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METAMORPHIC MOBILIZATION OF SULFUR IN THE DUCKTOWN DISTRICT, TENNESSEE, U.S.A.

(Figs. 11)

Abstract: The sulfidic metasedimentary rocks of the Precambrian Great Smoky Group in the Ducktown mining district show a typical Barrovian series of metamorphism and host a number of pre- or syn-metamorphic massive sulfide deposits in the staurolite-kyanite zones. Systematic sampling of the metasediments from chlorite to staurolite zones shows a fairly systematic decrease in total sulfide content (pyrite + pyrrhotite) and pyrite /(pyrite + pyrrhotite) ratio with increasing metamorphic grade. These variations can be explained by loss of sulfur during regional metamorphism due to transformation of pyrite to pyrrhotite and development of differentiation cleavage.

Резюме: Сульфидные метаосадочные породы докембрийской серии ,,Great Smoky" в дактаунском горном районе показывают типичную баровскую метаморфическую свиту и содержат много до- и синметаморфических массивных сульфидных месторождений ставролит-кианитовых зон. Систематический отбор метаосадков из хлоритовых до ставролитовых зон показывает довольно систематическое понижение общего содержания сульфидов (пирит + пирротин) и отношения пирит/(пирит + пирротин) с повышающейся степенью метаморфизма. Эти вариации можно объяснить потерью серы во время регионального метаморфизма вследствие трансформации пирита в пирротин и развития дифференциационного кливажа.

Introduction

Sulfur mobilization, or mass transfer of sulfur, during prograde metamorphism is a controversial issue. Some authors have found evidence for mobilization of sulfur around metamorphosed sulfide deposits (e. g., Fullagar — Brown — Hagner, 1967; Popp — Gilbert — Craig, 1977), whereas others have argued that mass transport of sulfur does not normally occur during regional metamorphism (Thompson, 1972; Nesbitt — Essene, 1983).

From a recent study of graphitic, sulfide-rich schists from Maine, Ferry (1981) concluded that significant mass transfer of sulfur occurred during metamorphic transformation of pyrite to pyrrhotite through desulfidation reactions. The present study, which was in progress concurrently but in another area of comparable geologic setting, has yielded similar conclusions (Runyon, 1983; Runyon — Misra, 1981, 1984).

Our study was conducted in the Ducktown mining district of the southern Appalachian by systematic sampling of the regionally metamorphosed sulfidic metasediments of the Precambrian Great Smoky Group across the metamorphic isograds. Such a study is of particular significance in the Ducktown district

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because of the possible role sulfur mobilization may have played in the formation or subsequent evolution of the massive sulfide deposits in the district.

The Ducktown mining district

Geologic setting

The Ducktown mining district is located near the junction of Tennessee, North Carolina, and Georgia (Fig. 1). The district lies in the Blue Ridge belt, composed of metasedimentary and metaigneous rocks of Precambrian—Paleozoic age and is underlain by a basement complex of Granville age (about 1 billion years old). To the west, the Blue Ridge is separated from the Valley and Ridge Belt, a terrane of unmetamorphosed Paleozoic clastic and carbonate rocks, by the Great Smoky fault zone; to the east, it is separated from the Inner Piedmont Belt, a terrane of high-grade metamorphic rocks, by the Brevard Zone (Fig. 1).

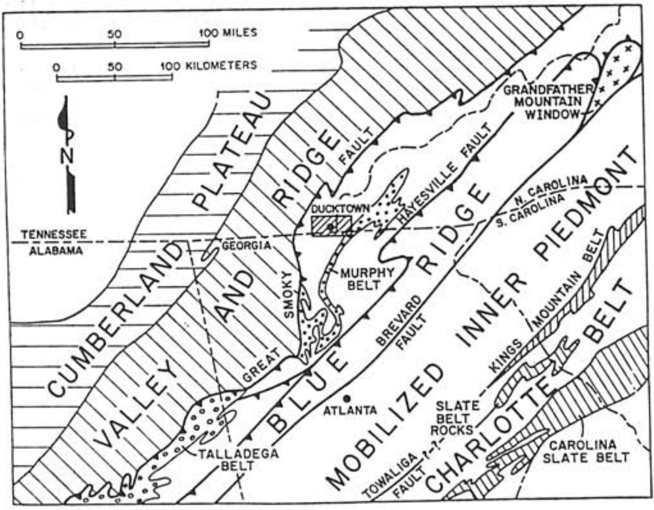

Fig. 1. Map of a portion of the southern Appalachian orogen showing major subdivisions (adapted from Hatcher – Butler, 1979) and location of the Ducktown mining district. The box around Ducktown approximately represents the area shown in Fig. 2.

Rocks of the Ducktown district belong to the Great Smoky Group of the Precambrian Ocoee Supergroup which rests unconformably on the Grenville basement (not exposed in the Ducktown area). The Great Smoky Group is a thick sequence of metasediments composed of metagreywacke, mica schist, metasandstone, and metaconglomerate. This clastic sequence has been interpreted as turbidites derived from a dominantly granitic source (Hadley, 1970). Disseminated sulfides (predominantly pyrrhotite and pyrite) constitute a minor

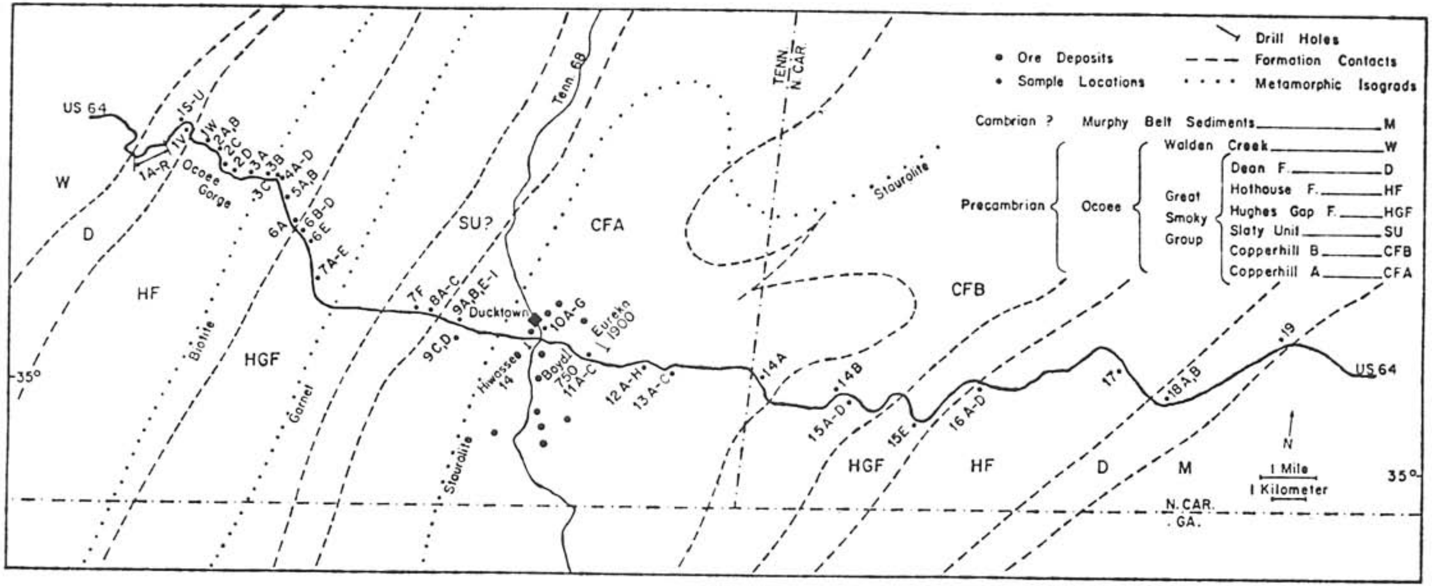

Fig. 2. Regional geologic map of the Ducktown mining district showing stratigraphic units, metamorphic isograds of known sulfide ore bodies in the district (geologic data from Hurst, 1955; Hurst – Schlee, 1962; Hernon, 1968; Magee, 1968; and Holcombe, 1973).

but noticeable constituent of the Great Smoky Group metasediments, especially in the quartz-rich, coarse-grained layers in the lower metamorphic zones.

The stratigraphy of the Great Smoky Group is controversial. The interpretation preferred for the present purpose (Fig. 2) is adapted from the earlier studies of Hurst (1955), Hurst — Schlee (1962), Hernon (1968), and Holcombe (1973) which provide evidence for a large anticlinal structure centered around the Ducktown area. To the east of the Ducktown area, rocks of the Murphy Marble Belt occuping the Murphy Syncline overlie the Great Smoky Group with conformable contact. Most workers regard the Murphy Belt rocks as Cambrian, although its lower section may be correlative with the Late Precambrian Walden Creek Group (Mohr, 1973).

In contrast to equivalent Precambrian stratified sequences in other parts of the southern Appalachian Blue Ridge belt (for example, the Ashe Formation of North Carolina and the Lunchburg Formation of Virginia), the Ocoee Supergroup is characterized by a conspicuous lack of mafic-ultramafic rocks (Misra — McSween, 1984). In the Ducktown district, the known igneous rocks are limited to amphibolites exposed in the mines and as discontinuous surface outcrops. The amphibolite units, presumably metamorphosed basaltic flows, show a close spatial association with the sulfide deposits of the district (Slater, 1982); their genesis and significance are being investigated at present.

Metamorphism and deformation

The Ducktown district, along with the Blue Ridge Belt, experienced several periods of deformation and metamorphism during the Paleozoic (Carpenter, 1970; Holcombe, 1973). Metamorphism in the district is characterized by a typical Barrovian series, from chlorite grade in the western part to staurolite/kyanite grade in the eastern part. Due to infrequent occurrence of kyanite in surface exposures, location of the kyanite isograd is not well defined and therefore this isograd is not shown in Fig. 2. Invariably, the finer-grained lithologies display greater effects due to metamorphism and deformation than their coarser-grained counterparts. Units showing lower than staurolite grade metamorphism show well-preserved sedimentary features (grading bedding, cross-bedding, and scour channels), whereas most units from the staurolite zone have retained only the crudest sedimentary features. In many cases what appears to be original sedimentary bedding is actually transposed bedding, making stratigraphic correlations in this complexly folded area much more difficult (Holcombe, 1973).

Addy — Ypma (1977) suggested three periods of metamorphism in the area: a prograde metamorphism (M1) reaching garnet grade during the Taconic deformation (Ordovician), a second prograde metamorphism (M2) reaching staurolite-kyanite grade during the Acadian deformation (Devonian), and a retrograde phase (M3) to chlorite and biotite grades during the Alleghanian deformation (Mississippian—Pennsylvanian). However, most workers believe that the main regional metamorphic episode in the Blue Ridge was Taconic (450—480 Ma) and was followed by one or more retrograde events (Butler, 1972, 1973; Dallmeyer, 1975; Hatcher — Butler, 1979). Based on carbonate thermometry and silicate phase equilibria, Nesbitt — Essene (1982) have inferred a temperature of 540 °C ± 40 °C and a pressure of 6 ± 1 kb for the peak metamorphic event at Ducktown.

The rocks of the Ducktown district have a general strike of N35°E with dips of 50° to 80° toward southeast. The structure of the district is dominated by two major isoclinal folds (Taconic?) — the Burra antiform and the Coletown synform — which plunge toward northeast (Fig. 3). Two sets of post-ore faults affect the previous structures: an E-W set, dipping 60° toward south, with dexteral displacement; and a N30°W set, dipping 60° to 80° toward northeast, with sinistral displacement. A NE-SW set of faults, believed by earlier workers to be pre-ore (Magee, 1968), is not well defined. This NE-SW set is typically found along the hanging wall and footwall contacts ore-bodies and is now believed to have formed in response to differential movement by the less competent sulfide ore during deformation (Slater — Misra — Acker, 1985).

Sulfide deposits

The Duckown district, which contains one of the largest concentration of sediment-hosted, strata-bound, pyritic massive sulfide deposits, has been in operation almost continuously since the late 1800' s. Of the nine ore-bodies known in the district, all located in the staurolite-kyanite metamorphic zones, only two (Cherokee and Boyd) are currently active, with a combined output of about 2.2 million tons of ore from which the Tennessee Chemical Company produces sulfuric acid, liquid sulfur dioxide, copper metal, copper chemicals, and zinc concentrate (Slater — Misra — Acker, 1985).

The massive sulfide mineralization is composed of pyrrhotite (60 %), pyrite (30 %), chalcopyrite (4 %), sphalerite (4 %) and magnetite (2 %), with traces of lead (galena), silver and gold (Magee, 1968). The major gangue minerals are calcite, quartz, dolomite, actinolite and tremolite, with subordinate amounts of diopside, garnet, zoisite, talc and hornblende. Many of the ore-bodies have a discontinuous envelope of chlorite- and sericite-rich schists which have been interpreted variously as evidence of post-metamorphic hydrothermal emplacement of ore (Magee, 1968), metamorphic sulfidation reactions (Nesbitt, 1982), or sea-floor exhalations (Slater — Misra — Acker, 1985).

The origin of the Ducktown sulfide deposits is highly controversial. Metamorphic and deformation textures of the sulfide ores (Kinkel, 1967; Runyon — Misra, 1981; Craig, 1983) and mineralogical zoning around the ore-bodies (Nesbitt — Kelley, 1980) indicate that the sulfide deposits are not post-metamorphic. For the Ore Knob deposit, North Carolina, which is very similar to the Ducktown deposits, Fullagar — Brown — Hagner (1967) suggested a synmetamorphic sulfide deposition by a combination of iron depleted from the country rocks with sulfur from hydrothermal solutions ascending through shear zones. Recently, several authors have argued for a syngenetic origin on the basis of sulfur isotope data (Mauger, 1972) or metal and lithochemical zoning (Slater, 1982; Slater — Misra — Acker, 1985). Actually, the evolution of the Ducktown sulfide deposits is much more complicated than these simple models tend to imply. Combining oxygen-carbon-hydrogen isotope data with published studies, Addy — Ypma (1977) proposed that "the sulfides are partly pre-tectonic, probably syngenetic, and patrly hydrother-

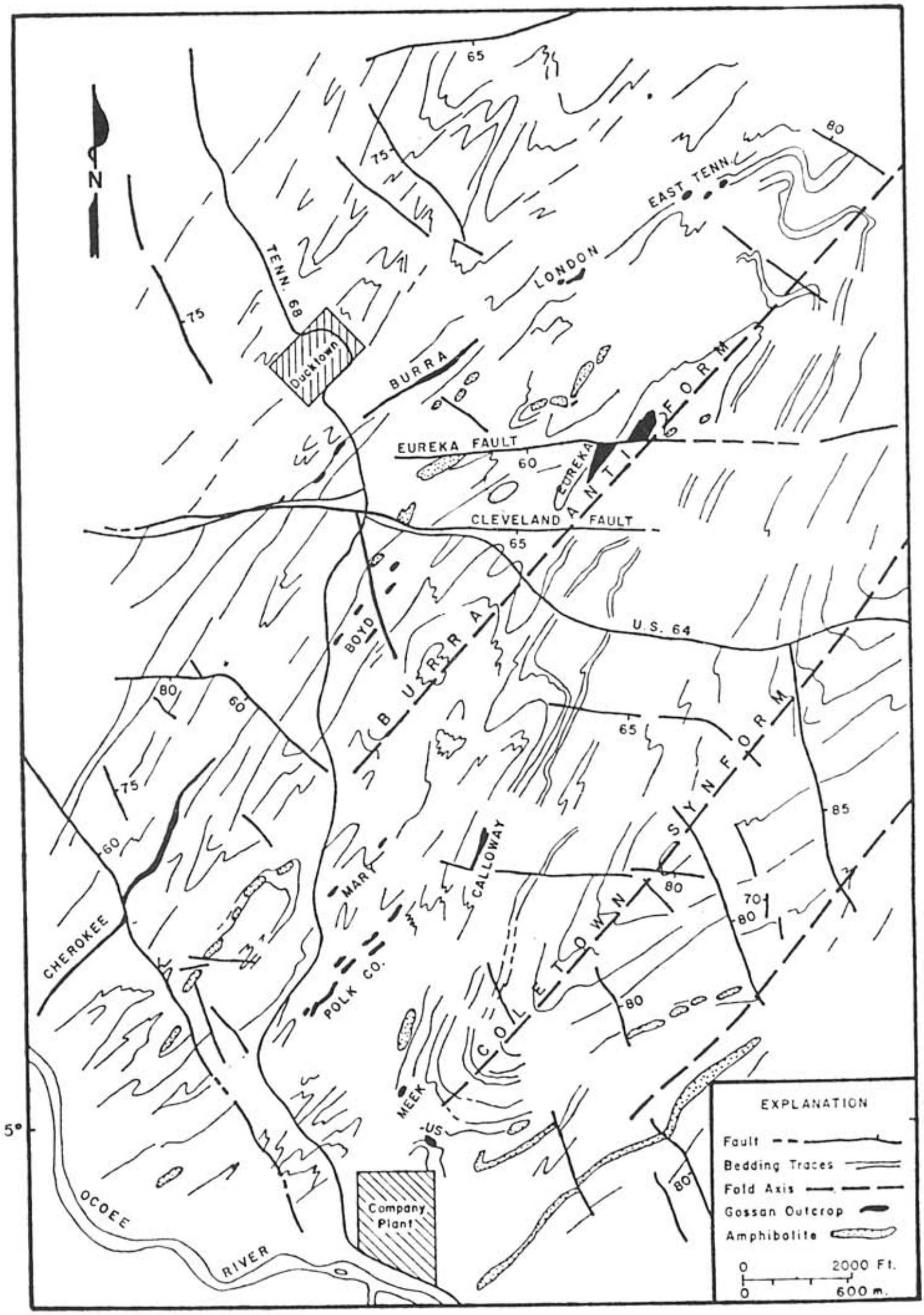

Fig. 3. Generalized structural map of the Copper Basin, Ducktown mining district (modified from Magee, 1968). Gossan and amphibolite outcrops are exaggerated.

mal, formed by remobilization of trace sedimentary sulfides and metals leached from the rocks during the period of regional metamorphism". According to Le Huray (1984), the lead and sulfur isotope data provide evidence for mixing of hydrothermal ore fluids from two sources, one derived from the clastic sediments and the other from deep-seated mafic igneous rocks.

The Great Smoky Group metasediments

Samples

The present investigation was designed primarily to evaluate variations in the abundance and nature of disseminated sulfide constituents across metamorphic isograds in the Great Smoky Group metasediments. Samples for this study were collected from exposures along Highway U.S. 64, from the western exposure of the Dean formation (Ocoee Gorge) eastwards to the contact of the Dean formation with the Murphy Marble Belt (Fig. 2). Where good outcrop exposures did not exist, drill core samples supplied by the Cities Services Company (previous owners of the Ducktown property) were used. At each exposure samples were collected from sulfide-poor to sulfide-rich lithologies so as to represent the range of sulfide contents. In all areas, there are lithologies which essentially contain no sulfide material.

Opaque petrography

In the chlorite and biotite zones, sulfide-bearing horizons are found in most outcrops. Characteristically, the sulfides are concentrated in the coarser-grained, quartz-rich layers whereas the adjacent finer-grained, mica-rich layers are practically devoid of sulfides (Fig. 4a). Sulfides are quite common in the garnet zone, but the contact between sulfide-rich and sulfide-poor layer tend to be gradational. Although lithologies in the staurolite zone and very similar to those in the lower grade zones, rocks of the staurolite zone are noticeably barren of sulfides, except for occasional minute patches in some outcrops.

The main opaque phases in the metasediments include pyrite (Py), pyrrhotite (Po), ilmenite (Ilm) and graphite (Gr), with minor amounts of chalcopyrite (Ccp), galena (Gal), sphalerite (Sph), marcasite (Ms), hematite (Hem), magnetite (Mg), and rutile (Rt). Sphalerite and galena are quite rare; galena was observed only in the samples from the chlorite zone. As expected, the opaque and non-opaque assemblages show a systematic variation across the metamorphic isograds (Fig. 5).

The texture of pyrite varies systematically with the metamorphic grade of the metasediments. In the chlorite and biotite zones, pyrite usually occurs as euhedral cubic crystals which are often partially replaced along crystallographic directions and margins by pyrrhotite and metamorphic minerals such as quartz, chlorite, muscovite, and calcite/ankerite (Fig. 4b). Many of the pyrite cubes show development of pressure shadows; occasionally, the pyrite is rimmed by muscovite and an Fe-rich, berlin-blue, chlorite phase. These features suggest that the pyrite is pre-metamorphic (M1). In contrast, the small amount of pyrite found in the garnet zone occurs as lenticular patches without pressure shadows.

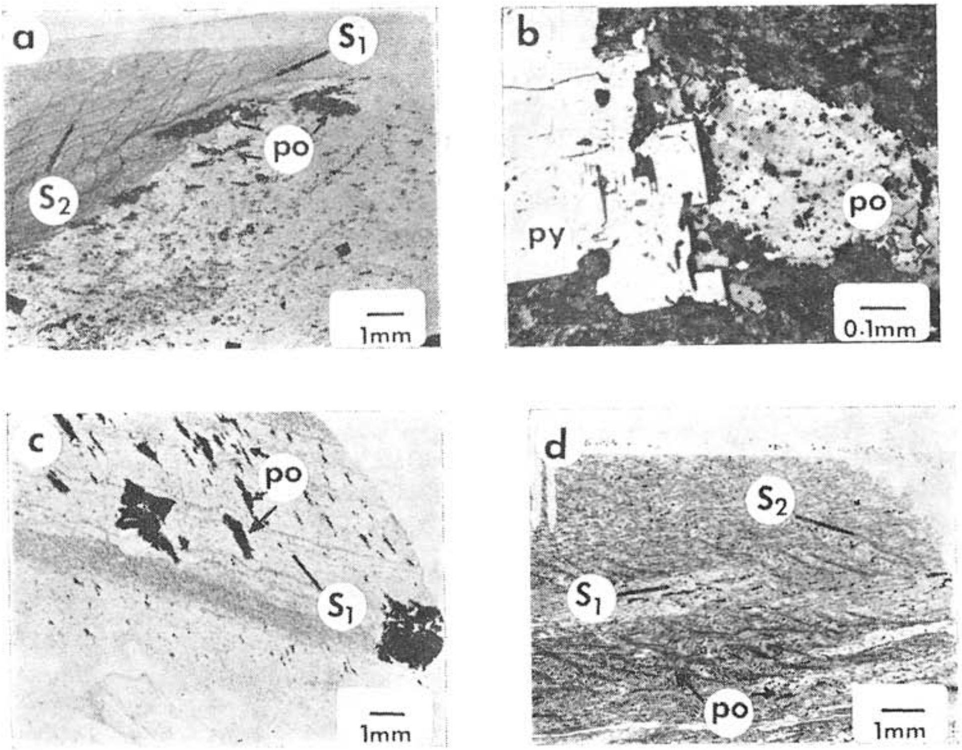

Fig. 4. Photomicrographs showing sulfide-silicate textures in the Great Smoky Group metasediments (plane polarized light unless stated otherwise).

Explanations: a) concentration of sulfides (black) in the quartz-rich layer (chlorite zone). Note the preferred orientation of pyrrhotite (po) parallel to S_1 and lack of sulfides in the adjacent mica-rich layer; b) partial replacement of pyrite (py) by silicates and pyrrhotite (chlorite zone) (reflected light); c) well-developed preferred orientation (S_1) of pyrrhotite streaks in metasiltstone (chlorite zone); d) preferred orientation of pyrrhotite along S_1 and S_2 cleavages (biotite zone). Photographs by G. A. Runyon.

Alignment of these patches with S_1 cleavage suggests local development of metamorphic (M1) pyrite in the garnet zone. The rare occurrence of pyrite in the staurolite-kyanite zones is limited to late-stage fractures and weathering of pyrrhotite.

Pyrrhotite is pervasive throughout the area studied. Some of the pyrrhotite occurs as polycrystalline aggregates, with 120° triple junctions indicative of annealing. More typically, pyrrhotite is found as lenticular patches or streaks aligned parallel to schistosity (S_1) in the chlorite and biotite zones (Fig. 4c) and also to differentiation crenulation cleavage (S_2) in biotite through staurolite zones (Fig. 4d). In the chlorite and biotite zones, the pyrrhotite contains abundant inclusions of quartz, mica and chlorite, which appear to have been engulfed by pyrrhotite during its metamorphic (M1) growth. S_1-oriented streaks of pyrrhotite are also common in the garnet and staurolite zones, but these are

CHLORITE	BIOTITE	GARNET	STAUROLITE — KYANITE					
Country Rocks				Alteration Zone ⟶ Ore Zone				
Py+Po+Rt+ Gr+Mag+Ccp	Py+Po+Ilm +Gr+Ccp	Po+Ilm+Gr +Py+Ccp	Po+Ilm+Gr	Po+Ilm	Po+Rt	Po+Py+Rt	Po+Py	Po+Py+Mag
Ms+Qtz+ Pl+Carb	Ms+Qtz+Pl+ Cc+Bt	Qtz+Grt+ Pl+Bt+Spn	Ms+Qtz+St +Bt+Chl	Ms+Qtz+ Bt+Chl	Ms+Qtz+Grt +Bt+Chl		Ms+Qtz +Bt+Chl +Clz	
				Fe Silicates ⟶ Low Fe Silicates				

Fig. 5. Variations in opaque-nonopaque assemblages across metamorphic isograds. The alteration and ore zone assemblages are from Nesbitt — Kelly (1980).

not as irregular in shape or inclusion-ridden (Fig. 6a). Occasionally in the staurolite zone, pyrrhotite is interstitial to recrystallized silicates (Fig. 6b).

As stated previously, in the chlorite and biotite zones, sulfides are predominantly confined to the coarser, more quartz-rich layers of these metasediments. However, when pyrrhotite is observed in the finer-grained sediments, it is commonly surrounded by a pod of polycrystalline quartz (Fig. 6c). The pyrrhotite and quartz lie parallel to the S_1 cleavage. Pyrite in close proximity to this pyrrhotite shows little association with quartz other than poorly developed pressure shadows. The alignment of quartz and pyrrhotite parallel to S_1 suggests a synmetamorphic development.

In several samples, ferromagnesian minerals are partially replaced by pyrrhotite (Fig. 6d). Such textures, also noted by other workers (Chinner, 1960; Fullagar — Brown — Hagner, 1967; George, 1969) suggest that during and after the metamorphic formation of these ferromagnesian silicates sulfur reacted with these silicate minerals to produce iron sulfides and magnesium-enriched silicates (Mallio — Gheith, 1972; Tso — Gilbert — Craig, 1979).

Sulfide modal analysis

As the conventional point counting method is not reliable for modal analysis of lineated and coarse-grained constituents, an alternate technique, based on comparison of the area occupied by sulfides with the total area of a thin section (Fitch, 1959), was used for modal analysis of the sulfide constituents. Modal data were obtained only for pyrrhotite and pyrite as they account for more than 90 % of the sulfides in the Great Smoky Group metasediments. All samples with greater than 0.1 % sulfide content (visual estimate) were analyzed (Runyon, 1983).

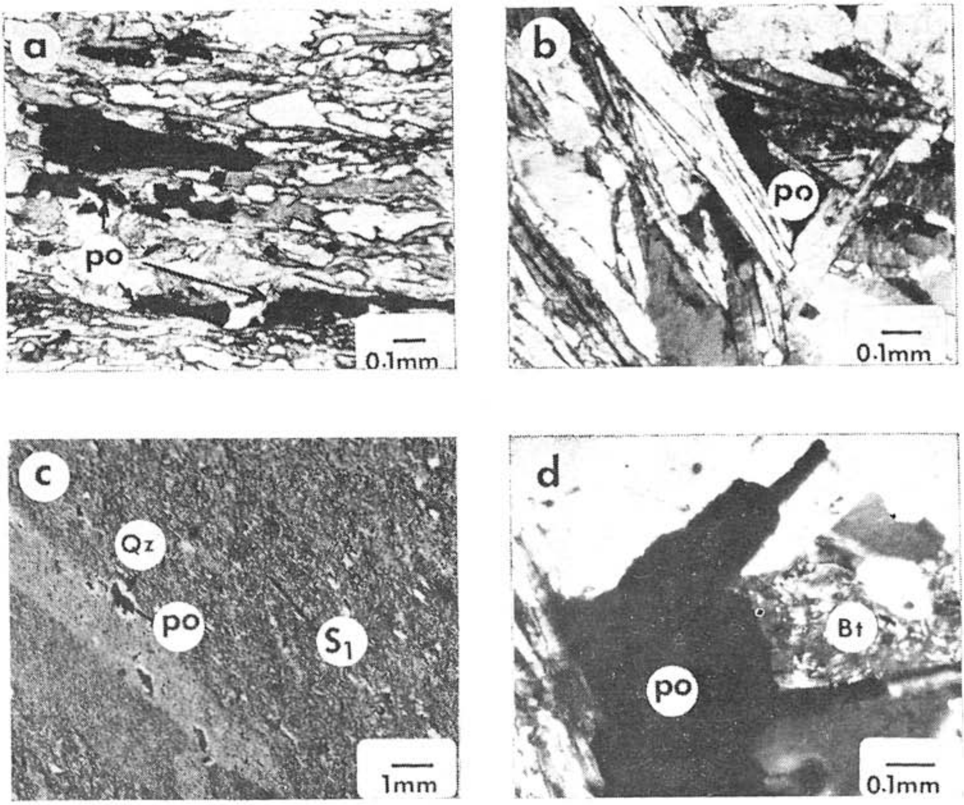

Fig. 6. Photomicrographs showing sulfide-silicate textures in the Great Smoky Group metasediments (plane polarized light).

Explanations: a) oriented streaks (S_1) of inclusion-free pyrrhotite (po) (staurolite zone); b) pyrrhotite interstitial to silicates (staurolite zone); c) streaks of pyrrhotite in a quartz-rich pod, both oriented parallel to S_1 (biotite zone). Note the quartz (Qz) envelope around pyrrhotite; d) replacement of biotite (Bt) by pyrrhotite (staurolite zone). Photographs by G. A. Runyon.

Fig. 7 shows the variation in total sulfide content (pyrrhotite + pyrite) with metamorphic grade — a decrease in the average sulfide content from 3.7 % in the chlorite zone to 1.11 % in the staurolite zone. Despite the rather large standard deviations associated with the means (arithmetic) for the various metamorphic zones, the overall trend is quite clear: a fairly systematic decrease in the total sulfide content with increasing metamorphic grade. A Student's t-test confirms that the differences between pairs of means are significant at 95 % confidence level.

The trend in Fig. 7 can be explained by (1) variation in the content of syngenetic-diagenetic sulfides, or (2) mobilization of sulfide constituents during regional metamorphism. Reconnaissance traverses show that formations along strike to the north and south have sulfide contents similar to the samples used in the study. Also, studies by Hale (1974), Mohr (1973), and Poppelreiter (1980) on the Great Smoky Group to the north and by Weiner — Merschat (1978) to the south of the Ducktown area suggest that sulfides are prominent over a wide area. Thus, it appears unlikely that the significant and systematic decrease in sulfide content is merely a reflection of variation in the sulfide contents of the pre-metamorphic protoliths.

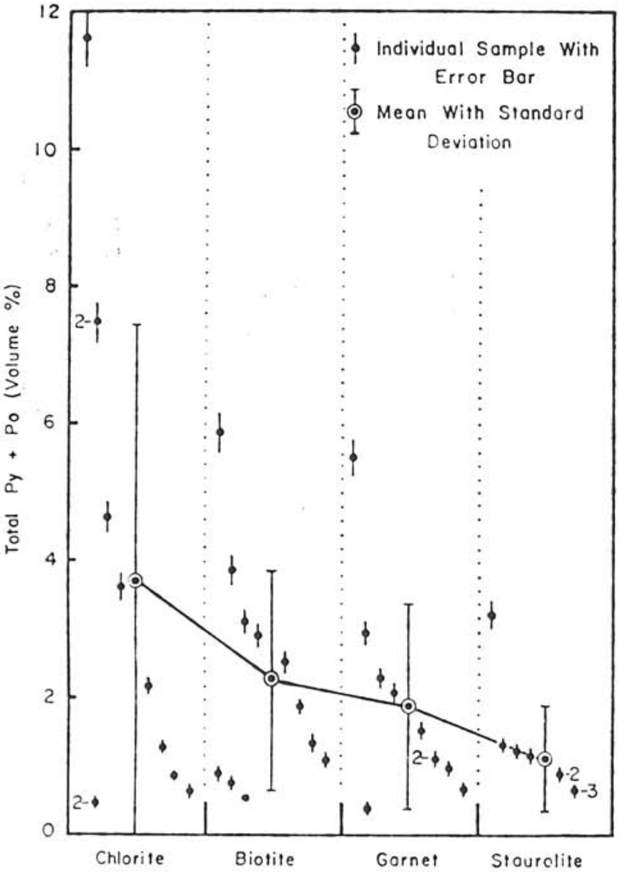

Fig. 7. Variation in total (volume %) sulfide content (pyrite + pyrrhotite) in metasedimentary rocks of the Ducktown area with increasing grade of metamorphism. *Explanations:* Small numbers denote the number of samples, if more than one, that plot at the same value.

Another approach to the problem is illustrated in Fig. 8. In this Fig., average sulfide contents of the various formations below the staurolite grade are compared with average sulfide contents of the same formations within the staurolite zone. If the decrease in sulfide content is a feature of sedimentation, then the average sulfide content for each formation should be relatively similar regardless of the metamorphic grade. Most of the formations have a large variation in sulfide content as expressed by the large standard deviations. However, the average sulfide content in the formations from the staurolite zone is noticeable lower than the average sulfide content in their less metamorphosed counterparts. This supports field observations that staurolite zone lithologies are sulfide-poor relative to lower grade lithologies. The decrease in sulfide content in the staurolite zone formations suggests that the variation in sulfide content is related mainly to metamorphic mobilization of sulfide constituents rather than sedimentation-diagenesis.

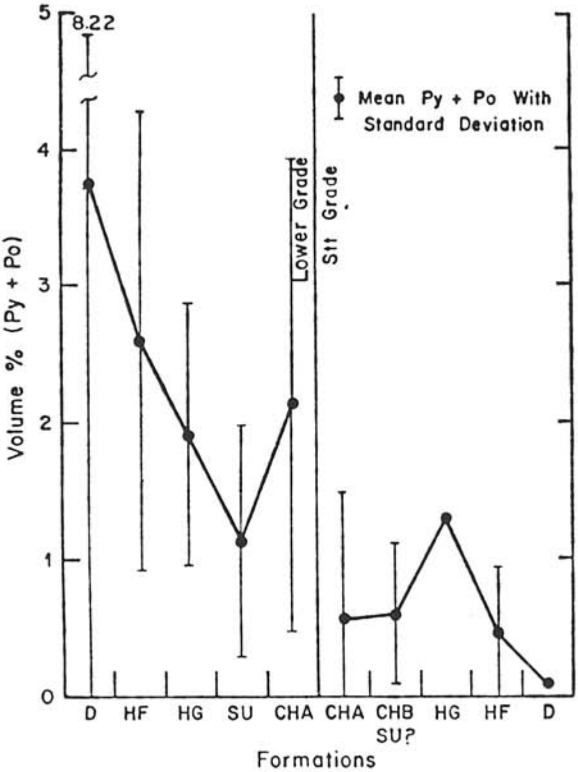

Fig. 8. Comparison of average sulfide contents (volume % pyrite + pyrrhotite) of formations below the staurolite grade with average sulfide contents of the same formations within the staurolite zone.

The decrease in sulfide content during metamorphism could have occurred in two ways: 1) removal of sulfide constituents from the host rocks by some process; or 2) dispersion of sulfides into sulfide-poor horizons, resulting in low sulfide contents of individual samples. To resolve this question, for each of three main lithologies in the district (metagreywacke, metasandstone, and metaconglomerate), the average sulfide content for the chlorite-biotite zones is compared with the average for the staurolite zone (Fig. 9). If the decrease in sulfide content is caused by a dispersive process, at least one of the lithologies should not display a decrease in sulfide content. On the other hand, if the decrease is caused by removal of sulfide constituents from the host rocks, all lithologies should show a decrease in sulfide content. Data presented in Fig. 9 show apparent decreases in sulfide content in all three lithologies. A Student's t-test on sample means shows that in all lithologies the differences are significant at 99 % confidence limit. The conclusion is that the decrease in sulfide content has been caused probably by removal of sulfide constituents from these rocks rather than by dispersion of sulfide constituents within these rocks. Also, a consistent pattern of decrease in sulfide content with grade of metamorphism for

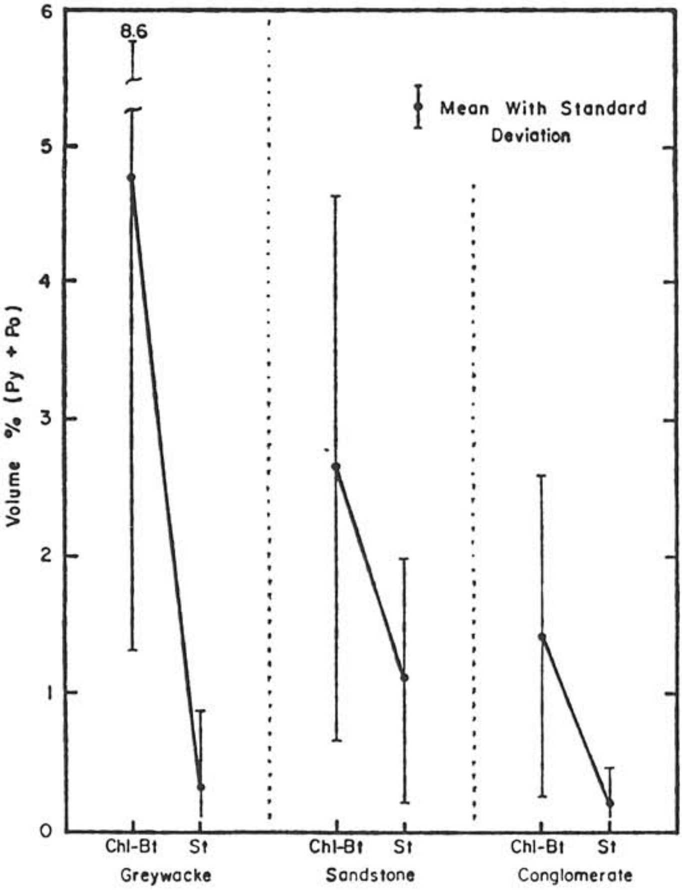

Fig. 9. Comparison of average sulfide contents (volume % pyrite + pyrrhotite) of metagreywackes, metasandstones, and metaconglomerates in chlorite-biotite zones with those of staurolite zone.

each lithology reinforces the earlier conclusion about metamorphic mobilization of sulfide constituents in this area.

Pyrite/pyrrhotite ratio

From observations in outcrops and polished sections of samples collected, it is fairly obvious that the pyrite/pyrrhotite ratio decreases from chlorite to staurolite zones. However, for a quantitative illustration of the trend and evaluation of possible reaction relationship between pyrite and pyrrhotite in the area, the molar ratios of pyrite/(pyrite + pyrrhotite) were calculated from the modal data and plotted as function of metamorphic grade (Ferry, 1981). This plot (Fig. 10) shows a wide variation in the ratio, but the ratio does appear to decrease with increasing metamorphic grade, especially when the average (arithmetic) ratios are considered.

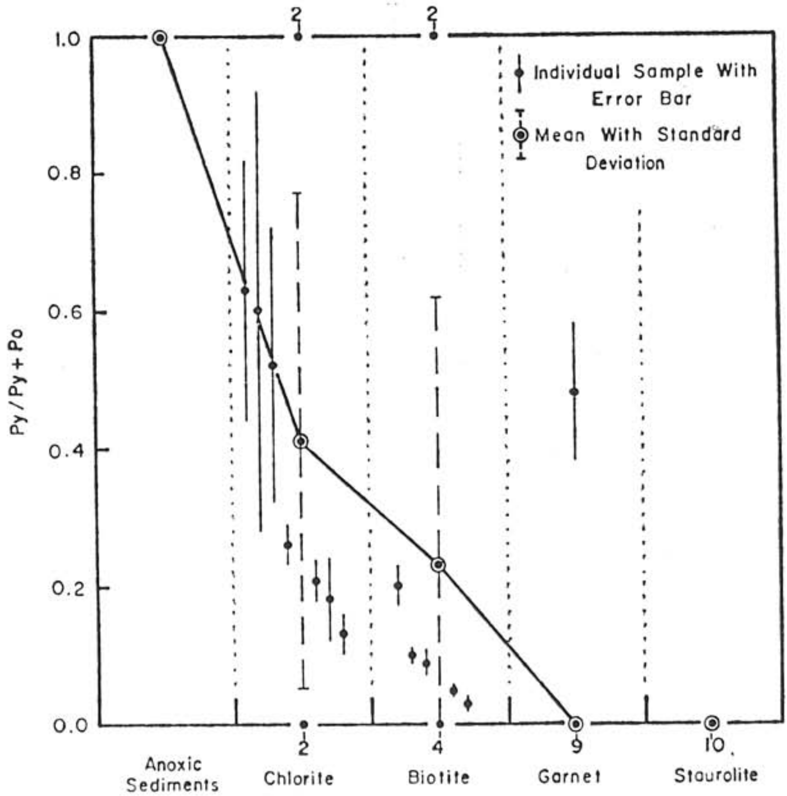

Fig. 10. Variation in molar pyrite/(pyrite + pyrrhotite) ratio in metasedimentary rocks of the Ducktown area with increasing metamorphic grade.
Explanations: Small numbers denote the number of samples, if more than one, that plot at the same value.

Pyrrhotite is quite rare in marine sedimentary rocks (Kaplan — Emery — Rittenberg, 1963), whereas pyrite is the ubiquitous sedimentary-diagenetic iron sulfide phase in sedimentary rocks (Berner — Baldwin — Holdren, 1979). Also, Carpenter (1974) has shown that pyrite is practically the only iron sulfide phase in the low grade rocks of the Great Smoky Group. Thus, it is unlikely that the systematic trend in Fig. 10 is inherited from the pre-metamorphic pyrite/pyrrhotite ratios in the sediments. In view of the similarity of the lithologies in the different metamorphic zones and the sampling procedure adopted, such a systematic trend suggests conversion of pyrite to pyrrhotite during progressive metamorphism. The predominantly metamorphic origin of pyrrhotite in the Ducktown district is also supported by textural evidence discussed earlier: growth of pyrrhotite in the pressure shadows of diagenetic pyrite cubes, incipient replacement of such pyrite cubes to pyrrhotite, and pronounced preferred orientation of pyrrhotite along metamorphic foliation planes in all the metamorphic zones. Conversion of pyrite to pyrrhotite during regional metamorphism has been noted by previous workers in the Ducktown area as well as in other areas around the world (Kanehira — Bano — Nishida, 1964; Thompson — Norton, 1968; Mohr, 1973; Holcombe, 1973; Carpenter, 1974; Nesbitt — Kelly, 1980; Ferry, 1981).

Discussion

What sort of reactions were responsible for the pyrite to pyrrhotite transition during metamorphism? To evaluate this we consider three representative reactions (A, B, C) for the transition from chlorite to biotite and biotite to garnet zones, as the transformation from pyrite to pyrrhotite is essentially complete by the garnet isograd (disregarding one anomalous pyrite-bearing sample from the garnet zone). All of these reactions involve graphite which is a minor but persistent phase in the metasediments.

A) $2\ \mathrm{FeS_2} + 2\ \mathrm{H_2O} + \mathrm{C} = 2\ \mathrm{FeS} + 2\ \mathrm{H_2S} + \mathrm{CO_2}$
pyrite pyrrhotite

B) $4\mathrm{Fe_{4.5}\,Al_3Si_{2.5}\,O_{10}\,(OH)_8} + 6\mathrm{KAlSi_3O_8} + 18\mathrm{FeS_2} + 4\mathrm{C}$
chlorite K-feldspar pyrite
$= 6\mathrm{KAl_2\,AlSi_3O_{10}(OH)_2} + 36\mathrm{FeS} + 10\mathrm{SiO_2} - 20\mathrm{H_2O} + 4\mathrm{CO_2}$
muscovite pyrrhotite quartz

C) $6\mathrm{Fe_{4.5}\,Al_3Si_{2.5}\,O_{10}(OH)_2} + 4\mathrm{KFe_3\,AlSi_3\,O_{10}(OH)_2} + 24\mathrm{FeS_2} + 12\mathrm{C}$
chlorite biotite pyrite
$= 5\mathrm{Fe_3Al_2\,(SiO_4)_3} + 4\mathrm{KAl_2AlSi_3O_{10}(OH)_2} + 48\mathrm{FeS}$
garnet muscovite pyrrhotite
$+ 24\mathrm{H_2O} + 12\mathrm{CO_2}$

Reaction A) is an example of desulfidation-type reactions which could occur in the chlorite and biotite zones for a system open with respect to sulfur. Ferry (1981) considered this to be the most appropriate pyrite-pyrrhotite reaction for similar graphite-bearing sulfidic schists in Maine. Reaction B) represents progressive metamorphism from chlorite to biotite zone in a system closed to sulfur, and reaction C) represents transition from biotite to garnet zone in a system closed to sulfur.

These reactions represent oversimplification of a much more complex system. For the sake of simplicity, pyrrhotite in these reactions is represented by FeS and the silicate phases are represented by their ideal compositions. Nevertheless, the above reactions, in conjunction with the sulfide modal data, can be used to test whether the system was open or closed during progressive metamorphism. We can do this by calculating the theoretical change in pyrite content between chlorite-biotite and biotite-garnet zones expected from these reactions and comparing them with the changes actually observed (modal data). The basis of the calculation is that the conversion of one mole of pyrite to one mole of pyrrhotite is accompanied by a 25 % reduction in volume (Mason — Berry, 1968).

Consequences of reaction A) are: 1. exactly one mole of pyrrhotite forms for every mole of pyrite consumed; and 2. whole rock sulfur contents decrease as the reaction progresses. Consequences of reactions B) and C) are: 1. exactly two moles of pyrrhotite forms for every mole of pyrite consumed; and 2. whole rock sulfur contents are unaffected by the reaction.

Fig. 11 shows the observed versus calculated changes in the sulfide (pyrrhotite + pyrite) content across the metamorphic zones. Note that the difference between the mean (pyrrhotite + pyrite) content and the mean pyrrhotite content represents the mean pyrite content. If the metamorphic system was closed to sulfur, a reaction of the type B) or C) should show an increase in the average sulfide content from the chlorite to the biotite zone, and from the biotite to the garnet zone. On the other hand, if the metamorphic system was open to sulfur, a reaction of the type A), the average sulfide content should decrease from the chlorite to the garnet zone, as is seen in Fig. 11. The continuous decrease in sulfide content from the chlorite to the garnet zone supports an open system during metamorphism. Given the large standard deviations about the means, the observed differences between measured sulfide content versus the calculated decrease in sulfide content for an open system may not be significant. Therefore, the measured decrease in sulfide content from the chlorite to the garnet zone can be explained by volume reductions in desulfidation type of reaction of pyrite to pyrrhotite in an open system.

Since the pyrite-to-pyrrhotite conversion was essentially complete by the garnet grade condition, such desulfidation type of reactions cannot explain the decrease in sulfide content from the garnet zone to the staurolite zone. For this we propose formation of differentiation cleavage as a likely mechanism. Many studies (Williams, 1972; Holcombe, 1973; Glasson — Keays, 1978; Stephens — Glasson — Keays, 1979) have shown that development of differentiation cleavage during metamorphism is accompanied by selective removal of quartz, calcite, feldspar and sulfide constituents from micaceous layers by fluid migration. The effect of such a process would be most profound in the staurolite zone, the zone of most intense metamorphism and pervasive development of differentiation cleavage. Such a conclusion is supported by: 1) lack of sulfide in the micaceous layers whereas the adjacent quartz rich layers are quite rich in metamorphic pyrrhotite with a preferred orientation parallel to the schistosity (S_1) (Fig. 4a); and 2) quartz envelopes around pyrrhotite shears (Fig. 6c), interpreted to be the result of mobilization of both quartz and sulfide constituents during development of differentation cleavage.

From the data obtained in this study, it is not possible to adequately assess the role of sulfur mobilized during regional metamorphism in the genesis of sulfide deposits of the Ducktown district. Isotope data suggest that a part of the sulfur (as well as lead, and probably other metals such as Zn and Cu) were derived from the Great Smoky Group clastic sediments, either during initial, pre-metamorphic emplacement of the sulfide deposits (LeHurray, 1984) or during regional metamorphism (Addy — Ypma, 1977). Nesbitt (1982) interpreted the iron-depleted alteration zone around the Ducktown ore-bodies as a consequence of reaction between sulfur and ferromagnesian silicates during

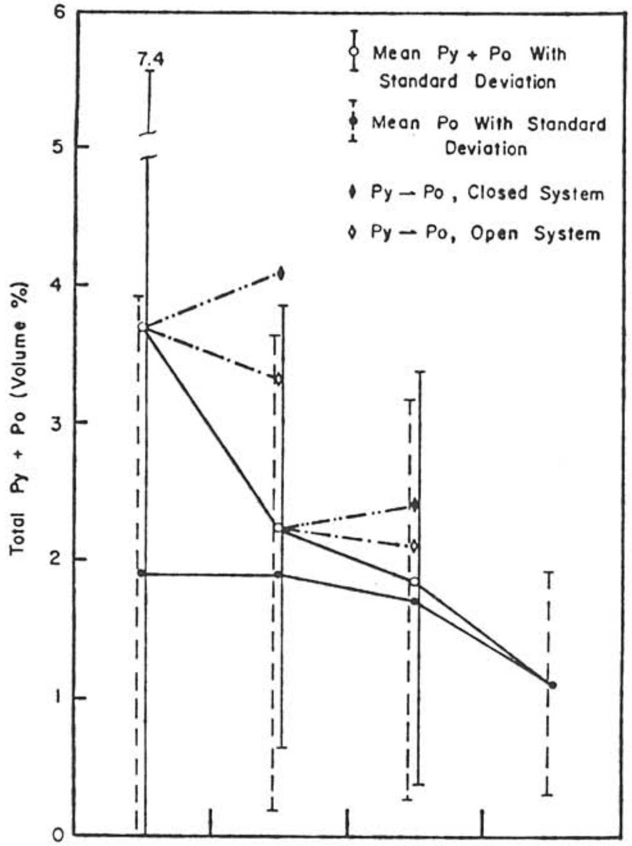

Fig. 11. Comparison of mean pyrite and pyrrhotite contents of metasediments of the different metamorphic zones with the calculated changes in sulfide contents for open and closed metamorphic reaction systems.

metamorphism, either because of sulfur enrichment in the wallrocks during emplacement of the ores or because of sulfur diffusion outward from the ore zone during metamorphism. However, the present study shows that a significant portion of the sulfur for the sulfidation reactions could have been mobilized from the country rocks during metamorphism. From the available data it is difficult to say if this process made any significant contribution to the ore zone, but the common presence of paragenetically-late, large, pyrite porphyroblasts in ore assemblages suggest the possibility of influx of sulfur from an external source during metamorphism.

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REFERENCES

ADDY, S. K. — YPMA, P. J. M., 1977: Origin of massive sulfide deposits at Ducktown, Tennessee: An oxygen, carbon, and hydrogen isotope study. Econ. Geol. (Lancaster, Pa), 72, pp. 1245—1268.

BERNER, R. A. — BALDWIN, I. — HOLDREN, G. R., Jr., 1979: Authigenic iron sulfides as paleosalinity indicators. J. Sed. Petrology (Tulsa, OK), 49, pp. 1345—1350.

BUTLER, J. R., 1972: Age of Paleozoic metamorphism in the Carolinas, Georgia and Tennessee, Southern Appalachians. Amer. J. Sci. (New Haven, Conn.), 272, pp. 319—333.

BUTLER, J. R., 1973: Paleozoic deformation and metamorphism in part of the Blue Ridge thrust sheet, North Carolina. Amer. J. Sci. (New Haven, Conn.), 273—A, pp. 78—88.

CARPENTER, R. H., 1970: Metamorphic history of the Blue Ridge Province of Tennessee and North Carolina. Geol. Soc. Amer. Bull. (Boulder, Co), 81, pp. 749—762.

CARPENTER, R. H., 1974: Pyrrhotite isograd in southeastern Tennessee and southwestern North Carolina. Geol. Soc. Amer. Bull. (Boulder, Co), 85, pp. 451—456.

CHINNER, G. A., 1960: Pelitic gneisses with varying ferrous/ferric ratios from Glen Clova, Angus, Scotland. J. Petrology (London), 1, pp. 178—217.

GRAIG, J. R., 1983: Metamorphic features in Appalachian massive sulfides. Mineral. Mag. (London), 47, pp. 515—525.

DALLMEYER, R. D., 1975: ^{49}Ar/^{39}Ar incremental release ages of biotite from Cherokee orebody, Ducktown, Tennessee; Their bearing on the age sulfide mineralization. Econ. Geol. (Lancaster, Pa), 70, pp. 341—344.

FERRY, J. M., 1981: Petrology of graphitic sulfide-rich schists from south-central Maine; an example of desulfidation during prograde metamorphism. Amer. Mineralogist (Richmond, Va), 66, pp. 908—930.

FITCH, F. J., 1949: Macro point counting. Amer. Mineralogist (Richmond, Va), 44, pp. 667—669.

FULLAGAR, P. D. — BROWN, H. S. — HAGNER, A. F., 1967: Geochemistry of wallrock alteration and the role of sulfurization in the formation of the Ore Knob sulfide deposit. Econ. Geol. (Lancaster, Pa), 62, pp. 798—825.

GEORGE, R. J., 1969: Sulphide-silicate reactions during metamorphism of the Nairne pyrite deposit. Proc. Austr. Inst. Min. Met., 230, pp. 1—7.

GLASSON, M. J. — KEAYS, R. R., 1978: Gold mobilization during cleavage development in sedimentary rocks from the auriferous Slate Belt of Central Victoria, Australia: Some important boundary conditions. Econ. Geol. (Lancaster, Pa), 73, pp. 496—511.

HADLEY, J. B., 1970: The Ocoee Series and its possible correlatives. In Fisher, G. W. — Pettijohn, F. J. — Redd, J. C. Jr. — Weaver, K. N., eds.: Studies of Appalachian geology, Central and Southern, Intersci. Publishers, New York, pp. 247—259.

HALE, R. C. 1974: Gold deposits of the Coker Creen district, Monroe County, Tennessee. Tenn. Div. Geology Bull. (Nashville, Tn), 93 pp.

HATCHER, R. D. — BUTLER, J. R., 1979: Guidebook for southern Appalachian Field Trip in the Carolinas, Teneessee, and northern Georgia (International Geological Correlation Program, Project 27), North Carolina Geological Survey (Raleigh, NC), 117 pp.

HERNON, R. M., 1968: Geology of the Ducktown, Isabella, and Persimmon Creek quadrangles, Tennessee and North Carolina. U.S. Geol. Survey Open File Report, 71 pp.

HOLCOMBE, R. J., 1973: Mesoscopic and microscopic analysis of deformation and metamorphism near Ducktown, Tennessee. Ph. D. Thesis, Standford Univ., Standford, California, 225 pp.

HURST, V. J., 1955: Stratigraphy, structure, and mineral resources of the Mineral Bluff quadrangle, Georgia Geol. Surv., Bull., 63, 137 pp.

HURST, V. — SCHLEE, J. S., 1962: Ocoee metasediments, North Central Georgia--Southeast Tennessee. Guidebook No. 3, Geol. Soc. America, Southeastern Sec. Annual Mtg., 10 pp.

KANEHIRA, K. — BANNO, S. — NISHIDA, K., 1964: Sulfide and oxide minerals in some metamorphic terranes in Japan. Jap. J. Geol. Geogr. (Tokyo), 35, pp. 175—191.

KAPLAN, I. R., — EMERY, K. O. — RITTENBERG, S. C., 1963: The distribution of isotopic abundance of sulfur in recent marine sediments of southern California. Geochim. cosmochim. Acta (London), 27, pp. 271—331.

KINKEL, A. Jr., 1967: The Ore Knob copper deposit, North Carolina, and other massive sulfide deposits of the Appalachians. U.S. Geol. Survey Prof. Paper (Washington, D. C.), 558, 58 pp.

LEHURAY, A. P., 1984: Lead and sulfur isotopes and a model for the origin of the Ducktown deposit, Tennessee. Econ. Geol. (Lancaster, Pa), 79, pp. 1561—1573.

MAGEE, N., 1968: Geology and ore deposits of the Ducktown district, Tennessee. In Ridge, J. D., ed.: Ore deposits of the United States, 1933—1967 (Graton-Sales Vol.). Am. Inst. Min. Metall. Pet. Eng., New York, pp. 207—341.

MALLIO, W. J. — GHEITH, M. A., 1972: Textural and chemical evidence bearing on sulfide-silicate reactions in metasediments. Mineralium Depos. (Berlin), 7, pp. 13—17.

MASON, B. — BERBY, L. G., 1968: Elements of Mineralogy. W. H. Freeman and Company, San Francisco, 550 pp.

MAUGER, R. L., 1972: A sulfur isotope study of the Ducktown, Tennessee district, U.S.A. Econ. Geol. (Lancaster, Pa), 76, pp. 497—510.

MISRA, K. C. — McSWEEN, H. Y. Jr., 1984: Mafic rocks of the southern Appalachians: a review. Amer. J. Sci. (New Haven, Conn.), 294, pp. 294—318.

MOHR, D. W., 1973: Stratigraphy and structure of part of the Great Smoky and Murphy Belt Groups, Western North Carolina. Amer. J. Sci. (New Haven, Conn.), 273-A, pp. 41—71.

NESBITT, B. E., 1982: Metamorphic sulfide-silicate equilibria in the massive sulfide deposits at Ducktown, Tennessee. Econ. Geol. (Lancaster, Pa), 77, pp. 364—378.

NESBITT, B. E. — ESSENE, E. J., 1982: Metamorphic thermometry and barometry of a portion of the southern Blue Ridge province. Amer. J. Sci. (New Haven, Conn.), 282, pp. 701—729.

NESBITT, B. E. — ESSENE, E. J., 1983: Metamorphic volatile equilibria in a portion of the southern Blue Ridge province. Amer. J. Sci. (New Haven, Conn.), 293, pp. 135—165.

NESBITT, B. E. — KELLY, W. C., 1980: Metamorphic zonation of sulfides, oxides, and graphite in and around the ore bodies at Ducktown, Tennessee. Econ. Geol. (Lancaster, Pa), 75, pp. 1010—1021.

POPP, R. K. — GILBERT, C. M. — CRAIG, J. R., 1977: Stability of Fe-Mg amphiboles with respect to sulfur fugacity. Amer. Mineralogist (Richmond, Va), 62, pp. 13—30.

POPPELREITER, B. S., 1980: A structural analysis of metasedimentary rocks of the Ocoee Supergroup above the Great Smoky Overthrust in southeast Tennessee. Unpub. Mater's Thesis. Univ. of Tenn., Knoxville, Tennessee, 111 p.
RUNYON, G. A., 1983: The distribution and variation of sulfide constituents of the Great Group, Ducktown area, Tennessee, with respect to metamorphic grade. Unpub. M. S. Thesis. Univ. of Tennessee, Knoxville, Tennessee, 112 pp.
RUNYON, G. A. — MISRA, K. C., 1981: Metamorphic mobilization of sulfide constitutents in metasediments of the Great Smoky Group, Ducktown area, Tennessee. Geol. Soc. America Abstracts with Programs (Boulder, Co), 13, 33 pp.
RUNYON, G. A. — MISRA, K. C., 1984: Sulfur mobilization during regional metamorphism: evidence from the Ducktown mining district, Tennessee, U.S.A. Proc. 27th Int. Geol. Congress, Moscow, 6, p. 281.
SLATER, W. R., 1982: Massive sulfide deposits of the Ducktown mining district, Tennessee. In: Exploration for metallic resources in the southeast. Univ. of Georgia, Athens, Georgia, pp. 91—99.
SLATER, W. R. — MISRA, K. C. — ACKER, C. P., III, 1985: Massive sulfide deposits of the Ducktown district, Tennessee. Geol. Soc. Am. Field Guidebook, Southeast Section Annual Meeting, Knoxville (in press).
STEPHENS, M. B. — GLASSON, M. J. — KEAYS, R. R., 1979: Structural and chemical aspects of metamorphic layering development in metasediments from Clunes, Australia. Amer. J. Sci (New Haven, Conn.), 278, pp. 129—160.
THOMPSON, J. B., Jr., 1972: Oxides and sulfides in regional metamorphism of pelitic schists. Internat. Geol. Cong. 24th, Montreal, 10, pp. 27—35.
THOMPSON, J. B. — NORTON, S. A., 1968: Paleozoic regional metamorphism in New England and adjacent areas. In Zen, E. — White, W. S. — Hadley, J. B. — Thompson, J. B. Jr., eds.: Studies of Appalachian geology, Northern and Maritime. John Wiley and Sons, New York, pp. 319—327.
TSO, J. L. — GILBERT, C. — CRAIG, J. R., 1979: Sulfidation of synthetic biotite. Amer. Mineralogist (Richmond Va), 64, pp. 304—316.
WEINER, L. S. — MERSCHAT, C. E., 1978: Summary of geology between the Great Smoky Mountain fault at Parksville, Tennessee and basement rocks of the Blue Ridge at Glade Gap, North Carolina. Tennessee Div. Geol. Rept. Invs. (Nashville, Tn), 37, 86 pp.
WILLIAMS, P. F., 1972: Development of metamorphic layering cleavage in low grade metamorphic rocks at Bermagui, Australia. Amer. J. Sci. (New Haven, Conn.), 272, pp. 1—47.

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