American Mineralogist, Volume 72, pages 599–604, 1987

Oxygen in pyrrhotite: 1. Thermomagnetic behavior and annealing of pyrrhotites containing small quantities of oxygen

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ABSTRACT

As an extension of previously described work on natural pyrrhotites, we have used a magnetic balance to observe magnetite solution-exsolution phenomena and to ascertain the magnitude of the oxygen solubility. Oxygen is soluble in pyrrhotite to the extent of at least 0.37% at 700°C (1.35% magnetite), and magnetite exsolves at lower temperatures. Oxygen moves freely over short distances at temperatures near 300°C, and since metal vacancies are also known to be mobile at low temperatures, natural pyrrhotite cannot be expected to reflect its conditions of formation with any degree of reliability. The activation energy for diffusion of oxygen in pyrrhotite (106 kJ/mol) is only slightly greater than that for vacancy diffusion (86.8 kJ/mol). "Abnormal" pyrrhotite formed by quenching is probably a mixture of two phases and may be stabilized by oxygen. Limited annealing experiments indicate that the presence or absence of oxygen may affect the phase stability.

INTRODUCTION

Magnetite is the only iron oxide in equilibrium with pyrrhotite in the temperature range from room temperature to above 700°C (Taylor and Kullerud, 1971). Its appearance and disappearance from a phase mixture can be detected with a magnetic thermobalance, which provides a convenient means to study some of the reactions in the system Fe-S-O. Interpretation is not always straightforward because of order-disorder changes in the sulfides, but at temperatures above 300°C, these cease to be important. The magnetic thermobalance has been used as a detection device for magnetite.

MAGNETIC BEHAVIOR OF MONOCLINIC PYRRHOTITE

Samples run in the electromagnetic thermobalance consist of about 50 mg of material sealed under a vacuum of $\sim 10^{-4}$ torr in a silica tube as described in Bennett and Graham (1980, 1981). If magnetite is present in a pyrrhotite sample at levels much above 1%, the thermomagnetic curves are approximately the sum of the curves for the individual minerals. Hysteresis of the Curie point of the magnetite in pyrrhotite is of the order of 10 deg at 200 deg/h rate of temperature variation. When magnetite is present in much smaller amounts, variations in the amount of magnetite present, and of its Curie temperature and thermal hysteresis, become apparent. We have not been able to detect magnetite in samples of hexagonal pyrrhotite.

There are often small differences in the magnetic properties of magnetites from different sources, which may be associated with particle size and shape, degree of oxidation, or chemical impurities. For magnetite in pyrrhotite, quite large reductions in Curie point are often observed; Figure 1 gives an example in which the Curie point (T_c) has been lowered by ~50 deg from its bulk value, but the hysteresis is still only about 8 deg. When first formed by reaction of oxygen with the pyrrhotite, this magnetite had a T_c of 550°C, but this decreased to 533°C with thermal cycling. This behavior makes it difficult to recognize magnetite and to determine it quantitatively from its magnetic moment.

Experiments showed that the hysteresis for magnetite could be as much as 140 deg for a sample that was a synthetic mixture of pyrrhotite and pyrite, about 50:50 by weight, containing a small undetermined amount of oxygen. A single sealed sample yielded the thermomagnetic curves shown in Figure 2, and as the temperature was above T_c for pyrrhotite, the magnetism shown in Figure 2 refers almost entirely to the magnetite component. The magnetic force, in combination with thermal demagnetization effects, may be looked on as a measure of the quantity of magnetite in the sample.

The heating curves are not strongly dependent on rate of heating between 50 and 400 deg/h, but cooling curves are rate- and history-dependent. A description of the individual curves in Figure 2 may help to explain their interpretation.

Curve A. Slow heating and cooling at 50 deg/h. Magnetite dissolves at temperatures up to about 560°C but does not reprecipitate until 450°C on cooling [Note that solution of magnetite with increasing temperature could be due to increasing proportion of pyrrhotite (Toulmin and Barton, 1964)].

Curve B. Normal heating and cooling at 200 deg/h.

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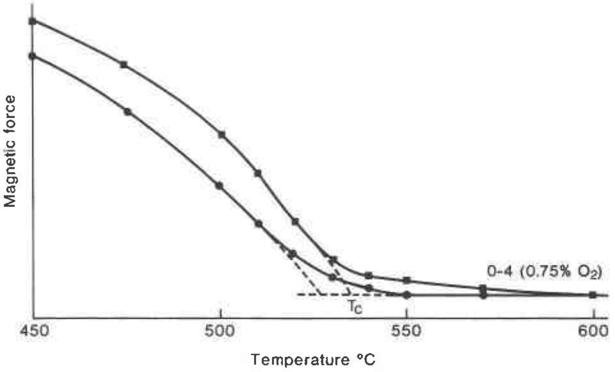

Fig. 1. Thermomagnetic curves for pyrrhotite 0-4, containing 0.75% oxygen. The Curie point (T_c) of magnetite, 533°C, has been depressed by about 50 deg, and hysteresis is about 8 deg.

Little change, except the temperature of reprecipitation is slightly depressed.

Curve C. Fast heating and cooling at 400 deg/h. Further depression of reprecipitation temperature.

Curve D. Cycle reversed at 550°C. Very similar to Curve C, so most of the magnetite has dissolved in pyrrhotite at 550°C and does not need annealing at higher temperatures.

Curve E. In order to differentiate magnetite solution from a depressed Curie point, the cycle was reversed at 525°C. Even when the temperature was decreasing, the magnetism continued to decrease, showing unequivocally that the decrease in magnetism was at least in part due to solution of magnetite in pyrrhotite.

Curve F. A similar experiment to E but with a 10-min annealing at 525°C, confirming the above conclusion.

Curve G. Rapidly air-cooled specimen in which some magnetite was quenched in.

Curve H. Subsequent heating curve showing magnetite continuing to precipitate up to 400°C, followed by resolution. Not all the magnetite exsolved, as shown by the area of the hysteresis loop.

Despite uncertainties already mentioned, it is possible to estimate the amount of magnetite exsolving, by using a calibration series. Such a series was made up using specially prepared low-oxygen pyrrhotite of composition Fe_7S_8 and synthetic magnetite. Using the magnetization at 325°C as a measure of magnetite percentage, the calibration was linear up to 6% Fe_3O_4; the detection limit with a 50-mg sample is better than 0.007% Fe_3O_4 or 0.002% oxygen, corresponding to about 0.001-mg oxygen in the sample. The greatest amount of magnetite observed in the series of Figure 2 (pyrrhotite plus pyrite) is 0.09%. The magnetite has all dissolved by 560°C when the sample is still of the order of 50% pyrrhotite, so the solubility at 560°C in pyrrhotite is at least 0.18% Fe_3O_4. The dramatic reduction in solubility at lower temperatures that is apparent in these curves, however, could be triggered by the precipitation of pyrite in the sulfide at these temperatures. [The composition is in a two-phase region at room temperature.] As pyrite forms on cooling, it rejects solid-solution oxygen that was in the pyrrhotite, producing nuclei and resulting in a sudden burst of magnetite formation.

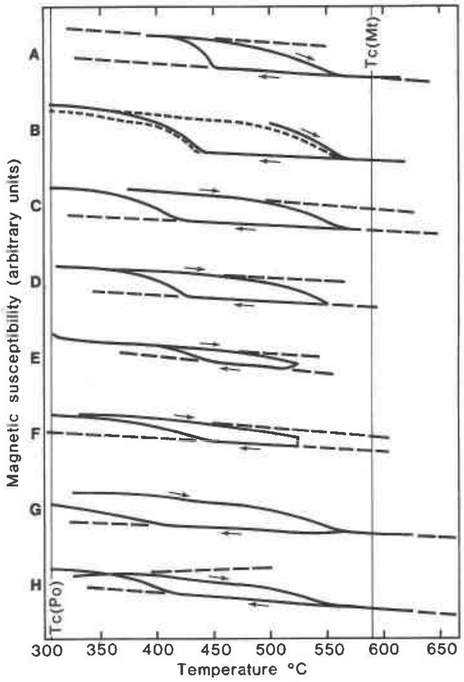

Fig. 2. Thermomagnetic curves (heating and cooling) for a synthetic pyrite-pyrrhotite mixture of overall composition approximately $Fe_{11}S_{16}$. The magnetic susceptibilities are due largely to magnetite produced by the reaction of oxygen with pyrrhotite. (A) 50 deg/h to 620°C and return. (B) 200 deg/h to 620°C (dashed curve is the second run); (C) 400 deg/h to 650 °C; (D) 400 deg/h to 550°C; (E) 400 deg/h to 525°C; (F) 400°C/h held 10 min at 525°C; (G) 400 deg/h to 625°C and rapid air cool; (H) 400 deg/h next run after run G. In each case, the upper curve is the heating curve. Dashed lines show the slope of significant parts of the curves.

The calibration standards described above were used to arrive at a solubility limit of magnetite in pyrrhotite. After a single thermomagnetic run to 600°C during their synthesis, some of the magnetite had dissolved, and after only a few hours annealing at 600°C, the standards appeared to have reached equilibrium. The amount of undissolved magnetite after quenching was measured from the magnetic curve at 325 and 350°C, leading to a solubility of 0.75 ± 0.07% magnetite in pyrrhotite at 500°C, and 1.00% at 600°C. These values correspond to a solubility of 0.21 ± 0.02% oxygen and 0.28% oxygen, respectively (the uncertainty represents the variation in this set of samples and is not a measure of accuracy). The magnitude of the solubility was confirmed by sealing some low-oxygen synthetic pyrrhotites under known pressures of oxygen gas in the magnetic balance capsules. In some cases, the pyrrhotite was preheated with SiS_2 to remove all traces of oxygen, but this made no detectable difference. Magnetite that formed by reaction between the oxygen and pyrrhotite during the thermomagnetic runs, after equilibration, suggested a solubility of 0.85 ± 0.26% magnetite at 600°C. The greater variation reflects the difficulty of sealing off the sample with a specified amount of gas.

Table 1 gives the results of a series of quenching runs on sample STD3 containing 1.81% added Fe_3O_4, indicating that the solubility of oxygen increases markedly with temperature. As before, the measured quantity is the amount of magnetite *not* in solution. At lower temperatures, data cannot be obtained in this way because oxygen does not diffuse in a reasonable time. If our synthetic pyrrhotite was not completely free of oxygen, the high-temperature solubility must be correspondingly adjusted. Some or all of the oxygen present at room temperature may be locked in metastable solution owing to the slowness of diffusion, but above 500°C, oxygen moves freely. At the higher temperatures, slow reactions occur between the pyrrhotite and magnetite to form nonmagnetic phases, and this phenomenon, which results in increased uncertainty for the solubility at 700°C in Table 1, is the subject of a separate study.

Table 1 shows that the movement of oxygen is sluggish below 550–575°C, whereas we have seen that in a pyrrhotite-pyrite mixture, solution and exsolution occur down to about 300–350°C. The difference may be due to dynamic effects caused by pyrite solution and exsolution. Further kinetic experiments are being carried out to confirm this, in a way similar to those described below for single-phase pyrrhotite.

Synthetic pyrrhotite of nominal composition Fe_7S_8 was sealed in glass capsules with sufficient oxygen to form approximately 2% magnetite. The samples were reacted during a slow temperature cycle from room temperature to 620°C until magnetite formation ceased. They were then annealed at 700°C for 20 min and quenched into water. A good deal of the magnetite dissolved in the pyrrhotite at 700°C, and when the quenched samples were annealed at intermediate temperatures, the precipitation of magnetite could be observed in the magnetic balance. The technique is broadly equivalent to the kinetic experiment described in Bennett and Graham (1981), but this time the experiment monitors diffusion of oxygen ions rather than vacancies. We must apologize for an arithmetic error in the value of the activation energy reported in the previous paper. The value should be 86.8 kJ/mol, and not 50.2 as printed.

Figure 3 shows kinetic curves for precipitation of magnetite in samples quenched from 700°C and then re-annealed at the stated temperatures from 325 to 450°C. There appear to be nucleation difficulties at the lower temperatures, and induction periods of 50 and 60 min, respectively, were observed at 350 and 325°C, prior to the commencement of the kinetic curves.

An activation energy for diffusion of oxygen can be calculated from an Arrhenius plot (Fig. 4) as before, and it turns out to be 106 kJ/mol, only a little higher than that for diffusion of vacancies. A diffusion coefficient cannot be derived because the distances involved are not known. However, the fact that oxygen diffusion even at 325°C can be observed using a time scale in seconds emphasizes that the oxygen distribution as well as the Fe and vacancy distribution in pyrrhotite is subject to low-temperature modification. There is little chance that either the phases present or the oxygen distribution can confidently be taken to represent conditions of formation.

TABLE 1. Solubility of magnetite in Fe_7S_8

Temperature of quench	Magnetite detected (%)	Magnetite in solution (%)
Slow cooled	1.11	0.70
400	1.02	0.79
450	1.02	0.79
475	1.02	0.79
500	1.05	0.76
550	0.97	0.84
575	0.89	0.92
600	0.81	1.00
625	0.66	1.15
700	0.46	1.35

Note: Total magnetite in sample, 1.81%.

METASTABLE "ABNORMAL" PYRRHOTITE

If a pyrrhotite with Fe content ≤46.67 atomic percent (Fe_7S_8 composition) is quenched rapidly from temperatures above about 500°C, "abnormal" pyrrhotite (nomenclature from Clark, 1966, 1970) is formed, in which the high-angle member of the pair of "102" X-ray reflections is more intense than the low-angle member. The magnetic curve for our quenched material shows its magnetism at room temperature to be variable, but it apparently has a very low Curie point of about 250°C. Figure 5 shows thermomagnetic heating curves for two different materials showing this phenomenon. The quenched material has an X-ray powder-diffraction pattern characteristic of "abnormal pyrrhotite" (Clark, 1970), but if heating is continued, some kind of atomic rearrangement occurs before T_c is reached, and the material reverts to a pyrrhotite (monoclinic?) with a T_c in excess of 300°C. If the quenched sample is annealed at 240–250°C, the magnetism also rises over 1 or 2 h to a value typical of monoclinic pyrrhotite.

There is some evidence of a number of phases of differing magnetic properties that give the abnormal X-ray diffraction pattern (Clark, 1970). One occurs as rims around monoclinic pyrrhotite in deposits of low-temperature aspect and could therefore result from low-temperature oxidation of pyrrhotite. We have made a synthetic material by annealing S-rich pyrrhotite for months at temperatures below 200°C, and like the natural material, it is nonmagnetic. Taylor (1971) has produced another variety as an oxidation product of pyrrhotites at 250 and 200°C.

The powder X-ray diffraction pattern of each of these materials is consistent with the presence of two phases, a "monoclinic" phase and a more S-rich "hexagonal" phase; the "102" reflection of the latter may superimpose on the

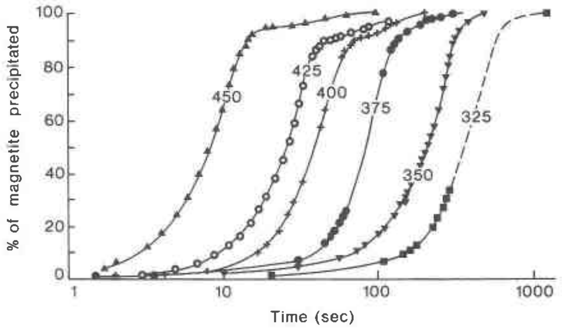

Fig. 3. Kinetic curves showing percent of magnetite precipitated in a given time at six different temperatures. Synthetic Fe_7S_8 with ~2% Fe_3O_4 added, annealed at 700°C, quenched, then annealed at the specified temperatures.

"228" reflection of the former, resulting in a typical "abnormal" powder pattern. In the case of our synthetic samples, including those shown in Figure 5, this is a probable explanation, because the phenomenon only occurs on quenching from a temperature where pyrite nuclei are absent, above the pyrite solvus. Apparently in our case, the high-temperature solid solution is unmixing into two compositions with related structures, there being insufficient time to nucleate pyrite. One of the phases is therefore more S-rich than the initial composition (already S-rich) and may remain hexagonal. The other is relatively S-poor and is probably fairly normal monoclinic pyrrhotite. It is possible that this kind of explanation can be extrapolated to explain other anomalous pyrrhotites. The S-rich phase must be nonmagnetic, so that the overall sample has a low magnetic moment. At first we thought that oxygen was necessary to allow the formation of the abnormal metastable phase in pyrrhotites of composition Fe_7S_8, but it now seems likely that the effect of oxygen is merely to inhibit atomic movements, since "abnormal pyrrhotite" has been observed in oxygen-free stoichiometric material (Fig. 5). The quenching rate is more critical in the absence of oxygen.

EFFECT OF OXYGEN ON STABILITY OF MONOCLINIC PYRRHOTITE

In order to test whether the presence of oxygen affects the stability of monoclinic pyrrhotite, it is desirable to control the partial pressures of S_2 and O_2 during annealing. At temperatures below 300°C, where the monoclinic ⇌ hexagonal transition is expected, the fugacities of S_2 and O_2 are so low as to require extremely sophisticated and specialized control techniques. Instead, we used SnS_2 and SiS_2 as buffers that set a low f_{O_2} and do not, at the same time, act as a getter for S_2. Unfortunately, the long-range diffusion of oxygen in pyrrhotite is very slow at the temperatures of interest. The anneals were carried out at 290°C, because this is below the transition temperature of 292°C recorded by Taylor (1970), and it is at least possible to retain a monoclinic structure for extended periods at this temperature.

If pyrrhotite is heated in a vessel with SnS_2 or SiS_2, a reaction of the type $SnS_2 + O_2 = SnO_2 + S_2$ (−75 kcal/mol) is possible. Oxygen will transfer from the pyrrhotite to the SnS_2 or SiS_2 until an f_{O_2} of 10^{-40} or 10^{-70} atm, respectively, is reached at 290°C. Any oxygen in solid solution will be replaced by sulfur, and magnetite will be converted to pyrrhotite with an increase in f_{S_2} (e.g., $14SiS_2 + 7Fe_3O_4 \rightarrow 3Fe_7S_8 + 14SiO_2 + 2S_2$). Any movement toward hexagonal pyrrhotite cannot, therefore, be due to removal of sulfur from the sample. Thermodynamic data have been extracted from Reed (1971), Darken and Gurry (1953), and Mills (1974).

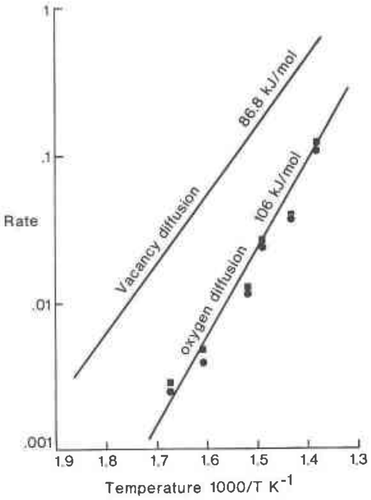

Fig. 4. Arrhenius plot derived from Fig. 4 giving an activation energy for oxygen diffusion in pyrrhotite. The points at each temperature represent the times for 25% and 75% precipitation. Vacancy diffusion from Bennett and Graham (1981).

SnS_2 and SiS_2 were synthesized shortly before use. With both buffers, it was found that a few hours at 600°C was sufficient to significantly reduce the magnetite content of pyrrhotite as measured on the magnetic balance. Effects at 290°C were more subtle, but temperatures as low as this were required to ensure that monoclinic pyrrhotite was present and reasonably stable.

It is not possible to differentiate between loss of oxygen and loss of sulfur on the basis of X-ray measurements alone, and an apparent increase in the Fe/S ratio, as mea-

TABLE 2. Magnetite (%) observed after treatment of a single natural pyrrhotite sample

Starting material	Treatment: Heated at 200 deg/h to 600°C	Treatment: Annealed in vacuo at 290°C for 3 weeks	Treatment: Annealed with SiS_2 at 290°C for 3 weeks
Natural Po with 3.4% Mt	3.6*	3.9 (1)*	2.6 (2)**
Product (1)	3.6†		
Product (2)	1.6‡		

* Reaction of adsorbed oxygen.
** Oxygen removed and Mt reduced by buffer.
† Solubility of oxygen greater at 600°C.
‡ Mt dissolves into oxygen-free Po.

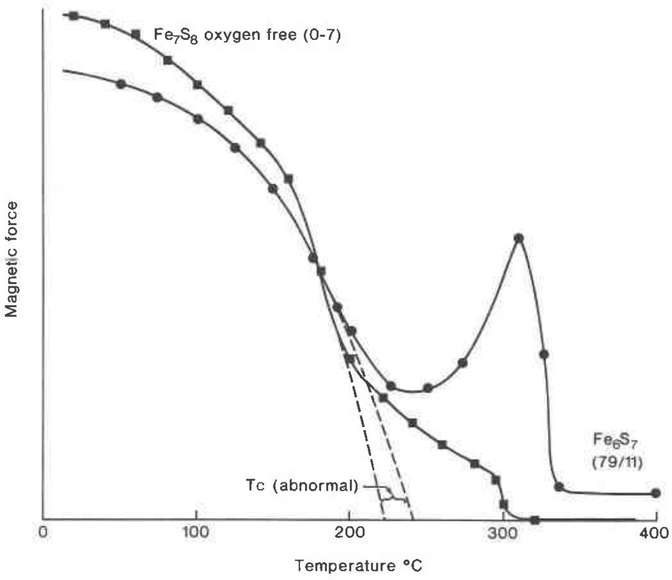

Fig. 5. Thermomagnetic heating curves for two metastable "abnormal" pyrrhotites. The first part of each curve is typical of thermal demagnetization, and the critical temperature of the quenched phase is given by extrapolation. Atomic rearrangement occurs at temperatures above about 180°C, resulting in normal monoclinic pyrrhotite.

sured from d_{102} by Arnold's determinative curve as modified by Yund and Hall (1969), may indicate loss of solid-solution oxygen or precipitation of pyrite. Loss of sulfur to the vapor is unlikely at 290°C because the vapor pressure is of the order of 10^{-12} atm (Burgmann et al., 1968) and the volume is small.

Preliminary experiments were carried out at 290°C for three weeks using two natural monoclinic pyrrhotites and a synthetic pyrite-pyrrhotite mixture. All samples were examined in the magnetic balance before and after the anneals (van Riessen, 1978). The material from Mount Morgan in Queensland contained the most magnetite initially, and the effect of the annealing is shown in Table 2. The samples were quenched after annealing. The comparatively slow heating and cooling during a thermomagnetic run allows a redistribution of phases. The results show that oxygen is removed preferentially by the buffer from solid solution rather than from existing magnetite; more magnetite then dissolves during the thermomagnetic run. The work also showed that SnS$_2$ removes some oxygen from the sample, but that SiS$_2$ is much more effective. Only one sample converted fully from monoclinic pyrrhotite to hexagonal during the anneal, even though other samples started with less oxygen and less sulfur. Oxygen diffusion in this sample may be assisted by movements in the sulfur array.

A variety of pyrrhotites was then annealed at lower temperatures (250–275°C) in evacuated capsules for periods of up to six months. There were minor changes in Curie points, and evidence of two magnetic phases in some samples, but all gave thermomagnetic behavior characteristic of monoclinic pyrrhotite.

Samples were also given long-term anneals at 290°C with an SiS$_2$ buffer. Portions were removed from the furnace at intervals, and some of these were X-rayed. The short-term changes in composition were found to continue until the pyrrhotite composition passed Fe$_9$S$_{10}$ and the material became hexagonal. Although all samples did not complete this change during the experiment, all compositions changed in the same direction, and the monoclinic β angle also moved closer to 90°. Annealing without the getter produced much smaller changes.

The results of annealing are shown by Figure 6. On the basis of these limited data, it can be said that in the ab-

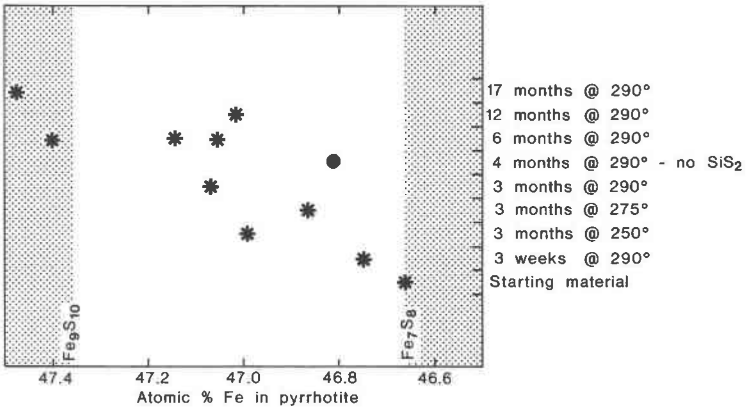

Fig. 6. Effect of annealing on pyrrhotite. The composition of the pyrrhotite determined from d_{102}, presumably coexisting with pyrite, is plotted with respect to annealing conditions. All samples marked with a star were annealed with SiS$_2$. Many other samples with different starting materials, not shown, are consistent with this scheme.

sence of oxygen, monoclinic pyrrhotite is unstable at 290°C with respect to hexagonal pyrrhotite and pyrite, and probably also at temperatures down to 250°C. In the absence of a buffer, the same trend occurs at 290°C, but at a slower rate. This was confirmed by several measurements of four different pyrrhotites annealed for three weeks in different batches. In every case, the change of composition was approximately twice as rapid when the SiS_2 buffer was present. SnS_2 produced an intermediate effect. It thus appears that for our natural samples, the transition temperature is somewhat below 290°C. The mechanism by which oxygen stabilizes the monoclinic pyrrhotite is not known.

SUMMARY

Oxygen is soluble and mobile in monoclinic pyrrhotites even at low temperatures. Its solubility increases markedly with temperature. If oxygen is excluded, the transformation from monoclinic to hexagonal pyrrhotite is accelerated, but it is not yet known whether this is due to enhancement of the relative stability of the hexagonal phase in the absence of oxygen, or to the fact that oxygen in solution impedes kinetic changes. The presence of oxygen seems also to make certain "abnormal" pyrrhotites more stable. Again, this could be a kinetic effect.

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MANUSCRIPT RECEIVED MARCH 29, 1985
MANUSCRIPT ACCEPTED JANUARY 26, 1987