CRYSTALLOGRAPHY AND MINERALOGY OF THE PYRRHOTITE GROUP

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1. **Iron Sulphides in the Earth and Mineral Sciences**

The iron sulphides pyrite and pyrrhotite are by far the most common sulphide minerals and are commonly associated with economic ores. The properties of these minerals are therefore of great importance to mineral exploration and extractive metallurgy. A useful review of the structure and properties of some iron sulphides and their relevance to geological and industrial applications has been published by Ward (1970). Other useful compilations have been given by Flinter (1970), Ribbe (1974), Shuey (1975), Power and Fine (1976) and Vaughn and Craig (1978).

Some applications of the properties of iron sulphides will now be briefly mentioned.

(i) **Anomalous geophysical response** - mineralisation is often detected by the anomalous response of pyritic or pyrrhotitic ore bodies to various geophysical techniques. Pyrite and pyrrhotite are dense (S.G. = 5.0 and 4.6 respectively), have high electrical conductivity ($\rho ~ 10^{-3} - 3 \times 10^{-2}$ ohm-m and $\sim 5 \times 10^{-5}$ ohm-m respectively) and monoclinic pyrrhotite is highly magnetic.

(ii) **Gossan formation** - the gossans sought by exploration geologists as indicators of ore at depth are largely due to complex interactions of iron sulphides with groundwater, the atmosphere and organic matter, possibly with bacterial involvement.
(iii) Reactivity of pyrrhotitic ores - oxidation of pyrrhotite in broken ores or concentrates can cause agglomeration and spontaneous combustibility. The safety problems of mining reactive pyrrhotitic ores using ammonium nitrate explosives are also well known. Reactivity of pyrrhotite appears to depend on composition and structure.

(iv) Mineral processing and extractive metallurgy - the flotability of sulphide ores can be greatly affected by the composition and structure of pyrrhotite. Removal of fine-grained pyrite and non-magnetic pyrrhotite from ores is often a major metallurgical difficulty, but these minerals can be converted to magnetic pyrrhotite by roasting, allowing subsequent magnetic separation. The flotability of haematite can be improved by sulphidation, producing a surface of iron sulphide.

(v) Ore genesis - the chemistry of iron sulphides is critical to understanding of mineralisation processes.

(vi) Industrial applications - solid state diffusion of iron in $\text{Fe}_{1-x}\text{S}$ is a major mechanism of sulphidic attack on steels. The properties of iron sulphides are therefore important in understanding and preventing corrosion in sulphide atmospheres, for example in coal burning power stations using high sulphur coal.

(vii) Coal beneficiation and liquefaction - inorganic sulphur in the form of pyrite and marcasite in coal can be a major environmental hazard. Reduction of these iron sulphides to pyrrhotite allows magnetic separation of much of the sulphur. On the other hand pyrrhotite produced
during coal liquefaction appears to have beneficial catalytic effects on coal conversion, the benefit possibly being correlated with pyrrhotite composition (Jagadeesh and Seehra 1981).

(viii) **Rock magnetism** - most magnetic anomalies associated with sulphide mineralisation are due to monoclinic pyrrhotite. Applications of rock magnetism include analysis of pyrrhotite composition, crystal structure and grain size by magnetic methods; palaeomagnetic studies of pyrrhotite-bearing rocks; magnetic fabric of pyrrhotite-bearing rocks as an aid to interpretation of geological structure; magnetic petrophysics of pyrrhotite-bearing rocks to improve interpretation of magnetic surveys. The rock magnetism of pyrrhotite has been reviewed by Schwarz (1974) and Clark (1983a, b, c, ; 1984).

2. **Crystal structure in the pyrrhotite group**

Iron sulphides with compositions ranging from stoichiometric FeS (troilite) to Fe$_7$S$_8$ (monoclinic pyrrhotite) are referred to as pyrrhotites. The general formula is generally written Fe$_{1-x}$S with $0 \leq x \leq 0.125$. Several alternative notations exist and the relationships between them are illustrated for a number of compositions in Table 1.

Pyrrhotite crystal structures are based on the NiAs structure depicted in Fig. 1. The sulphur atoms are in the hexagonal close-packed arrangement (repeating every two layers) with the iron atoms occupying octahedral interstices. The smaller tetrahedral interstices are vacant. Non-stoichiometry
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<th>Formula</th>
<th>FeS</th>
<th>Fe₁₁S₁₂</th>
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<th>Fe₉S₁₀</th>
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<td>(Troilite)</td>
<td>(Intermediate pyrrhotites)</td>
<td>(Monoclinic po)</td>
<td>(Smythite)</td>
<td>(Greigite)</td>
<td>(Pyrite, marcasite)</td>
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<td>46.67</td>
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<td>53.33</td>
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<td>x in Fe₁₋ₓS</td>
<td>0.000</td>
<td>0.083</td>
<td>0.091</td>
<td>0.100</td>
<td>0.125</td>
<td>0.182</td>
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<td>y in FeS₁₊y</td>
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<td>0.091</td>
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<td>0.143</td>
<td>0.222</td>
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Fig. 1(a). Hexagonal unit cell of the NiAs structure on which structures of the pyrrhotite group are based. Closed circles indicate iron atoms, open circles with dots are sulphur atoms. The iron atoms are stacked in identical layers forming hexagonal prisms, each consisting of six trigonal prisms. The sulphur atoms are at the centre of alternate trigonal prisms, which are indicated by shading of the triangular faces. The sulphur layers follow the stacking sequence ABABA...

The unit cell has been expanded to show the atomic arrangement clearly. In fact the atoms are in contact, the sulphurs are arranged in the hexagonal close-packed configuration with the iron atoms occupying all the octahedral interstices.

This structure is known as 1C and is adopted by troilite above about 215°C and by the Fe$_{1-x}$S solid solution at high temperatures.

1(b). The central iron atom of 1(a), illustrating the 6-fold octahedral (antiprismatic) co-ordination of sulphur atoms about the iron atoms in the 1C structure.

1(c). The 6-fold prismatic co-ordination of iron atoms about the sulphur atoms in the 1C structure.
FIG. 1
Troilite (2C Superstructure)

The structure of troilite was first defined by Bertaut (1956) and refined by Evans (1970). The 2C superstructure results from small displacements of the Fe and S atoms from their ideal positions. Above the $\alpha$-transformation at $-140^\circ C$ troilite adopts the 1C NiAs structure with an accompanying change in the lattice parameters, the unit cell volume and the thermal expansion coefficient.

Although stoichiometric FeS is believed to be the only composition with 2C structure which is stable, other compositions with 2C structure have been prepared. For homogeneous 2C Fe$_{1-x}$S with 0 ≤ x ≤ 0.09 the temperature of the $\alpha$-transition, $T_\alpha$, decreases systematically with increasing x from $-140^\circ C$ to $-50^\circ C$. The transition becomes less pronounced with increasing iron deficiency and is practically unobservable for $x > 0.09$.

The picture has been complicated by recent studies which reveal the presence of a transitional polymorph of troilite in the region of the $\alpha$-transition. Putnis (1974) described the transitional structure with a hexagonal 2A, 1C cell but Töpel-Schadt and Müller (1982) show that the true structure probably has an orthorhombic cell with lattice parameters $A$, $\sqrt{3} A$, $C$, the apparent hexagonal symmetry arising from threefold twinning about the c-axis. Neither the high-temperature (1C) nor the transitional structure can be quenched to room temperature. The experimental data are ambiguous, however, as to whether the transitional state is a stable phase or whether it results from alternative metastable behaviour.
High-temperature (1C) pyrrhotite

Between 300°C and the maximum melting point of 1190°C there exists a continuous solid solution Fe$_{1-x}$S over a wide range of compositions from FeS (x=0) to the pyrite-pyrrhotite solvus (e.g. x=0.1 at 300°C and x=0.18 at 743°C, above which temperature pyrite breaks down to 1C pyrrhotite + sulphur). The stability field of this phase also extends to lower temperatures, but with a more restricted composition range.

The hexagonal 1C structure of high-temperature pyrrhotite is a result of disordered of the iron vacancies. On cooling, the random distribution of vacancies gives way to various vacancy ordering schemes (depending on composition and thermal treatment) accompanied by formation of superstructures, usually with a lowering of crystal symmetry. The 1C structure cannot be quenched.

Arnold (1962) and Toulmin and Barton (1964) determined the composition of 1C pyrrhotite in equilibrium with pyrite from 300-743°C. A geothermometer based on measured composition of pyrrhotite coexisting with pyrite was proposed on the basis of these data. However there is a number of problems with this approach (Scott, 1974), including re-equilibration of pyrrhotite during cooling due to rapid diffusion of vacancies, and the pyrite-pyrrhotite geothermometer is now generally discredited.

Monoclinic 4C Pyrrhotite

From the point of view of rock magnetism the most important iron sulphide is natural monoclinic 4C pyrrhotite, which approximates
Fig. 2 The structure of monoclinic 4C pyrrhotite Fe₇S₈ (after Bertaut, 1953). Alternate iron layers contain vacancies which are ordered as shown. The orthorhombic (4C) unit cell is shown with the sulphur atoms and the complete iron layers omitted for clarity. Iron layers are numbered. There is a slight monoclinic distortion of the orthorhombic unit cell ($\beta = 90.5^\circ$), which has space group $F2/d$. A smaller monoclinic cell (indicated by dashed lines) which has symmetry $C2/c$ and lattice parameters $a' = 2\sqrt{3}A$, $b = 2A$, $c = 2C$, $\beta' = 118^\circ$ may also be chosen. The hexagonal subcell corresponding to the NiAs (1C) structure is also shown.
FIG. 2
ordered structure, whereas twins are orientational variants.

The properties of Fe₇S₈, in particular the spontaneous magnetisation, are often discussed on the basis of an ionic formula Fe⁵⁺Fe³⁺vS₈, where v represents an iron vacancy. The distribution of ferric and ferrous ions between the iron sublattices (filled layers and vacancy layers) can be inferred from the spontaneous magnetisation. This ionic formula is highly misleading, however, as it ignores the predominantly covalent nature of bonding in the NiAs structure. Accordingly it is more satisfactory to fulfill the requirements of electrical neutrality by writing the formula as Fe⁷⁺vS₈h⁺₂, where the h⁺ represent electron holes, the location of which must be determined by experiment.

**Intermediate Pyrrhotite (nC superstructure)**

Intermediate pyrrhotites are generally referred to in geological literature and older mineralogical literature as (low-temperature) hexagonal pyrrhotite. However the true crystal symmetry of the intermediate pyrrhotites is lower than hexagonal and a wide variety of superstructures are found, rendering the term "hexagonal pyrrhotite" obsolete.

The composition range of intermediate pyrrhotites extends approximately from Fe₁₁S₁₂ (x = 0.083 or 47.83 atomic % Fe) to Fe₉S₁₀ (x = 0.10 or 47.37 atomic % Fe). Phases which are possibly stable at room temperature are Fe₁₁S₁₂ with 6C superstructure and Fe₉S₁₀ (5C).

The crystal structure of 6C pyrrhotite has been determined by Koto et al. (1976). The true symmetry is monoclinic with apparent hexagonal symmetry resulting from twinning at 60°.
Fig. 3. The structures of 4C (Fe7S₈) and 6C (Fe11S₁₂) pyrrhotites, showing all iron layers. The dots indicate iron atoms, open circles denote vacancies and the half-filled circles in the 6C superstructure denote vacancy sites with 50% occupation probability. Magnetic moments of iron atoms in the alternate layers are oppositely directed. Ordering of vacancies onto alternate layers in 4C pyrrhotite produces a nett ferrimagnetic moment as shown. In 6C pyrrhotite the magnetic moments (not shown) of the two sublattices (even and odd Fe layers) cancel. Therefore 6C pyrrhotite is antiferromagnetic.
Nett spontaneous magnetisation

Magnetic moments of Fe layers

FIG. 3
commonly found intergrown with either 2C or 4C pyrrhotite, but rarely with each other (Morimoto et al., 1975).

**Non-integral pyrrhotites (NC, NA and MC superstructures)**

Above room temperature but below the stability field of 1C pyrrhotite, three polymorphs with non-integral superstructures are found (Nakazawa and Morimoto, 1971). NC pyrrhotite is stable over the composition range $x = 0.06$ to $x = 0.10$ below 210°C and is metrically hexagonal with $a = 2A$ and $c = NC$ ($3.0 < N < 6.0$). The value of N changes continuously with varying composition and temperature. NA pyrrhotite is stable between -210°C and -270°C and is apparently hexagonal with $a = NA$, $c = 3C$ where $40 < N < 90$. The composition ranges approximately from $x = 0.106$ to $x = 0.084$ (47.2 - 47.8 atomic % Fe).

NA pyrrhotite has been reviewed by Francis and Craig (1976). The value of N varies with temperature and the NA superstructure represents one stage in the progressive ordering of vacancies with decreasing temperature with the ultimate formation of intermediate (nC) and monoclinic (4C) pyrrhotites. The integral 3C repeat of the NA superstructure shows that the ordering sequence of metal layers is regular and the diffraction pattern requires that adjacent metal layers are non-equivalent. The NA structure is probably related to that of trigonal (3C) pyrrhotite.

The MC structure is stable only over a narrow temperature (-260 - 310°C) and compositional ($x = 0.905$) range. The MC structure is also apparently hexagonal with $a = 2A$, $c = MC$ where M varies continuously from 3.0 to 4.0.
Although the properties and stability fields of non-integral pyrrhotites have been established from work on synthetic samples both the NC and NA types have been found in nature.

**Trigonal pyrrhotite (Fe\textsubscript{7}S\textsubscript{8} with 3C superstructure)**

The structure of Fe\textsubscript{7}S\textsubscript{8} with 3C superstructure has been investigated by Fleet (1971) and Nakano et al. (1979). The structure is trigonal with \( a = 2A, c = 3C \), the apparent hexagonal symmetry resulting from twinning in which platy domains stacked along the c-axis are related by 180° rotations about the c-axis.

The 3C superstructure results from stacking of alternate filled and vacancy layers in the sequence \( \text{FD}_a \text{FD}_b \text{FD}_c \text{F} \ldots \). 4C pyrrhotite can be converted to the 3C type by heating until the structure inverts to 1C (above 308°C) and rapidly quenching. The 3C structure is metastable at low temperatures, but has been found in natural assemblages.

Collin et al. (1980) have discussed the structural basis of twinning in 3C pyrrhotite and the formation of imbricated sequences of 3C and 4C domains.

**Anomalous pyrrhotite**

Clark (1966) described a type of pyrrhotite containing 46.4 atomic % Fe, the most iron-deficient type of pyrrhotite found, with a number of anomalous properties. It is characterised by the intensity of 408 X-ray reflection being greater than 408, the reverse of the usual situation with monoclinic pyrrhotite. This fairly common mineral may
a stable triclinic phase or may be a metastable, strained structure resulting from incipient pyrite exsolution.

Other iron-sulphide minerals

Pyrite and marcasite are polymorphs with the formula FeS₂. Pyrite is the most common sulphide mineral and plays an important role in the phase equilibria of many sulphide systems which also involve pyrrhotite (e.g. Fe-S, Fe-Zn-S, Fe-Cu-S, Fe-Ni-S). Marcasite is believed to be metastable.

Mackinawite (FeS₁₋ₓ) is a relatively rare tetragonal mineral of near-FeS composition, found either with troilite or low-temperature pyrrhotites in a variety of geological environments including: black iron sulphide muds, contact metasomatic and hydrothermal deposits, bedded cupriferous iron-sulphide deposits within metamorphic rocks and in certain ultrabasic rocks. The thermal stability of mackinawite is unknown.

Smythite (Fe₉S₁₁) has a pseudorhombohedral structure related to that of monoclinic pyrrhotite, and perhaps should be included in the pyrrhotite group. Smythite invariably contains small quantities of nickel.

Greigite (Fe₅S₄) is iron thiospinel, the sulphide analogue of magnetite. It is frequently found in clays and muds but also occurs in sulphide ores. Greigite possibly exhibits cation deficiency analogous to the magnetite-maghaemite solid solution.
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<th>Thermal stability, °C</th>
<th>Structure type (cell edges in Å)</th>
<th>Space group</th>
<th>Remarks</th>
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<td>Troilite</td>
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<td>140</td>
<td>Hexagonal 2C</td>
<td>P62c</td>
<td>Inverts to transitional FeS</td>
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<tr>
<td>Transitional FeS</td>
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<td>Orthorhombic</td>
<td>Pmcn</td>
<td>MnP structure. Possibly metastable</td>
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<td>High-temperature</td>
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<tr>
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<td>Composition</td>
<td>Thermal stability, °C</td>
<td>Structure type (cell edges in A.U.)</td>
<td>Space group</td>
<td>Remarks</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
<td>-----------------------</td>
<td>-------------------------------------</td>
<td>-------------</td>
<td>---------</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>743</td>
<td>Cubic, a=5.417</td>
<td>Pa3</td>
<td>Breaks down to lC pyrrhotite + liquid S</td>
</tr>
<tr>
<td>Marcasite</td>
<td>FeS₂</td>
<td>-</td>
<td>Orthorhombic</td>
<td>Pnmm</td>
<td>Metastable</td>
</tr>
</tbody>
</table>

*Data from Evans (1970), Tokonami et al. (1972), Scott (1974), Morimoto et al. (1975), Koto et al. (1976), Power and Fine (1976), Nakano et al. (1979), Töpel-Schadt and Müller (1982).
3. **Distribution and abundance of pyrrhotite**

Pyrite and pyrrhotite are by far the most common sulphide minerals and are the only sulphides abundant enough to be termed rock-forming minerals.

Pyrrhotite occurs mainly in basic igneous rocks but is also found in pegmatites, in contact metamorphic deposits, in high temperature hydrothermal veins and in sediments (Deer, Howie and Zussman, 1966, p. 153). Ramdohr (1980) states that pyrrhotite occurs in ore deposits of very different origins (particularly high temperature deposits) and is more widespread than previously assumed. Many ore deposits containing pyrite or marcasite contain only pyrrhotite at great depth, where they are truly fresh. Terrestrial occurrences fall mainly into the following categories:

(i) Liquid-magmatic - platinum segregations in ultrabasic rocks; magmatic cyrstallisation differentiates of chromite, titanomagnetite-spinel and ilmenite; magmatic exsolution segregations (nickel-pyrrhotite occurrences ± platinum etc.); main plutonic sequence (mostly gabbro and diorite).

(ii) Pegmatitic-pneumatolytic - pegmatites, contact metasomatic limestones, tin veins.

(iii) Hydrothermal deposits - gold quartz veins; lead-zinc-copper deposits; some siderite and silver-tin veins.

(iv) Unaltered sediments and sedimentary ore deposits.

(v) Metamorphosed ore deposits - pyrrhotite is very abundant in contact deposits of intrusives and extrusives, and is formed in the epi-, meso- and catazones of dynamic metamorphism.
Troilite is relatively rare in terrestrial rocks, as it is formed only under strongly reducing conditions, and is found mainly in serpentinised rocks. In layered gabbros and norites the distribution of pyrrhotite is thought to result from sulphide liquid immiscibility with the magma. Nickel deposits associated with these intrusions usually consist of a pyrrhotite-pentlandite assemblage formed by breakdown of the high temperature (Fe,Ni)$_{1-x}$S solid solution.

Pyrite and/or chalcopyrite are commonly associated with pyrrhotite whereas bornite and pyrrhotite are almost never found together. Based on their composition natural pyrrhotites tend to be divided into three groups (Arnold, 1967):

(i) 49.8 - 50.0 atomic % Fe, representing troilite
(ii) 47.5 - 48.1 atomic % Fe, corresponding to intermediate pyrrhotites
(iii)  46.7 atomic % Fe, representing 4C monoclinic pyrrhotite.

Type (i) generally occurs with type (ii), often with no other sulphides, whereas types (ii) and (iii) are usually associated with pyrite and/or chalcopyrite.

Based on 82 samples, Arnold (1967) gives as the relative abundances of pyrrhotite assemblages: troilite and intermediate pyrrhotite (5%); intermediate pyrrhotite (13%); intermediate + monoclinic pyrrhotite (73%); monoclinic pyrrhotite (9%).

Berner (1970) has discussed formation of iron sulphides in sedimentary environments. Iron sulphides form by the
reaction of detrital iron minerals with bacteriogenic sulphide in anoxic sediments. The initial products are metastable iron monosulphides (mackinawite and/or greigite) which react with elemental sulphur to produce pyrite. Pyrite is the stable phase in most sedimentary environments, particularly in marine sediments, but survival of authigenic monosulphide phases, which are precursors to pyrrhotite, is favoured by stagnant anaerobic conditions and the absence of sulphur or sulphate. For this reason the ratio of FeS$_2$/FeS may serve as a palaeosalinity indicator (Berner et al., 1979), values greater than 10 characterising marine sediments whereas values less than one are typical of brackish or fresh-water environments. However deposition rate may also be an important factor as evidenced by very young saltmarsh sediments cemented by iron monosulphides and siderite (Pye, 1981). Authigenic pyrrhotite along with pyrite in strongly-reducing conditions is found at depth in sediment cores from the Sea of Japan (Kobayashi and Nomura, 1972) correlated with a more restricted palaeoecography and a reducing palaeoenvironment during the last glacial period.

Precipitation of pyrrhotite from hydrothermal vents at present-day spreading centres has been observed (e.g. Lonsdale et al., 1980). Older and deeper-water submarine exhalative ore deposits tend to be pyrrhotite-bearing whereas pyrite is favoured in more recent and shallower water deposits (Plimer and Finlow-Bates, 1978). Pyrite tends to be the
dominant iron sulphide in proximal stratabound deposits whereas pyrrhotite is abundant in distal deposits (Plimer, 1978).

The origin of pyrrhotite in metamorphosed ore deposits has often been ascribed to metamorphic breakdown of pyrite (e.g. Vokes, 1969). Willan and Hall (1980) discuss the evidence for occurrence of authigenic synsedimentary pyrrhotite in stratiform ores and conclude that formation of pyrrhotite during regional metamorphism of pyrite ores is minor. Pyrrhotite is often produced during contact metamorphism, however. The removal of sulphur from pyrite is aided by degassing of the igneous intrusion and/or outward movement of hydrothermal fluids, whereas during regional metamorphism escape of sulphur is hindered by low porosities and high confining pressure.

Possible reactions occurring in contact aureoles are \(2\text{FeS}_2 \rightarrow 2\text{FeS} + S_2\) and sulphur (liberated from \(\text{FeS}_2\) or organic matter) + ferromagnesian silicates + pyrrhotite + Fe-depleted ferromagnesian silicates.

4. **Phase relations in the Fe-S system**

The Fe-S system is the most studied binary sulphide system, both in geology and metallurgy, and it forms a foundation for the understanding of phase relations and thermochemistry of many other economically important systems, such as Zn-Fe-S, Cu-Fe-S, Fe-Ni-S. Knowledge of phase relations is essential to understanding processes of ore
genesis and to interpretation of natural mineral assemblages in terms of genesis and thermal history.

The phase relations of the Fe-S system above 300°C were well established by about 1970 and are discussed in many places (e.g. Ward, 1970; Scott, 1974). Above 308°C only two phases, 1C pyrrhotite and pyrite, exist between 33.3 and 50.0 atomic % Fe. Below 300°C, however, the phase relations are complex and it is only relatively recently that the many uncertainties and apparent contradictions have made way for a relatively clear and consistent picture.

A phase diagram for the region 33.3 - 50.0 atomic % Fe below 350°C is given in Fig. 4 (after Power and Fine, 1976). Although nC pyrrhotites (5C, 11C and 6C pyrrhotites) are depicted as stable phases, separated by two-phase regions, below 100°C, this may be an artefact of sluggish kinetics.

Morimoto et al. (1975) conclude that 2C and 4C pyrrhotites are the truly stable phases at low temperature, based on their abundance, well-ordered structure, constancy of composition and intergrowth textures. Putnis and McConnell (1980, pp. 241-243) argue that the well-ordered 2C and 4C structures should be stable at low temperatures and cite field evidence that 2C + 4C is stable with respect to intermediate pyrrhotite at ambient temperatures.

Natural pyrrhotites may therefore frequently represent metastable assemblages. Metastable phase relations, however, can be reproducible and may be even more useful than stable ones in deciphering some aspects of geological history, particularly where low temperatures are concerned.
Fig. 4. Phase diagram of the central portion of the Fe-S system below 350°C (after Power and Fine, 1976). The nomenclature is as in Table 1.2. A possible stability field for transitional troilite with MnP structure is not shown.
FIG. 4
5. References


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