CSIRO

INSTITUTE OF ENERGY AND EARTH RESOURCES

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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 ($\rho \sim 10^{-3} - 3 \times 10^{-2}$ 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 $Fe_{1-x}S$ 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 inter-

pretation 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 stoichio-

metric FeS (troilite) to Fe_7S_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

TABLE 1

COMPOSITION UNITS FOR IRON SULPHIDES

Formula	FeS	$Fe_{11}S_{12}$	$Fe_{10}S_{11}$	Fe_9S_{10}	Fe_7S_8	Fe_9S_{11}	Fe_3S_4	FeS_2
	(Troilite)	(Intermediate pyrrhotites)			(Monoclinic po)	(Smythite)	(Greigite)	(Pyrite, marcasite)
Atomic % Fe	50.00	47.83	47.62	47.37	46.67	45.00	42.86	33.33
Atomic % S	50.00	52.17	52.38	52.63	53.33	55.00	57.14	66.67
x in $Fe_{1-x}S$	0.000	0.083	0.091	0.100	0.125	0.182	0.250	0.500
y in FeS_{1+y}	0.000	0.091	0.100	0.111	0.143	0.222	0.333	1.000
Atomic ratio Fe/S	1.000	0.917	0.909	0.900	0.875	0.818	0.750	0.500
Atomic ratio S/Fe	1.000	1.091	1.100	1.111	1.143	1.222	1.333	2.000
Mole fraction FeS	1.000	0.957	0.952	0.947	0.933	0.900	0.857	0.667
Weight % S	36.47	38.51	38.71	38.94	39.62	41.23	43.36	53.45

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 $215^{\circ}C$ 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
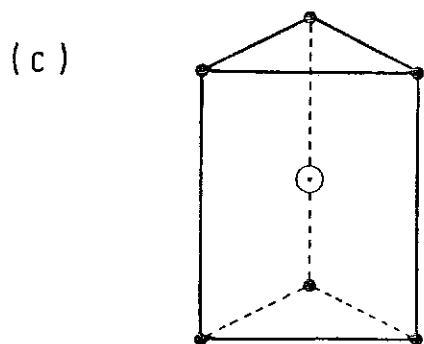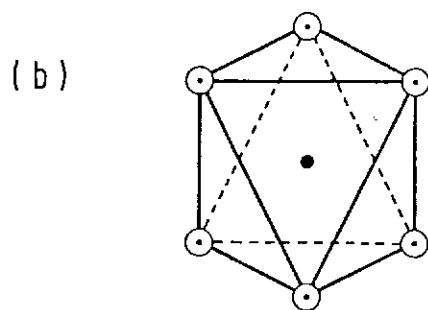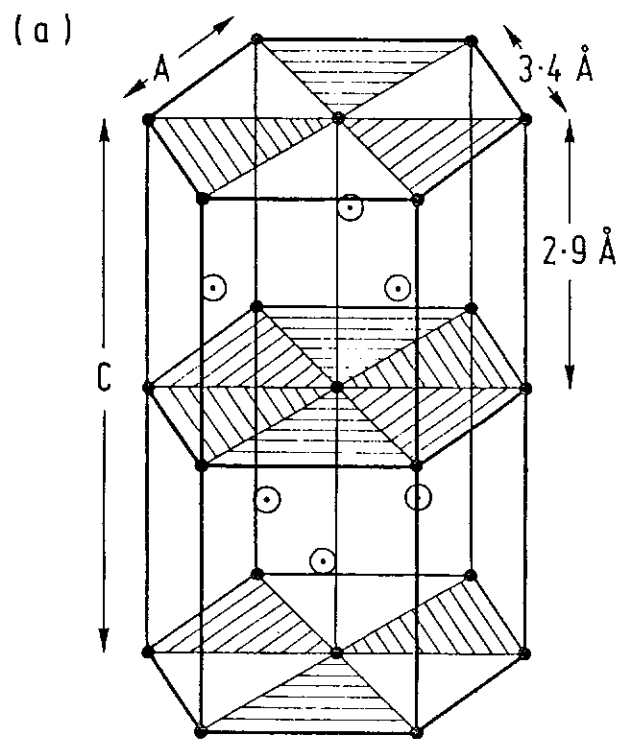
about the sulphur atoms in the 1C structure.

(a)

A

3·4 Å

2·9 Å

C

(b)

(c)

FIG.I

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 α-transformation at $\sim 140^{\circ}$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 $0 \leq x \leq 0.09$ the temperature of the α-transition, T_{α} , decreases systematically with increasing x from $\sim 140^{\circ}$C to $\sim 50^{\circ}$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 α-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 disordering 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 Fe_7S_8 (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 ($\beta = 90.5^O$), which has space group F2/d. A smaller monoclinic cell (indicated by dashed lines) which has symmetry C2/c and lattice parameters $a=2\sqrt{3}A$, $b=2A$, $c=2C$, $\beta' =118^O$ may also be chosen. The hexagonal subcell corresponding to the NiAs (1C) structure is also shown.
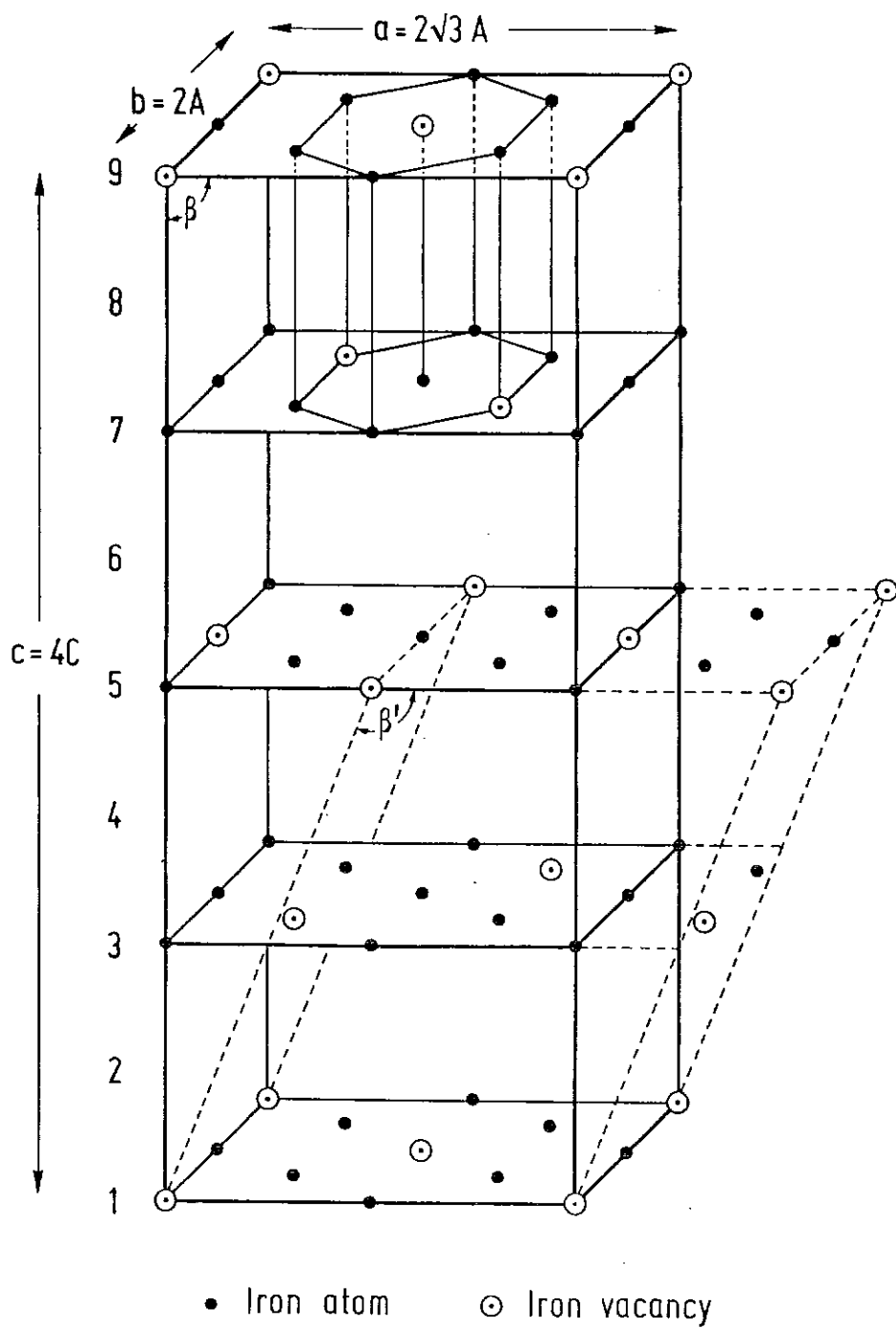
FIG. 2

ordered structure, whereas twins are orientational variants.

The properties of Fe_7S_8, in particular the spontaneous magnetisation, are often discussed on the basis of an ionic formula $Fe_5^{2+}Fe_2^{3+} v S_8$, 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 $Fe_7^{2+}vS_8h_2^{+}$, 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 $Fe_{11}S_{12}$ (x = 0.083 or 47.83 atomic % Fe) to Fe_9S_{10} (x = 0.10 or 47.37 atomic % Fe). Phases which are possibly stable at room temperature are $Fe_{11}S_{12}$ with 6C superstructure and Fe_9S_{10} (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 (Fe_7S_8) and 6C ($Fe_{11}S_{12}$)

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)
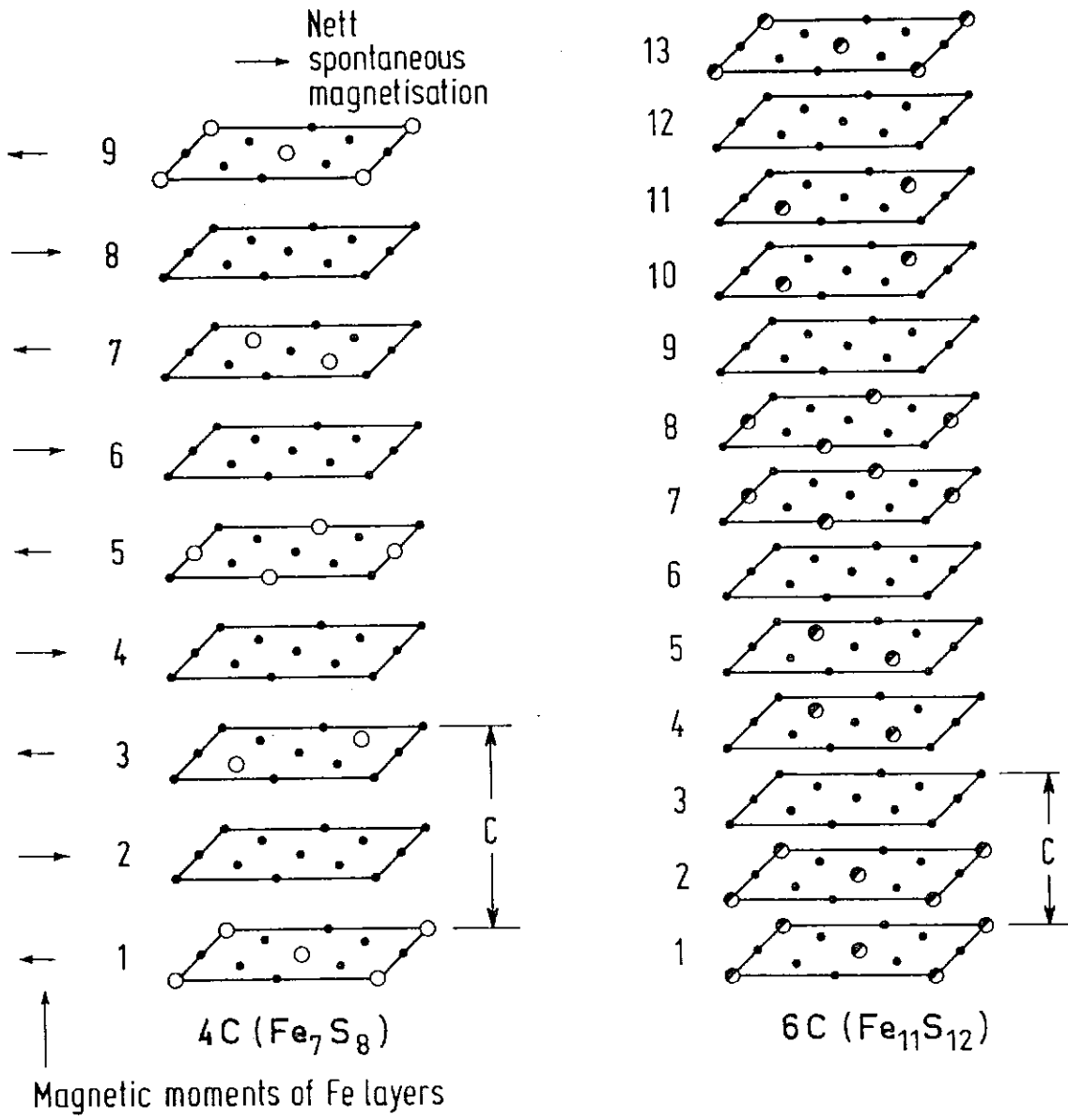
cancel. Therefore 6C pyrrhotite is antiferro-

magnetic.

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 super-structures are found (Nakazawa and Morimoto, 1971). NC pyrrhotite is stable over the composition range $x = 0.06$ to $x = 0.10$ below $210^{\circ}C$ 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 $\sim 210^{\circ}C$ and $\sim 270^{\circ}C$ 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 ($\sim 260 - 310^{\circ}C$) and compositional ($x \sim 0.905$) 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_7S_8 with 3C superstructure)

The structure of Fe_7S_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 $FD_aFD_bFD_cF$ ... 4C pyrrhotite can be converted to the 3C type by heating until the structure inverts to 1C (above $308^\circ C$) 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 $40\bar{8}$ 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 FeS_2. 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 (FeS_{1-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 (Fe_9S_{11}) 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 (Fe_3S_4) 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.

TABLE 2   CRYSTALLOGRAPHIC DATA*

Mineral Name	Composition	Thermal stability, °C Maximum	Thermal stability, °C Minimum	Structure type (cell edges in AU)	Space group	Remarks
Troilite	FeS	140	–	Hexagonal 2C $a=\sqrt{3}A=5.962$ $c=2C=11.750$	$P\bar{6}2c$	Inverts to transitional FeS
Transitional FeS	FeS	~215	140	Orthorhombic $a=A, b=\sqrt{3}A, c=C$	Pmcn	MnP structure. Possibly metastable
High-temperature hexagonal pyrrhotite	$Fe_{1-x}S$ $0\leq x<0.185$	m.p.=1190	100	Hexagonal 1C $a=3.45$ $c=5.75$	$P6_3/mmc$	NiAs structure
MC pyrrhotite	$Fe_{1-x}S$ $0.088\leq x<0.099$	308	262	Hexagonal ? $a=2A, c=MC$	?	$3.0\leq M\leq 6.0$
NA pyrrhotite	$Fe_{1-x}S$ $0.084<x<0.106$	~266	209	Trigonal ? $a=NA, c=3C$	$P3_121$?	$40<N<90$
NC pyrrhotite	$Fe_{1-x}S$ $0.073\leq x\leq 0.106$	~213	~100	Orthorhombic ? $a=2A, b=2\sqrt{3}A, c=NC$	Cmca or C2ca	$3.0<N<6.0$
5C pyrrhotite	Fe_9S_{10}	~100	–	Orthorhombic ? $a=2A=6.885$ $b=2\sqrt{3}A=11.944$ $c=5C=28.676$	Cmca or C2ca	Possibly unstable at room temperature

TABLE 2 (continued)

Mineral Name	Composition	Thermal stability, °C Maximum	Minimum	Structure type (cell edges in A.U.)	Space group	Remarks
6C pyrrhotite	$Fe_{11}S_{12}$	~100	—	Monoclinic $a=2\sqrt{3}A=11.954$ $b=2A=6.895$ $c=6C=34.518$ $\beta=90.0°$	Fd or F2/d	Possibly unstable at room temperature
4C monoclinic pyrrhotite	Fe_7S_8	~254	—	Monoclinic $a=2\sqrt{3}A=11.902$ $b=2A=6.859$ $c=4C=22.787$ $\beta=90.5°$	F2/d	
Trigonal pyrrhotite	Fe_7S_8	~266	209	Trigonal 3C $a=2A=6.865$ $c=3C=17.046$	$P3_121$	Related to NA pyrrhotite
Anomalous pyrrhotite	$\sim Fe_{0.866}S$	?	—	Triclinic ?	?	Possibly produced by oxidation of intermediate po
Smythite	$\sim Fe_9S_{11}$	~75	—	Rhombohedral ? $a=3.47, c=34.4$	$R\bar{3}m$	
Greigite	Fe_3S_4	?	?	Spinel, $a=9.876$	Fd3m	Sulphide analogue of magnetite
Mackinawite	FeS_{1-x} $0.04<x\leq0.07$	?	—	Tetragonal $a=3.675, c=5.030$	P4/nmm	

TABLE ..2 (continued)

Mineral Name	Composition	Thermal stability, $^\circ$C Maximum	Minimum	Structure type (cell edges in A.U.)	Space group	Remarks
Pyrite	FeS$_2$	743	–	Cubic, a=5.417	Pa3	Breaks down to 1C pyrrhotite + liquid S
Marcasite	FeS$_2$	–	–	Orthorhombic a=4.445, b=5.425, c=3.388	Pnnm	Metastable

*Data from Evans (1970), Tokonami et al. (1972), Scott (1974), Morimoto et al. (1975), Koto et al. (1975), 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 - platimum 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 palaeogeography
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 $2FeS_2 \rightarrow 2FeS + S_2$ and sulphur (liberated from FeS_2 or organic matter) + ferromagnesian silicates $\rightarrow$ 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 $300^{O}C$ were well established by about 1970 and are discussed in many places (e.g. Ward, 1970; Scott, 1974). Above $308^{O}C$ only two phases, 1C pyrrhotite and pyrite, exist between 33.3 and 50.0 atomic % Fe. Below $300^{O}C$, 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 $350^{O}C$ 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 $100^{O}C$, 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 $350^{O}C$ (after

Power and Fine, 1976). The nomenclature

is as in Table 1.2. A possible stability

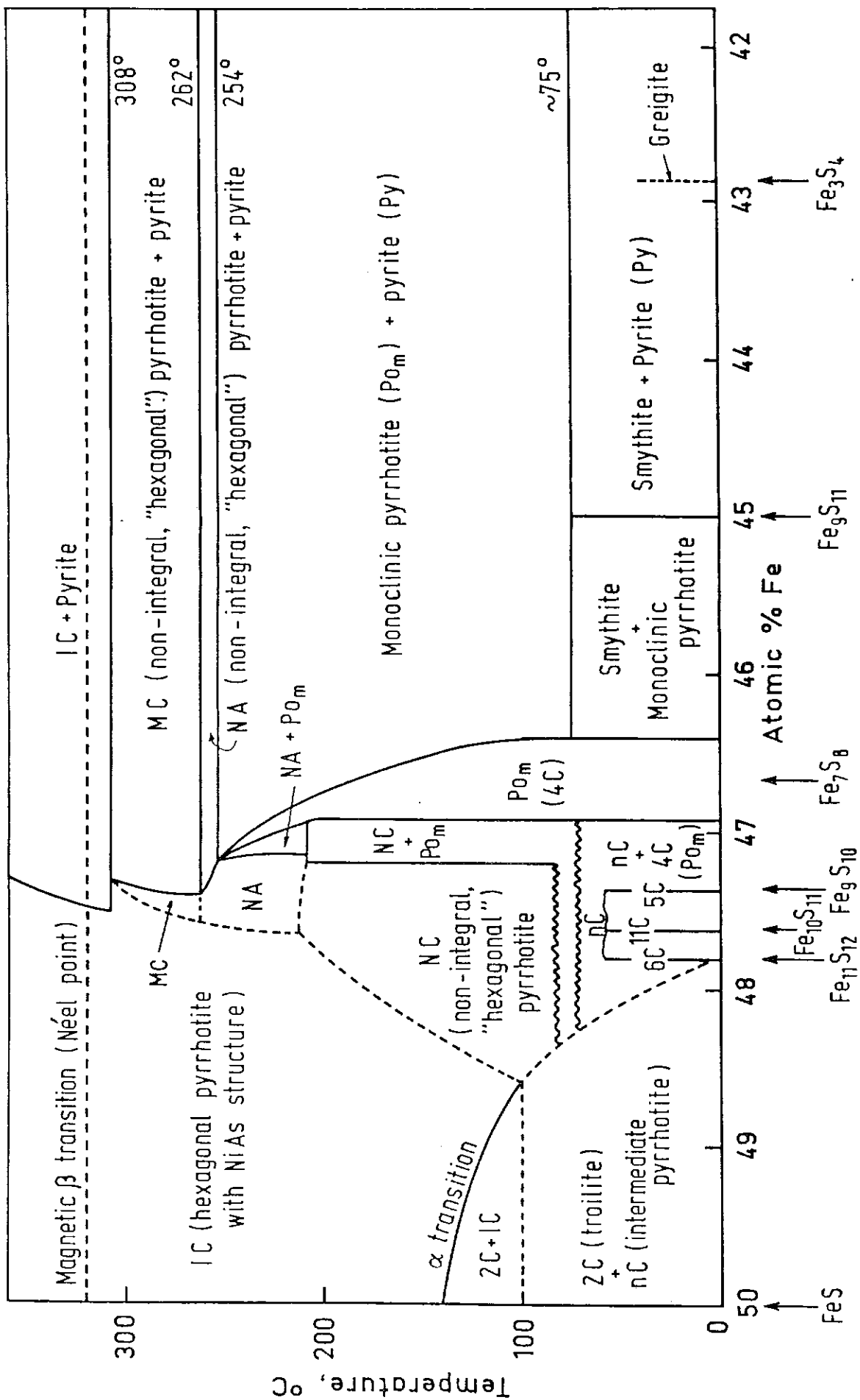field for transitional troilite with MnP

structure is not shown.

FIG. 4

5. References

Arnold, R.G., 1962. Equilibrium relations between pyrrhotite and pyrite from 325° to 743°C. Econ. Geol., 57: 72-90.

Arnold, R.G., 1967. Range in composition and structure of 82 natural terrestrial pyrrhotites. Can. Mineral., 9: 31-50.

Barton, P.B. and Skinner, B.J., 1979. Sulfide mineral stabilities. In: H.L. Barnes (Editor), Geochemistry of Hydrothermal Ore Deposits. Holt, Rinehart and Winston, New York, pp. 278-403.

Berner, R., 1970. Iron. In: Handbook of Geochemistry, Springer-Verlag, Berlin, 26-A-1 to 26-M-5.

Berner, R.A., Baldwin, T. and Holdren, G.R., 1979. Authigenic iron sulfides as paleosalinity indicators. J. Sed. Petr., 49: 1345-1350.

Bertaut, E.F., 1953. Contribution à l'étude des structures lacunaires: la pyrrhotine. Acta Cryst., 6: 557-561.

Bertaut, E.F., 1956. Structure de FeS stoichiométrique. Bull. Soc. Franc. Minér. Crist., 79: 276-292.

Clark, A.H., 1966. Stability field of monoclinic pyrrhotite. Inst. Min. Metal. Trans. 75B: 232-235.

Clark, D.A., 1983a. Hysteresis properties of sized dispersed monoclinic pyrrhotite grains. CSIRO Restricted Investigation Report 1411R.

Clark, D.A., 1983b. Palaeomagnetism of pyrrhotite-bearing rocks. CSIRO Restricted Investigation Report 1438R.

Clark, D.A., 1983c. Magnetic fabric of pyrrhotite-bearing rocks. CSIRO Restricted Investigation Report 1462R.

Clark, D.A., 1984. Magnetic petrophysics of pyrrhotite-bearing rocks. CSIRO Restricted Investigation Report 1531R.

Collin, G., Chavant, C. and Keller-Besrest, F., 1980. Défauts planaire et non-stoechiométrie dans les composés NiAs lacunaires. Bull. Minéral., 103: 380-386.

Deer, W.A., Howie, R.A., Zussman, J., 1966. An Introduction to the Rock Forming Minerals. Longmans, London, 528 pp.

Evans, H.T., 1970. Lunar troilite: crystallography. Science, 167: 621-623.

Fleet, M.E., 1971. The crystal structure of a pyrrhotite (Fe_7S_8). Acta Cryst., B27: 1864-1867.

Fleet, M.E., 1978. The pyrrhotite-marcasite transformation. Canadian Mineralogist, 16: 31-35.

Flinter, B.H., 1970 (Editor). Proceedings of the CSIRO Symposium on Iron Sulphides, Held at North Ryde, New South Wales, November, 1968. CSIRO Division of Mineral Chemistry, North Ryde.

Francis, C.A. and Craig, J.R., 1976. Pyrrhotite: the nA (or 2A, 3C) superstructure reviewed. Amer. Mineralogist, 61: 21-25.

Jagadeesh, M.S. and Seehra, M.S., 1981. Thermomagnetic studies of conversion of pyrite and marcasite in different atmospheres (vacuum, H_2, He and CO). J. Phys. D, 14: 2153-2167.

Kobayashi, K. and Nomura, M., 1972. Iron sulfides in the sediment cores from the Sea of Japan and their geophysical implications. Earth Planet. Sci. Lett., 16: 200-208.

Koto, K., Morimoto, N. and Gyobu, A., 1976. The superstructure of the intermediate pyrrhotites. I. Partially disordered distribution of metal vacancy in the 6$\underline{C}$ type, $Fe_{11}S_{12}$. Acta Cryst., B31: 2759-2764.

Lonsdale, P.F., Bischoff, J.L., Burns, V.M., Kastner, M. and
Sweeney, R.E., 1980. A high-temperature hydrothermal deposit
on the seabed at a Gulf of California spreading center.
Earth Planet. Sci. Lett., 49: 8-20.

Morimoto, N., Gyobu, A., Mukaiyama, H. and Izawa, E., 1975.
Crystallography and stability of pyrrhotites. Econ. Geol.,
70: 824-833.

Morimoto, N., Nakazawa, H. and Watanabe, E., 1974. Direct
observations of metal vacancy in pyrrhotite, $Fe_{1-x}S$, by
means of an electron microscope. Proc. Japan. Acad., 50:
756-759.

Nakano, A., Tokonami, M. and Morimoto, N., 1979. Refinement
of 3C pyrrhotite, Fe_7S_8. Acta Cryst., B35: 722-724.

Nakazawa, H. and Morimoto, N., 1971. Phase relations and
superstructures of pyrrhotite, $Fe_{1-x}S$. Mat. Res. Bull.,
6: 345-358.

Pierce, L. and Buseck, P.R., 1974. Electron imaging of pyrrhotite
superstructures. Science, 186: 1209-1212.

Plimer, I.M., 1978. Proximal and distal stratabound ore deposits.
Mineral. Deposita, 13: 345-353.

Plimer, I.R. and Finlow-Bates, T., 1978. Relationship between
primary iron sulphide species, sulphur source, depth of
formation and age of submarine exhalative sulphide deposits.
Mineral. Deposita., 13: 399-410.

Power, L.F. and Fine, H.A., 1976. The iron-sulphur system.
Part I. The structure and physical properties of the
compounds of the low-temperature phase fields. Minerals
Sci. Engng., 8: 106-128.

Putnis, A., 1974. Electron-optical observations on the α-transformation in troilite. Science, 186: 439-440.

Putnis, A. and McConnell, J.D.C., 1980. Principles of Mineral Behaviour. Blackwell, Oxford, 257 pp.

Pye, K., 1981. Marshrock formed by iron sulphide and siderite cementation in saltmarsh sediments. Nature, 294: 650-652.

Ramdohr, P., 1980. The Ore Minerals and Their Intergrowths, 2nd ed., Pergamon, 1207 pp.

Ribbe, P.H., 1974 (Editor). Sulfide Mineralogy. Mineralogical Society of America Short Course Notes, Volume 1.

Schwarz, E.J., 1974. Magnetic properties of pyrrhotite and their use in applied geology and geophysics. Geol. Surv. Canada Paper, 74-59.

Scott, S.D., 1974. The Fe-S system. In: P.H. Ribbe (Editor), Sulfide Mineralogy. Mineralogical Society of America Short Course Notes, Volume 1, CS-21 to CS-40.

Shuey, R.T., 1975. Semiconducting Ore Minerals. Elsevier, Amsterdam, 415 pp.

Taylor, P., 1980. The stereochemistry of iron sulfides - a structural rationale for the crystallization of some metastable phases from aqueous solution. American Mineralogist, 65: 1026-1030.

Tokonami, M., Nishiguchi, K. and Morimoto, N., 1972. Crystal structure of a monoclinic pyrrhotite (Fe_7S_8). American Mineralogist, 57: 1066-1080.

Töpel-Schadt, J. and Müller, W.F., 1982. Transmission electron microscopy on meteoritic troilite. Phys. Chem. Minerals, 8: 175-179

31.

Toulmin, P. and Barton, P.B., 1964. A thermodynamic study of
    pyrite and pyrrhotite. Geochim. Cosmochim. Acta, 28: 641-671.

Vaughn, D.J., Schwarz, E.J. and Owens, D.R., 1971. Pyrrhotites
    from the Strathcona Mine, Sudbury, Canada: a thermomagnetic
    and mineralogical study. Econ. Geol., 66: 1131-1144.

Vaughn, D.J. and Craig, J.R., 1978. Mineral Chemistry of Metal
    Sulfides. C.U.P., 493 pp.

Vokes, F.M., 1969. A review of the metamorphism of sulphide
    deposits. Earth-Sci. Rev., 5: 99-143.

Ward, J.C., 1970. The structure and properties of some iron
    sulphides. Rev. Pure Appl. Chem., 20: 175-206.

Willan, R.C.R. and Hall, A.J., 1980. Sphalerite geobarometry
    and trace-element studies on stratiform sulphide from
    McPhun's Cairn, Loch Fyne, Argyll, Scotland. Inst. Min.
    Metal. Trans., 89: B31-B40.