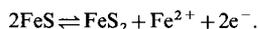


Pyrite–pyrrhotine redox reactions in nature

A. J. HALL

Department of Applied Geology, University of Strathclyde, Glasgow G1 1XJ

ABSTRACT. The origin in rocks of the common iron sulphides, pyrrhotine, Fe_{1-x}S and pyrite, FeS_2 and their behaviour during geochemical processes is best considered using the simplified redox reaction:



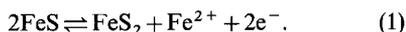
Thus pyrrhotine is more reduced than pyrite and is the stable iron sulphide formed from magmas except where relatively high oxygen fugacities result from falling pressure or hydrothermal alteration. Pyrite, on the other hand, is the stable iron sulphide in even the most reduced sedimentary rocks where it usually forms during diagenesis through bacteriogenic reduction of sulphate; it is stable throughout the pressure/temperature range endured by normal sedimentary rocks. Pyrrhotine after pyrite or sulphate in metasediments of regional metamorphic origin results mainly from progressive reduction on metamorphism due to the presence of graphite-buffered fluids. Pyrrhotine and/or pyrite may be precipitated from hydrothermal solutions on epigenetic or syngenetic mineralization but pyrrhotine will only be preserved if protected from oxidation to pyrite or to more oxidized species. Exhalative pyrrhotine appears to have been more common in Precambrian times and/or in depositional environments destined to become regionally metamorphosed. FeS can be considered to be the soluble iron sulphide, rather than FeS_2 , in reduced aqueous systems although pyrite may precipitate from solution as a result of redox reactions. The relatively soluble nature of FeS explains the observed mobility of iron sulphides in all rock types.

KEYWORDS: pyrite, pyrrhotine, redox reactions, iron sulphides.

THE common iron sulphide minerals are pyrite (cubic FeS_2), marcasite (orthorhombic FeS_2), and pyrrhotine (monoclinic and hexagonal Fe_{1-x}S). They are found as accessory minerals in the three major categories of rocks: igneous, sedimentary, and metamorphic. In addition they are often major minerals in hydrothermal ore deposits. The origin of the iron sulphides and their behaviour during geochemical processes has been the subject of much research but the redox aspect of their reactions has been relatively neglected. The objective of this paper is to emphasize the value of considering iron sulphide reactions as redox reactions by presenting a general redox equation and demonstrating its

application to provide a better understanding of the occurrence and origin of iron sulphide minerals. The approach adopted here stems from study of the complex relationships exhibited by iron sulphides in metasediments.

Iron sulphide reactions. The relationship between pyrite and pyrrhotine can be expressed by the general redox equation:



The formula of pyrrhotine is simplified for the present discussion and FeS_2 will be called pyrite. It is the distribution of FeS_2 relative to pyrrhotine that is of concern here and not the distinction between pyrite and marcasite, which have a similar distribution.

Pyrrhotine is reduced compared to pyrite and their relative stabilities in nature depend on oxidation reactions, i.e. electron transfer reactions which may or may not involve oxygen. A schematic fugacity–fugacity diagram for Fe–S–O phases following the method of Holland (1959) and Ohmoto and Kerrick (1977) is presented in fig. 1. This emphasizes that pyrite coexists with iron oxides indicative of relatively high oxygen fugacity, whereas pyrrhotine coexists with iron oxides indicative of relatively low oxygen fugacity (Barnes and Kullerud, 1961).

The relationships illustrated in fig. 1, based on thermodynamic calculations, are confirmed by observation of coexisting iron sulphide and iron oxide minerals in nature. Although the numerical value of the fugacities vary with temperature, there is no significant change in the geometry within the P – T range of interest in the outer crust of the Earth. A version of this diagram was used by Froese (1971) who emphasized the value of fixing oxygen fugacity when describing sulphide–silicate phase relations.

Barnes and Kullerud (1961) explained how the pyrrhotine + pyrite + magnetite equilibrium assemblage fixes sulphur and oxygen fugacity at a given temperature; the useful reference point representing this special assemblage is marked by an asterisk in fig. 1.

The effect of pH is not of major concern here;

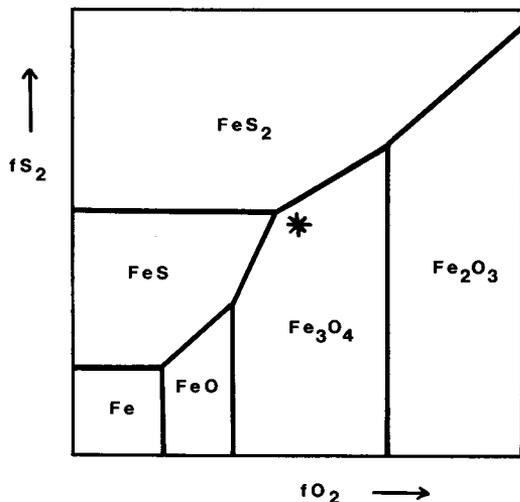


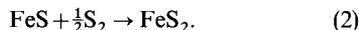
FIG. 1. f_{S_2} (fugacity)- f_{O_2} diagram for the main phases in the Fe-S-O system. The asterisk marks the point where pyrite, FeS_2 , and pyrrhotine, $Fe_{1-x}S$, coexist with magnetite, Fe_3O_4 . The diagram is simplified and does not indicate the non-stoichiometry of pyrrhotine and wüstite, $Fe_{1-x}O$. The axes are left unlabelled as the values of f_{S_2} and f_{O_2} (usually expressed in units of $-\log_{10}$ bars) vary greatly with temperature, but the geometry of the diagram changes little.

Barnes and Kullerud (1961) explained in detail the interaction between f_{S_2} , f_{O_2} , pH and dissolved sulphur in relation to the deposition of pyrrhotine + pyrite + magnetite from solutions. In essence, this assemblage is indicative of highly alkaline solutions at low temperatures (25 °C) and less alkaline solutions at high temperatures (250 °C). However, pH is not an independent variable; increasing alkalinity (at constant f_{O_2}) leads to decreasing f_{S_2} and the assemblage will dissociate to produce pyrrhotine and/or magnetite in association with fluid with a high sulphur content (Barnes and Kullerud, 1961). Changing pH can therefore be considered as a mechanism of changing sulphur fugacity at constant f_{O_2} .

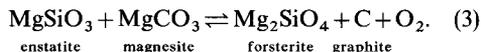
Iron sulphides in igneous rocks. Both pyrrhotine and pyrite are major components of magmatic orebodies but, although they also occur in normal igneous rocks, their study therein has been rather neglected; they are usually scarcely mentioned in texts on igneous petrology. Pyrrhotine is the primary iron sulphide in unaltered basaltic rock which represents the dominant igneous lithology in the Earth's crust. Pyrrhotine is also found in mantle xenoliths and diamonds (Harris and Gurney, 1979). Troilite, stoichiometric FeS, is the iron sulphide found in meteorites and lunar basalts in association

with ferro-nickel alloys (Craig and Vaughan, 1981) and troilite is probably the stable iron sulphide in the Earth's mantle and core (Rama Murphy, 1976). However, at high pressure and temperatures, magmatic iron sulphide hosts copper and nickel in a metal monosulphide solid solution. Cooling and exsolution lead to the common magmatic association of pyrrhotine with pentlandite, $(Fe,Ni)_9S_8$, and chalcopyrite $CuFeS_2$. These minerals usually occur as rounded inclusions or masses due to sulphide liquid immiscibility in silicate magma (Naldrett, 1973).

Pyrite is found in basaltic rocks but can be interpreted as crystallizing late. An increase in sulphur activity perhaps due to concentration of H_2S on magma fractionation may lead to destabilization of pyrrhotine and produce late pyrite:

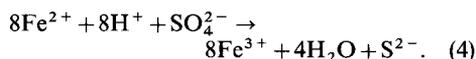


However, an alternative view is that pyrrhotine becomes unstable in association with cooling basaltic magma due to an increase in oxidation state driving reaction (1). Mathez (1984) outlined the effects of increasing oxidation state on oxides and silicates in basaltic magmas but excluded sulphides; the fugacity of oxygen was considered to increase on falling pressure by degassing of CO. Since CO is dissolved with O^{2-} and $\frac{1}{2}O_2$ in the magma as CO_3^{2-} , it was considered (BVSP, 1981) that the oxygen fugacity of basaltic magma is controlled by the EMOG buffer:



This pressure-dependent buffer gives f_{O_2} (fugacity) values for basaltic magma close to that of the iron-wüstite (Fe-FeO) buffer at mantle pressures but close to the fayalite-magnetite quartz (Fe_2SiO_4 - Fe_3O_4 - SiO_2) buffer (FMQ) at low crustal pressures (BVSP, 1981) and is an alternative way of expressing the increasing f_{O_2} of evolving basaltic magma.

Interaction with sea-water or other sulphate-bearing waters is an additional, lower temperature syn- or post-crystallization process leading to more oxidized assemblages in igneous rocks. At temperatures above ~300 °C sulphate is reduced inorganically by ferrous iron in silicates (Barnes, 1979; Trudinger, 1981):



This is a major process taking place in submarine hydrothermal systems related to ocean-floor spreading (Cann, 1980) and can result in pyrite and/or magnetite in basaltic rocks.

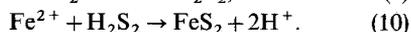
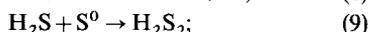
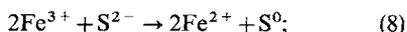
Pyrrhotine is particularly prone to alteration to

FeS₂ (marcasite or pyrite) on weathering but the characteristic alteration texture usually permits the former presence of pyrrhotine to be recognized. In each case outlined above, an increase in oxygen fugacity permits the electron loss necessary to drive reaction (1) leading to the occurrence of pyrite in basaltic rocks with, or at the expense of, pyrrhotine. Pyrite rather than pyrrhotine is the iron sulphide of sulphide-enriched felsic igneous rocks such as 'copper porphyrys' (Craig and Vaughan, 1981) but such iron sulphide is of a special hydrothermal origin and can result from late magmatic fluid or by reduction of circulating sulphate-bearing fluids.

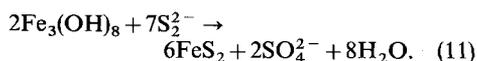
Iron sulphides in sedimentary rocks. The principal origin of pyrite, often as framboidal pyrite, in sedimentary rocks is by bacteriogenic reduction of sea-water sulphate during diagenesis (Trudinger, 1981). Sulphur-deficient iron sulphides, such as pyrrhotine are extremely rare in sedimentary rocks (Ferry, 1981); Curtis and Spears (1968) predicted this observation from the low Eh and limited stability field of FeS. High alkalinity would in theory, however, stabilize FeS (Barnes and Kullerud, 1961). Mackinawite (a low-temperature form of FeS) and the sulphospinel greigite, Fe₃S₄, have been described as low-temperature transitory phases in reducing organic-rich sediments (Berner, 1964). The generally accepted (Curtis, 1980) simplified reactions for bacteriogenic reduction of sulphate to pyrite are those of Berner (1970, 1978):



Experimental studies of pyrite formation led Roberts *et al.* (1969) to conclude that the free sulphur, S⁰ is made available by oxidation of S²⁻ by Fe³⁺ and this leads to the formation of transitory H₂S₂ which combines with Fe²⁺ to produce pyrite:

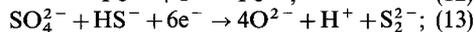
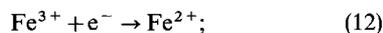


Taylor (1982) suggested that magnetic ferrosiferrous hydroxide might be a framboidal precursor to framboidal pyrite which could result from the following reaction that also involves Fe³⁺ (charge unbalanced as published):

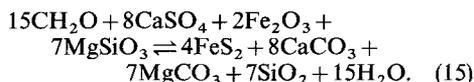


Whatever the details of the reaction kinetics, FeS is unstable at the oxidation fugacities of even the most reduced sedimentary rocks (Curtis and Spears, 1968), so pyrite is the expected stable iron sulphide.

This can be expressed using reaction (1) which requires a corresponding reduction reaction. Three possibilities that may take place during diagenesis are:



An overall reaction representing the geochemical balance of relatively reduced and oxidized sulphur is given in Berner and Raiswell (1983):



Consideration that Fe²⁺ and S²⁻ (or HS⁻) exist as transitory soluble products of bacteriogenic sulphate reduction resolves the problem of supplying all the contributing materials: sulphate, iron salts, organic debris, and bacteria *at* the site of growing pyrite crystals. Thus sulphate reduction and pyrite growth need not take place at the same place in the sediment. This is borne out by petrographic studies of pyrite which may occur interstitially, within detrital iron-bearing minerals, within organic debris, as replacements of shell fragments and even in veinlets (Stach *et al.*, 1982). Raiswell and Plant (1980) showed that diagenetic pyrite is usually either framboidal and precipitated by reaction of dissolved H₂S with iron-bearing minerals, or euhedral and precipitated by reaction of dissolved H₂S and dissolved iron. Pyrite and marcasite concretions require a more obvious supply of mobile iron and sulphur from a large reservoir as the concretion grows by digestion and dissolution of sedimentary debris.

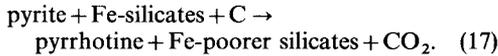
The soluble nature of FeS compared to FeS₂ will be discussed further below. Once formed, pyrite is stable throughout the low-temperature, low-pressure conditions encountered in sedimentary rocks. An oxidation process, e.g. weathering, will, however, lead to the breakdown of pyrite.

Iron sulphides in metamorphic rocks. Both pyrrhotine and pyrite occur in metasediments from the lowest to the highest grades of regional metamorphism therefore, pyrrhotine must be produced in the anchizone, between diagenesis and greenschist facies metamorphism. Consideration of the phase relations of iron sulphides (Kullerud and Yoder 1959) would suggest the following reaction;



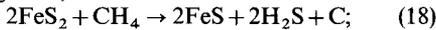
However, there is no simple temperature-controlled desulphidation reaction leading to the breakdown of pyrite and providing a pyrite/pyrrhotine metamorphic reaction isograd as suggested by Carpenter (1974).

Lambert (1973) demonstrated experimentally that carbonaceous material catalyses reaction (16) leading to the thermal transition taking place at lower temperatures from $\sim 750^\circ\text{C}$ in the condensed system down to $\sim 350^\circ\text{C}$ with carbonaceous matter present. The role of carbon is therefore an important aspect of pyrite reduction. Mohr and Newton (1983) discussed iron sulphide-silicate reactions in metamorphic rocks and concluded that metamorphic mineral assemblages developed in a *closed* system are greatly influenced by the involvement of iron sulphides and carbon. The general reaction given, following that of Thompson (1972) was:



Ferry (1981) proposed that the following reactions took place on *open* system progressive metamorphism of graphitic pelites:

at low grades,

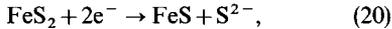


at high grades,



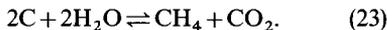
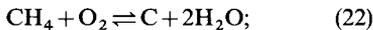
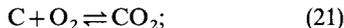
Removal of H_2S by syn-metamorphic fluid-flushing was considered to be the driving force of the reactions so this can be considered as a special case on metamorphism.

All these reactions may be represented by the reduction process



and I suggest that progressive reduction during regional metamorphism can be considered to be the driving force of reaction (20). Note that iron is generally available in fluid/rock interactions and the addition of Fe^{2+} on the left hand side of reaction (20) will lead to the proposed general redox equation (1).

The equilibrium oxygen fugacity in metamorphic rocks depends on the controlling buffer but carbon is the most effective reducing substance in meta-sedimentary rocks (Frost, 1979). In graphitic rocks the controlling buffer reactions are:



These reactions can lead to the lowest oxidation states observed in metasediments. Eugster (1981) reviews buffer reactions in metamorphic fluids in detail.

Using published methods and thermodynamic data (Barnes and Kullerud, 1961; Scott, 1974; Ohmoto and Kerrick, 1977; Crerar *et al.*, 1978;

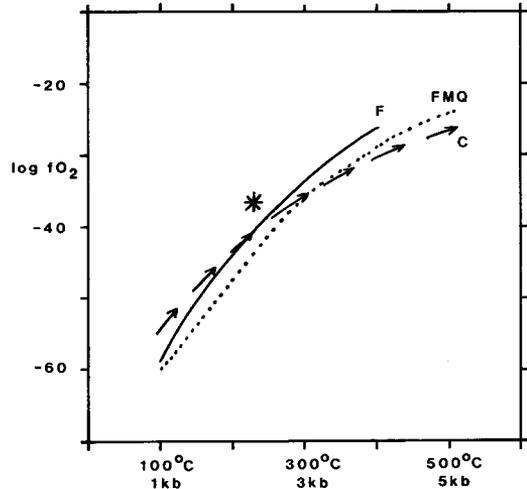


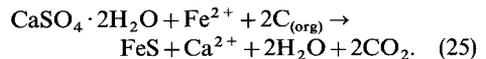
FIG. 2. Diagram illustrating how progressive reduction by graphite results in the production of pyrrhotine at the expense of pyrite in metasediments. The diagram is based on calculations and data referenced to in the text, and using a geothermal gradient of $33^\circ\text{C}/\text{km}$. F (solid line) represents the pyrite to pyrrhotine reaction in the presence of magnetite. C (dashed line) represents the graphite to carbon dioxide reaction. FMQ (dotted line) represents the fayalite to magnetite + quartz reaction. The asterisk marks the point, at the intersection of the graphite/ CO_2 and pyrite/pyrrhotine lines, where pyrite coexists with pyrrhotine in the presence of magnetite.

Vaughan and Craig, 1978; Barnes, 1979; Henley *et al.*, 1984) and assuming a reasonable geothermal gradient of $33^\circ\text{C}/\text{km}$, calculations show (fig. 2) that the graphite buffer will begin to reduce pyrite to pyrrhotine above about 200°C . The progressive reduction corresponds to a movement down the central line separating iron sulphides from iron oxides in fig. 1. Thus in graphitic metasediments, progressive metamorphism on burial will result in the reduction of relatively oxidized sulphide minerals as well as oxides and silicates because of the *relative* fall in f_{O_2} of the graphite buffer with increase in temperature (and pressure).

At temperatures above $\sim 200^\circ\text{C}$ sulphate can be reduced inorganically by organic matter (Kiyosu, 1980):

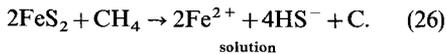


Petrographic evidence for a similar reaction leading to pyrrhotine-bearing pseudomorphs of gypsum in dolomitic slates was presented by Hall (1982):

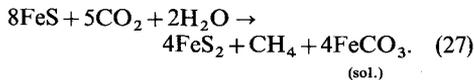


Pyrite will persist in metasediments which do not attain a low enough oxidation state for the formation of pyrrhotine. Obviously, graphite-free lithologies are more likely to contain original pyrite but reaction with mobile reduced metamorphic fluid would be a means of converting pyrite in graphite-free lithologies to pyrrhotine.

During metamorphism pyrite may not simply change *in situ* to pyrrhotine but the iron and sulphur can dissolve as FeS in the reduced metamorphic fluid. Textural features that are interpreted as being due to 'remobilization' of sulphides (Vokes, 1969; Carpenter, 1974) lend support to this view and the equation (16) from Ferry (1981) can be adapted to express the soluble nature of FeS:



The growth of pyrite porphyroblasts in metamorphic rocks as in the Ballachulish Slates, where late pyrite grows in lithologies containing disseminated pyrrhotine (Hall, 1982), and the Great Gossan Lead, where pyrite has a complex growth history during metamorphism (Craig, 1983; Craig and Vaughan, 1981), may be due to dissolution of pyrrhotine followed by oxidation and precipitation as pyrite. This proposed process can be represented by the reaction:



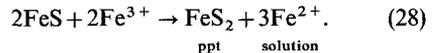
This oxidation process may be considered to be a retrogressive metamorphic or 'epidiagenetic' (Fairbridge, 1967) process when pyrite is seen to grow at a late stage in metamorphic rocks.

Appreciation of the possible complex reactions and remobilization of iron sulphides in metamorphic rocks as outlined above is important in the study of, for example, trace elements, stable isotopes, geothermometry and geobarometry. Careful textural interpretation is therefore a prerequisite of such studies; pyrite and pyrrhotine may occur together in the same rock but this does not imply that they are in equilibrium (Hall, 1982).

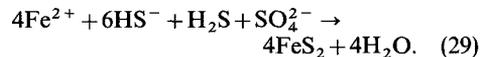
Contact or thermal metamorphism is a much more restricted geological process than regional metamorphism. The breakdown of pyrite to pyrrhotine is a characteristic process in thermal aureoles and can be represented adequately by reaction (16) (Neumann, 1950); the possible associated sulphurization of iron-silicates has been discussed by MacRae (1974).

Iron sulphides in hydrothermal ore deposits. Pyrrhotine and pyrite are considered to be common hydrothermal precipitates from solutions on epigenetic vein and exhalative synsedimentary

mineralization (Finlow-Bates *et al.*, 1977). The solubility product of FeS greatly exceeds that of FeS₂ (Crerar *et al.*, 1978) and it is evident from activity values that FeS is more soluble than all other common metal monosulphides (Barnes, 1979). It is therefore reasonable to consider FeS as the dissolved component, whereas FeS₂ may precipitate from solution as a result of redox reactions such as the following:



Increasing oxidation of exhalative hydrothermal solutions was considered by Lydon (1983) to be the principal reason for pyrite precipitation at Rammelsberg. On pyrite precipitation, biogenic sulphide may contribute to the pyrite, leading to exhalative pyrite in the synsedimentary environment carrying a variable bacteriogenic sulphur isotope signature (Trudinger, 1981). Extremely negative sulphur isotope values provide evidence that biogenic sulphur predominates in pyrite from the exhalative chimneys at Ballynoe, Silvermines, Eire, and this biogenic pyrite in the exhalative seafloor environment was considered by Boyce *et al.* (1983) to form in the relatively oxidizing seafloor conditions by way of the following notional reaction based on that of Barnes (1979):



The exhalative synsedimentary environment therefore involves an interplay of both biogenic and inorganic processes that generally lead to pyrite rather than pyrrhotine.

Exhalative mineralization containing disseminated or massive pyrrhotine is, however, found in metasediments and in some cases the pyrrhotine is considered to be a primary precipitate (Finlow-Bates *et al.*, 1977; Craig, 1980, 1983; Sunblad, 1981). This implies that the precipitation took place from submarine exhalative fluids without any significant mixing with seawater and that the chemical precipitates escaped oxidation during diagenesis. Credence in this view is supported by the soluble nature of FeS discussed above and by the observation (Speiss *et al.*, Hayman, 1983) that FeS is being actively precipitated at the present day from exhalative fluids at East Pacific Rise sites. But here the FeS is either rapidly oxidized to produce limonite or is involved in reactions to produce pyrite and Cu-Fe sulphides (Hayman, 1983).

The lack of stratiform pyrrhotine deposits in unmetamorphosed (less than lowest greenschist facies) sedimentary rocks remains intriguing and may imply that conditions for pyrrhotine precipitation and preservation are more favourable in

sediments destined to become metamorphic rocks, i.e. sediments deposited in relatively deep water in rapidly subsiding basins. In addition, conditions may have been more favourable for the genesis and preservation of pyrrhotine in the Archaean and Proterozoic than in the Phanerozoic; such conditions would be a higher geothermal gradient resulting in higher-temperature, more reduced and therefore FeS-rich exhalative fluid and less oxygenated, more stratified marine waters (Finlow-Bates and Large, 1978; Plimer and Finlow-Bates, 1978). Hence, massive pyrrhotine is more likely to be of exhalative origin than disseminated pyrrhotine (Willan and Hall, 1980). As noted above, deposition under alkaline conditions will also favour pyrrhotine formation; highly alkaline seabottom conditions have been suggested by Russell *et al.* (1984) to explain the origin of celsian, $\text{BaAl}_2\text{Si}_2\text{O}_8$ in the late Proterozoic, Aberfeldy baryte deposit, where pyrrhotine-rich layers and pods are also found.

It is noteworthy that pyrrhotine and baryte, BaSO_4 , do not occur in close association, i.e. in contact, in stratiform deposits. At Aberfeldy for example, pyrite is the iron sulphide associated with baryte but both pyrite and pyrrhotine can occur in celsian and some other lithologies (Willan and Coleman, 1984). The sulphate for baryte is generally provided by seawater on mixing with Ba-bearing hydrothermal solutions when the baryte inherits the sulphur isotope signature of the seawater (Claypool *et al.*, 1980; Willan and Coleman, 1984). Oxidation of hydrothermal sulphide is an alternative source of sulphate for baryte (Lydon, 1983) and in this case baryte sulphur-isotope values would not simply represent seawater sulphate but would depend on the original dissolved sulphide isotopic value and the degree of isotopic fractionation on oxidation.

While primary exhalative pyrrhotine remains an attractive hypothesis, the increasing recognition of the role of mobile fluids during metamorphism may necessitate reconsideration of the possible metamorphic origin of massive pyrrhotine in stratiform ore deposits. Pervasive migrating reduced fluids could perhaps convert massive pyrite to pyrrhotine.

Iron oxides may accompany iron sulphides in hydrothermal mineralization but hematite does not occur in close association with pyrrhotine, an association which is forbidden by consideration of fig. 1. The correlation of f_{S_2} and f_{O_2} has been observed directly in present-day hydrothermal systems (D'Amore and Gianelli, 1984) but the decrease in both f_{S_2} and f_{O_2} values with falling temperature is an artefact of the thermodynamic calculation, as fugacity values are temperature dependent. Mineral assemblages observed to be in

equilibrium with cooler fluids indicate higher oxidation states than assemblages in equilibrium with warmer fluid (D'Amore and Gianelli, 1984). Also, it is clear that as pyrrhotine is stable at high temperatures and pyrite at lower temperatures in the active geothermal systems, the fugacities of cooling hydrothermal solutions correspond to a relative increase in f_{S_2} and f_{O_2} and a movement up the central line of co-existing iron sulphides and iron oxides in fig. 1.

Conclusions. The distribution of iron sulphides in nature can thus be best understood if pyrrhotine is taken to be indicative of lower, and pyrite indicative of higher sulphur and oxygen fugacities which appear to be generally interdependent and positively correlated in natural systems. Changes in pH of solutions provides a mechanism of changing f_{S_2} at constant f_{O_2} . Pyrrhotine can be considered to be the molten iron sulphide in reduced magmas and the dissolved iron sulphide in aqueous solutions, although pyrite may be precipitated in each case rather than pyrrhotine, due to increased oxygen and sulphur fugacities. Pyrite is the stable iron sulphide in normal sedimentary rocks but meta-sediments may carry disseminated pyrrhotine which results mainly from progressive reduction on progressive metamorphism.

Acknowledgements. Discussions with staff and research students of the Department of Applied Geology, University of Strathclyde, is greatly appreciated. Thanks also to the Head of Department, Mike Russell, for critical reading of the manuscript and for the useful comments provided by Rob Willan, Chris Stanley, and an anonymous referee.

REFERENCES

- Barnes, H. L., ed. (1979) *The Geochemistry of Hydrothermal Ore Deposits*. Wiley, New York.
 — and Kullerud, G. (1961) *Econ. Geol.* **56**, 648–88.
 BVSP (1981) *Basaltic Volcanism Study Project. Basaltic Volcanism on the Terrestrial Planets*. Pergamon Press, New York.
 Berner, R. A. (1964) *J. Geol.* **72**, 826–34.
 — (1970) *Am. J. Sci.* **268**, 1–23.
 — (1978) *Earth Planet. Sci. Lett.* **37**, 492–8.
 — and Raiswell, R. (1983) *Geochim. Cosmochim. Acta*, **47**, 855–62.
 Boyce, A. J., Coleman, M. L., and Russell, M. J. (1983) *Nature*, **306**, 545–50.
 Cann, J. R. (1980) *J. Geol. Soc. London*, **137**, 381–4.
 Carpenter, R. H. (1974) *Geol. Soc. Am. Bull.* **85**, 451–6.
 Claypool, G. E., Holser, W. T., Kaplan, I. R., Sakai, H., and Zak, I. (1980) *Chem. Geol.* **28**, 199–260.
 Craig, J. R. (1980) *Norges Geol. Unders.* **360**, 295–325.
 — (1983) *Mineral. Mag.* **345**, 515–26.
 — and Vaughan, D. J. (1981) *Ore Microscopy and Ore Petrography*. Wiley, New York.
 Crear, D. A., Susak, N. J., Borcsik, M., and Schwartz, S. (1978) *Geochim. Cosmochim. Acta.* **42**, 1427–37.

- Curtis, C. D. (1980) *J. Geol. Soc. London*, **137**, 189–94.
- and Spears, D. A. (1968) *Econ. Geol.* **63**, 257–70.
- D'Amore, F., and Gianelli, G. (1984) *Geochim. Cosmochim. Acta*, **48**, 847–57.
- Eugster, H. P. (1981) In *Chemistry and Geochemistry of solutions at high temperature and pressure: Physics and Chemistry of the Earth* (F. E. Wickman and D. T. Richard, eds.) Pergamon Press, New York, 461–507.
- Fairbridge, R. W. (1967) In *Diagenesis of Sediments* (G. Larsen and G. V. Chillinger, eds.), Elsevier, 19–89.
- Ferry, J. M. (1981) *Am. Mineral.* **66**, 908–30.
- Finlow-Bates, T., and Large, D. E. (1978) *Geol. Jahrb.* **30**, 27–39.
- Croxford, N. J. W., and Allan, J. M. (1977) *Mineral. Deposita*, **12**, 143–9.
- Froese, E. (1971) *Econ. Geol.* **66**, 335–41.
- Frost, B. R. (1979) *Am. J. Sci.* **279**, 1033–59.
- Hall, A. J. (1982) *Mineral. Deposita*, **17**, 401–9.
- Harris, J. W., and Gurney, J. J. (1979) In *The Properties of Diamond* (J. E. Field, ed.) Academic Press, London, 555–91).
- Hayman, R. M. (1983) *Nature*, **301**, 695–8.
- Henley, R. W., Truesdell, A. H., and Barton, P. B. Jr. (1984) *Fluid-mineral equilibria in hydrothermal systems. Reviews in Economic Geology*, **1**, Soc. of Econ. Geologists, USA.
- Holland, H. D. (1959) *Econ. Geol.* **54**, 184–233.
- Kiyosu, Y. (1980) *Chem. Geol.* **30**, 47–56.
- Kullerud, G., and Yoder, H. S. (1959) *Econ. Geol.* **54**, 533–72.
- Lambert, I. B. (1973) *J. Geol. Soc. Austral.* **20**, 205–15.
- Lydon, J. W. (1983) In *Sediment-hosted stratiform lead-zinc deposits* (D. F. Sangster, ed.) Mineral. Assoc. Can. Short Course Handbook, **9**, 175–250.
- MacRae, N. D. (1974) *Can. J. Earth Sci.* **11**, 246–53.
- Mathez, E. A. (1984) *Nature*, **310**, 371–75.
- Mohr, D. W., and Newton, R. C. (1983) *Am. J. Sci.* **283**, 97–134.
- Naldrett, A. J. (1973) *Can. Mining Metall. Bull.* **66**, 45–63.
- Neumann, H. (1950) *Mineral. Mag.* **29**, 234–8.
- Ohmoto, H., and Kerrick, D. (1977) *Am. J. Sci.* **277**, 1013–44.
- Plimer, I. R., and Finlow-Bates, T. (1978) *Mineral. Deposita*, **13**, 399–410.
- Raiswell, R., and Plant, J. (1980) *Econ. Geol.* **75**, 584–99.
- Rama Murthy, V. (1976). In *The Early History of the Earth* (B. F. Windley, ed.) Wiley, London, 21–32.
- Roberts, W. M. B., Walker, A. L., and Buchanan, A. S. (1969) *Mineral. Deposita*, **4**, 18–29.
- Russell, M. J., Hall, A. J., Willan, R. C. R., Allison, I., Anderton, R., and Bowes, G. (1984) In *Prospecting in areas of glaciated terrain 1984, symposium volume*. Instn. Mining Metall., London, 159–70.
- Scott, S. D. (1974) In *Sulfide Mineralogy*, Mineralogical Society of America Short Course Notes, **1** (P. H. Ribbe, ed.), MSA, Washington, S1–S38.
- Speiss, F. N., MacDonald, K. C., Atwater, T., Ballard, R., Carranza, A., Cordoba, D., Cox, C., Diaz Garcia, V. M., Francheteau, J., Guerrero, J., Hawkins, J., Haymon, R., Hessler, R., Juteau, T., Kastner, M., Larson, R., Luyendyk, B., MacDougall, J. D., Miller, S., Normakr, W., Orcutt, J., and Rangin, C. (1980) *Science*, **207**, 1421–33.
- Stach, E., Mackowsky, M.-Th., Teichmuller, M., Taylor, G. H., Chandra, D., and Teichmuller, R. (1982) *Coal Petrology*. Gebruder Borntraeger, Berlin.
- Sunblad, K. (1981) *Mineral. Deposita*, **16**, 129–46.
- Taylor, G. R. (1982) *Ibid.* **17**, 23–36.
- Thompson, J. B., Jr. (1972) *Proc. 24th Intern. Geol. Congress*, **10**, 27–35.
- Trudinger, P. A. (1981) *BMR J. Austral. Geol. Geoph.* **6**, 279–85.
- Vaughan, D. J., and Craig, J. R. (1978) *Mineral chemistry of metal sulphides*. Cambridge University Press, England.
- Vokes, F. M. (1969) *Earth Sci. Rev.* **5**, 99–143.
- Willan, R. C. R., and Coleman, M. L. (1984) *Econ. Geol.* **78**, 1619–56.
- and Hall, A. J. (1980) *Trans. Instn. Min. Metall. (Sect. B: Appl. Earth Sci.)* **89**, 31–40.

[Manuscript received 24 April 1985;
revised 26 September 1985]