

# The metamorphism of pyrite and pyritic ores: an overview

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## Abstract

Pyrite, the most widespread and abundant of sulphide minerals in the Earth's surficial rocks, commonly constitutes the primary opaque phase in ore deposits. Consequently, an understanding of the behaviour of pyrite and its relationships with coexisting phases during the metamorphism of pyrite-bearing rocks is vital to the interpretation of their genesis and post-depositional history. Metamorphism is commonly responsible for the obliteration of primary textures but recent studies have shown that the refractory nature of pyrite allows it to preserve some pre-metamorphic textures. Pyrrhotite in pyritic ores has often been attributed to the breakdown of pyrite during metamorphism. It is now clear that pyrrhotite can be primary and that the presence of pyrrhotite with the pyrite provides a buffer that constrains sulphur activity during metamorphism. Pyrite-pyrrhotite ratios change during metamorphism as prograde heating results in sulphur release from pyrite to form pyrrhotite and as retrograde cooling permits re-growth of pyrite as the pyrrhotite releases sulphur. Retrograde growth of pyrite may encapsulate textures developed during earlier stages as well as preserve evidence of retrograde events. Sulphur isotope exchange of pyrite with pyrrhotite tends to homogenise phases during prograde periods but leaves signatures of increasingly heavy sulphur in the pyrite during retrograde periods.

**KEYWORDS:** metamorphism, pyrite, pyrrhotite, sulphur isotopes.

## Introduction

PYRITE is the most well known and widespread of the iron sulphides in surficial rocks. It occurs in rocks of every geologic age and of virtually every geologic realm, including rocks of virtually all grades of metamorphism. It is also an occasional corrosion product of ferroalloys when attacked by H<sub>2</sub>S-bearing gases or aqueous solutions (Ramanarayanan and Smith, 1990). Furthermore, pyrite has recently been found being formed within magnetotactic bacteria (Mann *et al.*, 1990) and has even been proposed as having provided the surface on which life may have originated (Morgan, 1991).

There can be little doubt that pyrite constitutes the most, or at least one of the most, dominant minerals formed or modified during a broad spectrum of ore-forming processes. Because of

the ubiquitous occurrence of pyrite, an understanding of its behaviour under a variety of conditions is important. The present paper attempts to contribute toward an understanding of pyrite in metamorphic environment.

## Pyrite in the metamorphic environment

The occurrence and behaviour of pyrite in the metamorphic environment are topics about which much has been written. It has received so much attention because it is the most abundant and widespread of the sulphides and constitutes the dominant phase in many ore deposits and because it serves as a major control on the activity of sulphur in the mineral phases and the metamorphic fluids. Furthermore, its high thermal stability (742°C) Kullerud and Yoder, 1959) and its high

physical strength ensure that it will survive all but the highest grades of metamorphism. Thus pyrite is quite stable in the greenschist to amphibolite grades to which so many ores have been metamorphosed (Fig. 1) provided that the activity of sulphur remains high.

More than 20 years ago Vokes (1969) noted the difficulty of deciphering the true origin of many metamorphosed deposits. Subsequently, Stanton (1972) has stressed that original textures are commonly lost, and Plimer (1987) has noted that most mineralogical and textural features observed in metamorphosed massive sulphide deposits form after the peak of metamorphism. Scott (1976, 1983) has, however, pointed out that pyrite is one of the most refractory sulphides and that it thus offers an opportunity of preserving some evidence of pre- or syn-metamorphic development.

The present paper is intended to bring together observations on the physical and chemical nature of pyrite which are useful in interpreting the behaviour of pyrite during metamorphism. To what extent does it retain characteristics through a metamorphic event? And what features, if any, permit us to interpret changes occurring during the metamorphism? In doing this we are building on and extend some observations made in several of our earlier papers (Vokes, 1969; Craig, 1983; Craig and Vokes, 1986, and in press; Craig *et al.*, 1991) and leaning heavily upon the fine work of

many others whose papers are referenced throughout.

The observations and discussions that follow are separated in typical fashion and for convenience into physical and chemical aspects. It is fair to note that such a separation is rather artificial because the physical and chemical behaviour are commonly interdependent. Furthermore, the discussion has been restricted to the megascopic and optical microscopic realms and has not delved into the submicroscopic domain.

### Physical properties of pyrite

Two characteristics of pyrite dominate its physical behaviour during metamorphism—its bond strength (observable in its microhardness and resistance to ductile deformation) and its proclivity to form idiomorphic (usually cubic) crystals. The Vickers hardness number (VHN) for pyrite is 1505–1620, whereas those for the sulphides with which pyrite commonly occurs are: pyrrhotite, 230–318; sphalerite, 218–227; chalcopyrite, 187–203; and arsenopyrite, 715–1354 (Vaughan and Craig, 1978). Hence, pyrite withstands deformation far better than most of the other typically associated sulphides, as shown in Fig. 2, and better than many silicates. There is no doubt that structural defects may also affect the strength of pyrite, but little is known of the

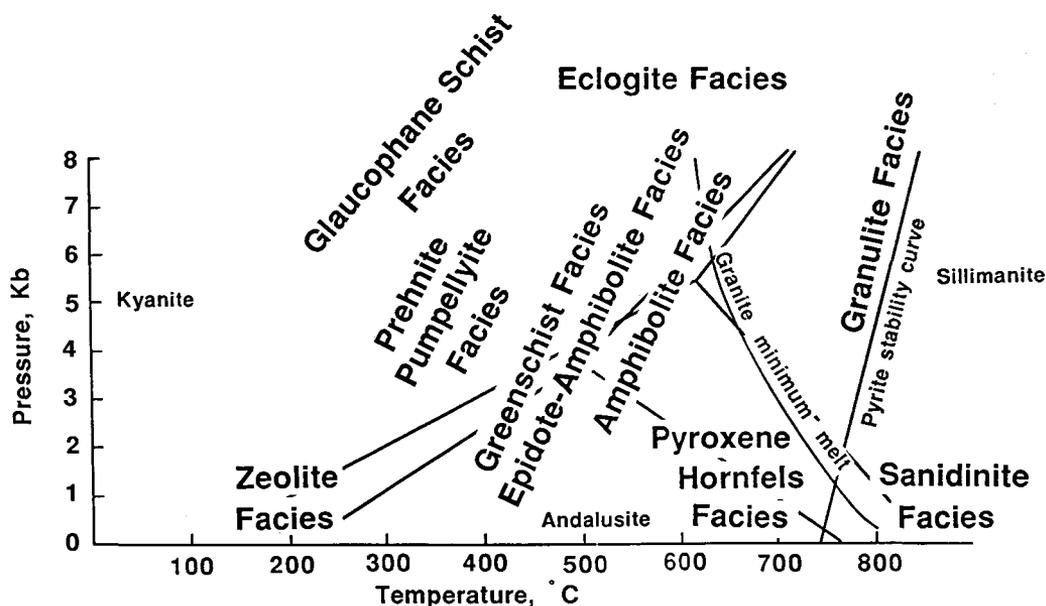


FIG. 1. Schematic depiction of metamorphic facies and the upper stability curve for pyrite illustrating that pyrite is stable under all but the highest grades of metamorphism. Data derived from many sources.

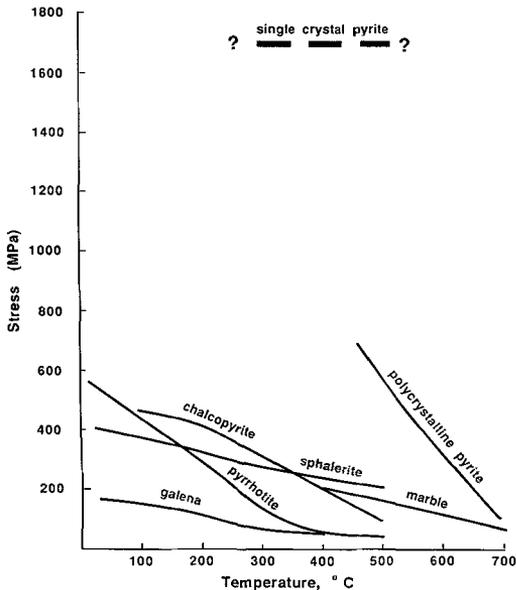


Fig. 2. Strength of some common sulphides in terms of differential stress and temperature. The much greater strength of pyrite is responsible for its much more refractory behaviour during metamorphism. Data from Graf and Skinner (1970), Atkinson (1975), and Kelly and Clark (1975).

distributions of defects, and the authors know of no reports of anomalous pyrite where softness is attributable to defects.

The mechanisms of pyrite deformation during metamorphism have been the subject of numerous studies and have been mapped in stress versus temperature space by McClay and Ellis (1983). Graf and Skinner (1970) note that pyrite behaves as a brittle substance under all conditions of deformation in the earth's crust, and Siemes *et al.* (1991) note that pyrite would remain rigid through a stress differential-temperature path of 60 MPa + 600 °C. Although this conclusion was challenged by Mookherjee (1971) and although some ductile behaviour of pyrite has been demonstrated by Atkinson (1975) and Cox *et al.* (1981) the general observation by Graf and Skinner remains largely correct. Brittle deformation is very commonly noted where pyrite is dominant or where pyrite euhedra are forced against one another. Generally, the brittle deformation results in randomly fractured fragments in a cataclastic texture (Fig. 3A) but locally it results in a well developed cleavage as described by England (1979) and as shown in Fig. 3B. Over the past ten years, several workers (e.g. McClay and Ellis, 1984; Cox, 1987; Marshall and Gilligan,

1987) have pointed out that pressure solution also appears to play a major role in the modification of textures. McClay and Ellis (1984) note there is strong evidence that pressure solution and cataclastic flow are the dominant deformation mechanisms in pyrite in low-grade metamorphic environments. Furthermore, Marshall and Gilligan (1987) suggest that solution-transfer is an important mechanism in retrogressive deformation. The subject of retrograde effects is discussed in greater detail below.

Pyrite, despite its hardness and its generally refractory nature, exhibits a tendency to recrystallise in response to metamorphism at greenschist grades and above. The recrystallisation manifests itself in the development of annealed textures and in changes of grain size. Several authors (e.g. Vokes, 1968; Templeman-Kluit, 1970; Mookherjee, 1976; McClay and Ellis, 1983) have documented that there is a general increase in pyrite grain size with increasing grade of metamorphism. However, the effects of annealing depend upon the other phases which occur together with the pyrite. Where it occurs as monomineralic polycrystalline masses, the pyrite tends to develop annealing textures characterised by 120° dihedral angles (Fig. 4A) as described by Stanton and Gorman (1968), Stanton (1972), and Lawrence (1972). If there are only small quantities of accompanying sulphides or gangue phases, these have little effect upon the gross texture and may be confined to lenses and triangular masses interstitial to the pyrite (Fig. 4B). On the other hand, the presence of significant to dominant amounts of other sulphides usually allows the pyrite to recrystallise into euhedral grains as shown in Fig. 5. Once developed, the pyrite crystals may readily serve as buttresses if there is significant deformation; in such cases softer minerals such as chalcopyrite may be mobilised and reprecipitated in the adjacent low pressure zones (Fig. 6). The mechanisms for such movement have been described by Selkman (1983).

Less obvious than the megascopic textural changes are subtle but potentially important submicroscopic lattice changes which occur in the pyrite. Loberg *et al.* (1985) in a detailed study of pyrites from a variety of metamorphic environments found that with increasing metamorphic grade pyrites generally exhibited an increase in VHN, and an increase in reflectance. It is probable that these changes result from differences in the numbers and/or types of dislocations present within the lattice; this is consistent with the findings of Cox *et al.* (1981) who pointed out that pyrite undergoes significant work hardening during plastic deformation.

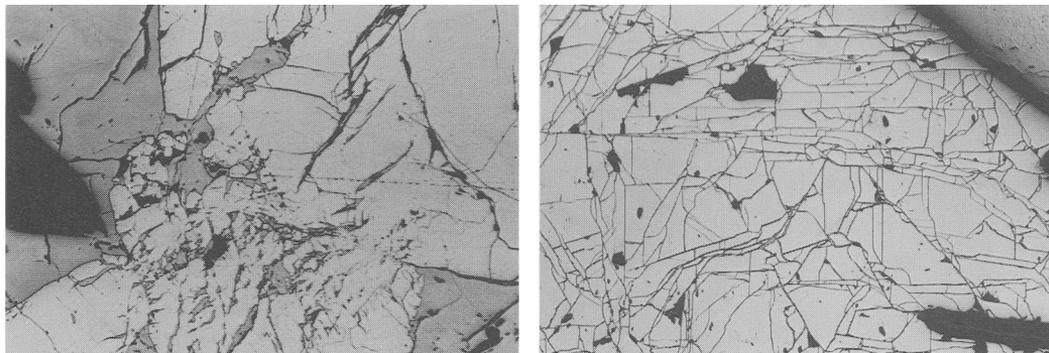


FIG. 3. (A, *left*) Cataclastic deformation of pyrite where adjacent crystals impinge upon one another during deformation (Ducktown, Tennessee, U.S.A.). (B, *right*) Orthogonal cleavage planes in pyrite crystals that have been rolled during deformation of the massive ores at Sulitjelma, Norway (width of field is 1.2 mm in both photomicrographs).

Marcasite, the orthorhombic dimorph of pyrite, is a moderately common phase in sedimentary ores and low-temperature vein deposits but is absent as a primary mineral in moderate to high-grade metamorphosed ores. Although thermodynamic data (Grønvoold and Westrum, 1976) indicate that marcasite has no field of true stability, its tendency to form in low-temperature acid environments has been reported for many years. It appears that natural annealing, even at relatively low temperatures, results in the transformation of the marcasite to pyrite. Thus, for example, marcasite is a common constituent of the sulphide chimneys and mounds that have been observed forming at black smoker sites along oceanic spreading centres (Edmond and Von Damm, 1983; Haymon, 1983; Zierenberg and Shanks, 1983), but the metamorphosed equivalents contain abundant pyrite but little or

no marcasite. Kullerud (1967) found that marcasite converts readily to pyrite if heated in the presence of excess sulphur between 150 and 400 °C and that marcasite could be synthesised (with pyrite) in the presence of water up to 432 °C by reaction of sulphur with iron hydroxide. Rising (1973) found that the inversion rate of marcasite to pyrite above 157 °C is proportional to temperature but is inversely proportional to grain size. Much more recently, Murowchick (1992) has examined the textures of marcasites which have been thermally converted to pyrite and found distinctive characteristics which may prove useful in deciphering the paragenesis of some pyrites.

#### Chemical aspects

Innumerable chemical analyses of pyrite by a host of analytical techniques confirm the metal to

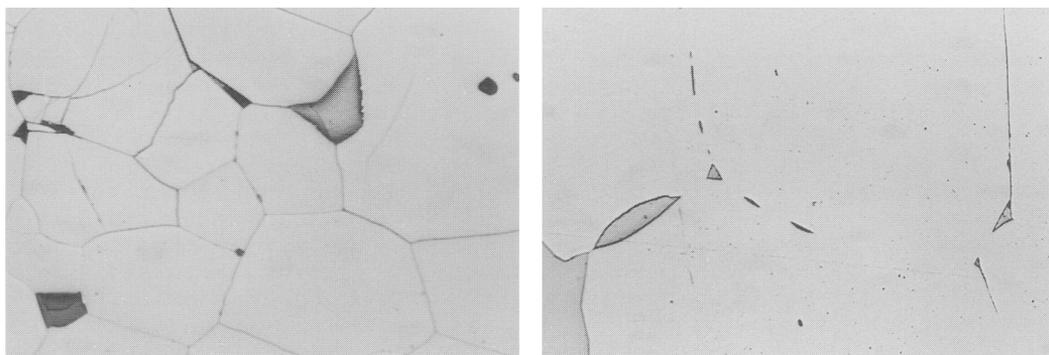
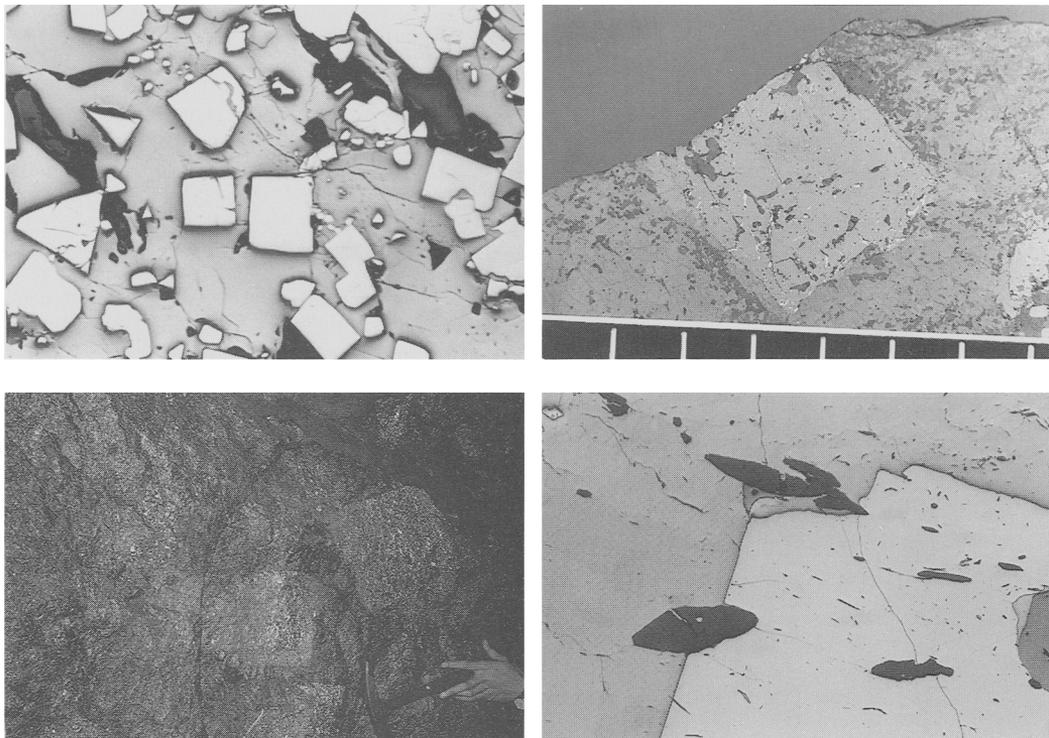


FIG. 4. (A, *left*) Typical annealed texture in polycrystalline mass of pyrite subjected to amphibolite grade metamorphism but to little or no deformation. (B, *right*) Polycrystalline pyrite where interstitial galena has been trapped as lens like and triangular masses during the annealing of pyrite (Mineral District, Virginia, U.S.A.; width of field is 1.2 mm in both photomicrographs).



FIGS. 5–8. FIG. 5 (*top left*) Recrystallisation of pyrite into euhedral crystals when hosted in a matrix of pyrrhotite and chalcocyanite and when metamorphosed at amphibolite grade (Mineral District, Virginia, U.S.A.; width of field is 1.2 mm). FIG. 6 (*top right*) Concentrations of chalcocyanite developed in the low-pressure shadow zones adjacent to a 3 cm pyrite crystal Ducktown, Tennessee, U.S.A. FIG. 7 (*lower left*) Large pyrite porphyroblasts such as this one 25 cm across occur in the massive pyrrhotite–pyrite ore in the Cherokee Mine, Ducktown, Tennessee, U.S.A. The largest exceeded 30 cm, but the average size in the deposit does not exceed 1 cm. FIG. 8 (*lower right*) The presence of amphibole laths completely or partially overgrown by pyrite indicates that pyrite growth did not occur until metamorphic conditions had been raised sufficiently for amphibole growth (Cherokee Mine, Ducktown, Tennessee, U.S.A.; width of field is 1.2 mm).

sulphur ratio of 1:2. Substitution of cobalt and nickel, and other metals to a very much smaller degree, occurs readily in synthetic systems but is relatively rare in natural occurrences because of the very low abundance of cobalt (25 ppm), nickel (75 ppm) and the other metals in most geologic environments. Bravoite-type zoning, in which alternating growth bands are enriched in  $\text{CoS}_2$  and or  $\text{NiS}_2$  has been reported from numerous low-temperature ores, especially Mississippi Valley Type carbonate-hosted lead–zinc deposits (Ramdohr, 1969), but has not been observed in metamorphosed ores. In fact, most metamorphosed pyrite are remarkable pure  $\text{FeS}_2$ . Probably the greatest occurrence of metamorphosed pyrites with significant contents of other transition metals is in the Central African Copper Belt where the cobalt contents may commonly average more than 10 wt.% (Annels *et al.*, 1983). The

cobalt is now uniformly distributed in the pyrites; hence, if any bravoite-type zoning existed originally, it has subsequently been homogenised by the metamorphism.

The anomalous relationships between arsenic and gold have been investigated for many years. Recently, these investigations have carried over to the relationships of arsenic in pyrite, especially gold-bearing pyrites. It appears that most pyrites, even those coexisting with arsenopyrite, do not contain significant arsenic but Fleet *et al.* (1989) do report hydrothermal vein pyrite with as much as 8 wt.%. As in oscillatory zonal patterns. They also note the occurrence of some idiomorphic growth zones in the centres of pyrite grains in stratabound–stratiform gold deposits.

The homogenisation of macroscopic and microscopic physical textural changes noted above, obviously result from a variety of chemical

reactions in which sulphur and/or iron move by diffusion or by solution and redeposition. Even in ore bodies or rock volumes where pyrite reactions appear to be isochemical, it is likely that some fluid phase played a role in sulphur or iron exchanges. The precise nature of such fluids is, without doubt, variable from one deposit to another, but many studies have demonstrated that metamorphic fluids are generally aqueous with significant proportions of CO<sub>2</sub> (e.g. Hollister and Crawford, 1981; Roedder, 1984). This is borne out by calculations of fluids and by detailed studies of fluid inclusions in the Ducktown, Tennessee, ores (Nesbitt and Essene, 1983; Hall *et al.*, 1991) and is evidenced by the presence of abundant hydrous phases within the massive sulphide ores. The emphasis of this paper is not so much on the mechanisms but rather upon the textures of the solid phases that retain evidences of the pre-, syn-, or post-metamorphic history.

Mechanical crushing may bring about cataclasis in pyrite with essentially no chemical transport. However, recrystallisation of pyrite into annealed textures or the increase in pyrite grain size requires movement of iron and sulphur to permit nucleation or growth on pre-existing surfaces or the movement of sulphur to convert pre-existing pyrrhotite to pyrite by a sulphidation process. Supergene reactions commonly form pyrite through extraction of iron from the pyrrhotite lattice but this process has not been recognised in metamorphism.

#### Pyrite crystals and porphyroblasts

Pyrite exhibits a strong tendency to crystallise in euhedral forms. The dominant form is that of a cube, especially in metamorphosed ores, but a broad variety of other forms, including the pyritohedron, have been reported (Gait, 1987). The size of pyrite crystals varies widely within and between deposits depending upon metamorphic grade and coexisting mineralogy but is generally in the 1 mm to 1 cm range. Over the past 10 years the authors have encountered a few metamorphosed deposits which contain extraordinarily large pyrite crystals. The largest observed occur at Ducktown, Tennessee, where cubes as large as 30 cm (12 inches) on a side have been reported. The only other locality with pyrite crystals as large is the Black Angel Mine in Greenland (K. McClay, pers. comm.); unfortunately, there are no reports in the literature on the Black Angel pyrites. The remarkable Ducktown crystals occurred in areas where they had been severely fractured by blasting and were not safely removable but have been documented by photographs

(Fig. 7). Unfortunately, the mines are now flooded and inaccessible. Pieces of single crystals up to 18 cm (7 inches) were extracted and complete crystals as large as 10 cm (4 inches) have been preserved. The next largest crystals known to the authors occur at the small Grøslid deposit near Kongsberg in southern Norway. At that site the crystals achieved sizes up to 15 cm (6 inches) across. Ramdohr (1969) cites, but does not figure, crystals from Sulitjelma in Norway as large as 15 cm (6 inches). Crystals such as those noted above are exceptional both in the conditions of formation and in having survived post-ore deformations and mining activities.

The earlier cited comments noting the difficulty of interpreting the histories of ores prior to their metamorphism were based on the assumptions that the physical deformation and the low temperature post-peak re-equilibration had obliterated primary textures. To a large extent this is true in all metamorphosed rocks. However, where primary minerals have persisted through a metamorphic episode, albeit somewhat tectonised or altered, they present the potential of retaining interpretable information. Even minerals which have developed during the metamorphic cycle offer the possibility of yielding information relevant to at least a part of the history of a deposit.

All workers who have examined pyrite-containing ores are aware that pyrites from all types of settings commonly contain inclusions of other sulphides and gangue phases. Because these are so common and because polished surfaces represent only two-dimensional views of three-dimensional textures, the inclusions are often taken for granted. Sometimes, however, the nature of even randomly oriented inclusions can yield useful information. Thus, the presence of amphibole laths or inclusions (Fig. 8) in pyrite from a regionally metamorphosed terrain indicates that the pyrite formed after temperatures and pressures were high enough for the amphibole to form. The nature of inclusions also becomes important if they contain gold because their setting may readily contribute to the refractory nature of an ore when it comes to gold extraction. What has been largely unnoticed, or unnoted, is that the inclusions within pyrite commonly display distinctive patterns. The patterns, when noted, have usually been from sedimentary or vein deposits. The tacit assumption has been that pyrite in metamorphosed ores either never contained patterned inclusions or that such inclusions were obliterated in the metamorphism.

It is likely that some other earlier workers noted concentrically disposed inclusions in pyrite

from metamorphosed deposits but the earliest good illustration known to the authors is that of Carstens (1941) from Follidal in Norway. In the intervening years, little additional comment about such features seems to have been recorded in the literature. However, studies of the massive ores of the Ducktown, Tennessee, ores in the past several years (Brooker *et al.*, 1987; Craig and Vokes, in press) have shown that numerous pyrite crystals, ranging from less than one millimetre to more than one hundred millimetres, contain concentric rows of inclusions (Fig. 9*a,b*). Subsequently, the present authors have found that such textures occur in pyrite crystals in a large number of metamorphosed deposits.

The combination of the pattern of the inclusions and their mineralogy may provide insight into the timing of crystal growth. Hence concentric zones of minerals that would not have been stable until near peak metamorphic conditions were reached are indicative of pyrite growth only at or after that time. On the other hand, pyrites that contain concentric bands of inclusions which are the size of pre-metamorphism grains may be preserving textures through the metamorphic episode.

The investigation of metamorphic minerals, especially garnet, has also revealed the occurrence of helical rows of inclusions which are believed to have been incorporated by the host mineral as it rotated and grew at or near the metamorphic peak (Spry, 1963; Rosenfeld, 1970; Schoneveld, 1977). Bell and Johnson (1989) and Bell *et al.* (1992) have offered an alternative explanation based on alternating stress fields, but this remains to be confirmed or evaluated by other workers. Such garnet porphyroblasts, were viewed as little more than curiosities until Spear

and Selverstone (1983) and Spear *et al.* (1984) recognised the potential of using the inclusions to interpret a portion of the metamorphic cycle. It thus became apparent that inclusions within many types of metamorphic minerals, including pyrite, might yield interpretable information. Accordingly, the authors initiated a detailed study of the pyrite crystals from metamorphosed ore deposits along the Appalachian-Caledonian orogen. Early in the study, it became apparent that the pyrites from several deposits contained inclusions in concentric patterns. In addition, we discovered in the ores of the Cherokee Mine at Ducktown, Tennessee, several 1–2 cm and one 10 cm pyrite porphyroblasts which contain inclusions in spiral patterns. The only other locality, known to the authors, where such a texture has been described is Follidal in Norway where Carstens (1944) figured a pyrite with a 'bow-like or circle-like' arrangement of inclusions. He attributed them to rotation during growth. The smaller samples observed in this study, like the one illustrated by Carstens (*loc. cit.*) exhibited a semicircular to bow-like arrangement of inclusions. In contrast the largest porphyroblast (Fig. 10) exhibits an inclusion pattern which indicates the porphyroblast rotated through 360° relative to its matrix during its growth period; this has been described in detail by Craig *et al.* (1991).

There was an early expectation that the systematic examinations of the sphalerite inclusions within both concentrically and spirally grown pyrites might yield data which could be interpreted in terms of the metamorphic cycle. Previous sphalerite geobarometric studies on the Ducktown ores had yielded rather widely variable to scarcely believable results (summarised in Brooker *et al.*, 1987). Heeding the precautions of

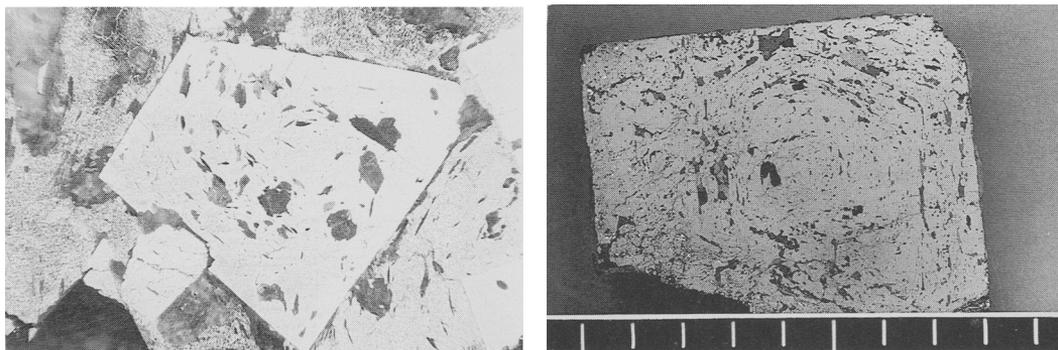


Fig. 9. (A, left) 10 mm pyrite crystal exhibiting concentric pattern of amphibole inclusions (B, right) 7.5 cm long pyrite crystal displaying concentric pattern of amphibole, quartz, sphalerite, and calcite inclusions (cm scale visible at bottom of photograph). Samples from Cherokee Mine, Ducktown, Tennessee, U.S.A.

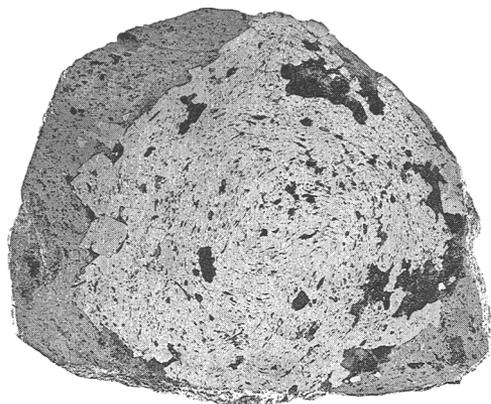


Fig. 10. 10 cm, equant, pyrite crystal which contains a double spiral inclusion pattern indicative of pyrite rotation of  $360^\circ$  relative to its enclosing host pyrrhotite during growth. This sample from the Cherokee Mine, Ducktown, Tennessee, U.S.A., is described in detail in Craig *et al.* (1991).

Hutchison and Scott (1980) regarding the problems of sphalerite re-equilibration, Brooker *et al.* (1987) found that the most reliable sphalerites for geobarometry indicated essentially constant pressure conditions during pyrite porphyroblast development. Although the time span for porphyroblast growth is unknown, the presence of amphibolite grade mineral inclusions defining the growth features indicates that growth occurred near or after peak conditions. Brooker *et al.* (1987) and Craig *et al.* (1991) observed that the pyrite porphyroblasts contained pyrite cores and satellite crystals (Fig. 9a,b) that had been overgrown in the development of the principal portion of the porphyroblasts. The cores are rounded, irregularly distributed, and exhibit no compositional difference from the rest of the pyrite but do have a distinctly higher polishing hardness. In addition, Craig *et al.* (1991) observed that the inclusions commonly contained more than one kind of amphibole, calcite, and stibnomelane, as well as quartz and other sulphides. Many of the larger pyrite crystals have been found to contain not only small rounded cores of pyrite but also subhedral to euhedral pyrite crystals totally or partially encapsulated within them (see Figs. 14B and 16 later in this manuscript). Metallurgists and mineralogists have for many years demonstrated that chemical etching can make visible the internal structures of some phases. Indeed, the etching of pyrite grains from several types of deposits, including metamorphosed massive sulphides, can reveal growth structures which are not visible, or only poorly visible, after normal polishing (Fig.

11). These are very similar to etched pyrites described by Shadlum (1971). The difficulty is in deciphering when the growth actually occurred.

#### The sulphur budget during metamorphism

The prograde phase of a metamorphic cycle of pyrite-bearing rocks or ores is accompanied by a rise in temperature and hence by a rise in the activity of sulphur (generally expressed as  $a_{S_2}$ ), a general increase in reaction rates, and an increased potential for sulphur to be lost as a fugitive phase. The degree to which rock packets or ore bodies remain as isochemical units or are open systems during metamorphism clearly varies from one place to another and with the scale of observation. The recrystallisation of pyrite to yield typical annealed textures with  $120^\circ$  dihedral angles as described by Stanton (1972) appears to be an isochemical system relative to iron and sulphur even if some fluids were expelled or passed through the rocks.

On the other hand, there are many accounts proposing open systems in which the decomposition of pyrite by loss of sulphur has resulted in the formation of pyrrhotite. Prior to the recognition that pyrrhotite can be a major primary phase in massive stratiform ores (Plimer and Finlow-Bates, 1978), the 85+ million tons of pyrrhotite-rich massive sulphide at Ducktown, Tennessee (Gair and Slack, 1980), were considered to have formed by hydrothermal replacement (Weed and Watson, 1906; Ross, 1935). Similarly, Stose and Stose (1957) considered the tens of millions of tons of massive pyrrhotite in the Great Gossan Lead, Virginia, U.S.A., to have formed after, and in part, from pyrite. Pyrite crystals pseudomorphed as pyrrhotite and attributed to sulphur loss have been described (Vokes, 1963; Nilsen, 1978) and Carpenter (1974) has described a pyrrhotite isograd in southeastern Tennessee and southwestern North Carolina which he believed represented a metamorphic boundary above which pyrite had decomposed to pyrrhotite.

Sulphur lost from pyrite would be available for reaction with other phases and has been considered as responsible for iron depletion in iron-bearing silicates around metamorphosed ore bodies. Such reactions may occur locally but their significance on any major scale is not supported by field observations. The size of bleached zones, if present at all, around massive pyrite/pyrrhotite ore bodies such as Ducktown, Tennessee, or the Great Gossan Lead, Virginia, are far too small to correspond with the quantities of pyrrhotite in the mineralised zones. Hence, it appears that many massive pyritic sulphide bodies have behaved

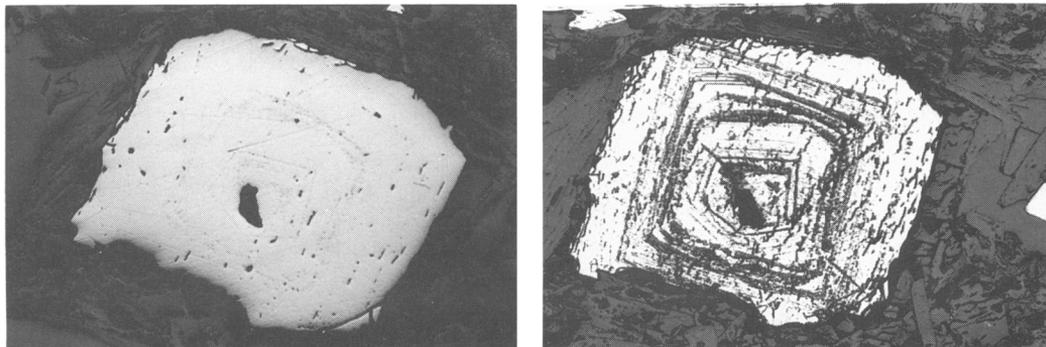


Fig. 11. The same pyrite grain shown (A, left) before and (B, right) after etching with conc.  $\text{HNO}_3$ . Etching has brought out a detailed zonal growth pattern that was barely discernable in the grain after normal polishing. The grain is from the ores of the Mineral District, Virginia, U.S.A., that have been metamorphosed to amphibolite grade (width of field is 1.2 mm).

more-or-less isochemically during metamorphism. This is further supported by the presence of pyrite grains in rocks which have been subjected to high grades of metamorphism. Thus, for example, Plimer (1977), in a study of granulite facies metamorphism at the Thackaringa, N.S.W. deposit, found no desulphurisation reactions. It is also clear from the abundance of hydrous phases, especially amphiboles and micas, of carbonates, and of fluid inclusions, that fluids are present during metamorphism and that they may well facilitate sulphide dissolution and reprecipitation as suggested by Gilligan and Marshall (1987), Marshall and Gilligan (1987), and Plimer (1987). Hall (1986) has proposed that pyrite forms during retrogressive metamorphism by pyrrhotite solution in  $\text{CO}_2$ -bearing fluids, oxidation, and subsequent reprecipitation of the pyrite with methane an ferrous carbonate generation. Some volatile phases may well diffuse in and out of the ores (Hall *et al.*, 1991) but the loss of sulphur does not seem to be significant.

Many massive sulphides contain significant quantities of coexisting pyrite and pyrrhotite which are interpreted as primary phases. In this situation, metamorphism of the bodies drives them along the pyrite–pyrrhotite buffer curve as shown in Fig. 12. Barton (1970) aptly included a portion of the pyrite–pyrrhotite buffer in his ‘mainline of ore formation’ because of the ubiquity of the coexisting phases and hence the large number of deposits constrained by the buffer. Only if one or other of the minerals was decomposed, could any ore body or sulphide-bearing rock move off the pyrite–pyrrhotite buffer during the metamorphic cycle. At low temperatures, reaction kinetics may not be sufficient to maintain equilibrium, but at tempera-

tures above  $300^\circ\text{C}$  it is almost certain that pyrite and pyrrhotite would remain in equilibrium.

Pyrite remains stoichiometric  $\text{FeS}_2$  throughout the range of thermal conditions experienced in normal regional metamorphism but the composition of the pyrrhotite in equilibrium with pyrite changes quite markedly along the pyrrhotite solvus shown in Fig. 13A. Using the pyrrhotite solvus composition data of Toulmin and Barton (1964) for 700, 600, 500 and  $400^\circ\text{C}$  and that of Kissin and Scott (1982) for  $300^\circ\text{C}$ , the calculations used herein are based upon the following pyrrhotite compositions:  $700^\circ\text{C}$ —45.35 at.% Fe (59.106 wt.% Fe);  $600^\circ\text{C}$ —46.00 at.% Fe (59.737 wt.% Fe);  $500^\circ\text{C}$ —46.65 at.% Fe (60.365 wt.% Fe);  $400^\circ\text{C}$ —47.00 at.% Fe (60.70 wt.% Fe);  $300^\circ\text{C}$ —47.58 at.% Fe (61.254 wt.% Fe). Thus, if a pyrite–pyrrhotite assemblage maintains equilibrium as it is heated into the  $300$ – $600^\circ\text{C}$  range during prograde metamorphism, the activity of  $\text{S}_2$  rises (i.e. the assemblage moves along the pyrite–pyrrhotite curve on Fig. 13A), the pyrrhotite composition becomes more sulphur-rich, and some pyrite is decomposed. This is shown in a highly schematic form in Fig. 13A. Reactions of this type, if frozen at this point, would yield corroded pyrites or pyrites appearing to be replaced by pyrrhotite as shown in Fig. 13B.

In contrast, the constant re-equilibration of a pyrite–pyrrhotite assemblage during retrograde cooling would result in a drop in the activity of  $\text{S}_2$ , a decrease in the sulphur content of the pyrrhotite, and growth of pyrite. This is illustrated schematically in Fig. 14A and would likely be evidenced in natural ores by the development of euhedral crystals as shown in Figure 14B.

The obvious question arises as to how much pyrite could form as a result of retrograde cooling

as schematically shown in Fig. 14. The answer is dependent upon two factors—the initial pyrite–pyrrhotite ratio and the temperature range over which re-equilibration was maintained during cooling. One can calculate the percentage of pyrite that could form, but it is important to recognise that different parts of ore bodies probably re-equilibrated down to different temperatures and that we do not know the size of the realm over which equilibration occurs. Furthermore, the size of that realm probably decreases rapidly as temperature drops.

Although the conditions of peak metamorphism have been examined in many deposits, there is considerably less information on the

cooling cycle and the lowest temperatures to which retrograde reactions continue to occur. However, the presence of hexagonal pyrrhotite with pyrite and the absence of monoclinic pyrrhotite in many ores suggests that re-equilibration ceased on cooling before the temperatures had dropped to 252 °C, which appears to be the upper stability limit of monoclinic pyrrhotite (Kissin and Scott, 1982). At Ducktown, Tennessee, independent studies of the pyrrhotite compositions adjacent to pyrite (Brooker *et al.*, 1987) and of the sulphur isotopic fractionation (Mauger, 1972) both indicate re-equilibration down to approximately 270 °C.

Therefore, recognising that many pyrite–pyr-

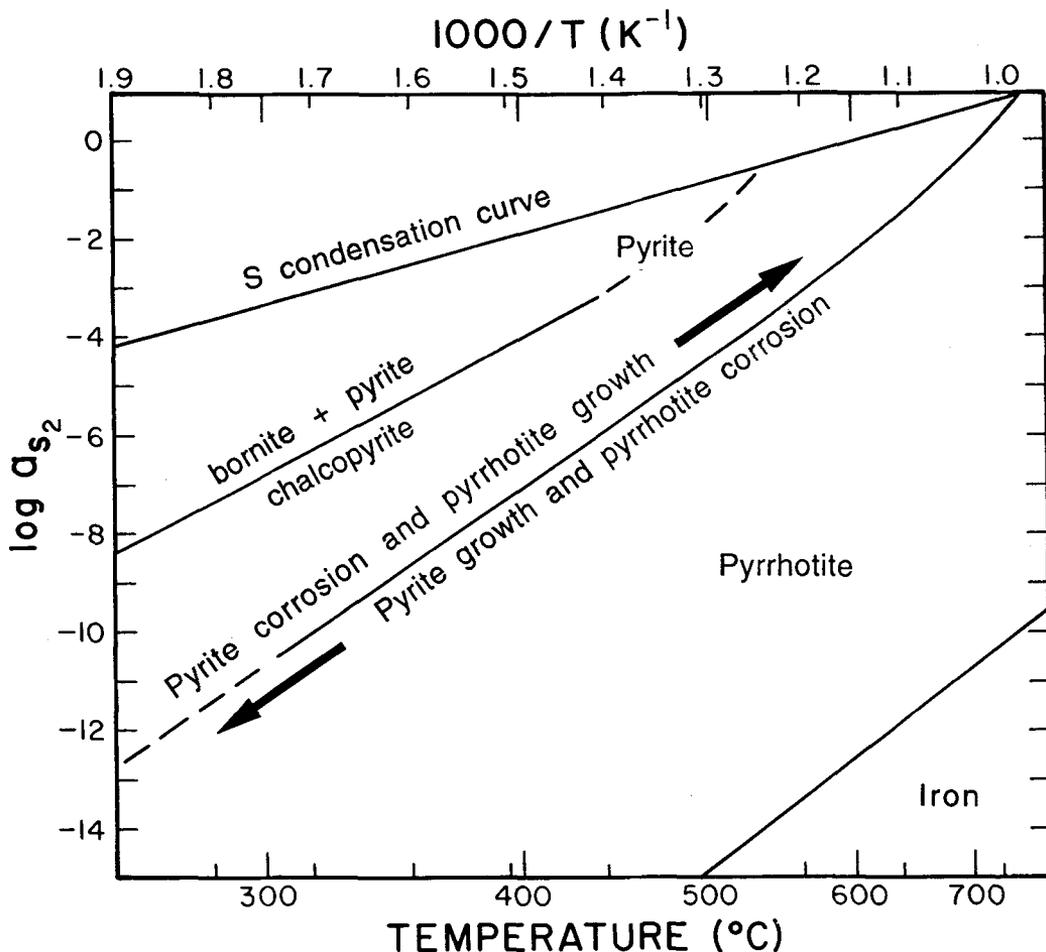


FIG. 12. A  $\log a_{S_2}-1/T$  plot showing the pyrite–pyrrhotite sulphidation curve which buffers the sulphur activity during the metamorphism of pyrite–pyrrhotite ores. As temperature rises during prograde metamorphism pyrite suffers corrosion and pyrrhotite grows; the reverse occurs during the retrograde phase of metamorphism (adapted from Barton and Skinner, 1979).

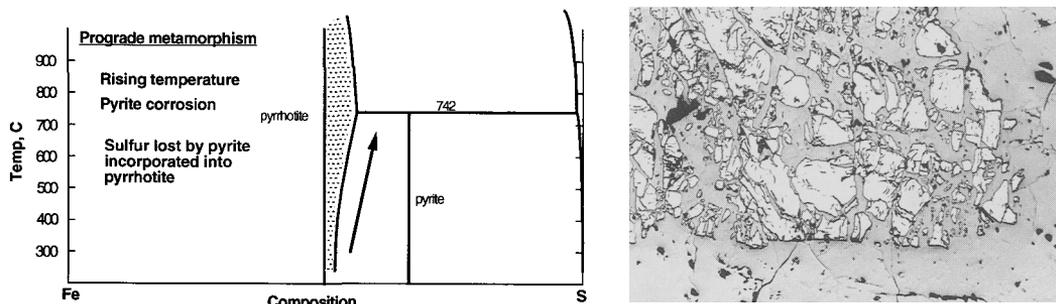


Fig. 13. (A, left) Highly schematic diagram of the Fe-S system noting that the rise in temperature during prograde metamorphism results in pyrrhotite growth (by becoming more sulphur rich) and pyrite corrosion. (B, right) Fractured pyrite exhibiting corrosion and decomposition to form pyrrhotite (Cherokee Mine, Ducktown, Tennessee, U.S.A.; width of field is 1.2 mm).

pyrite bearing ores have been metamorphosed to greenschist and amphibolite facies in the realms of 400–600 °C and assuming that natural re-equilibration often does continue to 300 °C or below, we have calculated pyrite growth between 600 and 300 °C. These limits are arbitrary and could easily be extended using the 700 °C pyrrhotite composition data and extrapolating the solvus below 300 °C.

Two sets of curves have been prepared (one shown in Fig. 15), to illustrate the degree to which sulphur liberated from pyrrhotite might form pyrite during retrograde metamorphism. On each diagram are presented three curves labelled 600° → 300 °C, 500° → 300 °C, 400° → 300 °C. These indicate respectively the degree to which pyrite could form on cooling from a peak of 600 °C to a quenching at 300 °C, from a peak of 500 °C to 300 °C, and from a peak of 400 °C to 300 °C. The total amount of sulphur released, and hence available to cause pyrite growth, depends upon the relative amounts of pyrite and pyrrho-

tite in the ore. If pyrrhotite is dominant, there is much more sulphur released than if there is only a small amount of pyrrhotite. Other sulphide phases are not considered because they generally constitute only very small quantities of the ore mass and because the others of any importance (e.g. sphalerite, galena, chalcopyrite) exhibit little or no change in sulphur content as a function of temperature.

Hence, consider an ore, which after re-equilibrating from 600 °C down to 300 °C during retrograde metamorphism, is found to contain 10% pyrite and 90% pyrrhotite (top curve of Fig. 15). The sulphur released during the cooling would have been sufficient to have formed 52% of the total pyrite that the observer finds in the ore. In contrast, if an ore that cooled from 600 to 300 °C is found to contain 20% pyrite and 80% pyrrhotite, the top curve of Fig. 14 shows that the pyrrhotite would have released sufficient sulphur to account for 24% of the observed pyrite. However, if ore that equilibrated from 600 °C to

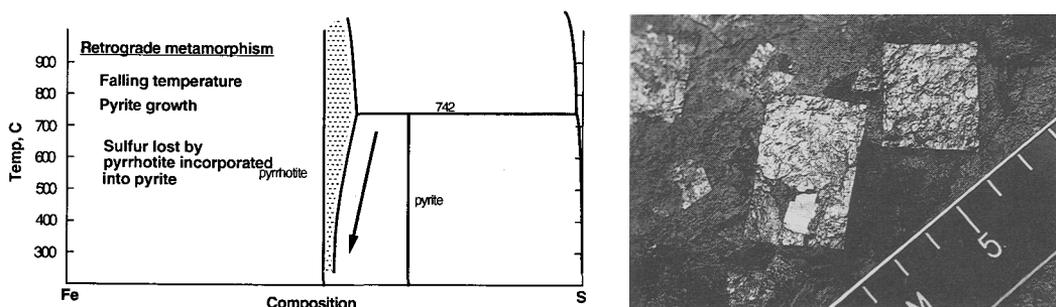


Fig. 14. (A, left) Highly schematic diagram of the Fe-S system, noting that the decrease in temperature accompanying retrograde metamorphism results in pyrite growth at the expense of pyrrhotite as the pyrrhotite readjusts to less sulphur rich compositions. (B, right) 1 to 4 cm euhedral pyrite crystals in the Ducktown, Tennessee, U.S.A., ores that reached amphibolite grade metamorphism. Note the sharpness of the crystal terminations and the 1 cm crystals that has been overgrown in the formation of the 4 cm crystal.

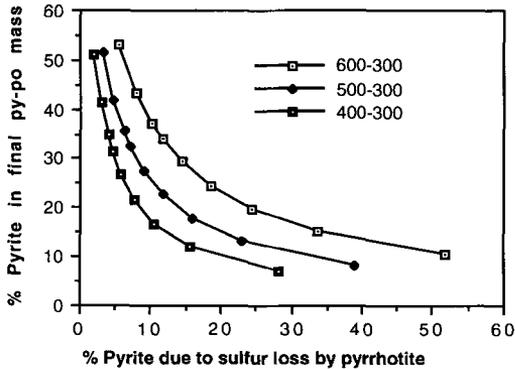


Fig. 15. The percentage of pyrite observed in a pyrite–pyrrhotite ore plotted against the percentage of the pyrite which would have formed due to the sulphur released by the pyrrhotite during cooling from 600° to 300°C (top curve), 500° to 300°C (middle curve), and 400° to 300°C (bottom curve) in the retrograde phase of a metamorphic cycle. Thus, if one can estimate the relative pyrite and pyrrhotite contents of the ore mass (vertical axis), one can estimate what percentage of the pyrite formed during cooling down to 300°C, at which temperature many ores appear to cease re-equilibrating. See text for additional discussion.

300°C was found to contain 50% pyrite and 50% pyrrhotite, the sulphur released during cooling would have only been sufficient to have formed 6% of the total pyrite. Thus, it is evident that the percentage of the total observed pyrite that could form by sulphur release from pyrrhotite decreases markedly as the pyrite to pyrrhotite ratio of ores rises.

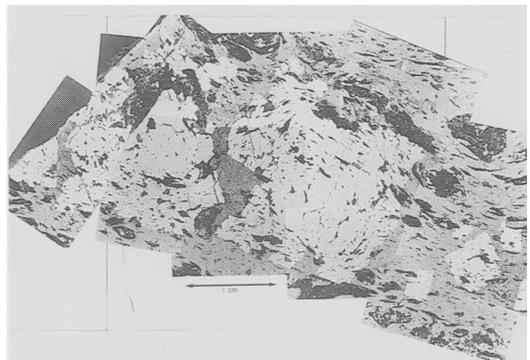
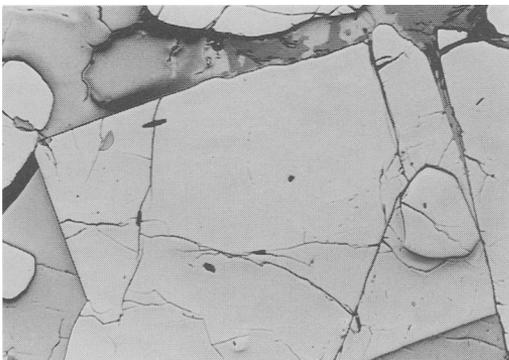
It is logical to consider if there is sufficient evidence to support pyrite growth during the

cooling, or retrograde, part of a metamorphic episode. There are several pieces of evidence, including: (1) phase equilibria data, (2) lack of evidence of sulphur loss from the ore bodies, (3) pyrite crystal form, (4) pyrite overgrowths, (5) lack of metamorphism of pyrite cubes, (6) mineral inclusions in pyrite, (7) sulphur isotopic data.

(1) It is clear from the well established phase equilibria in the Fe–S system that pyrrhotite on cooling from amphibolite or greenschist facies temperatures must release significant quantities of sulphur. There are no other sulphide minerals in the massive ore deposits which could absorb this sulphur. Pyrite forms readily from the sulphur released by pyrrhotite in laboratory cooling experiments; it must also do this in natural deposits. Mohr and Newton (1983) report the change in pyrrhotite composition on retrograde cooling and the concurrent exsolution of pyrite.

(2) Most massive pyrrhotite–pyrite containing massive sulphides have very small, if any, surrounding alteration zones which could be attributable to sulphur loss and subsequent wall rock reaction. The bodies appear to have behaved nearly isochemically relative to iron and sulphur contents. Isolated pyrite grains survive granulite grade metamorphism without breaking down to form pyrrhotite.

(3) Many pyrite crystals, small and large in metamorphosed sulphide bodies possess euhedral outlines (Fig. 14B) and hence evidence growth rather than corrosion textures. Prograde metamorphism must have corroded pyrites if pyrite and pyrrhotite remained at equilibrium. Euhedral growth could occur best during peak or post-peak periods.



Figs. 16 and 17. Fig. 16 (left). Typical example of a somewhat rounded core of pyrite (right centre) that has been incorporated in a larger subhedral grain (Ducktown, Tennessee, U.S.A.; width of field is 1.2 mm). Fig. 17 (right). The persistence of the general fabric of the highly contorted ores at Ducktown, Tennessee, U.S.A., through both the plastic pyrrhotite and the refractory pyrite indicates that pyrite growth occurred at the expense of the pyrrhotite after the last major deformation event (width of field is 6 cm).

(4) Many pyrite crystals in metamorphosed deposits contain clear zonal growth patterns (Fig. 9) and/or cores (Fig. 16) of apparently earlier formed pyrite. At present, it is not clear how to unequivocally identify pyrite over-growth that would have formed from sulphur released by cooling pyrrhotite or to separate it from pyrite overgrowth resulting from metamorphic resorption of small grains of pyrite. Besides, it is likely that both processes were occurring simultaneously. The round or euhedral shapes of the small pyrite cores found within the euhedral crystals suggests that they formed, or persist, from a different set of conditions. Barton and Skinner (1979) allude to this situation in reference to pyrrhotite-bearing, pyrite-poor assemblages by noting conditions under which pyrite is no longer able to nucleate, but where it may continue to grow on previously existing nuclei. Also, McClay and Ellis (1983) state that clear, inclusion-free, euhedral pyrite overgrowths are commonly found in areas of low mean stress.

(5) There are reports of post-metamorphic pyrite crystals in some deposits. Thus Ramdohr (1969) states that the occurrence of non-cataclastic pyrite cubes up to 15 cm edge length in the intensively deformed deposits of Sulitjelma, Norway, indicate clearly that the formation of that pyrite is younger in age than the deformation process. Lianxing and McClay (in press), in a study of pyrites from the Sullivan deposit state that porphyroblastic pyrite euhedra are commonly rich in pyrrhotite inclusions and are obviously later than the pyrrhotite matrix. Certainly, some of the large euhedral pyrite crystals of the Ducktown, Tennessee, ores bear no evidence whatever of mechanical distortion despite their occurrence in pyrrhotite masses that exhibit *durchbewegung*. When pyrites have been subjected to intense ore mobilisation, the evidence is clear, as the exhibit abrasion or rounding (e.g. the rolled pyrites of Sulitjelma, Norway; Vokes, 1971, 1973).

(6) Many pyrite crystals, of all sizes, contain inclusion of a broad variety of other minerals. The inclusion of other sulphides has not yet proved informative in determining the age of incorporation. In contrast, the incorporation of high-grade metamorphic minerals indicates that the incorporation could not have occurred until after a sufficient grade of metamorphism to form those minerals had been reached. Furthermore, minerals such as amphiboles are commonly observed as only partly overgrown and sometimes it is clear that the pyrite growth postdates the last deformation because the pyrite overprints the oriented inclusions (Fig. 17). Examination of the inclu-

sions within the large pyrite porphyroblast exhibiting spiral growth (see Fig. 10) revealed the presence of abundant stilpnomelane (Craig *et al.*, 1991). This is generally recognised as a retrograde mineral that could not have existed at peak metamorphic conditions nor have survived as a trapped phase. It thus appears to have been incorporated as pyrite growth occurred during the retrograde metamorphic phase.

(7) The conclusions of most sulphur isotopic studies of pyrite-pyrrhotite-bearing ore bodies such as those at Ducktown, Tennessee, have been derived on the assumption that the pyrites are homogeneous (e.g. Mauger, 1972; LeHuray, 1984). However, some recent detailed studies of pyrites from massive sulphides and hydrothermal deposits have demonstrated that isotopic zoning may occur (Eldridge *et al.*, 1988; McKibben and Eldridge, 1990). Such detailed data from metamorphosed pyrites are scant, but three transects outward from the centre of the large (100 mm) rotated pyrite crystal (Craig *et al.*, 1991) shown in Fig. 10 reveal a persistent but not smooth increase in the weight of the sulphur in the pyrite from centre to rim (from about 0 to about 5.6  $\delta^{34}\text{S}$ ). Though not conclusive in terms of the time of porphyroblastic growth, this isotopic pattern is consistent with a decreasing temperature during growth. Preservation of isotopic values for pyrite and pyrrhotite if they grew or re-equilibrated at peak metamorphic conditions should reveal little difference between the minerals and no trend in the pyrite.

It is important to note, however, that even though one can calculate quite straightforwardly the precise amount of pyrite produced by a cooling pyrrhotite mass, the quantitative application is likely to be impractical. This results from the uncertainties of volumes of equilibration in a cooling ore mass and the ambiguity of determining the temperature at which re-equilibration ceased during cooling. These two factors are clearly related but are no doubt influenced by the presence of other mineral phases and the types and quantities of fluids in and moving through the mass. Hence, we wish to emphasise, in a more qualitative than quantitative manner, that significant quantities of pyrite do form during the retrograde phases of metamorphism and may record some decipherable information about the history of the deposits.

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### References

- Annels, A. E., Vaughan, D. J., and Craig, J. R. (1983) Conditions of ore mineral formation in certain Zambian Copperbelt deposits with special reference to the role of cobalt. *Mineral. Deposita*, **18**, 71–88.
- Atkinson, B. K. (1975) Experimental deformation of polycrystalline pyrite: Effects of temperature, confining pressure, strain rate, and porosity. *Econ. Geol.*, **70**, 473–87.
- Barton, P. B. (1970) Sulfide petrology. *Mineral. Soc. Am. Spec. Paper*, **3**, 187–98.
- and Skinner, B. J. (1979) Sulfide mineral stabilities. In *Geochemistry of Hydrothermal Ore Deposits*, 2nd Edition (H. L. Barnes, ed.), John Wiley and Sons, New York, p. 279–403.
- Bell, T. H. and Johnson, S. E. (1989) Porphyroblast inclusion trials: The key to orogenesis. *J. Metamorph. Geol.*, **7**, 279–310.
- Forde, A., and Hayward, N. (1992) Do smoothly curving, spiral-shaped inclusion trails signify porphyroblast rotation? *Geology*, **20**, 59–62.
- Brooker, D. D., Craig, J. R., and Rimstidt, J. D. (1987) Ore metamorphism and pyrite porphyroblast development at the Cherokee Mine, Ducktown, Tennessee. *Econ. Geol.*, **82**, 72–86.
- Carpenter, R. H. (1974) Pyrrhotite isograd in southeastern Tennessee and southwestern North Carolina. *Geol. Soc. Am. Bull.*, **85**, 451–56.
- Carstens, C. W. (1941) Zur frage der metamorphose der schwefelkieserze. *Det Kong. Norske Vidensk., Forhandl.*, **16**, 9–12.
- (1944), Om dannelsen av de norske svovelkieserforekomster. *Ibid.* **17**, 1–28.
- Cox, S. F. (1987) Flow mechanisms in sulphide minerals. *Ore Geol. Rev.*, **2**, 133–71.
- Etheridge, M. A., and Hobbs, B. E. (1981) The experimental ductile deformation of polycrystalline and single crystal pyrite. *Econ. Geol.*, **76**, 2105–17.
- Craig, J. R. (1983) Metamorphic features in Appalachian massive sulphides. *Mineral Mag.*, **47**, 515–25.
- and Vokes, F. M. (1986) The metamorphism of pyrite. *Int'l Mineral. Assoc. Program with Abstracts*, 135–6.
- (in press) Pyrite in the paragenesis of metamorphosed ores. *Proceedings 8th Quadrennial IAGOD meeting, Ottawa 1990*. Stuttgart, E. Schweizerbart'sche Verlagsbuchhandlung.
- and Simpson, C. (1991) Rotational fabrics in pyrite from Ducktown, Tennessee. *Econ. Geol.*, **86**, 1737–46.
- Edmond, J. M. and Von Damm, K. (1983) Hot springs on the ocean floor. *Scientific Am.*, **248**, 78–84, 86, 89–93.
- Eldridge, C. S., Compston, W., Williams, I. S., Both, R. A., Walshe, J. L., and Ohmoto, H. (1988) Sulfur isotope variability in sediment-hosted massive sulfide deposits as determined using the ion microprobe shrimp: I. An example from the Rammelsberg orebody. *Econ. Geol.*, **83**, 443–9.
- England, B. M. (1979) Cleavage in pyrite from Tasmania. *Mineral. Mag.*, **43**, 183–4.
- Fleet, M. E., MacLean, P. J., and Barbier, J. (1989) Oscillatory-zoned As-bearing pyrites from stratabound and stratiform gold deposits: An indicator of ore fluid evolution. *Econ. Geol. Monograph* **6**, 356–62.
- Gair, J. E. and Slack, J. F. (1980) Stratabound massive sulfide deposits of the U.S. Appalachians. In *Review of Caledonian–Appalachian Stratabound Sulphides* (F. M. Vokes and Zachrisson, eds.) Geol. Surv. Ireland Spec. Paper **5**, 67–81.
- Gait, R. I. (1987) The crystal forms of pyrite. *Mineral Record*, **9**, 219–29.
- Gilligan, L. B. and Marshall, B. (1987) Textural evidence for remobilisation in metamorphic environments. *Ore Geol. Rev.*, **2**, 205–29.
- Graf, J. L. and Skinner, B. J. (1970) Strength and deformation of pyrite and pyrrhotite. *Econ. Geol.*, **65**, 206–15.
- Grønvold, F. and Westrum, E. F. (1976) Heat capacities of iron disulfides. Thermodynamics of marcasite from 5 to 700 K, pyrite from 350 to 700 K, and the transformation of marcasite to pyrite. *J. Chem. Thermodynamics*, **8**, 1039–48.
- Hall, A. J. (1986) Pyrite–pyrrhotite redox reactions in nature. *Mineral. Mag.*, **50**, 223–9.
- Hall, D. L., Bodnar, R. J., and Craig, J. R. (1991) Evidence for postentrapment diffusion of hydrogen into peak metamorphic fluid inclusions from the massive sulfide deposits at Ducktown, Tennessee. *Am. Mineral.*, **76**, 1344–55.
- Haymon, R. M. (1983) Growth history of hydrothermal black smoker chimneys. *Nature*, **301**, 645–8.
- Hollister, L. S. and Crawford, M. L. (1981) Mineral. Assoc. Canada *Short Course in Fluid Inclusions: Application to Petrology*, 304 p.
- Hutchison, M. N. and Scott, S. D. (1980) Sphalerite geobarometry applied to metamorphosed sulfide ores of the Swedish Caledonides and the U.S. Appalachians. *Norges Geol. Unders.*, **360**, 59–71.
- Kelly, W. C. and Clark, B. R. (1975) Sulfide deformation studies: III. Experimental deformation of chalcopyrite at 2,000 bars and 500 degrees Celsius. *Econ. Geol.*, **70**, 431–53.
- Kissin, S. A. and Scott, S. D. (1982) Phase relations involving pyrrhotite below 350 °C. *Ibid.*, **77**, 1739–54.
- Kullerud, G. (1967) Sulfide studies. In *Researches in Geochemistry* (P. H. Adleson, ed.) **2**, Wiley, New York, pp. 286–321.
- and Yoder, H. S. (1959) Pyrite stability in the Fe-S system. *Econ. Geol.*, **54**, 533–72.
- Lawrence, L. J. (1972) The thermal metamorphism of pyrite. *Ibid.*, **67**, 487–96.
- LeHuray, A. P. (1984) Lead and sulfur isotopes and a model for the origin of the Ducktown deposit, Tennessee. *Ibid.*, **79**, 1561–73.
- Lianxing, G. and McClay, K. R. (in press) Pyrite deformation in stratiform lead-zinc deposits of the Canadian cordillera. *Mineral. Deposita*.

- Loberg, B. E. H., Háber, M., and Westberg, S. B. (1985) Microhardness, reflectance and unit cell length of pyrites from Swedish base metal ores. *Geol. Fören. i Stockholm Förhandl.*, **107**, 45–52.
- Mann, S., Sparks, N. H. C., Frankel, R. B., Bazylinski, D. A., and Jannasch, H. W. (1990) Biomineralisation of ferrimagnetic greigite ( $\text{Fe}_3\text{S}_4$ ) and iron pyrite ( $\text{FeS}_2$ ) in a magnetotactic bacterium. *Nature*, **343**, 258–61.
- Marshall, R. L. and Gilligan, L. B. (1987) An introduction to remobilisation: Information from ore-body geometry and experimental considerations. *Ore Geol. Rev.*, **2**, 87–131.
- Mauger, B. (1972) A sulfur isotope study of the Ducktown, Tennessee District, U.S.A., *Econ. Geol.*, **67**, 497–510.
- McClay, K. R. and Ellis, P. G. (1983) Deformation and recrystallisation of pyrite. *Mineral. Mag.*, **47**, 527–38.
- (1984) Deformation of pyrite. *Econ. Geol.*, **79**, 400–403.
- McKibben, M. A. and Eldridge, C. S. (1990) Radical sulfur isotope zonation of pyrite accompanying boiling and epithermal gold deposition: A shrimp study of the Valles caldera, New Mexico. *Ibid.*, **85**, 1917–25.
- Mohr, D. W. and Newton, R. C. (1983) Kyanite–staurolite metamorphism in sulfidic schists of the Anakeesta formation, Great Smoky Mountains, North Carolina. *Am. J. Sci.*, **283**, 97–134.
- Mookherjee, A. (1971) Deformation of pyrite. *Econ. Geol.*, **66**, 200.
- (1976) Ores and metamorphism. Temporal and genetic relationships. In *Handbook of Strata-bound and Stratiform Ore Deposits*, (K. H. Wolf, ed.), **4**, Elsevier, Amsterdam, pp. 203–60.
- Morgan, J. (1991) In the beginning. *Scientific Am.*, **264**(2), 116–25.
- Murovchick, J. B. (1992) Marcasite inversion and the petrographic determination of pyrite ancestry. *Econ. Geol.*, **87**, 1141–52.
- Nesbitt, R. E. and Essene, E. J. (1983) Metamorphic volatile equilibria in a portion of the Southern Blue Ridge province. *Am. J. Sci.*, **283**, 135–65.
- Nilsen, O. (1978) Caledonian sulphide deposits and minor iron-formations from the southern Trondheim region, central Norwegian Caledonides. *Norges Geol. Unders.*, **340**, 35–85.
- Plimer, I. R. (1977) The origin of the albite-rich rocks enclosing the cobaltian pyrite deposit of Thackaringa, NSW, Australia. *Mineral. Deposita*, **12**, 175–87.
- (1987) Remobilisation in high-grade metamorphic environments. In *Mechanical and chemical (re) mobilisation of metalliferous mineralisation* (B. Marshall and L. B. Gilligan, eds.), *Ore Geol. Rev.*, **2**, 231–45.
- and Finlow-Bates, T. (1978) Relationship between primary iron sulphide species, sulphur source, depth of formation and age of submarine exhalative deposits. *Mineral. Deposita*, **13**, 399–410.
- Ramanarayanan, T. A. and Smith, S. N. (1990) Corrosion of iron in gaseous environments and in gas-saturated aqueous environments. *Corrosion*, **46**, 66–74.
- Ramdohr, P. (1969) *The Ore Minerals and Their Overgrowths*, 3rd ed., Pergamon Press, Oxford, 1174 pp.
- Rising, B. A. (1973) Phase relations among pyrite, marcasite, and pyrrothite below 300°C. *Ph.D. thesis (unpubl.)*, The Pennsylvania State University, 192 pp.
- Roedder, E. (1984) *Fluid Inclusions*, Mineral. Soc. Am., *Reviews in Mineralogy*, **12**, 644 pp.
- Rosenfeld, J. L. (1970) Rotated garnets in metamorphic rocks. *Geol. Soc. Am. Spec. Paper*, **129**, 105 pp.
- Ross, C. S. (1935) Origin of the Copper deposits of the Ducktown type in the southern Appalachian region. *U.S. Geol. Surv. of Prof. Paper*, **179**, 165 pp.
- Schoneveld, C. (1977) A study of some typical inclusion patterns in strongly paracrystalline-rotated garnets. *Tectonophys.*, **39**, 453–71.
- Scott, S. D. (1976) Application of the spalerite geobarometer to regionally metamorphosed terrains. *Am. Mineral.*, **61**, 661–70.
- (1983) Chemical behaviour of sphalerite and arsenopyrite in hydrothermal and metamorphic environments. *Mineral. Mag.*, **47**, 427–35.
- Selkman, S. O. (1983) Stress and displacement distributions around pyrite grains. *Econ. Geol.*, **5**(1), 47–52.
- Shadlum, T. N. (1971) Metamorphic textures and structures of sulphide ores. *Soc. Mining Geol. Japan, Spec. Issue*, **3**, 241–50.
- Siemes, H., Hennig-Michaeli, C., and Martens, L. (1991) The importance of deformation experiments on minerals for the interpretation of metamorphic ore textures. *Ore Geol. Rev.*, **6**, 475–83.
- Spear, F. S. and Selverstone, J. (1983) Quantitative *P-T* paths from zoned minerals: Theory and tectonic applications. *Contrib. Mineral. Petrol.*, **83**, 348–57.
- Hickmott, D., Crowley, P., and Hodges, K. V. (1984) *P-T* paths from garnet zoning: A new technique for deciphering tectonic processes in crystalline terranes. *Geology*, **12**, 87–90.
- Spry, A. (1963) The origin and significance of snowball structure in garnet. *J. Petrol.*, **4**, 211–22.
- Stanon, R. L. (1972) *Ore Petrology*, McGraw Hill, New York, 713 p.
- and Gorman, H. (1968) A phenomenological study of grain boundary migration in some common sulphides. *Econ. Geol.*, **63**, 907–23.
- Stose, A. J. and Stose, G. W. (1957) Geology and mineral resources of the Gossan Lead District and adjacent areas in Virginia. *Virginia Div. Min. Res. Bull.*, **72**, 233 p.
- Templeman-Kluit, D. J. (1970) The relationship between sulphide grain size and metamorphic grade of host rocks in some stratabound pyritic ores. *Canadian J. Earth. Sci.*, **7**, 1339–45.
- Toulmin, P. and Barton, P. B. (1964) A thermodynamic study of pyrite and pyrrothite. *Geochim. Cosmochim. Acta*, **28**, 641–71.
- Vaughan, D. J. and Craig, J. R. (1978) *Mineral Chemistry of Metal Sulfides*, Cambridge Univ. Press, Cambridge, England, 493 pp.
- Vokes, F. M. (1963) Geological studies on the Caledonian pyritic lead-zinc orebody at Bleikvassli, Nordland, Norway. *Norges Geol. Unders.*, **222**, 126 pp.

- (1968) Regional metamorphism of the Paleozoic geosynclinal sulphide ore deposits of Norway. *Trans. Inst. Mining Metall., Sect. B, Appl. Earth Sci.*, B53–9.
- (1969) A review of the metamorphism of sulphide deposits. *Earth Sci. Rev.*, **5**, 99–143.
- (1971) Some aspects of the regional metamorphic mobilisation of pre-existing sulphide deposits. *Mineral. Deposita*, **6**, 122–9.
- (1973) 'Ball texture' in sulphide ores. *Geol. För. Stockholm Förh.*, **95**, 403–6.
- Weed, W. H. and Watson, T. L. (1906) The Virginia copper deposits. *Econ. Geol.*, **1**, 309–30.
- Zierenberg, R. A. and Shanks, W. C. (1983) Mineralogy and geochemistry of epigenetic features in metalliferous sediments, Atlantic II Deep, Red Sea. *Ibid.*, **78**, 57–72.

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