MONOCLINIC PYRRHOTITE

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Recent literature has produced much information on the thermal and compositional stability and on the natural occurrences and mineral associations of monoclinic pyrrhotite. These data together with those obtained from new field and laboratory studies have made it possible to derive the phase relations from 600° to about 200°C in the portion of the Fe-S-O system which involves the minerals hexagonal pyrrhotite, pyrite, monoclinic pyrrhotite and magnetite.

Monoclinic pyrrhotite is stable below 310 ± 5°C. Near the upper limit of its thermal stability range it can only be synthesized at rather low, closely controlled oxygen pressures, but over a fairly large variation in Fe/S ratios. Monoclinic pyrrhotite has an Fe/S+O ratio of, or near, 7/8.

Monoclinic pyrrhotite in the ternary system is stable with hexagonal pyrrhotite and pyrite below 310 ± 5°C. At about 220°C an invariant reaction involving hexagonal pyrrhotite, pyrite, monoclinic pyrrhotite, magnetite and vapor, takes place. Below this temperature monoclinic pyrrhotite and magnetite form a stable mineral pair. The maximum concentration of oxygen in solid solution in monoclinic pyrrhotite occurs at this invariant temperature. The monoclinic pyrrhotite solid solution composition may reach its closest proximity to the Fe-S boundary at the temperature where smythite becomes stable (about 75°C).

Hexagonal pyrrhotite takes a small amount of oxygen in solid solution. This oxygen may be responsible for the formation of hexagonal superstructures and may be the cause of the metastable behavior of supersaturated hexagonal pyrrhotite.

Key words: monoclinic pyrrhotite, phase relations, Fe-S-O system, oxygen in sulfides.

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Introduction

Of all binary sulfide systems, of interest to geologists and metallurgists alike, the one involving the two elements iron and sulfur has been investigated in the greatest detail and by the greatest number of researchers. From the point of view of frequency of occurrence of its minerals knowledge of the Fe-S system is more useful than that of any other binary system. Pyrite is the most commonly occurring sulfide mineral. Pyrrhotites are also very often observed in nature and are, in commonness of occurrence, second only to pyrite. Experimental studies have provided much information about the iron sulfide minerals. The most reliable data have been obtained at elevated temperatures where reaction rates are fast. The phase relations at low temperatures are more

complicated than those at high temperatures and laboratory experiments are hampered at low temperatures by slow rates of reactions.

The phase relations in this system remain a puzzle even at moderate temperatures and even after many years of studies.

It has gradually been realized that some of the minerals originally believed to be pure iron sulfides do contain other components. Thus, for instance mackinawite contains nickel and has the formula $(Fe,Ni)_{1.1}S$ (Evans *et al.* 1964; Fleischer 1983); smythite contains nickel, as well, and has the formula $(Fe,Ni)_9S_{11}$ (L. A. Taylor 1970 b; Fleischer 1983) and marcasite appears to contain hydrogen in its structure (Kullerud 1967). Recently convincing evidence has been presented to prove beyond reasonable doubt that monoclinic pyrrhotite contains oxygen in solid solution and that this oxygen may stabilize the monoclinic structure (Graham 1983).

The present paper attempts to evaluate the laboratory and field observations pertaining to the stability of monoclinic pyrrhotite, to derive the phase relation prevailing in the pertinent portion of the Fe-S-O system during formation of this mineral and to explain its association with other oxides and sulfides of iron.

Previous field and laboratory studies

Monoclinic pyrrhotite was first described by Byström (1945) who observed it as the only pyrrhotite phase in some Swedish ores. He identified mixtures of hexagonal and monoclinic pyrrhotites in other ores and hexagonal pyrrhotite only in yet others. Byström determined the cell dimensions of monoclinic pyrrhotites from 14 localities. On ten of these localities monoclinic pyrrhotite occurred in the absence of hexagonal pyrrhotite. The a values of these monoclinic pyrrhotites varied from 5.933 to 5.941 Å, the b dimensions varied from 3.425 to 3.430 Å, the c dimensions varied from 5.677 to 5.689 Å, and the β angle varied from 89.56° to 89.66°. The

compositions of these ten monoclinic pyrrhotites varied from 51.74 to 53.01 atomic %S. On the four localities where hexagonal and monoclinic pyrrhotites coexisted the latter had a values which varied from 5.936 to 5.942 Å, b values from 3.427 to 3.431 Å, c values from 5.685 to 5.689 Å, and β angles from 89.45° to 89.63°. The compositions of these four monoclinic pyrrhotites varied from 52.26 to 52.68 atomic %S. Byström heated one specimen of monoclinic pyrrhotite (from Yxsjö) for 15 hours at 600°C in an evacuated silica tube and obtained hexagonal pyrrhotite + pyrite. He also heated a mixture of hexagonal and monoclinic pyrrhotite (from Kleva) in the same manner also at 600°C for 15 hours and again obtained hexagonal pyrrhotite + pyrite. Byström did not discuss the minerals coexisting with pyrrhotite on these 14 Swedish localities, but he established monoclinic pyrrhotite as a magnetic mineral of rather common occurrence. He found that monoclinic pyrrhotite can coexist with hexagonal pyrrhotite, that it on heating to 600°C decomposes to hexagonal pyrrhotite and pyrite, and that its composition lies inside the range of 51.74 to 53.01 atomic %S.

Buerger (1947) investigated single crystals of ferromagnetic pyrrhotite from two localities by the precession method. These crystals revealed hexagonal superstructure characteristics with A = 2a = 6.87Å. C = 4c = 22.7Å (where a and c refer to the axes of pyrrhotite with the B-8 structure). Buerger found some indications pointing to a lower than hexagonal, possibly monoclinic, structure.

Bertaut (1952) confirmed that pyrrhotite with Fe_7S_8 composition has monoclinic structure and showed that it possesses a superlattice with parameters B = 6,865Å, A = B√3 = 11.9Å, C = 22.72Å and β = 89°33'. Based upon Byström's cell a = 5.94Å, b = 3.43Å, c = 5.68Å and β = 89.6°; A = 2a (2 × 5.94), B = 2b (2 × 3.43) and C = 4c (4 × 5.68). According to current nomenclature this ferromagnetic monoclinic pyrrhotite is loosely referred to as »4c» pyrrhotite.

Grönvold and Haraldsen (1952) synthesized a monoclinic pyrrhotite with $Fe_{0.877}S$ (53.27 at %S) composition at 290°C. This phase did not form at 325°C and was found to have broken down when heated to 360°C. Bertaut (1953) found monoclinic pyrrhotite to have an ordered vacancy structure. The unit cell contains 8 Fe_7S_8 molecules (or $4 \times 8 = 32$ NiAs unit cells). Natural crystals are almost always twinned which caused problems in the study of their crystallography. Wuench (1963) was able to unravel the twinning complications and found that the β angle is larger than 90°, not smaller, as reported by previous authors.

Corlett (1968) was successful in locating and studying untwinned crystals which were found to have an F-face-centered unit cell. The parameters for this cell a = 11.88 ± 0.01Å, b = 6.86 ± 0.01Å, c = 22.74 ± 0.01Å and β = 90°38' ± 4' were derived on material from Kisbanya with composition 46.8 ± 0.2 at %Fe. High temperature precession photographs show that the 4c structure of this material is retained only below 225 ± 10°C.

A considerable number of studies have been undertaken to determine the thermal and compositional range of stability of monoclinic pyrrhotite. Kullerud et al (1963) heated a number of natural monoclinic pyrrhotites in evacuated silica tubes and found that they invert to hexagonal pyrrhotites when kept at 260°C for one year. These monoclinic pyrrhotites have a nearly constant composition of 46.45 to 46.70 at %Fe. von Gehlen (1963) found that synthetic monoclinic pyrrhotite of Fe_7S_8 composition is stable to 300°C.

Carpenter and Desborough (1964) and Desborough and Carpenter (1965) found monoclinic pyrrhotite stable below 315°C and to have Fe_7S_8 composition. In the latter paper these authors comment that Fe_7S_8 can form at temperatures as high as 600°C and high Po_2 and state »It seems possible that at high temperature and high Po_2 oxygen enters the pyrrhotite structure and alters the phase relations between pyrrhotite and pyrite». Mariko (1965) heated natural monoclinic pyrrhotite at 400°C and reported that it inverted to hexagonal pyrrhotite which in turn was converted to monoclinic pyrrhotite when reheated at 200°C for 48 hours. Sugaki and Shima (1966) found that synthetic monoclinic pyrrhotite forms a homogeneous solid solution over the composition range from 46.95 to 46.51 atomic percent Fe. Clark (1966) found that synthetic monoclinic pyrrhotite with about 46.8 atomic percent Fe is stable between 150° and 308°C. His monoclinic pyrrhotite solid solution field extends from about 46.8 to 46.5 atomic percent Fe at 200°C. Kullerud (1967) in a tentative diagram showing the phase relations in the region from 30—50 atomic percent Fe in the condensed Fe-S system, includes monoclinic pyrrhotite as a stable phase below 310°C.

Hall and Yund (1966), Yund and Hall (1969) and Arnold (1969) pointed out that monoclinic pyrrhotite is metastable with respect to hexagonal pyrrhotite and pyrite. Experiments on synthetic materials lasting 111 days at 297 and 225°C produced coexistence of the three phases: monoclinic pyrrhotite, hexagonal pyrrhotite and pyrite. Arnold (1969) found monoclinic pyrrhotite to be stable below 304°C and Yound and Hall (1969) concluded that this phase is not stable above 290°C. Taylor (1970 a) found synthetic monoclinic pyrrhotite of Fe_7S_8 composition to be stable below 292°C. He heated synthetic monoclinic pyrrhotite of Fe_7S_8 composition at 330°C for 10 minutes in evacuated silica tubes. Hexagonal pyrrhotite was produced and was quenched by rapid chilling in cold water. When such tubes were cooled in air the hexagonal pyrrhotite reverted to monoclinic pyrrhotite. Similarly monoclinic pyrrhotite annealed at 304°C for 10 minutes and rapidly chilled in water produced monoclinic pyrrhotite, whereas rapid immersion in liquid nitrogen quenched the hexagonal structure. Taylor (1970 a) concluded that determination of upper stability temperature in this manner is a matter of cooling rate.

Ward (1970) who reviewed the data pertaining

to the stability of monoclinic pyrrhotite tentatively concluded that this phase is stable below about 230°C, that it forms metastably between 230 and 300—320°C and that kinetic studies are needed to obtain an understanding of its behavior. Yund and Hall (1970) observed that hexagonal pyrrhotite supersaturated with respect to pyrite (by as much as 0.18 at %Fe) did not exsolve pyrite even after annealing for more than a year and, thus, demonstrated metastable behavior.

Nakazawa and Morimoto (1970) synthesized pyrrhotites by heating iron and sulfur in evacuated silica glass tubes. They report that below 250°C monoclinic pyrrhotite appears to have essentially Fe_7S_8 composition. Above this temperature there is limited solid solution incorporating slightly more iron than indicated by the Fe_7S_8 formula. Monoclinic pyrrhotite of Fe_7S_8 composition (and coexisting with pyrite) was by Nakazawa and Morimoto (1970) found to be stable below 295°C whereas monoclinic pyrrhotite with maximum iron content (and coexisting with hexagonal pyrrhotite) was reported stable to 305°C.

Udodov and Kashaev (1971) synthesized monoclinic pyrrhotite from FeS + S mixtures and reported that this phase with Fe_7S_8 composition is stable below 220°C. Bennett *et al.* (1972 a) showed that the almost ubiquitous fine-scale twinning in natural monoclinic pyrrhotite is associated with a magnetic domain structure. They explained how smythite may exsolve from monoclinic pyrrhotite as a submicroscopic intergrowth, perhaps by a spinodal mechanism. Bennett et al. (1972 b) identified submicrometer thick lamellae of magnetite in monoclinic pyrrhotite from Norseman, Western Australia. The lamellae (111) surface of magnetite occurs parallel to (001) of pyrrhotite corresponding to a close fit of close-packed planes of the two structures. This perfect lamellar arrangement of magnetite in unaltered pyrrhotite indicates origin by exsolution which requires solid solution of oxygen in pyrrhotite.

Kissin and Scott (1972), Scott and Kissin (1973), Rising (1973) and Kissin (1974) utilized hydrothermal recrystallization methods to avoid the problems of metastability that previous researchers had encountered in their efforts to clarify the temperature and composition boundaries of the field of stability of monoclinic pyrrhotite. Rising (1973) found monoclinic pyrrhotite to be a stable phase below 251 ± 3°C and Kissin (1974) gives 254°C as the upper stability limit for this phase. These hydrothermal studies indicate that at 100°C the monoclinic pyrrhotite solid solution is about 0.5 at %Fe wide, and that Fe_7S_8 composition lies at, or near, its iron deficient limit.

Scott (1974) explains how these new methods produce internally consistent data delineating the phase relations for the monoclinic pyrrhotite phase. However, Sugaki *et al.* (1977) in hydrothermal type experiments found monoclinic pyrrhotite stable to 275°C. Bennett and Graham (1980) found monoclinic pyrrhotite to convert to hexagonal pyrrhotite in hydrothermal experiments at 280°C. Heating of this hexagonal pyrrhotite in an evacuated silica tube at 280° for 2—3 hours transformed it back to monoclinic pyrrhotite. Bennett and Graham (1980) inferred that »a component of water enters into the hexagonal pyrrhotite ⇌ monoclinic pyrrhotite reaction, and that the hydrothermal phase diagram is different from the dry phase diagram». Sugaki *et al.* (1980) analyzed natural monoclinic pyrrhotites and concluded that this phase has stoichiometric Fe_7S_8 composition. They did not find a field of solid solution such as reported by Kissin (1974).

Graham (1978) reports from observations of the Nairne pyrite formation, on the apparent ease with which small hexagonal pyrrhotite grains are oxidized to the monoclinic form. Monoclinic rims around hexagonal pyrrhotite grains are always present in the neighborhood of pyrite inclusions, and nowhere was a pyrite-hexagonal pyrrhotite assemblage observed. Graphite and monoclinic pyrrhotite were never observed together. Hex-

agonal pyrrhotite and graphite do coexist. Graphite and hexagonal pyrrhotite + pyrite seem to be commonly associated on many localities. Van Riessen (1978) provided evidence to indicate that monoclinic pyrrhotites contain a small concentration of oxygen in solid solution. He found that removal of oxygen from monoclinic pyrrhotite leads to a gradual change towards the hexagonal pyrrhotite structure. Bennett and Graham (1980), to test whether oxygen occurs in solid solution in monoclinic pyrrhotite, built a thermo balance which could be used to identify and quantify magnetite, hexagonal pyrrhotite, and monoclinic pyrrhotite. They provided experimental evidence for solid state exsolution of magnetite from monoclinic pyrrhotite which was postulated already in the Bennett et al. (1972 b) paper. This evidence strongly indicated that monoclinic pyrrhotite may take oxygen (or Fe_3O_4) in solid solution and, thus, extend into the ternary Fe-S-O system. The authors speculated that compositional differences between monoclinic pyrrhotite synthesized in the dry (Fe-S) system and monoclinic pyrrhotites synthesized in the hydrothermal system could explain the discrepancies in measured thermal stabilities. It was observed by Graham and Bennett (1983) that at 600°C the solubility of magnetite in pyrrhotite is 0.75 ± 0.07 %, corresponding to 0.21 ± 0.02 % oxygen. Graham (1983) found by neutron activation analysis measurable amounts of oxygen in natural monoclinic as well as in hexagonal pyrrhotites. Graham and McKenzie (1983) used the Harwell nuclear microprobe to determine the concentration of oxygen in pyrrhotites and were able to demonstrate a distribution of oxygen throughout the volume of both hexagonal and monoclinic pyrrhotite. Monoclinic pyrrhotite from Kambalda was found to contain about 0.1 wt% oxygen, whereas hexagonal pyrrhotite from Nairne contained about 0.06 wt% 0. Graham et al. (1983) annealed at 290°C synthetic monoclinic pyrrhotite of Fe_7S_8 composition with SiS_2 and SnS_2. SiS_2 was found to effectively remove oxygen from the pyrrhotite and produce SiO_2 at

the same time as monoclinic pyrrhotite changed composition towards Fe_9S_{10} and became hexagonal.

Graham (1983) expresses the opinion that »the monoclinic structure may be stabilized by the presence of magnetite lamellae as nuclei, or merely by the distorting effect of the smaller oxygen ions in solid solution». He concludes that the monoclinic phase is unstable in the absence of oxygen.

Phase relations

Monoclinic pyrrhotite has been recognized as a mineral for 40 years. Virtually hundreds of papers have been published during this period on the crystal structure, composition, thermal stability, magnetic properties and mode of occurrence of this mineral. In this paper the data are reviewed pertaining particularly to the composition and thermal stability of natural as well as synthetic monoclinic pyrrhotites. The pertinent literature data are shown in Table 1 a-e. It is noted from Table 1 a that natural monoclinic pyrrhotite appears stable below about 225°C. Table 1 b lists the results of dry silica tube experiments designed to delineate the stability of synthetic monoclinic pyrrhotite. These dry experiments, indicate that synthetic monoclinic pyrrhotite is stable below about 290°C. Udodv and Kashaev (1971) assume that monoclinic pyrrhotite is stable up to 220°C, but offer no experimental evidence or description. Table 1 c shows that in some hydrothermal experiments synthetic monoclinic pyrrhotite is stable below about 250°C. In others it is stable to 275°C. In one instance monoclinic pyrrhotite which at 280°C was converted to hexagonal pyrrhotite under hydrothermal conditions reverted to monoclinic pyrrhotite when reheated at the same temperature in an evacuated silica tube.

Table 1 d indicates that natural monoclinic pyrrhotites essentially contains iron and sulfur in the 7:8 atomic ratio and that in addition it contains about 0.1 wt.% oxygen in solid solution.

Table 1. Thermal stability and composition of natural and synthetic monoclinic pyrrhotites.

a. Stability of natural monoclinic pyrrhotite in dry experiments

Stable below 600°C (Byström, 1945)
»   »   260°C (Kullerud et al., 1963)
»   at   225 ± 10°C (Corlett, 1968)
»   at   200°C (Mariko, 1965)

b. Stability of synthetic monoclinic pyrrhotite in dry experiments

Stable below 315°C (Carpenter and Desborough, 1964)
»   »   310°C (Kullerud, 1967)
»   »   308°C (Clark, 1966)
»   »   304°C (Arnold, 1969)
»   at   300°C (von Gehlen, 1963)
»   »   300 ± 5°C (Nakazawa and Morimoto, 1970)
»   »   292°C (Taylor, 1970)
»   »   290°C (Grönvold and Haraldsen, 1952)
»   »   290°C (Yund and Hall, 1969)

c. Stability of synthetic monoclinic pyrrhotite in hydrothermal experiments

Stable below 280°C (Bennett and Graham, 1980)
»   at   275°C (Sugaki et al., 1977)
»   »   254°C (Kissin, 1974)
»   »   251 ± 3°C (Rising, 1973)

d. Composition of natural monoclinic pyrrhotite

45.99 — 48.26 atomic % Fe (Byström, 1945)
        46.8 ± 0.2 at.% Fe (Corlett, 1968)
        46.45 — 46.70 at.% Fe (Kullerud et al., 1963)
Fe_7S_8 (46.67 at.% Fe) (Sugaki et al., 1980)
Contains oxygen in its structure (Van Riessin, 1978)
Contains about 0.1 wt% oxygen (Graham and McKenzie, 1983)

e. Composition of synthetic monoclinic pyrrhotite

46.73 at.% Fe [$Fe_{0.877}S$] (Grönvold and Haraldsen, 1952)
46.67 at.% Fe [Fe_7S_8] and some oxygen (Desborough and Carpenter, 1965)
46.51 — 46.95 at.% Fe (Sugaki and Shima, 1966)
46.5 — 46.8 at.% Fe (Clark, 1966)
46.67 at.% Fe [Fe_7S_8] (von Gehlen, 1963)
46.67 at.% Fe [Fe_7S_8] (Taylor, 1970)
46.67 at.% Fe [Fe_7S_8] (Nakazawa and Morimoto, 1970)
46.67 at.% Fe [Fe_7S_8] (Sugaki et al., 1980)
0.5 at.% Fe solid solution near Fe_7S_8 composition (Rising, 1973)
0.5 at.% Fe solid solution near Fe_7S_8 composition (Kissin, 1974)
Contains oxygen in its structure (van Riessen, 1978)
Contains oxygen in its structure (Bennett and Graham, 1980)

Table 1 e indicates that synthetic monoclinic pyrrhotite contains iron and sulfur in, or near, the 7:8 atomic ratio. The variation in composition does not appear to exceed 0.5 at.%. This table also points out that synthetic monoclinic pyrrhotite contains oxygen in solid solution. Graham and Bennett (1983) found synthetic hexagonal pyrrhotite to contain as much as 0.2 wt.% oxygen at 600°C. At this temperature the hexagonal $Fe_{1-x}S$ solid solution spans from 50 to about 46 at.%Fe. Fe_7S_8 composition lies inside the hexagonal pyrrhotite solid solution field at 600°C and the composition of monoclinic pyrrhotite, containing 0.1 wt.% oxygen, falls inside the oxygen bearing $Fe_{1-x}S$ hexagonal solid solution field at this temperature. The phase relations at 600°C involving pyrite, hexagonal pyrrhotite, magnetite and hematite in the condensed Fe-S-O system as determined by Kullerud (1957) are shown in Figure 1. The phase relations
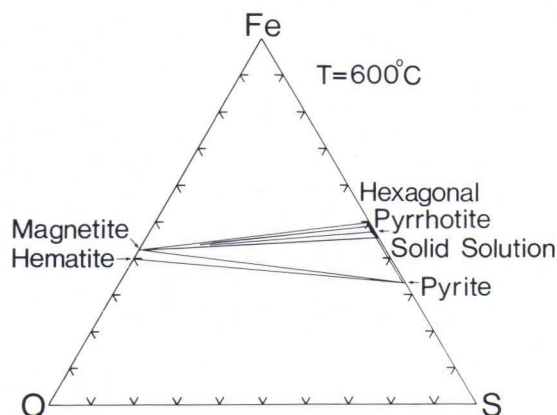
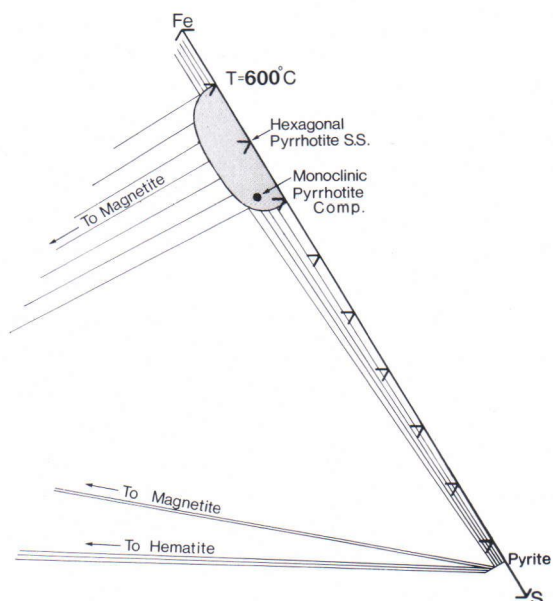Fig. 1. Phase relations in the Fe-S-O system at 600°C. All phases and phase assemblages coexist with vapor.

Fig. 3. Phase relations in a portion of the Fe-S-O system at 400°C. All phases and phase assemblages coexist with vapor. Note that monoclinic pyrrhotite composition at this temperature is situated in the divariant field between hexagonal pyrrhotite solid solution and pyrite and that this field extends into the ternary system.

Fig. 2. Phase relations in a portion of the Fe-S-O system at 600°C. All phases and phase assemblages coexist with vapor. Note that monoclinic pyrrhotite composition at this temperature is situated inside the hexagonal pyrrhotite solid solution field.

as shown in this figure and in the following ones (Figures 2—5) were derived under conditions where vapor is an inherent phase. Vapor, therefore, always occurs as a phase additional to those shown in the figures. It is noted in Figure 1 that tie-lines exist between magnetite and hexagonal
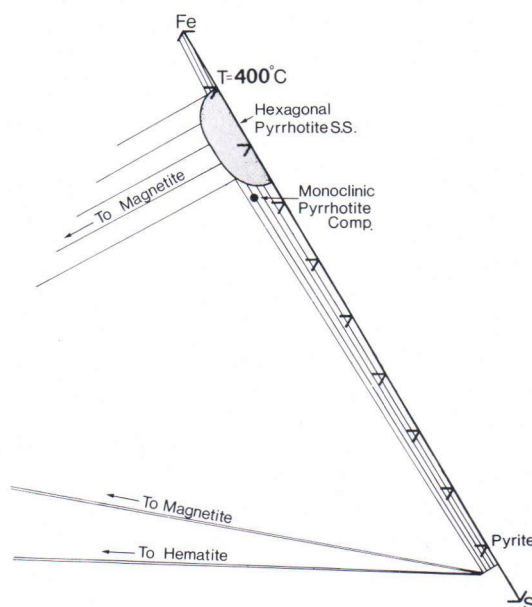
pyrrhotite, between magnetite and pyrite and between hematite and pyrite. The phase relations in the pyrrhotite-pyrite region are illustrated in detail in Figure 2. Monoclinic pyrrhotite composition, in which is included 0.1 % oxygen, is seen to lie well within the boundaries of the hexagonal pyrrhotite solid solution field at 600°C. It is also noted that the hexagonal pyrrhotite + pyrite + vapor divariant field has a real and measurable ternary width which near the hexagonal pyrrhotite solid solution boundary might extend to 0.2 wt.% oxygen. Data is not available on the solid solution of oxygen in pyrite. The width of the hexagonal pyrrhotite + pyrite + vapor divariant field near pyrite is not known, but the field probably is narrow (less than 0.1 % oxygen wide). This solubility has been exaggerated in Figures 2—5 to illustrate phase relations. On cooling below 600°C the hexagonal pyrrhotite solid solution field contracts towards

FeS composition along the Fe-S binary boundary and Fe_7S_8 composition is reached at about 470°C. This field at the same time gradually diminishes its ternary width because the hexagonal pyrrhotite solid solution loses its ability to dissolve oxygen with decreasing temperature. Monoclinic pyrrhotite composition for this reason may fall outside the hexagonal pyrrhotite solid solution field even at 500°C. This contraction of the hexagonal pyrrhotite field continues and at 400°C the phase relations may resemble those shown in Figure 3.

Monoclinic pyrrhotite composition is noted to lie in the hexagonal pyrrhotite + pyrite + vapor divariant field. Tie-lines between hexagonal pyrrhotite and magnetite, pyrite and magnetite and pyrite and hematite exist at 400°C as they did at 600°C. Cooling below 400°C leads to further contraction of the hexagonal pyrrhotite solid solution field. At about 310°C a reaction takes place whereby oxygen containing hexagonal pyrrhotite reacts with oxygen containing pyrite (in the presence of vapor) to produce monoclinic pyrrhotite. This reaction results in the formation of two new divariant fields (monoclinic pyrrhotite + hexagonal pyrrhotite + vapor and monoclinic pyrrhotite + pyrite + vapor) and two new univariant fields (monoclinic pyrrhotite + oxygen poor hexagonal pyrrhotite + oxygen poor pyrite + vapor and monoclinic pyrrhotite + oxygen rich hexagonal pyrrhotite + oxygen rich pyrite + vapor). The phase relations at about 300°C where monoclinic pyrrhotite is a stable ternary phase are shown in Fig. 4. The two univariant fields become wider with decreasing temperature. The one containing monoclinic pyrrhotite + oxygen poor hexagonal pyrrhotite + oxygen poor pyrite + vapor very gradually approaches the Fe-S boundary. The other containing monoclinic pyrrhotite + oxygen rich hexagonal pyrrhotite + oxygen rich pyrite + vapor broadens towards oxygen with decreasing temperature below 300°C. In this action the divariant field containing oxygen rich hexagonal pyrrhotite + oxygen rich pyrite + vapor grad-

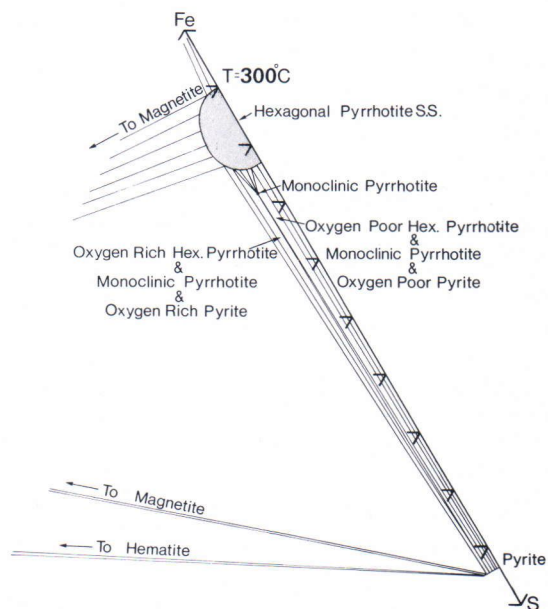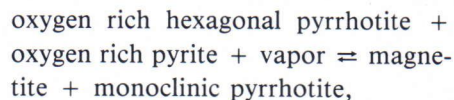

Fig. 4. Phase relations in a portion of the Fe-S-O system at 300°C. All phases and phase assemblages coexist with vapor. At this temperature monoclinic pyrrhotite is a stable phase. It contains about 0.1 wt% oxygen.

ually narrows and attains a single line width at some temperature below 250°C. At this temperature a reaction takes place whereby tie-lines between oxygen rich hexagonal pyrrhotite and oxygen rich pyrite are broken and replaced by tie-lines between monoclinic pyrrhotite and magnetite. This reaction, which involves the five phases: oxygen rich hexagonal pyrrhotite + oxygen rich pyrite + monoclinic pyrrhotite + magnetite + vapor, is invariant and can be written:

oxygen rich hexagonal pyrrhotite + oxygen rich pyrite + vapor ⇌ magnetite + monoclinic pyrrhotite,

where the assemblage to the left of the arrows is stable above and the assemblage to the right is stable below the invariant point temperature. The phase relations at about 200°C where tie-lines exist between magnetite and monoclinic pyrrhotite are shown in Figure 5. The exact temperature of this invariant point is not known.
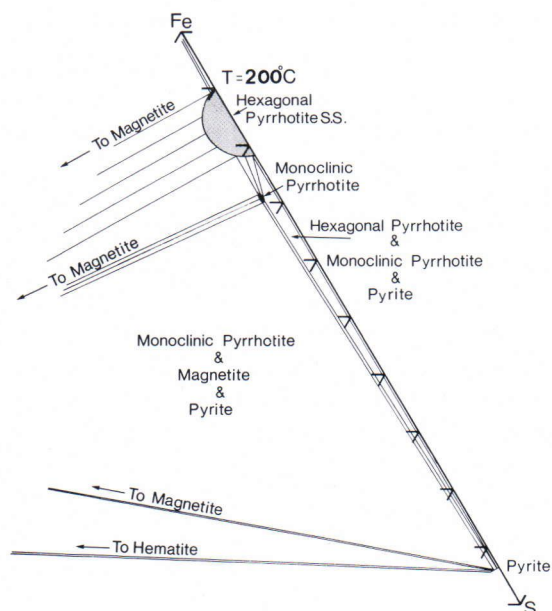
Fig. 5. Phase relations in a portion of the Fe-S-O system at 200°C. All phases and phase assemblages coexist with vapor. At this temperature monoclinic pyrrhotite is stable also with magnetite.

Some studies (Corlett 1968 and Mariko 1965) indicate that it may be situated at about 220°C.

Discussion

The phase relations as illustrated in Figures 2—5 may be used to explain the apparent contradictory experimental results listed in Table 1. First we may consider the experiments performed on natural monoclinic pyrrhotites. These experiments are listed in Table 1 a. Natural materials generally have been exposed to the oxygen and humidity of the atmosphere for long periods of time. They are not pure, monomineralic substances, but are intermixed with small amounts of other minerals. In spite of attempts to remove such impurities prior to heating experiments it is likely, not to say certain, that the bulk compositions of such silica tube experiments contain slightly more oxygen than that of pure monoclin-

ic pyrrhotite. Slow heating inside the temperature range where monoclinic pyrrhotite-magnetite coexist may produce a very small amount of magnetite in coexistence with the prevailing monoclinic pyrrhotite phase. Mariko (1965) heated natural monoclinic pyrrhotite in evacuated silica tubes and found it to be stable at 200°C. He did not report possible coexistence of magnetite. Corlett (1968) heated single crystals of natural monoclinic pyrrhotite with a stream of hot nitrogen and performed x-ray investigations at elevated temperatures. She reported monoclinic pyrrhotite to be stable at 225 ± 10°C and hexagonal pyrrhotite to be stable at 230 ± 10°C. It is likely that the composition of her experiment at 225 ± 10°C was situated inside the univariant field: monoclinic pyrrhotite + oxygen-rich hexagonal pyrrhotite + oxygen rich pyrite + vapor on Fig. 4. Whereas the bulk composition at 230 ± 10°C fell within the oxygen-rich hexagonal pyrrhotite + oxygen rich pyrite + vapor divariant field which widens rapidly with increasing temperature. It is possible that the nitrogen stream prevented further oxidation of the monoclinic pyrrhotite during the heating. However, the vapor over a compound of essentially Fe_7S_8 composition consists almost entirely of sulfur and the vapor pressure increases rapidly at elevated temperatures. This vapor was in Corlett's experiments removed by the nitrogen stream. Consequently there must have been some sulfur losses in these experiments.

The silica tube experiments performed by Kullerud et al. (1963) indicate that several natural monoclinic pyrrhotites after 1 year of heating at 260°C have converted to hexagonal pyrrhotites. These experiments, for reasons discussed above, also contained more oxygen than does pure monoclinic pyrrhotite. Their bulk compositions below 260°C were situated inside the univariant field: monoclinic pyrrhotite + oxygen-rich hexagonal pyrrhotite + oxygen rich pyrite + vapor. Above this temperature the bulk compositions fell within the divariant field: oxygen-rich hexagonal pyrrhotite + oxygen-rich pyrite + vapor.

These experiments on the thermal stability of natural monoclinic pyrrhotites did not provide the stability limit of pure monoclinic pyrrhotite because their bulk compositions were not that of the pure phase.

The numerous dry silica tube experiments performed to determine the thermal stability of synthetic monoclinic pyrrhotite were, without exception, based upon the assumption that monoclinic pyrrhotite is a phase in the pure Fe-S system. These experiments utilize high purity Fe and S, but it is very difficult, not to say impossible, to avoid oxygen contamination due to surface oxidation of sulfur and even of freshly reduced iron. It is not possible to completely evacuate the silica tubes. Some oxygen may enter the tubes during experimentation, the first step of which often consists of reacting Fe + S to produce a hexagonal pyrrhotite phase at 600°C or even higher temperature. The next step usually involves opening the tubes and grinding the material followed by reheating to assure product homogeneity. The final product is stored and small portions of it are used for numerous experiments at a variety of temperatures. It is understandable that this final product is oxidized; just how much depends upon the quality of the starting materials and the care taken during each step of the synthesis. With reasonable care in this type of synthesis the oxygen contamination should not exceed that of pure monoclinic pyrrhotite. The data listed in Table 1 b indicate that the Carpenter and Desborough (1964) experiments may have contained rather exactly the amount of oxygen contained in pure monoclinic pyrrhotite. The remaining experiments apparently contained lesser amounts of oxygen. In the experiments by Grönvold and Haraldsen (1952) as well as those by Yund and Hall (1969) the bulk compositions merged into the oxygen-poor hexagonal pyrrhotite + oxygen-poor pyrite + vapor divariant field at a temperature slightly above 290°C. The remaining dry silica tube experiments listed in Table 1 b on the stability of synthetic monoclinic pyrrhotite indicate such merger anywhere between 315 and 290°C.

In the hydrothermal experiments performed to determine the thermal stability of monoclinic pyrrhotite, as in the dry silica tube experiments, it was assumed that this phase is a pure iron sulfide. The experiments listed in Table 1 c were conducted under fo_2, fs_2 and pH conditions which permitted monoclinic pyrrhotite to exist as high as 275°C (Sugaki *et al.* 1977). In other experiments (Rising 1973 and Kissin 1974) it was found to be stable below about 254°C. The occurrence of monoclinic pyrrhotite in this type of experiment is again very much dependent on the oxygen concentration. The fo_2 in the Rising (1973) and Kissin (1974) runs was likely higher than that in the runs by Sugaki *et al.* (1977). If fs_2, pH and particularly fo_2 in such experiments are buffered exactly to produce only pure monoclinic pyrrhotite its breakdown temperature will coincide with that determined in dry experiments.

The experiment by Bennett and Graham (1980) listed in Table 1 c is interesting. They found that under certain hydrothermal conditions monoclinic pyrrhotite converted to hexagonal pyrrhotite at, or below 280°C. This hexagonal pyrrhotite was cleaned, dried and reheated at 280°C in an evacuated silica tube where it reverted to monoclinic pyrrhotite. This can be illustrated by Figure 4. In the first step monoclinic pyrrhotite is heated hydrothermally under fo_2 conditions which at 280°C lie in the oxygen-rich hexagonal pyrrhotite + oxygen-rich pyrite + vapor divariant field. Reheating dry in an evacuated silica tube where the fo_2 was lower than in the hydrothermal experiment permitted monoclinic pyrrhotite to form again.

The papers listed in Table 1 do not discuss at length the mechanism of monoclinic pyrrhotite formation or disappearance and do not mention whether pyrite occurs in the experiments as Figures 2—5 indicate it should under equilibrium conditions. Yund and Hall (1970) demonstrated that, in what they believed to be the pure Fe-S system, hexagonal pyrrhotite supersaturated with

respect to pyrite did not exsolve pyrite even after prolonged annealing. As seen above the Yund and Hall (1970) material must have containing a small amount of oxygen in solid solution. The very presence of oxygen may well have prevented pyrite exsolution. It is not unreasonable to assume that the oxygen content, however small, may be responsible for the metastable behavior described by Yund and Hall (1970). Such metastability may not occur in the pure Fe-S system. This should be investigated in the laboratory.

The compositions given by various authors for natural monoclinic pyrrhotites are listed in Table 1 d. The compositions given by Byström (1945), Kullerud et al. (1963), Corlett (1968) and Sugaki et al. (1980) all are close to Fe_7S_8. In addition Van Riessen (1978) points out that natural monoclinic pyrrhotite contains some oxygen and Graham and McKenzie (1983) reports oxygen content of about 0.1 wt.%. The compositions given by a number of authors for synthetic monoclinic pyrrhotites are listed in Table 1 e. Ten of the 12 references give the composition as, or very close to, Fe_7S_8. In addition Desborough and Carpenter (1965) believe this phase to contain some oxygen and the two remaining references, (Van Riessen, 1978 and Bennett and Graham, 1980) report that oxygen occurs in solid solution in monoclinic pyrrhotite.

The data of Table 1 d and e indicate that the $Fe/S + O$ atomic ratio of monoclinic pyrrhotite does not deviate from the 7:8 ratio by more than about 0.5 atomic percent. The Fe_7S_8 formula contains 39.62 wt.%S. If monoclinic pyrrhotite contains about 0.1 wt.%0 replacing sulfur, its Fe:S ratio increases from 0.875 (7/8) to 0.879. Graham et al. (1983) found that synthetic monoclinic pyrrhotite became hexagonal and changed composition towards an Fe:S ratio of 0.900 when its oxygen was removed. It is, therefore, likely that the Fe:S ratio of monoclinic pyrrhotite is slightly larger than 7:8, but that the $Fe/S + O$ ratio adheres rather closely to the 7:8 ratio.

It seems reasonable that oxygen may replace

some sulfur in the pyrrhotite structure. Graham (1983) entertains the idea that this oxygen, being smaller than sulfur, may cause distortion sufficient to stabilize the monoclinic structure. The solid solution of oxygen as derived by considering phase relations illustrated in Figures 2—4 would reach a maximum at the temperature of the invariant point (220°C) where the five phases : hexagonal pyrrhotite + pyrite + monoclinic pyrrhotite + magnetite + vapor coexist.

At temperatures below this invariant point the solubility of oxygen in monoclinic pyrrhotite decreases resulting in exsolution of magnetite; see Figure 5. Such exsolution in nature was reported by a number of authors such as Bennett et al. (1972 b). It is possible that the monoclinic pyrrhotite solid solution field may reach its nearest proximity to the Fe-S boundary at the temperature where smythite becomes stable which is about 75°C according to Taylor (1970 b). Below this temperature the monoclinic pyrrhotite solid solution field evidently withdraws from the Fe-S boundary as indicated by smythite exsolving from monoclinic pyrrhotite as shown to occur in ores by Bennett et al. (1972 a).

The literature is replete with references to exsolution of monoclinic pyrrhotite from hexagonal pyrrhotite. Such exsolution demonstrates that the hexagonal pyrrhotite field narrows considerably below the temperature at which monoclinic pyrrhotite becomes stable, as shown in Figures 2—5. The present author has not found any evidence in the literature for exsolution of hexagonal pyrrhotite from monoclinic pyrrhotite. This indicates that the slope of the monoclinic pyrrhotite solvus toward hexagonal pyrrhotite is very steep.

Numerous publications have appeared dealing with hexagonal pyrrhotite superstructures. Morimoto and his co-workers, perhaps more than anyone else, have performed excellent studies to explain the occurrence, crystallography and stability relations of these structures. To the present author's knowledge nobody, so far, has considered the effect oxygen may have on the oc-

currence and stability of such structures. It seems reasonable to assume that the structures occurring in oxygen-rich hexagonal pyrrhotite whether this is a single phase or coexists with one or both oxygen-rich pyrite and monoclinic pyrrhotite must be different from those occurring in oxygen-poor hexagonal pyrrhotite as a single phase or coexisting with one or both oxygen-poor pyrite and monoclinic pyrrhotite (see Fig. 4). Perhaps the oxygen-rich hexagonal pyrrhotite super-structures were recorded by Kissin (1974) who utilized hydrothermal procedures, whereas the oxygen-poor hexagonal pyrrhotite super-structures were

recorded by Morimoto's group (see for instance Nakazawa and Morimoto 1970). High priority should be given primarily to studies of hexagonal superstructures as function of temperature and composition in the pure (unoxidized) Fe-S system and secondarily to studies of such structures as function of temperature and composition in the Fe-S-O system.

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