Metamorphic features in Appalachian massive sulphides*

JAMES R. CRAIG

Department of Geological Sciences, Virginia Polytechnic Institute and State University,
Blacksburg, Virginia 24061, USA

ABSTRACT. Massive stratiform and stratabound sulphide bodies in the central Appalachians exhibit a wide variety of metamorphic features which are typical of similar deposits world-wide. The ores occur as lens- to plate-like bodies which are concordant with the enclosing meta-sediments and volcanics and are interpreted as products of Late Precambrian to Early Palaeozoic submarine volcanism. Sulphide mineralization ranges from pyritic to pyrrhotinic bodies with variable, but Zn- and Cu-dominant, base-metal contents. The deposits have been subjected to metamorphism ranging from greenschist to amphibolite grade. The metamorphism has been pervasive and has resulted in thorough recrystallization of most ores and intense deformation of pyrrhotinic ores, but does not appear to have significantly altered original sulphide assemblages. Recrystallization has homogenized most sulphide minerals including pyrite and sphalerite, so that any original compositional zoning is no longer seen. The presence of chalcopyrite has apparently promoted an increase in grain size and has facilitated post-metamorphic retrograde re-equilibration. Consequently, sphalerite geobarometry is not reliable in Cu-bearing assemblages. Pyrrhotines, mostly hexagonal, have re-equilibrated to low temperatures but commonly display pressure twins and kink-banding, apparently due to the late stages of deformation. Characteristic mineralogical changes in the host rocks include changes in the abundance of minerals, changes in the Fe:Mg ratios, and the presence of gahnite.

THE Piedmont and Valley and Ridge provinces of the Central and Southern Appalachians of the Eastern United States are hosts to numerous massive sulphide deposits (fig. 1) which have been subjected to one or more stages of regional metamorphism. Although the effects of the metamorphism, which ranges from lower greenschist to upper amphibolite in grade, are pervasive, the ores have responded in a variety of ways depending upon the the mineralogy, the temperature, and the stress. Surveys of the setting and sizes of these deposits have been prepared by Gair and Slack (1979, 1980).

* Invited contribution.

The comprehensive papers on the effects of metamorphism of ores by McDonald (1967), Vokes (1969), and Mookherjee (1976) have served as general bases for categorizing the effects discussed here. Kalliokoski (1965) emphasized the megascopic effects of metamorphism on some Canadian Appalachian massive sulphide deposits; this paper concentrates upon the smaller-scale predominately microscopic effects. Unfortunately, the pervasiveness of the metamorphism in terms of sulphide mineral re-equilibration often precluded the determination of the original ore mineral paragenesis. The degree to which individual minerals have preserved their original compositions and textures or have responded to the metamorphism ranges widely depending upon the type of mineral, the temperature, the amount of stress, and the associated minerals. The summary of the tendency for ore minerals to re-equilibrate at various temperatures, as presented by Barton and Skinner (1979), demonstrates that the response threshold for ore minerals corresponds, in general, with bond strength and hardness. Thus minerals such as pyrite, magnetite, and arsenopyrite have the greatest likelihood of preserving original compositional and textural data through a mild metamorphism. If these minerals are re-equilibrated during the metamorphism, they are also most likely to preserve some record of the metamorphic peak rather than totally re-equilibrating during the subsequent retrograde period. In contrast, the softer sulphides—e.g. pyrrhotine, chalcopyrite, tetrahedrite—and native metals—e.g. bismuth, electrum—rapidly re-equilibrate during the thermal rise to the metamorphic maximum and during the retrograde cooling and hence retain little evidence of their origins. Sphalerite is unique in that it is relatively soft (VHN ~ 220) but is yet sufficiently refractory to retain original growth features through mild metamorphism and to retain metamorphically equilibrated compositions through retrograde cooling periods.
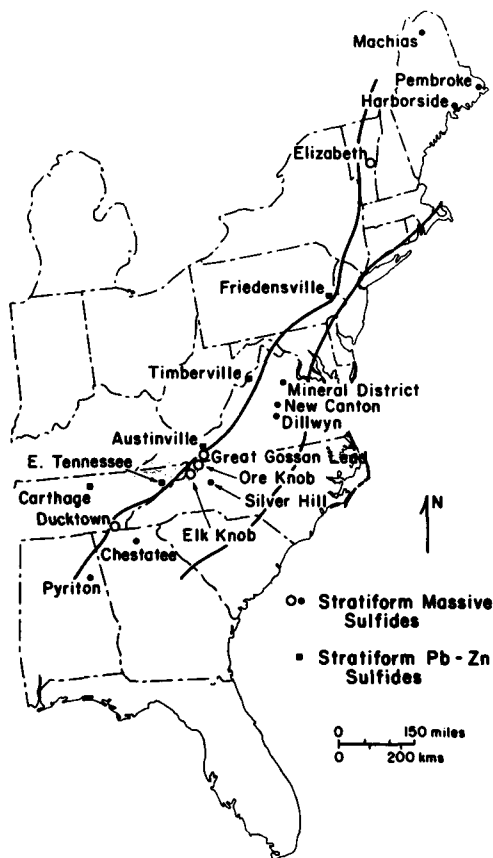
FIG. 1. Map of the eastern United States showing the locations of metamorphosed massive sulphide deposits (open circles are pyrrhotine-rich; solid circles are pyrite-rich) of the Piedmont and Blue Ridge provinces. The squares represent carbonate-hosted (Mississippi Valley-type) Zn–Pb deposits of the adjacent Valley and Ridge Province.

The Appalachian massive sulphides all reveal effects of regional metamorphism; contact effects are absent or have been overprinted by the regional effects. The metamorphic features can be generally grouped into (i) thermal or recrystallization effects, and (ii) deformational or stress effects. Although often described separately, both are present in many ores.
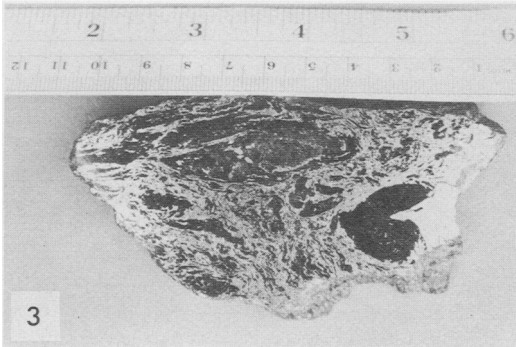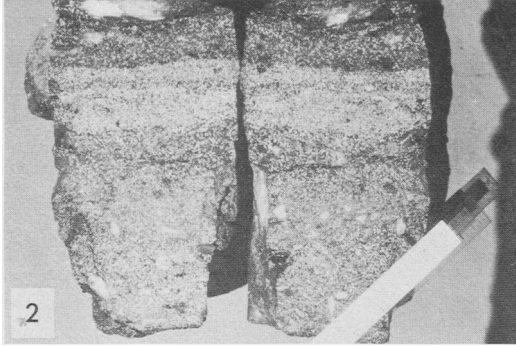
Origins of the deposits

Early interpretations of Appalachian massive sulphides generally suggested that they represented massive and thorough replacements of now missing beds or shear zones subparallel to bedding. In the past 20 years more detailed work on these deposits, new mapping of the Appalachian Blue Ridge and

Piedmont, new petrological data, and the recognition of numerous similar stratabound deposits as volcanogenic exhalites have dramatically altered the interpretation of the massive sulphides. It is now recognized that most of the Appalachian massive sulphides occur within metamorphosed volcaniclastic or mixed volcaniclastic–sedimentary beds and it is believed that the ores are attributable to submarine volcanic exhalations related to island arc formation. Such an interpretation has now been offered for the Central Virginia belt (Pavlides et al., 1982), the Great Gossan Lead (Henry et al., 1979; Craig, 1980), the Carolina Slate belt (Bell, 1982), Ducktown, Tennessee (Mauger, 1972), and Pyrition, Alabama (Stow and Tull, 1982). The age of the initial deposition varies from late Precambrian (Ducktown, The Great Gossan Lead) to Cambro-Ordovician (Central Virginia). A major metamorphic event in the Appalachians occurred in the Ordovician, with later more local deformations occurring from the early Devonian to the late Palaeozoic; hence all the massive sulphides are metamorphosed rather than metamorphic. With the possible exception of some small localized base- and precious-metal-bearing veins adjacent to the stratiform bodies, there appear to be few effects of metamorphism on the grade, size, or general stratigraphic setting of the massive sulphides. The principal megascopic effects are folding of the original, probably flat planar bodies into complex structures, an increase in grain size, and minor injection of the plastic sulphides into cross-cutting apophyses.

Megascopic ore textures

The ores of the Appalachian massive sulphides show wide variation in effects of metamorphic overprinting depending upon the stresses and the ore mineralogy. Thus the pyrite- and sphalerite-rich ores of the Mineral District in Central Virginia contain a nearly undisturbed primary sulphide banding with numerous inclusions of undeformed volcaniclastic debris (fig. 2). In contrast, the pyrrhotine-rich ores of the Great Gossan Lead, Virginia and of Ducktown, Tennessee commonly display durchbewegung and ball textures (fig. 3) which reveal a thorough mechanical destruction of the original texture. These textures, first named by Vokes (1969, 1973), result from the plastic deformation of pyrrhotine at high temperature and pressure. Kelly and Clark (1975) demonstrated that the strength of pyrrhotine drops markedly at temperatues above 100 °C; hence under greenschist or amphibolite grades of metamorphism, the pyrrhotine readily yields by flow to virtually any stress. During the flow, included layers and even
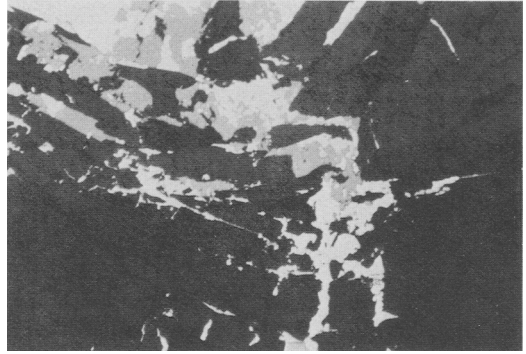
FIG. 4. Injection of sphalerite and chalcopyrite into fractured amphibole crystals as a result of metamorphic deformation at the Great Gossan Lead, Virginia. The field of view is 0.7 mm. (From Henry et al., 1979, p. 651.)

FIGS. 2 and 3. FIG. 2. Primary sulphide banding of pyrite- and sphalerite-rich layers with included volcanic fragments from the Cofer deposit, Mineral District, Virginia. FIG. 3. Durchbewegung texture resulting from plastic flow of pyrrhotine-rich ore in the Great Gossan Lead, Virginia. The sample is approximately 8 cm across.

portions of the hanging and footwall rocks, which are more brittle, are broken, deformed, and rotated in the pyrrhotine matrix.

Pyrrhotine, accompanied by chalcopyrite, sphalerite, and galena is commonly injected into the fractures and cleavages of the accompanying silicates, oxides, and carbonates (fig. 4). Minor remobilization of chalcopyrite is evidenced by its common presence in cross-cutting fractures and its concentration along grain boundaries of, and fractures in, large pyrite crystals. The similarity of lead isotopes (LeHuray, 1982) in the galena of the massive ores and the cross-cutting veins at Ducktown, Tennesse suggests, but does not prove, that the vein galena was remobilized from the pre-existing stratiform bodies.

The degree of homogenization and recrystalliza- tion varies markedly from one deposit to another and within short distances in one deposit. Thus, in the pyritic portions of the ores in the Mineral District of Virginia, the grain size of pyrite averages approximately one millimetre but over a distance of

ten centimetres may vary from 0.1 mm to 1 cm. The contrasts are even more striking at Ducktown, Tennessee where ores containing pyrite cubes (fig. 5) which can grow to more than 20 cm on a side are intermixed with ores containing pyrite crystals barely 0.1 mm across.

Microscopic ore textures

Microscopic investigations of the metamorphosed ores, in combination with a considerable amount of electron microprobe analysis, has revealed much that is not discernible on the megascopic scale. The microscopic study has been carried out using conventional polished sections prepared in the manner described by Craig and Vaughan (1981) and using doubly-polished thin sections. The latter are especially important in the study of transparent ore minerals such as sphalerite because they combine the best attributes of both conventional polished and thin sections; their preparation and use has recently been described by Heald-Wetlaufer et al. (1982). The following discussion begins with the most abundant of the ore minerals, the iron sulphides, and includes the most commonly observed and important base-metal and precious- metal phases, but exludes some of the minor minerals.

Pyrite. Pyrite is the dominant ore mineral in some deposits (e.g. the Arminius deposit of the Mineral District where it constitutes more than 90% of the massive ore) but is virtually absent in others (e.g. most of the Great Gossan Lead). The behaviour of the pyrite during metamorphism is determined by its abundance and its strong force of crystallization. Under dynamic metamorphism massive pyritic bodies display considerable amounts
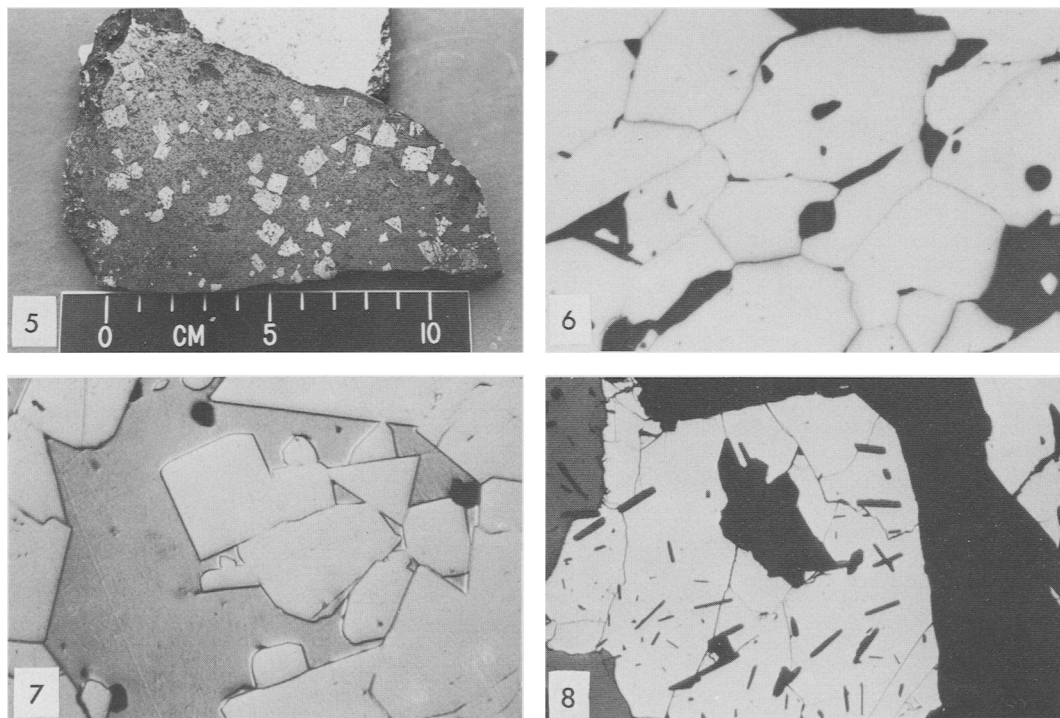
FIGS. 5–8. FIG. 5. Metablastic pyrite crystals in a matrix of pyrrhotine, a typical recrystallization texture in Appalachian massive sulphide ores. This sample is from the Calloway Mine at Ducktown, Tennessee but occurs in many massive pyrite-pyrrhotine ores. FIG. 6. Typical annealed texture resulting from recrystallization of a monomineralic (pyrite) massive ore. The dihedral angles tend toward 120° junctions. Sample from the Arminius Deposit, Mineral District, Virginia; the field of view is 0.6 mm. FIG. 7. Recrystallization of pyrite into euhedral forms where interstitial chalcopyrite offers little resistance to pyrite growth. Sample from the Cofer deposit, Mineral District, Virginia. Field of view is 1.3 mm. FIG. 8 Inclusions of mica in pyrite indicating that primary or metamorphic micas were present when recrystallization of pyrite occurred. Sample from the Cofer deposit, Mineral District, Virginia. Field of view is 0.45 mm.

of cataclasis because of the hardness and brittleness of the pyrite. Under thermal metamorphism massive pyritic bodies recrystallize with the development of 120° triple junctions characteristic of equilibrated annealed textures (fig. 6).

If significant amounts of pyrrhotine, chalcopyrite, sphalerite, or even gangue minerals such as micas or amphiboles occur interstitially, the pyrite readily assumes euhedral, usually cubic, forms (fig. 7). The occurrence of the euhedral pyrite crystals in the presence of hard minerals such as amphiboles and garnets attests to the strength of the force of crystallization of the pyrite and quite likely reflects an earlier development of the pyrite crystals than of the common large silicate crystals during prograde metamorphism. This timing is also suggested by the presence of numerous small inclusions of micas in pyrite crystals (fig. 8) but the general absence of amphiboles within the crystals. The recrystallization effects are also apparent where the growth of pyrite

grains during metamorphism has trapped base metal sulphide grains. Fig. 9 illustrates a typical instance in which interstitial galena has yielded to the growth force of the pyrite and now is isolated as lens-like grains between pyrite crystals.

Growth structures, probably reflecting metamorphic development, are abundant in pyrite (fig. 10) but may require etching to be made readily visible (fig. 11). Many pyrite crystals, with or without discernible growth zoning, possess a polycrystalline internal texture (brought out by etching) in spite of their external appearance as a single crystal. Because an initially polycrystalline aggregate is unlikely to have grown into a form which possessed the external morphology of a single crystal, the polycrystalline nature must be the result of recrystallization which occurred at the metamorphic maximum or during the retrograde period, after initial growth of a single crystal during prograde metamorphism.
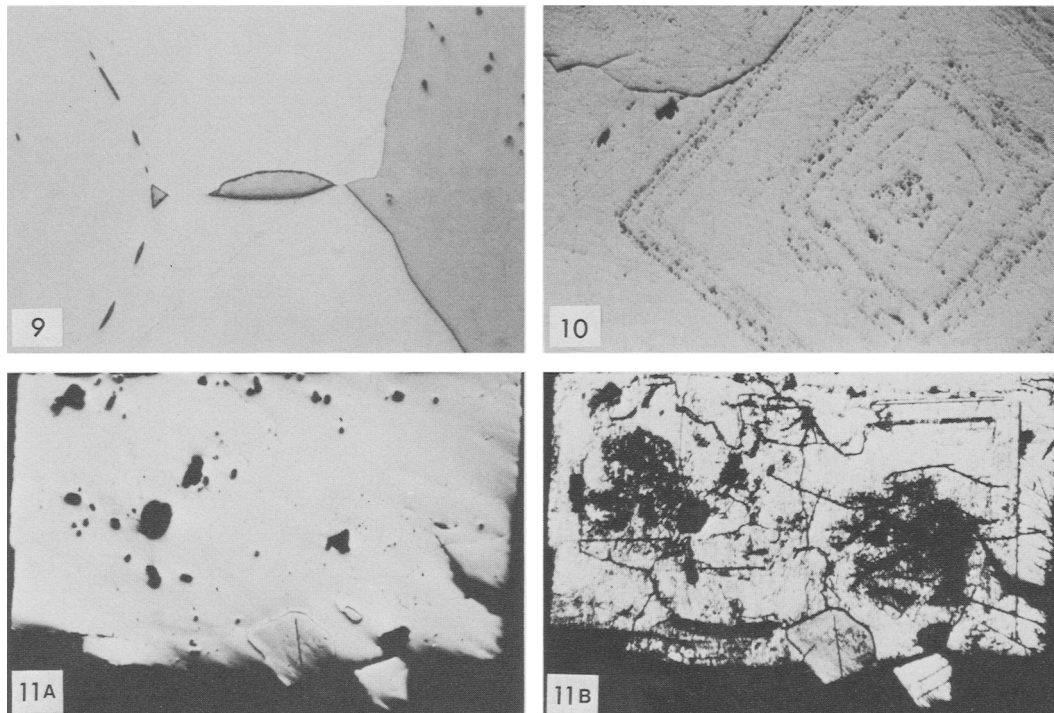
FIGS. 9–11. FIG. 9. Lens-like inclusions of galena defining the grain boundaries in recrystallized pyrite in the Cofer deposit of the Mineral District, Virginia. Field of view is 0.52 mm. (From Craig and Vaughan, 1981, p 279.) FIG. 10. Growth zoning in pyrite accentuated by the presence of fine clays and micas which concentrated along the crystal faces at various stages of growth. Cofer Deposit, Mineral District, Virginia. Field of view is 1.3 mm. FIG. 11. Recrystallized pyrite grains which appear homogeneous (A) commonly contain well-defined growth zoning (B) after etching with acids. Arminius Mine, Mineral District, Virginia. Field of view is 2.25 mm.

Pyrrhotine. Pyrrhotine is present in most Appalachian massive sulphides and ranges from a trace as in the base-metal-rich pyritic ores of the Mineral District to the overwhelmingly dominant sulphide phase as in the Great Gossan Lead. Despite its rapid rate of re-equilibration, pyrrhotine retains remarkably abundant evidence of the regional metamorphism to which it has been subjected. The constancy of pyrrhotine composition within very large ore masses (> 80 million tons) at Ducktown (Moh and Kullerud, 1964) and the Great Gossan Lead no doubt attests to its equilibration to a nearly constant activity of sulphur throughout each deposit. In contrast to the constancy of composition, the textures reflect significant differences in degree of equilibration over distances of less than 10 centimetres. Most massive pyrrhotinic ore have annealed textures with 120° dihedral angles, but deformation twin lamellae (fig. 12) and kink-banding (fig. 13) are common in those ores which display megascopic durchbewegung textures. Annealed and deformed textures are often found in the same polished section. A series of pyrrhotine-rich ore samples which ranged from one and a half to eighty centimeters from blast holes in an actively mined face at Ducktown, Tennessee, was examined to determine if blasting could have induced any of the features which are commonly interpreted to be metamorphic. Aside from intense fracturing, no metamorphic-like features attributable to blasting were evident. The pyrrhotine is apparently elastic enough to transmit the shock waves without distortion of the lattice. The tendency for pyrrhotine to yield plastically and to re-equilibrate is further seen in the work of Larson (1973) who found in both optical and X-ray studies that the crystallographic axes of the pyrrhotine were aligned in response to the stresses during recrystallization.

Many earlier workers have interpreted the abundant pyrrhotine in the Appalachian massive sulphides to be the result of desulphidation of pyrite during metamorphism. Carpenter (1974) has even defined a pyrrhotine-isograd, subparallel to
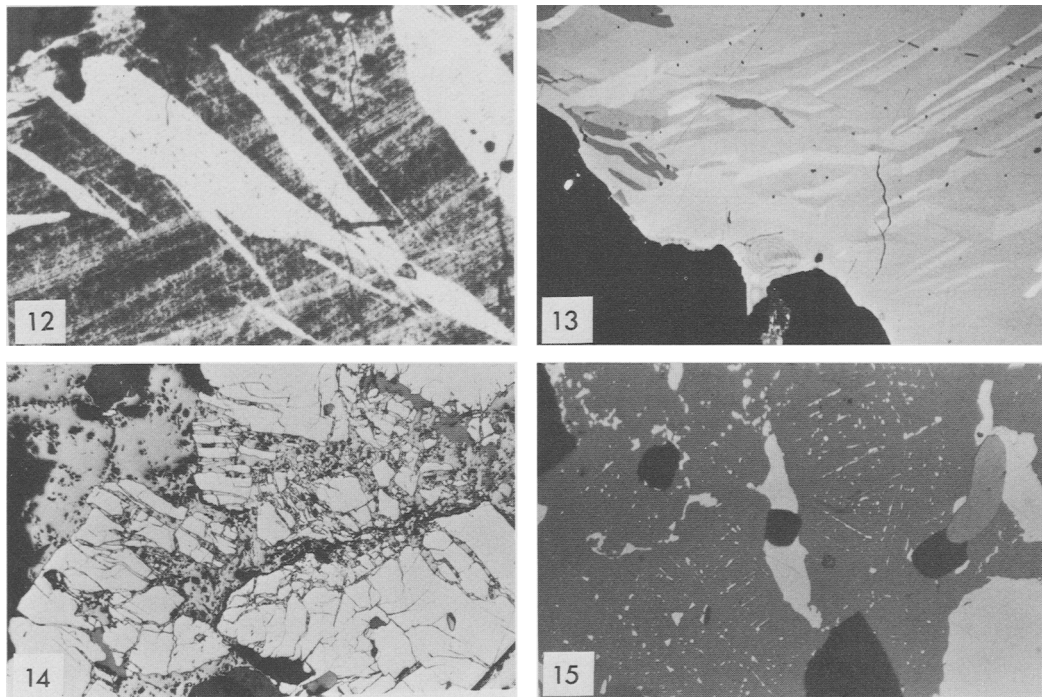
FIGS. 12-15. FIG. 12. Deformation twin lamellae in pyrrhotine from the Great Gossan Lead, Virginia. Differential oxidation on the surface of the polished section has enhanced the appearance of the lamellae. Field of view is 0.6 mm. FIG. 13. Kink-banding in deformed pyrrhotine from the Great Gossan Lead, Virginia. Field of view is 0.7 mm. (From Henry *et al.*, 1979, p. 648.) FIG. 14. Fractured pyrite with pyrrhotine injected between fragments. The sharpness and shape of the fragments indicates that little or no replacement or breakdown of the pyrite has occurred; Great Gossan Lead, Virginia. Field of view is 1.2 mm. FIG. 15. Chalcopyrite disease-like occurrence of grains and rods of chalcopyrite oriented within sphalerite from the Great Gossan Lead, Virginia. This texture, once interpreted as exsolution texture, is now believed to result from replacement or epitaxy. (From Craig and Vaughan, 1981, p. 128.)

and slightly above the biotite isograd, in the Ducktown, Tennessee area, at which pyrite has been converted to pyrrhotine in response to the metamorphism. There is little doubt that pyrite has been desulphidized locally; however, the interpretation of pyrrhotine as a primary phase in other massive sulphides (Scott *et al.*, 1977; Plimer and Finlow-Bates, 1978), the observation of pyrrhotine as a minor phase in modern sea-floor deposits and the main precipitate from 'black smokers' (Scott, pers. comm. 1982), and the very narrow alteration halos around some large sulphide bodies (Staten, 1976) all suggest that most of the pyrrhotine has not formed at the expense of pyrite. Careful microscopic examination of fractured pyrite grains which have internal cracks filled with pyrrhotine (fig. 14) usually reveals that the pyrrhotine has been injected into the cracks rather than having formed through desulphidation of the pyrite.

The most comprehensive studies on phase equilibria in the Fe-S system (Kissin and Scott, 1982) indicates that pyrrhotines re-equilibrated with pyrite during metamorphism (at least the retrograde stages below 250 °C) should be the monoclinic variety. However, monoclinic pyrrhotine is remarkably rare in the tens of millions of tons of ores in the entire US Appalachian belt. Very small amounts have been found in the Mineral District, Virginia (Cox, 1979; Craig, unpubl.) but none has been found in the massive pyrite-pyrrhotine ores at Ducktown, Tennessee or in the pyrrhotine and pyrrhotine–pyrite ores of the Great Gossan Lead.

Sphalerite. Sphalerite, the most abundant of the base metal sulphides in many Appalachian massive sulphide deposits, generally ranges from 1 to 15 % of the sulphide ore but may locally reach abundances of 70 %. Although sphalerite is known as one of the more refractory sulphide minerals (Barton and Skinner, 1979) and commonly contains complex growth banding in non-metamorphosed massive sulphide ores such as the Japanese Kuroko

deposits (Barton, 1978), the sphalerite in the Appalachian massive sulphides has been recrystallized and homogenized during metamorphism. Electron microprobe traverses across sphalerite grains in contact with pyrite and pyrrhotine generally reveal homogeneous Fe contents (Cox, 1979). Many of the sphalerites from these deposits contain randomly disseminated or aligned blebs of chalcopyrite, similar to chalcopyrite disease (fig. 15). These chalcopyrite grains, once thought to be the result of exsolution, are now interpreted as replacement or epitaxial features; the solubility of Cu in sphalerite is not sufficient (Wiggins and Craig, 1980; Hutchison and Scott, 1981) for exsolution to be responsible for their development. During metamorphism the chalcopyrite has commonly diffused from the interiors of the individual sphalerite grains to grain boundaries or to the periphery of the sphalerite aggregate where it remains as rims as shown in fig. 16. Diffusion of zinc in chalcopyrite, probably during retrograde metamorphism, also occurs to a limited extent and results in the local formation of dendrites which may coalesce to form star-like aggregates (fig. 17) up to 0.1 mm across.

The utility of sphalerite as a geobarometer was developed and calibrated by Scott and Barnes (1971) and Scott (1973). Although the original prerequisites for application of the sphalerite geobarometer were only that sphalerite be in contact with pyrite and pyrrhotine, subsequent work (Hutchison and Scott, 1980, 1981) has revealed that the presence of chalcopyrite often results in lower temperature re-equilibration of the sphalerite and hence renders it unusable for geobarometric interpretation. Hutchison and Scott (1980) further point out that only 'sphalerites which are totally encapsulated within metablastic pyrites represent preserved high P-T equilibrium assemblages. These sphalerites have been isolated from subsequent P-T conditions by the inert encapsulating pyrite, whereas sphalerites which occur in other "touching" assemblages in the ores often infer metamorphic pressures which are geologically unrealistic and interpreted to have retrograded to low temperatures.' The behaviour of sphalerites in the metamorphosed massive sulphides of the Appalachians is consistent with the above comments and warnings. Compositional ranges vary widely and often yield anomalously high-pressure values, especially where chalcopyrite is present (figs. 15 and 16). The most reasonable pressure values obtained from sphalerites, consistent with other geologic values, are 5.5 for the Great Gossan Lead (Henry et al., 1979), and 5.0 to 6.1 kbar for Ducktown (Hutchison and Scott, 1980; Nesbitt and Essene, 1982).

Galena. Galena, the least abundant of the major base-metal sulphides in the Appalachian massive sulphide deposits, occurs as locally disseminated grains and in cross-cutting veinlets. The isotopic similarity of the lead in the massive ores and that in the veins (LeHuray, 1982) suggests that the vein galena is most probably remobilized material from the massive stratiform bodies. All of the galena has no doubt been recrystallized but curved cleavage traces resulting from late-stage deformation are common. The galena may locally contain trace quantities of Ag in solid solution (e.g. Ducktown, Tenn.; Magee, 1968), especially if Bi or Sb is present, but most of the Ag in the deposits is contained in tetrahedrite which, if present, is always closely associated with the galena (fig. 18). Gasparrini and Lowell (1983) have recently demonstrated that some Ag-bearing galenas, long believed to hold the
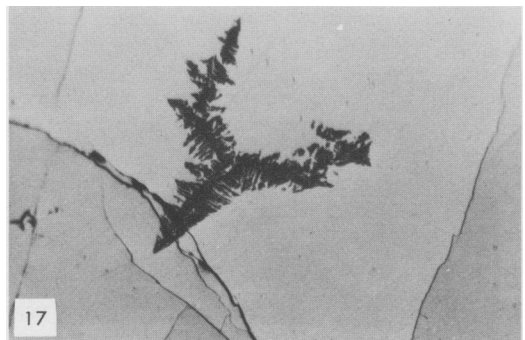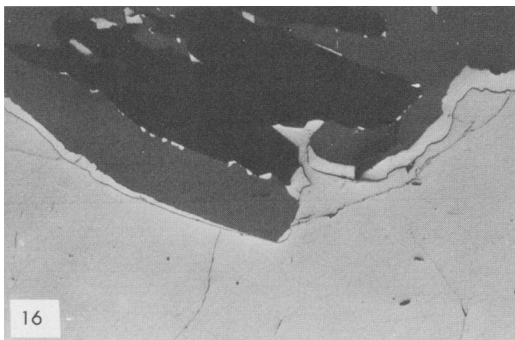
FIGS. 16 and 17. FIG. 16. Chalcopyrite rims developed on sphalerite grains as a result of recrystallization of sphalerite and a coalescing of the originally disseminated chalcopyrite grains. Sample from the Great Gossan Lead, Virginia; field of view is 0.7 mm. (From Henry et al., 1979, p. 649.) FIG. 17. Sphalerite star formed as a result of diffusion of zinc in chalcopyrite in the ores of the Cofer deposit, Mineral District, Virginia. Field of view is 0.33 mm. (From Craig and Vaughan, 1981, p. 139.)
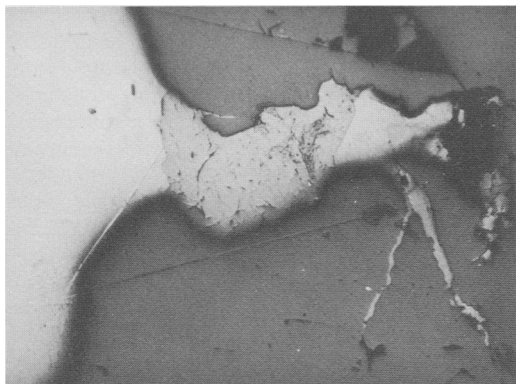
FIG. 18. Typical occurrence of tetrahedrite adjacent to galena (light gray at left) sphalerite (dark) and bournonite (light gray at right) in the Cofer deposit, Mineral District, Virginia. Field of view is 0.45 mm. (From Miller and Craig, 1983, p. 229.)

Ag in solid solution, actually contain discrete micron-sized inclusions of tetrahedrite or other silver minerals. The actual state of the silver in the galenas from Appalachian massive sulphides is not known.

Chalcopyrite. Chalcopyrite is ubiquitous in massive sulphide deposits where it occurs as disseminated anhedral grains interstitial to the dominant iron sulphides and silcates. Many of the ores (e.g. Ducktown, Great Gossan Lead) were, in fact, first mined for supergene copper minerals which formed from copper liberated during weathering of chalcopyrite in the primary ore. In the primary ores the migration of chalcopyrite to low pressure areas during metamorphism is evidenced by its frequent occurrence in fractures and cracks in pyrite grains and in the silicates included within, and peripheral to, the massive ores. Chalcopyrite also commonly occurs as randomly or aligned disseminated grains and rods dispersed within sphalerite (fig. 16). Recrystallization of the sphalerite has commonly resulted in migration and coalescence of the disseminated chalcopyrite, which may have had its origin as 'chalcopyrite disease', into discontinuous rims which now surround many sphalerite grains.

Tetrahedrite–tennantite. The tetrahedrite series minerals occur as minor to trace components of many massive sulphide deposits but their importance commonly exceeds their volume percentage because they may contain significant quantities of Ag. Miller (1978) has estimated that 90 % of the silver in the Cofer deposit of the Mineral District of Virginia is contained with tetrahedrite. This estimate is probably equally applicable to many other deposits. Tetrahedrite is generally

intimately associated with galena and occurs as rounded to anhedral grains interstitial to pyrite or gangue minerals (fig. 18). Yui (1971) found that the tetrahedrite in Kuroko ores may possess growth zones with significantly differing compositions. Tetrahedrites in the Appalachian massive sulphides, on the other hand, are homogeneous within each grain, metamorphic recrystallization having removed any initial inhomogeneities. Although the individual grains are homogeneous, there are commonly very marked differences between grains which are only tens of centimetres apart; thus the volume of metamorphic equilibration for tetrahedrite-series minerals is relatively small.

The tetrahedrite series minerals of the Cofer deposit in the Mineral District, the only deposit for which detailed data are avaiable, possess a compositional range which extends across the entire tetrahedrite $(Cu_{12}Sb_4S_{13})$–tennantite $(Cu_{12}As_4S_{13})$ solid solution (Miller and Craig, 1983). These minerals reveal reciprocal relationships betwen Cu and Ag, and Fe and Zn, as well as between As and Sb. They also show that the substitution of Ag for Cu is a permissive relationship dependent upon the Sb content (fig. 19). Thus, if the
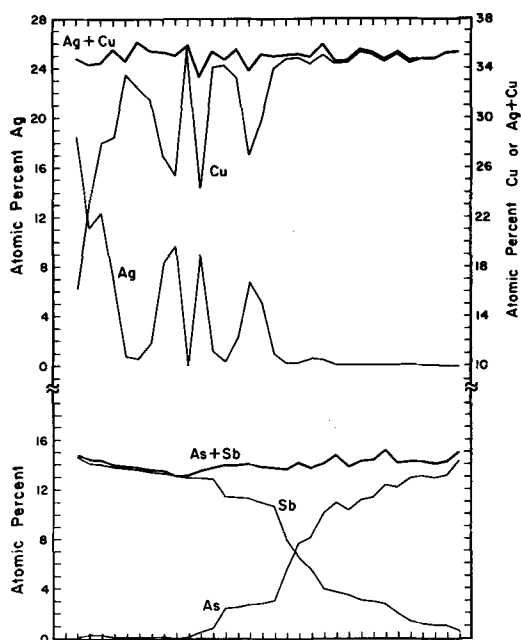

FIG. 19. Relationships between Cu, Ag, As, and Sb in tetrahedrites from the metamorphosed massive sulphide deposit at the Cofer deposit, Mineral District, Virginia. All values along any vertical line are from the same sample. Note that Ag contents may be, but are not necessarily, high only when Sb contents are high. (From Miller and Craig, 1983, p. 231.)

Sb content is less than about 10 atomic %, the Ag content never exceeds about 1 atomic % but, if the Sb content reaches 15 atomic %, the Ag value may rise to nearly 19 atomic % (= 29.5 weight %). The degree, if any, to which metamorphism mobilized Ag so that it could be scavanged by the tetrahedrite is not known, but the tetrahedrites in unmetamorphosed volcanogenic deposits typically contain less than 5% Ag.

Metamorphism appears to be responsible for the decomposition of some As-rich members of the tetrahedrite-tennantite series into complex graphic intergrowths of arsenopyrite, chalcopyrite, sphalerite and, rarely, berthierite (fig. 20). Similar intergrowths have been reported from other metamorphosed massive sulphide deposits by Juve (1974) and Shadlun (1981). The bulk compositions of such intergrowths are equivalent to the tetrahedrite-tennantite series except for a deficiency of sulphur and thus appear to have formed through a desulphidation reaction.

Arsenopyrite. Arsenopyrite, a common trace constituent in metamorphosed massive sulphide deposits, occurs as small (< 0.1 mm–1.0 mm) disseminated euhedral crystals. Kretschmar and Scott (1976) determined that the composition of arsenopyrite in equilibrium with pyrite and pyrrhotine is temperature dependent and hence could be used as a geothermometer. The presence of euhedral crystals (fig. 21) which are larger than those in unmetamorphosed volcanogenic deposits and which contain inclusions of other sulphides suggests that the crystal growth occurred in response to the metamorphism. Henry *et al.* (1979) found that the temperatures represented by the compositions of arsenopyrites in the Great Gossan Lead were in good agreement (15–50 °C) with temperatues indicated by Mg/Fe partitioning in garnet–biotite pairs.
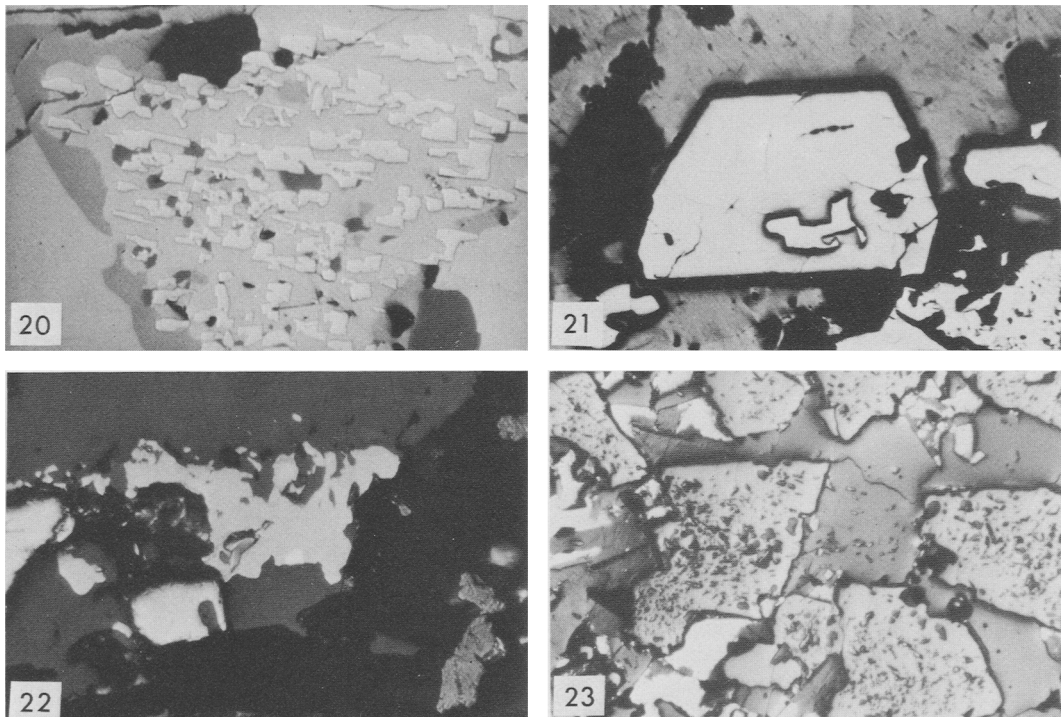
FIGS. 20–3. FIG. 20. Graphic intergrowth of arsenopyrite (white) with chalcopyrite (medium gray) and sphalerite (dark gray) which results from the decomposition of As-rich members of the tetrahedrite-tennantite series in many metamorphosed massive sulphide deposits. Sample from Cofer deposit, Mineral District, Virginia. Field of view is 0.45 mm. FIG. 21. Recrystallized arsenopyrite with inclusion of galena in a matrix of chalcopyrite; from Arminius Mine, Mineral District, Virginia. Field of view 2.25 mm. FIG. 22. Small grain of electrum (brightest phase) with chalcopyrite, sphalerite, and pyrite in the ore of Cofer deposit, Mineral District, Virginia. This is typical of gold occurrences in metamorphosed massive sulphide deposits. Field of view is 0.52 mm. FIG. 23. Poikiloblastic subhedral crystals of gahnite with small inclusions of quartz in the Julia deposit, Mineral District, Virginia. Field of view is 0.6 mm.

Precious metals. The behaviour of the precious metals during the metamorphism of massive sulphide deposits is not well understood. It is apparent, however, that Au is present in part (and perhaps totally) as disseminated grains of electrum. Although the data are few, the electrum generally occurs in close association with chalcopyrite (fig. 22). Ag, though present in electrum grains up to 40 weight %, appears to be held dominantly in tetrahedrite, at least in the Mineral District, Virginia (Miller and Craig, 1983). The massive sulphide ores at Ducktown have yielded significant amounts of Ag and Au but unfortunately the sources of these metals are not known (Magee, 1968).

Gangue minerals

The host rocks in close proximity to metamorphosed massive sulphide deposits are commonly characterized by increases in grain size, changes in the abundance of minerals, changes in iron content (and the Fe/Mg ratio), and the presence of specific minerals (e.g. gahnite). Several common metamorphic minerals (e.g. amphiboles, garnets, micas) display the development of larger than average crystal size in, and near, massive ores. Thus in the vicinity of the massive pyrrhotinic ores of the Great Gossan Lead, Virginia, amphiboles are much more abundant than in the surrounding country rocks and commonly occur as radiating sprays of fibrous crystals up to several centimetres in length. These amphiboles and the accompanying biotites, chlorites, and garnets all display compositional gradients such that approach of the ores corresponds with decreased iron contents of the minerals. Similar textural and compositional changes have been observed at Ducktown, Tennessee (Nesbitt, 1982; Nesbitt and Kelly, 1980).

The extent to which mineralogical changes and compositional zoning around massive sulphide ores are due to the metamorphism of the ores rather than to initial alteration haloes is not always clear. It is apparent, however, that the sulphur and oxygen activity gradients around the ores have influenced the chemical equilibrium over varying distances. The following discussion attempts to describe a few of the more important and recently studied gangue relationships.

Gahnite. Gahnite, nominally $ZnAl_2O_4$, has in recent years been recognized as an important accessory mineral in and immediately adjacent to many massive sulphide ores in metamorphosed terrains. Gahnite has been generally considered to be a mineralogical curiosity but Sheridan and Raymond (1977) and Spry and Scott (1982) have pointed out its potential as a guide to ore deposits. It is readily recognized when it forms 1 cm dark green octahedral crystals in cross-cutting quartz veins in and around ore deposits but is much less obvious in its more common mode of occurrence as 0.1 to 1.0 mm poikiloblastic crystals (fig. 23) and mixed with chlorite, garnet, quartz, and sulphides. In the only detailied study of gahnite in the Appalachian ores, Sandhaus (1981) and Sandhaus and Craig (1982) found that gahnite is nearly ubiquitous with the ore zones of the Mineral District of Virginia. A current study by Spry (in prep.) will provide much additional information. The gahnite occurs in virtually all rock and ore types and ranges from traces to as much as about 15% of the rock volume. Compositionally the gahnite in the massive ores is confined to a relatively narrow range near 6 weight % iron (fig. 24).
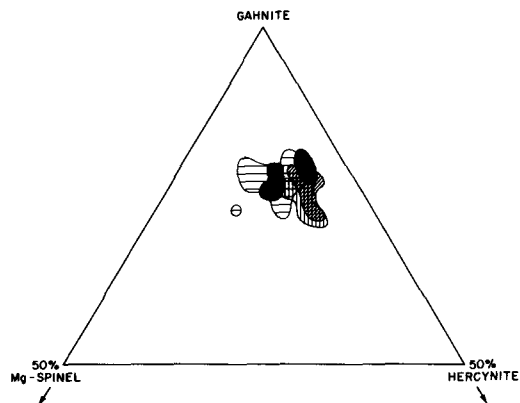

FIG. 24. Ternary plot showing the compositions of gahnites in four deposits in the Mineral District, Virginia (horizontal lines—Cofer deposit; vertical lines—Sulphur Mine; inclined lines toward lower right—Julia deposit; inclined lines toward lower left—Arminius Mine). (From Sandhaus, 1981.)

The origin of gahnite remains conjectural and the several alternatives offered are summarized by Sandhaus (1981) and Sundblad (1982). In the Mineral District, there is no correlation with sphalerite and the origin of the gahnite is attributed to the presence of a primary zinc oxide phase (Sandhaus, 1981). In similar settings in the Caledonides, the origin of the gahnite is attributed to metamorphic decomposition of sphalerite (Sundblad, 1982). Whatever the origin, the primary requirments for its formation appear to be proximity of a Zn-rich massive sulphide deposit and at least lower amphibolite-grade metamorphism (Sundblad 1982).

Gahnite has probably been overlooked in many

deposits because of its fine grain size and general megascopic similarity to other green metamorphic minerals. However, in thin section gahnite may be readily recognized because it is isotropic and pale green and because it has a characteristic euhedral shape and is commonly poikilitic. The reflectance ($\sim 8\%$), which is intermediate between magnetite or sphalerite and common silicates, provides a useful parameter for recognition in polished section.

Gahnite clearly has considerable potential as a guide to metamorphosed massive sulphide deposits because it appears to be confined to or concentrated near the massive ore zones, because it is readily recognizable, and because it has great persistence in weathered zones, in gossans, and in stream sediments.

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