magnetite in the sample. It soon became clear, however, that reactions and phase changes could occur during the thermomagnetic run, and that equilibrium was not necessarily attained at any temperature. There are still a number of unexplained observations, but it has proved possible to sort out several interesting features, and in general to identify phases as expected.

It is possible to distinguish three kinds of transitions on the basis of hysteresis and kinetic factors. The first is a pure spin reorientation which is rapid and takes place with little thermal hysteresis. The second is a short-range movement of vacancies such as that involved in a change of order at approximately constant composition, or an order/disorder transition. These transitions are somewhat slower, but still come to equilibrium in times of the order of hours at temperatures as low as 120°C. The third is a first-order phase change involving a complete change of basic structure, and requiring long-range diffusion of iron or sulfur. Times of the order of days or weeks at temperatures about 250°C are needed to produce unambiguous magnetic effects in a dry system, and months or years are required to reach equilibrium.

Reaction with air and adsorbed species

Van den Berg and Thiel (1969) went to extraordinary lengths to avoid contact between pyrrhotite and air, even at room temperature, and there have been remarks in the literature to the effect that the first thermomagnetic run on pyrrhotites should be disregarded because of transient effects. This run, however, gives important information on reaction with air and other adsorbed species, and on the re-equilibration of more or less oxidized samples. Figure 3(a) is a stylized heating curve for a stable sample, and shows the magnetic spectrum expected from a mixture of monoclinic and hexagonal pyrrhotites and magnetite. Figure 3(b) shows the first heating curve for a powdered sample which had been stored in air for a time, and (c) and (d) show variants of the effect in other samples. These samples are of pyrrhotite/

gangue tailings from commercial operations. Evidently a reaction occurs to form a magnetic iron oxide at different temperatures in the range 300°–600°C in different samples. On the cooling curve and subsequent runs, these samples give typical stable curves such as that in (a), in which the iron oxide is apparently magnetite. Of interest is the temperature at which the reaction occurs; in some pyrrhotites it can be as low as 350°C or less, and if the pyrrhotite is annealed isothermally at any temperature above that at which the reaction commences, it will reach equilibrium in a reasonably short time (a few hours).

It is thought that the temperature of onset of the reaction, which is very easily observed, is a measure of the "reactivity" of the pyrrhotite, and could be used to predict those samples where spontaneous ignition might be expected in transport or storage. However, the degree of reaction may be just as important in this application, and it will be seen that in the samples selected for Figure 3 there is a negative correlation between the temperature of reaction and the amount of magnetite formed. The latter can be gauged from the cooling curves.

Because the degree of oxidation is often very slight, it is not possible by X-ray diffraction to be sure that magnetite is the only oxide forming, but the magnetic curve is always consistent with the presence of magnetite, with some variations described later. Wüstite is not stable below 560°C, and a magnetite/pyrrhotite assemblage is consistent with the thermodynamic data (Scott, 1974).

As a result of these oxidation reactions the proportions of sulfide phases may vary considerably. (Compare the low-temperature regions of the heating and cooling curves.) For example, the amount of monoclinic pyrrhotite increases at the expense of the hexagonal variety if the sulfur content is low, while monoclinic pyrrhotite gives way to pyrite at higher sulfur contents. This decrease in metal/sulfur ratio is caused by the removal of iron to form the oxide. Hexagonal pyrrhotites with oxidized monoclinic rims may homogenize to a completely hexagonal phase. Any effects due to storage of powdered samples are immediately apparent in this way, and the stable state reached after the reaction is complete can be easily assessed.

Figures 3(b) to (d) all show the conversion from a typical hexagonal plus monoclinic mixture to a magnetic pyrrhotite, probably monoclinic. In (b) and (c), enough magnetite has formed to significantly alter the iron to sulfur ratio of the pyrrhotite, and the change is not unexpected. In (d), however, much of

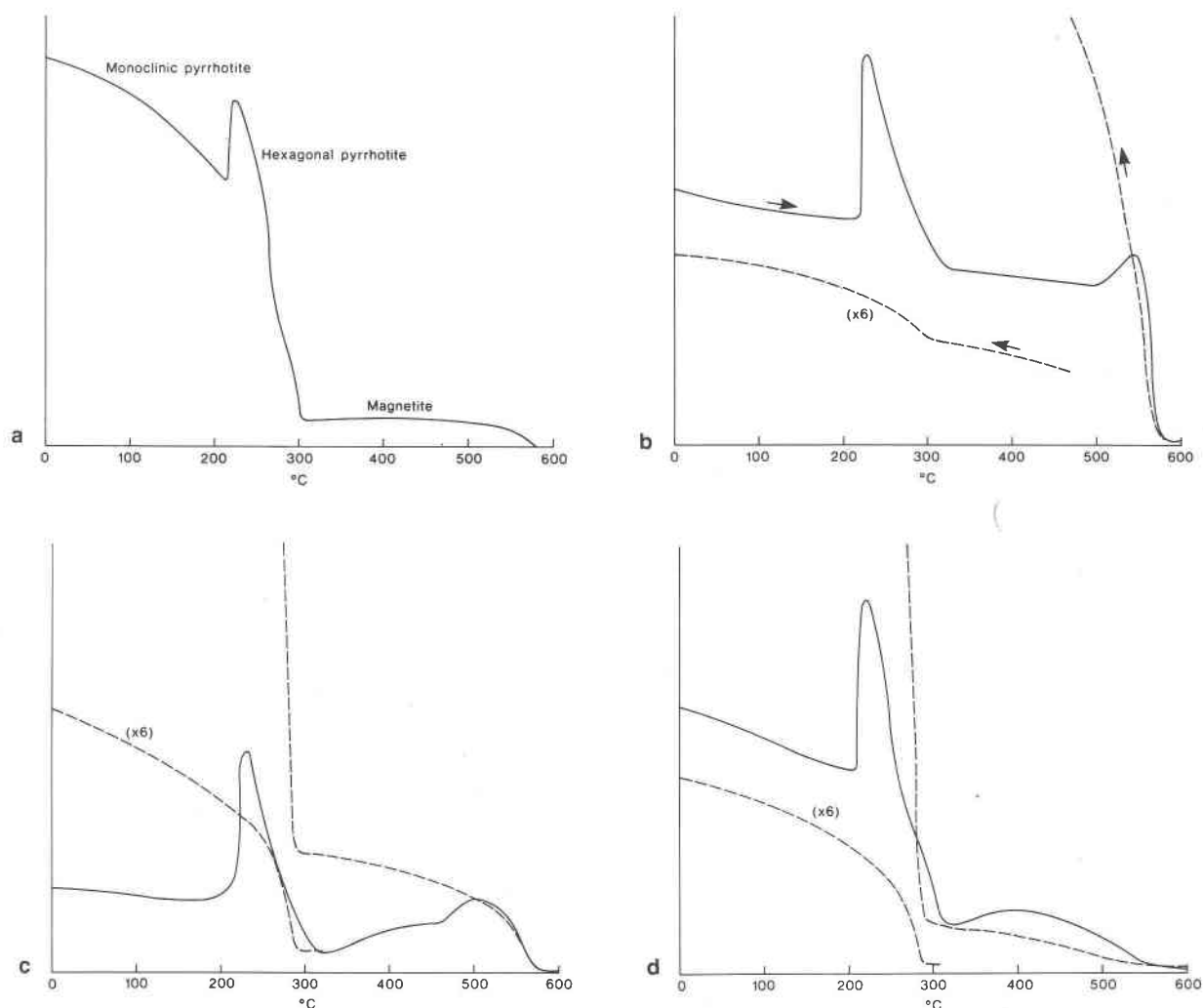


Fig. 3. Thermomagnetic curves of magnetization against temperature for pyrrhotite-magnetite mixtures. (a) Stylized stable heating curve showing a monoclinic plus hexagonal mixture with some magnetite. (b)-(d) Tailings containing pyrrhotite showing different reaction regimes which result in the formation of magnetite between about 350° and 600°C, and alteration of the composition and magnetic properties of the pyrrhotite. (Compare heating and cooling curves below 300°C.) Heating curves are full lines, cooling curves broken.

the magnetite formed has either entered into solid solution in the pyrrhotite, or has reacted to form some non-magnetic phase. There is not enough oxygen to convert the hexagonal pyrrhotite to monoclinic by iron depletion or by entering into solid solution, but X-rays show the presence of pyrite before the run. Evidently the hexagonal pyrrhotite has reacted with about 5% of pyrite to form monoclinic pyrrhotite in the two hours that the temperature was above 400°C; this was confirmed by X-ray diffraction after the run. A similar reaction occurs for Nepean (Western Australia) pyrrhotite, where a mixture apparently consisting of monoclinic pyrrhotite with a small admixture of hexagonal converts into pure hexagonal

pyrrhotite after the run (Fig. 4); see next section. This is probably due to pentlandite flames and lamellae re-entering the pyrrhotite phase during the first run. In this particular sample, pentlandite is not detected by X-ray diffraction, but about 5-10% is required to accomplish the transformation if the resulting pyrrhotite has an $(\text{Fe,Ni})_9\text{S}_{10}$ composition. The pyrrhotite was in fact separated from a mixture with pentlandite. From the X-ray result, the grain size of the residual pentlandite must be sub-micron.

"Hexagonal pyrrhotite"

Pyrrhotites of composition approximating Fe_9S_{10} undergo a transition from their normal anti-

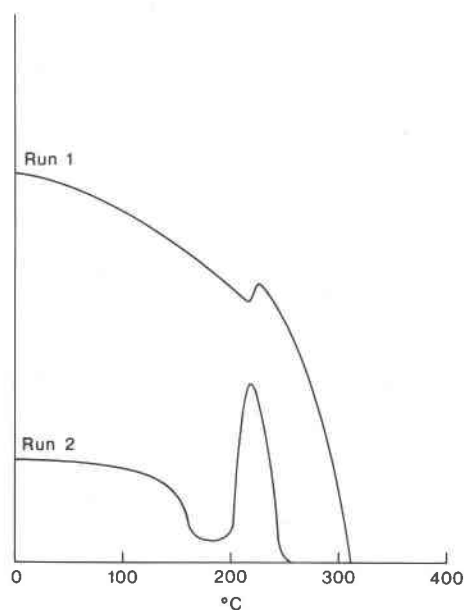


Fig. 4. The first and second heating curves for Nepean (Western Australia) pyrrhotite separated from a pentlandite/pyrrhotite ore. The magnetic monoclinic pyrrhotite has been converted to the hexagonal form.

ferromagnetic state to a ferrimagnetic one commencing at about 215°C, and they thermally demagnetize by a temperature of about 255°C. The temperature range of the magnetic phase corresponds approximately to the phase field of Kissin and Scott (Scott, 1974) for the "nA" structure (Fig. 1), and it is possible that the magnetic properties and the "nA" ordering are related. As described below, the transformation antiferromagnetic \rightleftharpoons ferrimagnetic can be rather sluggish, suggesting that a vacancy ordering process is occurring. There is, however, insufficient time for a first-order transition to occur, as required by Kissin and Scott's phase diagram. The ferrimagnetic phase may therefore be metastable.

Curve a of Figure 5 shows a thermomagnetic heating curve for a slow-cooled hexagonal pyrrhotite. The shape of the cooling curve depends on cooling rate. At rates less than 1°/min it approximates to curve a, curves b–e show the effect of increasing cooling rates, and curve f is a heating curve immediately following cooling curve d. The room-temperature magnetization in d is high because the vacancy structure is still that of the high-temperature phase, which was able to follow its normal thermal magnetization curve to room temperature. If we look closely at the magnetic transitions around 215° and 255°C, we notice that the former is associated with a two-phase region. A sample annealed in the magnetic

balance at 215°C slowly loses magnetism if it is magnetic and gains magnetism if it is antiferromagnetic. In addition, thermal magnetization and demagnetization can be observed in this two-phase region as a result of small temperature excursions caused by the temperature controller. Thermal magnetization is in the reverse sense to that due to the transformation, showing that the transformation is not due solely to magnetic order. Once the two-phase region has been passed in the upward direction, vacancy and magnetic ordering is very rapid indeed; it is complete within about a minute of commencement. The reverse transformation is slower, probably mainly because of the significantly lower temperatures.

Two observations may be made from these results.

(a) Because vacancies are ordering and disordering at temperatures below 120°C [Fig. 5(f)], it is obvious that the detailed crystal structure of the pyrrhotite can indicate nothing about the temperatures and pressures of formation. Vacancy ordering processes can occur in minutes, as shown in Figure 6. Note that the transformation is slower at 207° than at 190°C because the driving force is smaller. Below 190°C the rate again slows due to thermal factors.

(b) In industrial processing of minerals, magnetic separation is often used to remove pyrrhotite from other sulfide minerals such as pentlandite, but the technique has not been possible for non-magnetic varieties of pyrrhotite. It would be a simple matter to magnetically beneficiate ores containing non-magnetic hexagonal pyrrhotites by heating to 240°C for a few minutes, then cooling below about 120°C in less than about 15 minutes, possibly in a blast of air. (This procedure has recently been suggested by Townsend *et al.*, 1979.)

From the magnetic results the transition at 250° seems to be largely a thermal demagnetization; hysteresis is small and not strongly dependent on rate of change of temperature. The change to the mC structure is thus not amenable to study by the magnetic method, as both structures seem to be non-magnetic at the temperatures involved.

A few frustrating results have been obtained which have not been reproducible; these could be due to the presence in the sample tube of a grain or two of an unsuspected mineral. For example a sample of monoclinic plus hexagonal pyrrhotite from Mt. Morgan evolved through a hexagonal pattern to a non-magnetic pattern after a series of heat treatments. X-rays still showed a hexagonal pyrrhotite. The change in magnetic order may have resulted by reaction with chalcopyrite, for example.

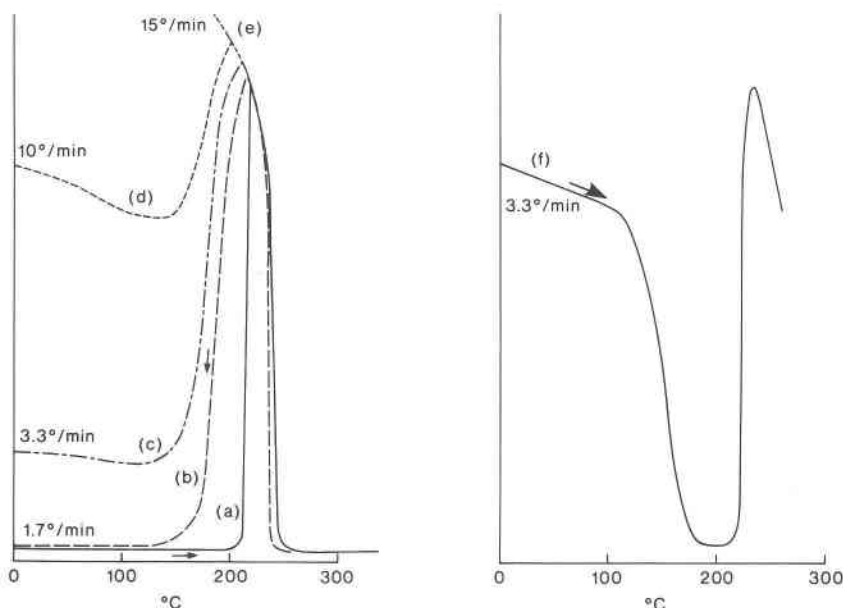


Fig. 5. Thermomagnetic curves for a hexagonal pyrrhotite from Nairne, South Australia. (a) is the initial heating curve, and (b)–(e) represent cooling curves at increasing rates. (f) is a heating curve immediately following curve (d).

Monoclinic pyrrhotite

In all natural materials we have investigated, a small proportion of a magnetic phase is still present at temperatures up to 570°C, and this has been shown to be magnetite. In some samples, including one from a single crystal of Chihuahua (Mexico) pyrrhotite, the magnetite was barely discernible.

In other respects, a thermomagnetic curve of material of composition approximately Fe_7S_8 is apparently typical of thermal demagnetization of magnetic materials. The Curie temperature is highly reproducible and is $310 \pm 4^\circ\text{C}$ (there is a slight hysteresis between heating and cooling curves, but the rate of temperature change from about 50 to 500°/hour has no marked effect).

Appearances are deceptive, however, and the magnetic pyrrhotite actually seems to be a metastable phase at temperature between 250° and 300°C, as annealing in this range modifies the magnetic curve as shown in Figure 7. The apparent Curie temperature is reduced to about 295°C, and an inflection in the magnetization curve at 270–285°C indicates that a new “high”-temperature ordered phase has been formed. After heating to 600°C and re-running, the original 310°C Curie temperature is observed. The cycle to 600°C seems to be a means of restoring the pyrrhotite to a homogeneous composition.

It should be emphasized that for natural materials so far tried, annealing in the absence of water at

250°, 265°, or 275°C does not result in the formation of hexagonal pyrrhotite and pyrite after six months, so this is not necessarily the stable assemblage.

The rearrangement of vacancies to form a superlattice requires little or no activation energy, and the free energy of the ordered phase is sufficient to reduce the driving force towards equilibrium. Schwarz (1975) attempted to grapple with this problem.

We have performed many experiments to verify the temperature of 254°C for the breakdown of

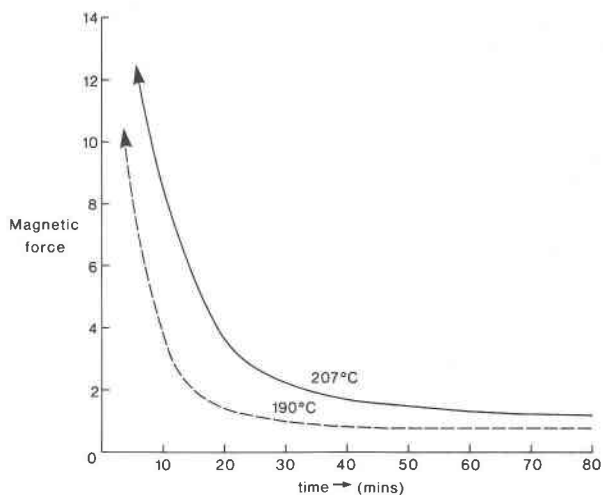


Fig. 6. Decay of magnetization with time for Nairne pyrrhotite quenched from 240°C and annealed at the specified temperatures. Initial magnetization is much higher.

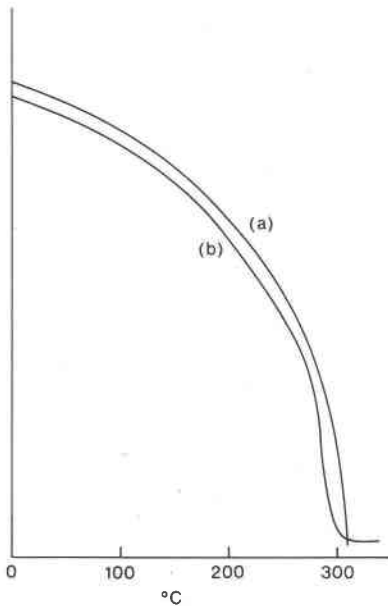


Fig. 7. Thermal demagnetization curve for monoclinic pyrrhotite from Renison Bell (Tasmania). (a) Normal curve, (b) after annealing at 275°C for 3 months.

monoclinic pyrrhotite given by Kissin (1974) and Scott (1974), but the results have not been definitive. In a series of hydrothermal experiments monoclinic pyrrhotite was sealed in gold capsules in aluminum bombs, and also in thick-walled glass capillary tubing, with ammonium iodide solution, while attached

to the magnet. There were difficulties in temperature calibration, and leaks and breakages occurred in the miniature bombs, but at 280°C, using a synthetic pyrite + pyrrhotite mixture, monoclinic pyrrhotite transformed to the hexagonal variety in less than 28 hours. After equilibration, the product was re-sealed in an evacuated silica capsule and re-annealed dry at 280°C. It transformed back to monoclinic pyrrhotite in only 2–3 hours. The hydrothermal transformation occurred at this temperature both in water and in 5 molal NH_4I solution, but was marginally slower in pure water. We may infer that a component of the water enters into the hexagonal pyrrhotite \rightleftharpoons monoclinic pyrrhotite reaction, and that the hydrothermal phase diagram is different from the dry phase diagram.

Samples from the Broadlands (New Zealand) geothermal field (kindly supplied by Dr. P. Browne of N.Z. DSIR) proved to be the magnetic "4C" structure if taken from borehole depths where the temperatures are $266 \pm 3^\circ\text{C}$ or below. No samples could be obtained between this temperature (BR4, 2550 ft) and 293°C (BR14, 3900 ft), where the sample was hexagonal. We feel that Kissin's hexagonal pyrrhotite from the hole BR4 must have been atypical—it was not from a pyrrhotite-rich zone, in any case, and the fact that the pyrrhotite was iron-rich may have been due to a low sulfur fugacity. These observations are consistent with a breakdown temperature be-



Fig. 8. Polished section of synthetic pyrrhotite formed by heating a synthetic iron-nickel sulphide melt in contact with a synthetic chromite and cooling over a period of 16 hours. Textures shown are of a grain boundary pyrrhotite/magnetite eutectic, and exsolution magnetite lamellae within the grains. Length of side 220μ , crossed nicols.

tween 266° and 293°C for natural hydrothermal pyrrhotite, but a further complicating factor is that we have synthesized hexagonal pyrrhotite at temperatures below 250°C in ammonium iodide solutions with excess ammonia. Impurities including H⁺ and OH⁻ thus seem to be important, and it is possible that the transformation temperatures of 254° (Kissin, 1974), 275° (Sugaki *et al.*, 1977), and 292°C (Taylor, 1970) all represent equilibrium for the particular conditions chosen.

Appendix

Synthetic magnetite lamellae

A synthetic iron-nickel sulfide melt which had been heated with synthetic chromite and then cooled over a period of 16 hours contained a graded series of spinel phases (Ewers *et al.*, 1976). The spinels ranged in composition from chromite to magnetite, some euhedral within grains of monosulfide solid solution. There was also some eutectic spinel between grains, and some eutectic in veinlets. The latter contained the least chromium, and all of the spinel phases evidently formed during solidification of the melt. Re-examination of the sections has shown that a lamellar solid exsolution phase is also present (see Fig. 8). If this phase is magnetite, a logical assumption, support is given to our previous conjecture (Part II) that magnetite lamellae observed in natural pyrrhotites result from exsolution of oxygen dissolved in the solid pyrrhotite, rather than from later oxidation processes.

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*Manuscript received, September 11, 1979;
accepted for publication, March 5, 1980.*