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I am submitting herewith a thesis written by Gary A. Runyon entitled "The Distribution and Variation of Sulfide Constituents of the Great Smoky Group, Ducktown Area, Tennessee, with Respect to Metamorphic Grade." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Geology.

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THE DISTRIBUTION AND VARIATION OF SULFIDE CONSTITUENTS
OF THE GREAT SMOKY GROUP, DUCKTOWN AREA, TENNESSEE,
WITH RESPECT TO METAMORPHIC GRADE

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ABSTRACT

The metasedimentary rocks of the Precambrian Great Smoky Group in the Ducktown mining district show a Barrovian metamorphism from the chlorite zone through the staurolite zone. Modal data of sulfide distribution and abundance in these metasedimentary rocks indicate that with increasing metamorphic grade: (a) pyrite is converted to pyrrhotite and (b) total sulfide content decreases. Premetamorphic cubic pyrite grains have pressure shadows of quartz, calcite, and pyrrhotite which parallel the S_1 cleavage. A syn-metamorphic origin of pyrrhotite is suggested by the alignment of pyrrhotite parallel to S_1 and S_2 cleavages. The absence of premetamorphic pyrite in lithologies from the garnet and staurolite zones therefore implies that the transition of pyrite to pyrrhotite is complete at garnet grade conditions. Mobilization of sulfur by some metamorphic process can explain the noted decrease in average sulfide content as a function of metamorphic grade. Comparison of average ratios of major element content versus aluminum content derived from whole-rock chemical analyses of representative samples does not discern mobilization of elemental constituents during metamorphism. However, because of the large variation of ratios in each metamorphic zone, the absence of significant trends of elemental ratios

cannot be used to support or repudiate the decrease in sulfide content with increasing grade as defined by modal data. Correlation coefficient analysis of S with other major elements shows that S content is not related to the Si, Ti, Al, Fe, Mn, Mg, Ca, K, and P content in these metasedimentary rocks.

The decrease in average sulfide content between lithologies in the chlorite zone through the garnet zone can be explained by volumetric decreases caused by the transition of pyrite to pyrrhotite in a reaction of:

$$2\text{FeS}_2 + 2\text{H}_2\text{O} + \text{C} \rightleftharpoons 2\text{FeS} + 2\text{H}_2\text{S} + \text{CO}_2$$

in an open metamorphic system. The removal of sulfide constituents in the development of differentiated cleavages during prograde metamorphism can account for the decrease in average sulfide content of lithologies in the garnet zone versus lithologies in the staurolite zone. The above data indicates that S was mobile during prograde metamorphism and that significant amounts of sulfide material within the Ducktown ore deposits could have been derived by this process.

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CHAPTER I

INTRODUCTION

The Ducktown mining district is located in the southeastern corner of Tennessee and consists of eight ore bodies which have produced total tonnages in excess of 200,000,000 metric tons. These massive sulfide deposits are tabular bodies, extensively folded and relatively conformable to the highly contorted and metamorphosed enclosing host rocks of the Great Smoky Group. Mineralization, which consists of pyrrhotite, pyrite, chalcopyrite, sphalerite, and magnetite, with minor amounts of galena, gold, and silver, is commonly located along shear zones in kyanite-staurolite grade metamorphosed Ocoee rocks (Magee, 1968). Alteration zones of chloritized country rocks up to 100 meters in thickness surround the ore bodies.

The origin of these deposits has remained an enigma despite several investigations. Many workers have favored a syngenetic formation for these ore bodies, but some of the features cannot be explained by this mode of origin. A few investigators have suggested that at least a portion of the sulfides present in the ore bodies may be attributed to metamorphic mobilization of disseminated sulfides from

the country rocks. However, no systematic study of the country rocks has been undertaken either in the Ducktown area or in other areas containing similar deposits to substantiate this hypothesis.

This study has been undertaken as an attempt to better understand the relationships between silicate and sulfide assemblages during prograde metamorphism. Data from petrographic, modal, and whole-rock chemical analyses have been used to examine the mobility of sulfide constituents in relation to metamorphic grade, formations, chemical composition, and genesis of ore deposits.

CHAPTER II

GEOLOGIC SETTING

The study area occurs in rocks of the Blue Ridge Belt. This belt is bounded on the southeast by the Brevard Zone which separates the Inner Piedmont igneous and metamorphic complex from the Blue Ridge Belt (Figure 1). To the northeast, the Blue Ridge Belt terminates in a series of low-angle thrust faults along which the Blue Ridge crystalline basement was thrust over the Paleozoic sediments of the Valley and Ridge Province (Rodgers, 1953).

The Blue Ridge Belt consists of lower Precambrian gneisses and granites (not exposed in the Ducktown area), overlain unconformably by the upper Precambrian metasedimentary rocks of the Ocoee Series and the upper Precambrian/Cambrian Murphy Marble Belt (King, 1955; Hadley, 1970).

Stratigraphy

In the vicinity of Ducktown, Tennessee, the metasedimentary rocks of the Ocoee Series and Murphy Marble Belt make up the exposed stratigraphic section.

The Ocoee Series is subdivided into four Groups. These are from oldest to youngest, the Snowbird Group, the Great Smoky Group, several unclassified formations, and the Walden Creek Group, all of late Precambrian age

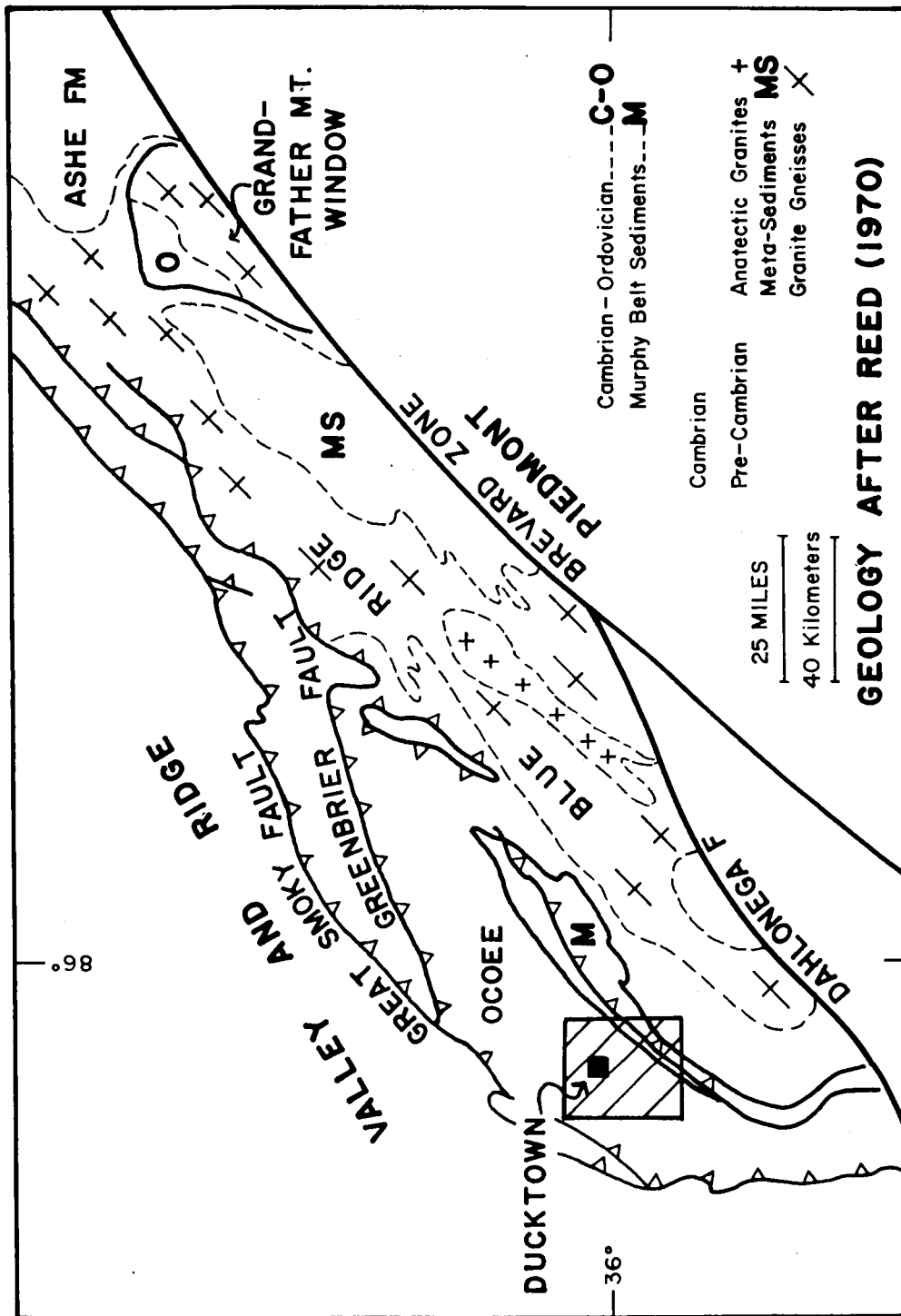


Figure 1. Location of study area in relation to major Tectonic provinces of the southern Appalachians, North America.

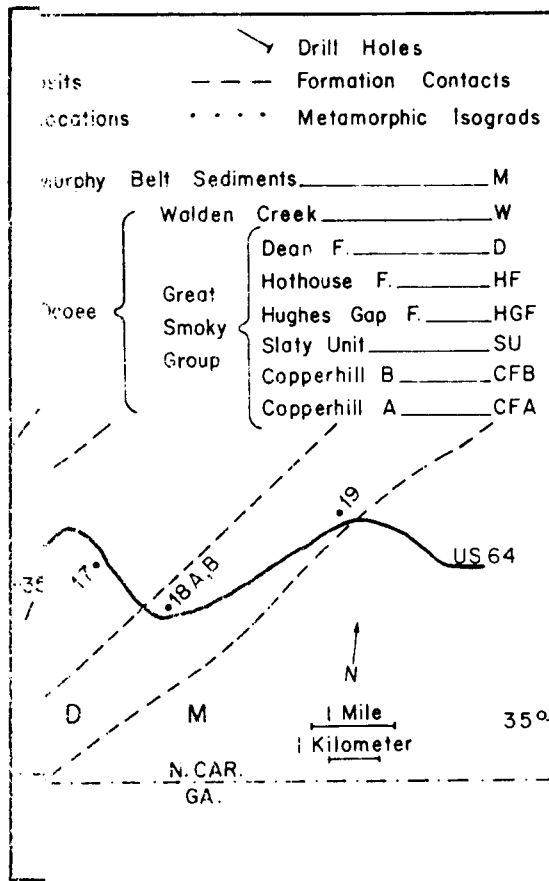
(Hadley et al., 1958). Within the study area only the Walden Creek and Great Smoky Groups are recognized.

The stratigraphy of the Ocoee Series and the Murphy Marble Belt has been studied by Hurst (1955) on the eastern side of the Ducktown region, and by Hurst and Schlee (1962), Hernon (1968), Holcombe (1973), and Weiner and Merschat (1978) on the western side of the region (Figure 2). The interpretation by Hurst (1955), Hurst and Schlee (1962), and Holcombe (1973) appears to be the most reasonable. They provide evidence for a large anticlinal structure centered around the Ducktown area (Figure 3). Formations of the Great Smoky Group are in conformable contact with the Murphy Marble Belt to the east of the Ducktown area and the Walden Creek Group to the west of the Ducktown area. The similarity of the strata of the Walden Creek Group with the lower section of the Murphy Marble Belt (Natahala Slate, Tusquitee Quartzite) and the conformable contact of both of these groups with the underlying Great Smoky Group suggests that the Walden Creek Group and the lower section of the Murphy Marble Belt are correlative (Mohr, 1973). This further supports an anticlinal structure for the Great Smoky Group in this region.

Weiner and Merschat (1978) provisionally correlate the Snowbird Group to rocks previously assigned to the Walden Creek Group by King et al. (1958), Hurst and

AGE	SERIES	GROUP	HURST 1955	HURST & SCHLEE 1962	HERNON 1968	MERSCHAT & WEINER 1978
Cambrian			Mineral Bluff Nottely Quartzite Andrews Murphy Marble Brasstown Formation Tusquitee Quartzite Nantahala Slate			Chilhowee & Sandsuck
	?					
Precambrian	Ocoee	Walden Creek		Walden Creek ? grey/green laminated Phyllite	Unit 3	Walden Creek
		Unassigned				Cades
		Great Smoky	Dean Formation	Dean Formation	Unit 2	Buck Bald
			Hothouse Formation	Hothouse Formation	Unit 1	Boyd Gap
			Hughes Gap Formation	Hughes Gap Formation		
			Copperhill Formation A	Copperhill Formation	Wehuty/Slaty Unit	Wehuty
			Copperhill Formation B		Copperhill	Copperhill
						Fault
				Not Exposed		Snowbird

Figure 2. Precambrian and Cambrian stratigraphy of southeastern Tennessee, southwestern North Carolina, and Georgia.



sograds, sample/
ng district,
ee, 1962; Hernon,

Schlee (1962), Holcombe (1973), and Hale (1974). Weiner and Merschat infer a continuation of the Greenbrier fault from the Great Smoky Mountains into the Ocoee Gorge (Figure 4). Due to the lithologic similarities between the Snowbird Group and the Walden Creek Group, they suggest that the rocks beneath the inferred thrust fault belong to the Snowbird Group. The inferred presence of the Snowbird Group led Weiner and Merschat (1978) to propose a different stratigraphic and structural interpretation for the Great Smoky Group in the Ducktown area. They suggest that formations decrease in age from west to east and that no anticlinal structure is present in this region (Figure 4).

The studies by Hurst (1955), Hurst and Schlee (1962), and Holcombe (1973), in the Ducktown region, and by Hale (1974) and Poppelreiter (1980) in areas directly north of the Ducktown area do not support the interpretation by Weiner and Merschat (1978). All of the above studies provide evidence for a conformable contact between the Walden Creek Group and Great Smoky Group and furthermore find no support in the rock fabrics for a major fault.

Structural and Metamorphic History

The structural and metamorphic history of the Ducktown area has been discussed by Carpenter (1970), Addy (1973), Holcombe (1973), and others. The Ocoee Series and the

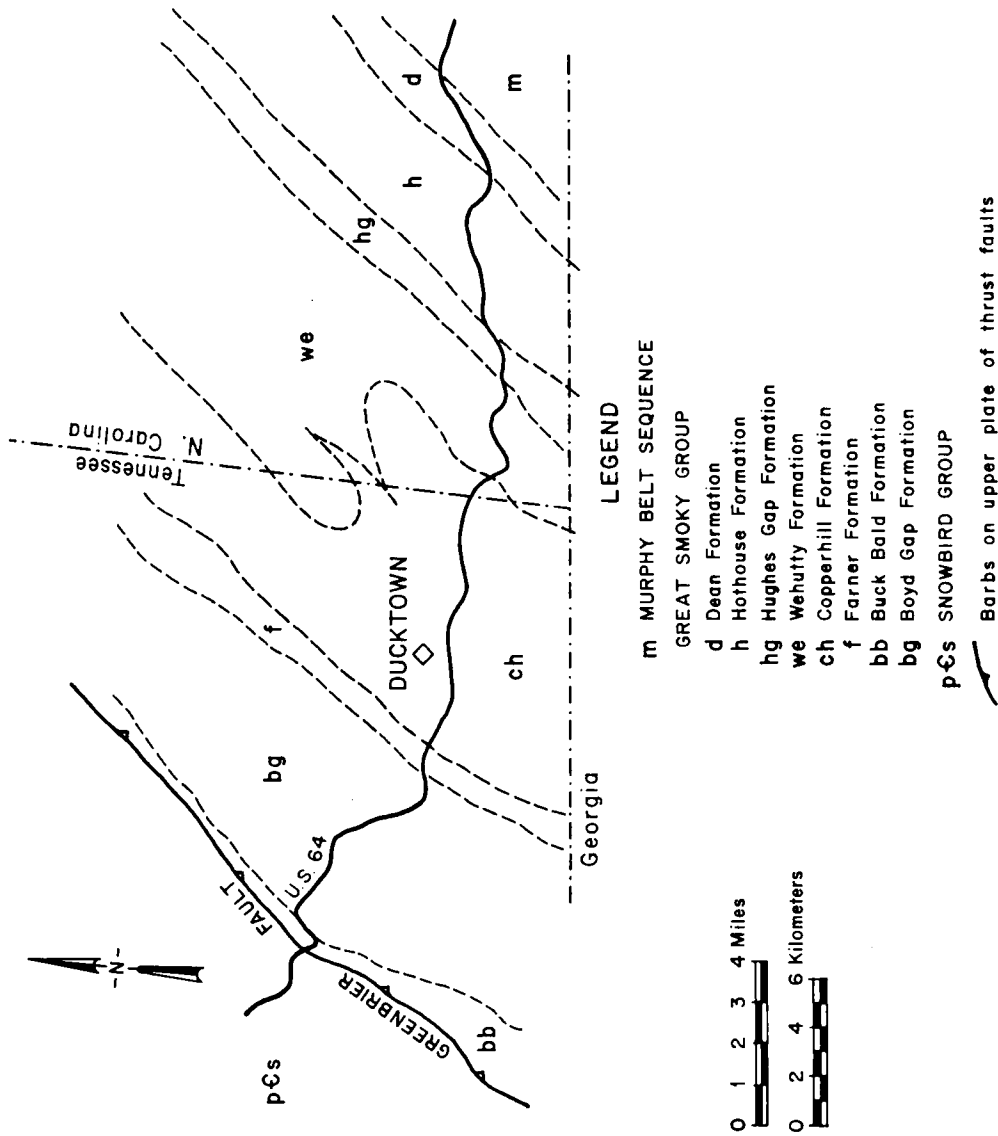


Figure 4. Provisional geological map of the Ocoee Gorge and the Ducktown mining district as proposed by Merschat and Weiner (1973) and Weiner and Merschat (1978).

Murphy Marble Belt sediments were deposited in late Precambrian to Cambrian time. During the middle to late Ordovician, a metamorphic and deformational event (F_1) moved the younger Ocoee and Murphy Marble Belt rocks northwards over the older Ocoee rocks and basement gneisses. Metamorphism attained almandine grade. The F_1 folds and faults were subsequently refolded in a later F_2 event. F_1 and F_2 are identified as the Taconic and Acadian orogenies, respectively, however F_1 and F_2 may be products of the same orogenic event (Hatcher, 1972). The metamorphic thermal peak occurred contemporaneously or slightly later than the F_2 deformation imposing the present metamorphic isograds (Figure 3, p. 7). This thermal peak reached kyanite-staurolite grade ($540^\circ \pm 40^\circ \text{ C}$, $6 \pm 1 \text{ Kb.}$, Nesbitt, 1979). A later event, during the Alleghanian orogeny, produced faulting ($F_3 - F_5$) and pervasive, retrograde alteration of staurolite, kyanite, almandine, and biotite. Figure 5 summarizes these deformational and metamorphic events.

The timing of the above metamorphic events has been documented by Dallmeyer (1975) using $^{40}\text{Ar}/^{39}\text{Ar}$ incremental release age patterns and K-Ar ages of biotite in the Ducktown ore district. The results indicate that M_1 occurred at $435 \pm 15 \text{ m.y.B.P.}$ and M_2 occurred at $372 \pm 15 \text{ m.y.B.P.}$

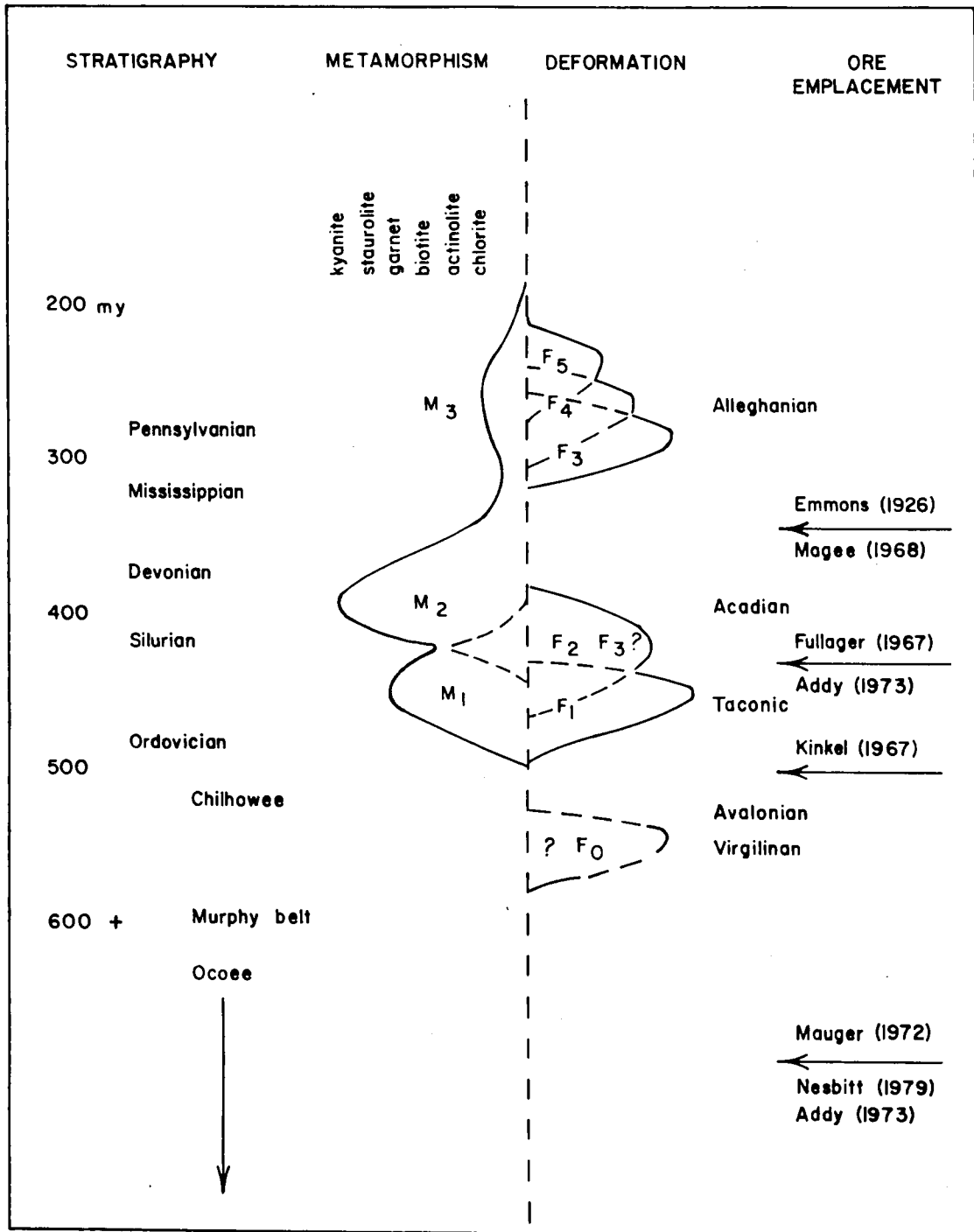


Figure 5. Schematic diagram showing deformational events, metamorphic events, and suggested times of ore emplacement (after Butler, 1972; Addy, 1973).

CHAPTER III

METHODS OF INVESTIGATION

Sampling

Samples for this study were collected from exposures along Highway 64 in southeastern Tennessee, from the western exposure of the Dean formation (Ocoee Gorge) eastwards to the contact of the Dean formation with the Murphy Marble Belt (Figure 3, p. 7). Where good outcrop exposures did not exist, drill core samples supplied by Cities Service Company 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.

Petrography

Polished thin sections (25 × 45 mm.) were prepared from representative samples from each exposure cut perpendicular to bedding or foliation. The petrography of silicate and opaque phases was determined using reflected and transmitted light microscopy.

Modal Analysis of Sulfide Constituents

Accepted point counting techniques for accurate modal analysis depend on two factors: (1) analyzed samples are not

foliated, banded, or lineated; and (2) point counting increments are larger than the phases to be counted (Chayes, 1956; Van de Plas and Tobi, 1965). Since the sulfide constituents of samples in the Ducktown region are both lineated and coarse-grained, modal analysis by conventional point counting techniques would not produce reliable results.

An alternate technique, based on the comparison of sulfide area versus whole rock area in a thin section, was used for modal analysis of sulfide constituents (Fitch, 1959; Barrett, per. comm., 1978). Modal data were determined only for pyrite and pyrrhotite, since these are the predominant sulfide phases present in the studied samples. Sulfur analysis of seven unknown and one USGS rock standard (as an internal standard) was performed using a LECO combustion furnace (courtesy of Brad Wheeler, EG&G ORTEC) to determine the reliability of this modal analysis technique. Details of the modal analysis technique used in this study are discussed in Appendix B along with a comparison of these analyses with typical point counting analyses and the LECO combustion analyses.

Whole-Rock Chemical Analysis

Thirty-eight representative samples (see Figure 3, p. 7, for locations) were prepared for X-ray fluorescence (XRF)

bulk chemical analysis using the techniques described by Wheeler (1979). Pressed powder pellets were analyzed with a EG&G ORTEC 6110 tube-excited fluorescence analyzer owned by EG&G ORTEC, Inc., Oak Ridge, Tennessee. The error of these analyses was determined by analyzing three USGS rock standards (Flanigan et al., 1969, 1976) and two South African rock standards (Russell et al., 1972) as unknowns. In Appendix A, Table A-1 lists results of duplicate analyses of these five standards and Table A-2 lists the range of differences between XRF analyses and published values for these standards. Total iron was calculated as Fe_2O_3 . Sodium, H_2O , and C were not determined. Totals reflect the absence of analyses for these elements. Systematic errors for SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , K_2O , TiO_2 , MnO , and P_2O_5 , established by the results of analyses of the above standards, were reduced in the study samples by a linear regression routine (Figure A-1). Results for CaO showed large nonsystematic deviations from published values and therefore can only be considered as semiquantitative.

XRF analyses for S showed major discrepancies when compared to results of modal analyses of sulfides and LECO combustion furnace results for these same samples. In all cases, analysed S (XRF) is significantly lower than S content determined by other means. The error in XRF analyses

for S necessitates the use of modal data for S content. To examine the possible control of other major elements on S concentration, Pearson correlation coefficients were determined using whole-rock analyses and modal S data (Barr et al., 1979).

CHAPTER IV

PETROGRAPHY

Silicate Petrography

Samples collected in this study represent the diverse lithologies produced in a turbidite depositional environment. Greywacke, argillaceous siltstones and sandstones, and conglomerates are prominent throughout the area. Some units are very carbonaceous having a sooty appearance. Calcareous-rich nodules and horizons are found in the finer-grained units, distinguished by their susceptibility to weathering. Quartz-filled fractures and veins with accessory calcite, chlorite, and sulfides are common throughout the region.

The uppermost unit of the Great Smoky Group which outcrops in the Ocoee Gorge consists of a zone of thin, argillaceous metasiltstones and metasandstones interbedded with thin greenish phyllites. Underlying these are massive metaconglomerates interbedded with metagreywacke and phyllites. These grade into a monotonous sequence of metagreywacke and mica schist with an occasional metaconglomerate unit. All formations contain representatives of all lithologic types.

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 prominent sedimentary features (graded bedding, cross-bedding, and scour channels), whereas most units from the staurolite zone retain only the crudest sedimentary features. In many cases what appears to be original sedimentary bedding is actually transposed bedding, making stratigraphic correlations much more difficult (Holcombe, 1973).

Chlorite zone. The chlorite zone is recognized by the presence of chlorite-muscovite-quartz assemblage (Figure 6), developed best in the metasilstone layers. Chlorite occurs in all samples as very fine-grained blades in the matrix and as sheaths surrounding detrital muscovite grains. Carbonate minerals are a common constituent of most samples, occurring as rhombs or as irregular, coarse-grained, reddish-brown patches in a finer-grained matrix. Microprobe analysis by Holcombe (1973) showed these to have an ankeritic composition with a small manganese component.

Detrital quartz, plagioclase, K-feldspar, and lithic grains show little recrystallization or overgrowth. Quartz has inclusions of rutile needles aligned along crystallographic directions which impart an opalescent blue coloring to the quartz grains. Feldspars occasionally show a slight sericitic alteration along twin planes.

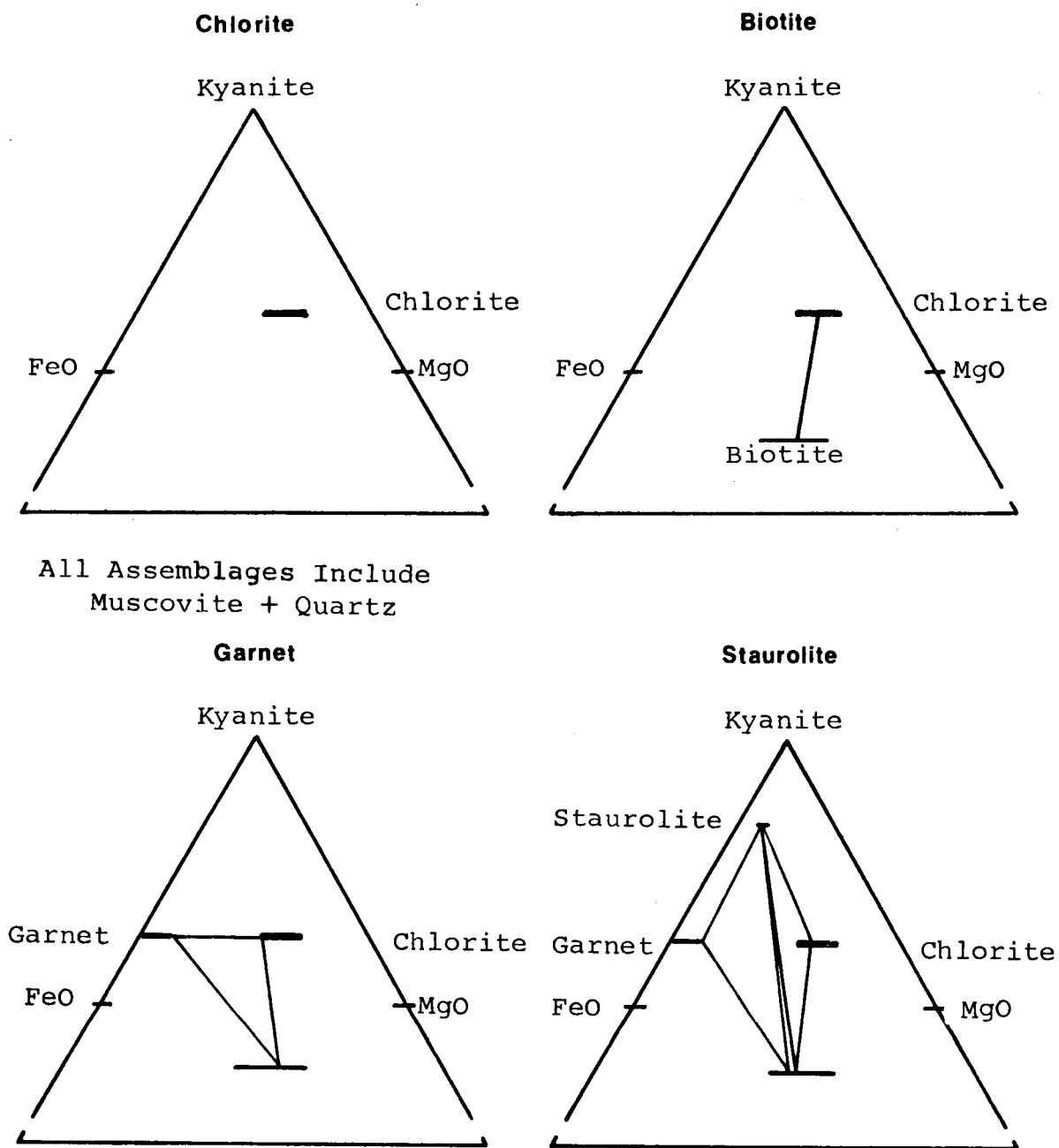
AKFM Facies Series

Figure 6. Generalized AKFM facies series defining stable metamorphic assemblages of pelitic sediments of the Ducktown area.

A marked concentration of sulfide phases is seen in the coarser-grained portion of most samples with very little sulfides, if any, seen in the finer-grained portions. The coarser-grained, more quartz-rich layers display little carbonaceous material or oxide phases, although occasional detrital ilmenite and rutile grains are seen with alteration rims of sphene. Carbonaceous material with associated detrital rutile is most prominent in the fine-grained phyllitic layers.

In the phyllitic layers a slaty cleavage, S_1 , is prominent. S_1 is offset by a later crenulation cleavage, S_2 . The coarser-grained metasiltsstones do not show a slaty cleavage, but S_1 is recognized by pressure shadows of quartz, ankerite, and pyrrhotite on pyrite grains and by lenticular patches of pyrrhotite which parallels the S_1 in the phyllitic layers (Figure 7a). S_2 is not distinguishable in the coarser-grained layers.

The metamorphic assemblages in this zone are:

(1) quartz + muscovite + chlorite + pyrite + pyrrhotite + rutile + graphite; (2) quartz + muscovite + ankerite + pyrite + pyrrhotite + rutile + graphite; and (3) quartz + muscovite + ankerite + plagioclase + pyrite + pyrrhotite + rutile + graphite.

- Figure 7. Photomicrographs and photographs of sulfide-silicate textures in the Great Smoky Group meta-sedimentary rocks, plane polarized light unless otherwise noted. Scales are shown at bottom of figure if not included in photograph. (a) Metasiltstone with lenticular patches of pyrrhotite (black) defining S_1 cleavage; chlorite zone. (b) Interlaminated phyllite/metasiltstone with concentration of sulfides (light grey) in metasiltstone layers (incident light). (c) Sulfide phases terminating at contact with phyllite. Note pyrrhotite (black, lenticular patches) parallel to S_1 cleavage. (d) Silicate phases replacing pyrite (Py) along crystallographic directions. Note embayments of silicates into pyrite, and the pyrrhotite (Po) pressure shadow on pyrite (reflected light). (e) Inclusions of chalcopyrite (Ccp), galena (Gn), and pyrrhotite (Po) in pyrite (light grey) (reflected light). (f) Irregular, metamorphic (?) pyrite (Py), aligned parallel to S_1 cleavage.

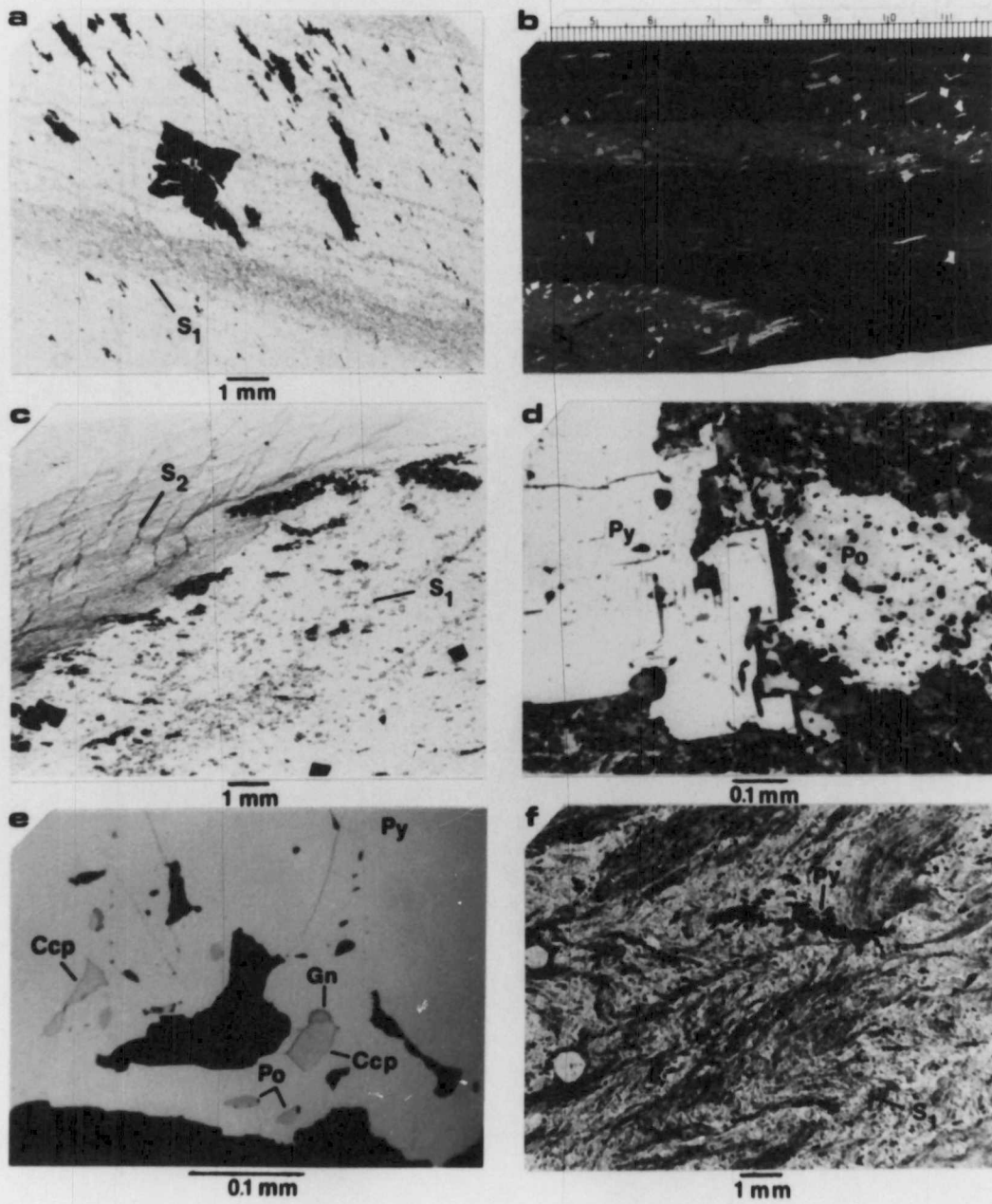


Figure 7

Biotite zone. The samples from this zone are well crystallized and display well developed schistosity due to the higher metamorphic grade. The first appearance of biotite occurs in the mica-rich edges of a differentiation crenulation cleavage attributed to the F_2 deformation, implying that biotite-grade conditions did not prevail in this region until at least the second deformation (Holcombe, 1973). The biotite isograd is shown in Figure 3, p. 7.

Conglomerates in this region exhibit a coarsening of the matrix with development of 1/2-1 mm sized muscovite and biotite grains. Detrital plagioclase shows sericitic replacement with occasional large crystals of muscovite surrounding plagioclase grains. Biotite occurs as single crystals and aggregates showing little crystallographic alignment to any of the schistositities. A few of the clastic quartz grains have been recrystallized, but most still remain relatively unaffected by the metamorphic events.

Rutile disappears from the carbonaceous laminae and ilmenite becomes the stable iron-titanium oxide phase. The ilmenite becomes quite prominent from this grade of metamorphism and shows dimensional, preferred orientation parallel to the S_1 and S_2 cleavages. It is usually found in the micaceous layers and is quite sparse in the quartz-rich layers.

Muscovite commonly develops as metacrysts in a finer-grained matrix. These are roughly oriented along S_2 cleavage directions. Biotite replaces detrital plagioclase grains, commonly extending into the feldspar along cleavage planes.

Assemblages noted in this zone are: (1) quartz + muscovite + biotite + chlorite + pyrite + pyrrhotite + rutile + graphite; (2) quartz + muscovite + biotite + ankerite + pyrite + pyrrhotite + rutile + ilmenite + graphite; and (3) quartz + muscovite + calcite + plagioclase + biotite + pyrite + pyrrhotite + ilmenite + graphite.

Garnet zone. This region displays the first occurrence of coarse-grained, biotite-garnet-muscovite schists. Sedimentary bedding is still evident with alternating beds of greywacke schists, metasandstone, and metaconglomerate in graded sets. Commonly these are very carbonaceous.

In the finer-grained greywacke schists, garnet appears as euhedral porphyroblasts associated with the M_2 metamorphism. Inclusions of quartz, biotite, ilmenite, and pyrrhotite are found in the garnet porphyroblasts. Garnet exhibits a two-stage growth reflected by an inclusion-free outer layer surrounding a sharply delineated, inclusion-ridden central portion (Spry, 1969). Some garnets are relatively free of inclusions except near the rim, which

has inclusions of pyrrhotite and ilmenite. Occasionally, garnet appears rotated. In metasandstones and metaconglomerates, garnet is found as irregular masses with ragged margins and partial crystal form.

Biotite exhibits two habits: (1) relatively small books and flakes parallel to schistosity; and (2) larger unoriented metacrysts cutting across and replacing earlier, oriented minerals. Muscovite is found in varying proportions in all but a few samples. Muscovite metacrysts are found as medium-grained sheaves of crystals in the ground mass.

Chlorite is present as a progressive phase oriented parallel to the dominant S_2 cleavage and is in textural equilibrium with biotite, muscovite, and garnet. Commonly, a late-kinematic chlorite is also present as porphyroblasts crossing the S_2 foliation. This chlorite replaces biotite and muscovite and often contains inclusions of sphene.

In the fine-grained metasedimentary rocks, quartz grains are usually parallel to schistosity, showing flattening, extension, and marginal recrystallization. Differentiation cleavage, S_1 and S_2 , are ubiquitous. Clastic feldspar grains retain their original shape but small aggregates of untwinned plagioclase overgrowths and matrix represent recrystallized material. Potassium feldspar is scarce to nonexistent in all samples. Detrital tourmaline grains are evident. These are zoned indicating partial recrystallization during metamorphism.

This metamorphic zone marks the first appearance of "calcsilicate granofels" (Hadley and Goldsmith, 1963), which is composed of coarse-grained amphibole, clinozoisite, garnet, and porphyroblasts of plagioclase. It is considered to be the metamorphic equivalent of a calcareous-rich concretion or lens (Hernon, 1968).

Assemblages from the garnet metamorphic zone include:

- (1) quartz + muscovite + garnet + biotite + chlorite + pyrrhotite + ilmenite + graphite;
- (2) quartz + muscovite + biotite + chlorite + pyrrhotite + ilmenite + graphite;
- (3) quartz + biotite + garnet + plagioclase + pyrrhotite + ilmenite + sphene + graphite;
- (4) quartz + muscovite + plagioclase + calcite + pyrrhotite + ilmenite + graphite;
- (5) quartz + muscovite + biotite + plagioclase + chlorite + pyrrhotite + ilmenite + graphite;
- (6) quartz + muscovite + plagioclase + calcite + biotite + pyrrhotite + ilmenite + graphite;
- and (7) quartz + biotite + K-spar + pyrrhotite + ilmenite + graphite.

Staurolite zone. Staurolite is found over a wide area (Figure 3, p. 7), although it is restricted to beds of favorable composition. It occurs as unoriented porphyroblasts from 0.5 mm to (reportedly) 16 cm in length commonly containing numerous quartz, garnet, and ilmenite inclusions (Hernon, 1968). Occasionally the quartz inclusions are graded in size possibly reflecting relict sedimentary

features. Staurolite metacrysts are surrounded by a zone of quartz, muscovite, and chlorite (chlorite may be retrograde). Commonly staurolite is partially to completely sericitized and chloritized, probably during a retrogressive event. For a more detailed description of staurolite occurrence and petrography, readers are referred to Emmons and Laney (1926), Hernon (1968), Hurst (1955), Hurst and Schlee (1962), Magee (1968), and Nesbitt (1979).

Garnets, common throughout the area, are more prominent in the finer-grained metasediments and sporadic in the metasandstones and metaconglomerates. All have abundant inclusions of quartz and ilmenite, and have been rotated and draped by micaceous minerals. In some samples, garnet has been partially to completely replaced by chlorite.

Biotite metacrysts are usually bent in crinkled and folded schists. Oriented and unoriented metacrysts of biotite occur in the same sample indicating different stages of formation. Occasionally, biotite is a deep brown-green color which is atypical of the medium-brown color usually present.

Metamorphic feldspar is relatively clear, lacking good cleavage or twinning. Hurst (1955) reported oligoclase to andesine compositions for feldspars in this area. Chlorite is pervasive throughout the staurolite zone, usually as a retrogressive phase. It occurs parallel to

foliation, selectively replacing biotite and muscovite and also as metacrysts crossing the foliation and replacing most silicate minerals. Zoned tourmaline grains are common in the matrix and as inclusions within chlorite and other metamorphic phases.

Ilmenite, pyrrhotite, and graphite are ubiquitous opaque phases throughout the staurolite zone. Ilmenite shows alteration to sphene in several samples. Magnetite has been reported by Nesbitt (1979) but was not observed in this study. Pyrite is found in one sample (DT-16a), but appears to be a late-stage fracture filling instead of a stable metamorphic phase.

Assemblages in the staurolite zone include: (1) quartz + muscovite + staurolite + garnet + biotite + pyrrhotite + ilmenite + graphite; (2) quartz + muscovite + staurolite + chlorite + biotite + pyrrhotite + ilmenite + graphite; (3) quartz + muscovite + plagioclase + calcite + K-spar + pyrrhotite + ilmenite + graphite; (4) quartz + muscovite + plagioclase + calcite + pyrrhotite + ilmenite + graphite; and (5) quartz + muscovite + garnet + biotite + chlorite + sphene + pyrrhotite + ilmenite + graphite.

Kyanite zone. Kyanite porphyroblasts have been found in portions of the Calloway mine near Ducktown, Tennessee, in close association with staurolite. It has also been reported by Hurst (1955) to occur along the contact between

the Hughes Gap and Hothouse formations south of the study area. Distance across regional strike between these two occurrences is approximately five miles with no known occurrence of kyanite between these two localities. From the information now available, a kyanite isograd cannot be delineated.

Figure 6, p. 18, delineates stable assemblages for metamorphic zones encountered in this study.

Opaque Petrography

Occurrence of opaque phases. The opaque phases in these samples consist of pyrite, pyrrhotite, ilmenite, and graphite with minor amounts of chalcopyrite, galena, sphalerite, marcasite, hematite, and rutile. In the chlorite and biotite zones, specific layers and beds are rich in sulfide phases. An outcrop, composed of interbedded phyllites and metasiltstone/sandstone will usually have noticeable sulfides in the coarser-grained metasiltstone/sandstone horizons with very little sulfides seen in the phyllitic beds (Figure 7b, p. 20). In rock slabs and polished thin sections, sulfide phases within a metasiltstone layer terminate abruptly at the contact with the phyllite (Figure 7c, p. 20). The concentration of these sulfides to specific beds and layers suggests control by sedimentary and diagenetic factors, such as porosity and permeability.

Within the chlorite, biotite, and garnet zone, sulfide-bearing horizons can be found in most outcrops. In the garnet zone, the concentration of sulfides to specific layers is not well developed. The contact between sulfide-bearing horizons and sulfide-poor horizons is usually gradational. There are instances where contact between sulfide-rich/sulfide-poor areas is sharply defined. When this occurs, sulfides are usually found in the coarser-grained, quartz-rich horizons.

Outcrops in the staurolite zone are noticeably impoverished in sulfides. In most cases, sulfides can be found only with great difficulty. They commonly occur as small patches in an otherwise sulfide-barren host rock. These areas appear identical to the surrounding material except for the addition of sulfide constituents. Other than the increase in metamorphic grade, lithologies from the staurolite zone are very similar to lithologies in lower grade areas. The paucity of sulfide in the high grade areas is therefore noteworthy. This observation has been supported by other studies (Hernon, 1968; Misra, per. comm., 1980).

Texture of opaque phases. Pyrite is found as individual cubes and as aggregates of small cubes which form irregular masses. The pyrite cubes usually show replacement by

quartz, muscovite, and calcite along crystallographic directions (Figure 7d, p. 20). In some samples, embayments are formed in pyrite which are filled with fine-grained quartz, micas, ankerite, and pyrrhotite (Figure 7d, p. 20). Many pyrite grains contain inclusions of pyrrhotite, galena, sphalerite, hematite, chalcopyrite, and silicate minerals (Figure 7e, p. 20).

As metamorphic grade increases, pyrite becomes more irregularly shaped occurring as lenticular masses aligned parallel to the S_1 cleavage. It envelops quartz, muscovite, and biotite grains (Figure 7f, p. 20). It is not in contact with pyrrhotite in any sample, possibly indicating non-equilibrium between the two.

In the staurolite zone, pyrite is seen filling late stage fractures and, rarely, surrounding pyrrhotite grains. When associated with pyrrhotite it appears to be an alteration product due to weathering. Pyrite is not found as a stable metamorphic phase in any sample from the staurolite zone.

Pyrrhotite is pervasive throughout the area studied. It is found as lenticular patches parallel to S_1 and S_2 cleavage. In the chlorite and biotite zone it contains inclusions of quartz, mica, and chlorite; these inclusions appear to have been engulfed by pyrrhotite at the time of its recrystallization during the M_1 metamorphic event

(Figure 8a). In samples from the garnet and staurolite zone, pyrrhotite is still seen as lenticles but these are not as irregular in shape nor as inclusion ridden as in those from the lower grade regions (Figure 8b). Occasionally in the staurolite zone, silicate phases control the shape of pyrrhotite producing an angular outline (Figure 8c).

Pyrrhotite consists of polycrystalline aggregates displaying polygonal boundaries and triple (120°) junctions indicative of annealing (Stanton, 1972). Surficial alteration along fractures and crystal boundaries to marcasite is observed in several samples.

Sphalerite is not a common phase, although small patches are found in some samples, usually associated with pyrrhotite. Inclusions of chalcopyrite in sphalerite are commonly aligned along crystallographic directions. Chalcopyrite is found as inclusions in pyrite and sphalerite grains and rimming pyrrhotite patches. Chalcopyrite and sphalerite in contact with pyrrhotite display smooth, mutual grain boundaries. Galena is rare in the meta-sedimentary rocks. It is found as inclusions, often with chalcopyrite, in pyrite grains from the chlorite zone (Figure 7e, p. 20). It was not observed in any sample from higher metamorphic zones.

Ilmenite, rare in chlorite zone rocks, becomes prevalent in the micaceous layers and laminae of the higher grade

Figure 8. Photomicrographs of sulfide-silicate textures in the Great Smoky Group metasedimentary rocks, plane polarized light. Scales are shown at bottom of figure. (a) Leaded-glass texture of pyrrhotite (black) replacing silicate minerals; chlorite zone. (b) Lenticular patch of pyrrhotite from staurolite zone. Note the more regular shape and lack of inclusions in comparison to (a) above. (c) Pyrrhotite shape controlled by silicate minerals; staurolite zone. (d) Pyrrhotite (Po) pressure shadow on pyrite (Py) parallel to S_1 cleavage; chlorite zone. (e) Chlorite (Chl) grain separated from pyrite grain (black) by quartz (Qtz) pressure shadow; biotite zone, (x-nichols). (f) Thin rim of muscovite (Ms) on pyrite grain; biotite zone.

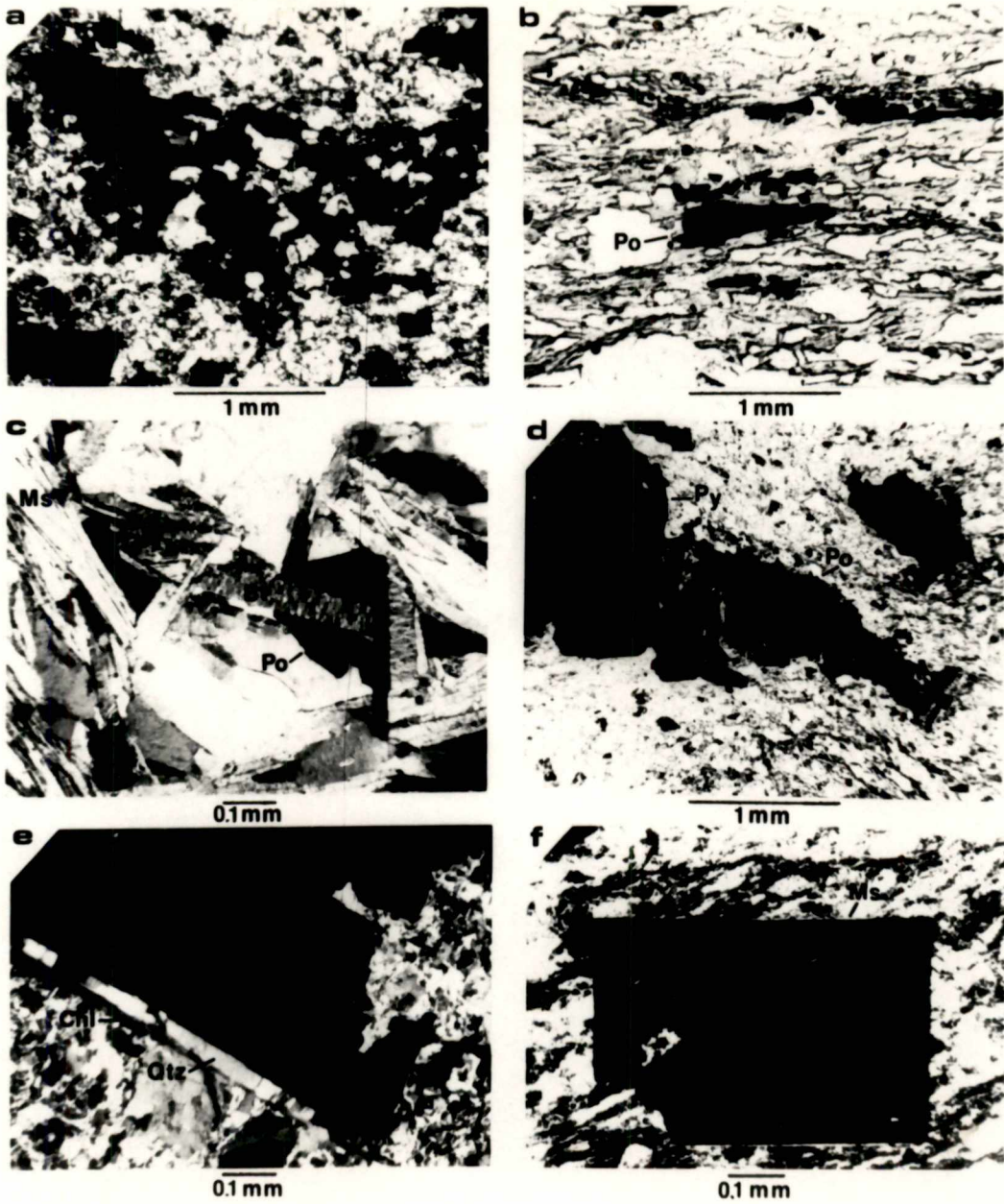


Figure 8

samples. It is found as small, ovoidal grains aligned parallel to S_1 and S_2 cleavages. In the higher grade areas, ilmenite occasionally shows boundary control by the surrounding silicate phases, losing its ovoidal character. This probably reflects recrystallization during the M_2 event. Commonly, it is rimmed by sphene, an alteration product.

Relationships of silicate minerals with opaque phases and variations with metamorphic grade. The opaque phases display several interesting features in terms of their associations with silicate phases and variations with metamorphic grade. These are listed below.

1. Pyrite cubes show quartz, calcite, and pyrrhotite pressure shadows which are parallel to the S_1 cleavage.
2. Pyrite is occasionally surrounded by muscovite and an Fe-rich chlorite.
3. Sulfide phases are usually found in the coarser-grained quartz-rich portions or are surrounded by a sheath of quartz.
4. Pyrrhotite commonly surrounds and invades detrital grains of albite and potassium feldspar.
5. Rutile is replaced by ilmenite as the stable Fe-Ti-O phase in samples above the chlorite zone of the greenschist facies.

6. Visually, ilmenite-rich samples have low sulfide content.

7. Pyrrhotite replaces ferro-magnesian silicate minerals.

Figure 9 summarizes the stable sulfide-oxide-graphite assemblage observed in each metamorphic zone.

Samples from the chlorite and biotite zones show development of pressure shadows on cubic pyrite grains. These pressure shadows are composed of quartz, calcite/ankerite, and pyrrhotite (Figure 8d, p. 32). They are aligned parallel to S_1 cleavage which indicates that these phases were mobilized during the first deformational event. It also suggests that pyrite was present prior to the first deformation, possibly as a sedimentary or diagenetic phase.

In the garnet zone, pyrite cubes disappear and pyrite is found as lenticular patches. Pressure shadows were not observed on the pyrite. This plus the fact that pyrite in this zone is aligned with the S_1 cleavage suggests that this pyrite is an M_1 metamorphic phase.

Pyrite grains occasionally show development of chlorite and muscovite rims. This feature has been observed in studies by Hale (1974) and Hall (1982). Figure 8e, p. 32, shows the growth of an Fe-rich, berlin blue, chlorite phase (Albee, 1962) parallel to the sides of the pyrite crystal. On the side of the pyrite grain lacking a pressure

STAUROLITE — KYANITE			
CHLORITE	BIOTITE	GARNET	
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+ Bt+Chl Ms+Qtz+Grt +Bt+Chl Ms+Qtz +Bt+Chl +Clz
			Fe Silicates → Low Fe Silicates

Figure 9. Distribution of sulfide-oxide-silicate assemblages observed in chlorite through staurolite zone. Assemblages in the staurolite zone displaying the transition from alteration zone into the ore zone of Ducktown deposits are from Nesbitt and Kelly (1978). The term "Carb" refers to carbonate phases of calcite and/or ankerite.

shadow, the chlorite is in contact with the pyrite. However, a separation exists between the chlorite and pyrite on the adjacent side of the crystal. It appears that the formation of the chlorite preceded the development of the pressure shadow. The formation of the pressure shadow forced the chlorite away from the pyrite. This implies that chlorite development probably occurred early in the M_1 metamorphic event whereas the growth of pressure shadows around pyrite took place later in the M_1 metamorphic event. A thin rim of muscovite around pyrite is shown in Figure 8f, p. 32. Possibly, the presence of sulfide material acts as a nucleus for the growth of silicate minerals (Hall, 1980).

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 (Figure 10a). 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. The pressure shadows on pyrite implies a premetamorphic formation of pyrite.

- Figure 10. Photomicrographs of sulfide-silicate textures in the Great Smoky Group metasedimentary rocks, plane polarized light, unless otherwise noted. Scales are shown at bottom of figure.
- (a) Pyrrhotite (black) and quartz (Qtz) pods parallel to S_1 cleavage; biotite zone.
 - (b) Pyrrhotite (black) segregated into quartz-rich, differentiated, S_1 and S_1 cleavages; garnet zone.
 - (c) Metaconglomerate, with pyrrhotite (black) surrounding and invading detrital albite (Ab) grains; garnet zone.
 - (d) Inclusions of pyrrhotite (Po) and quartz (Qtz) in albite grains; garnet zone (x-nichols). Note similar shape of the pyrrhotite and quartz inclusions.
 - (e) Replacement of biotite (Bt) by pyrrhotite (Po); staurolite zone.

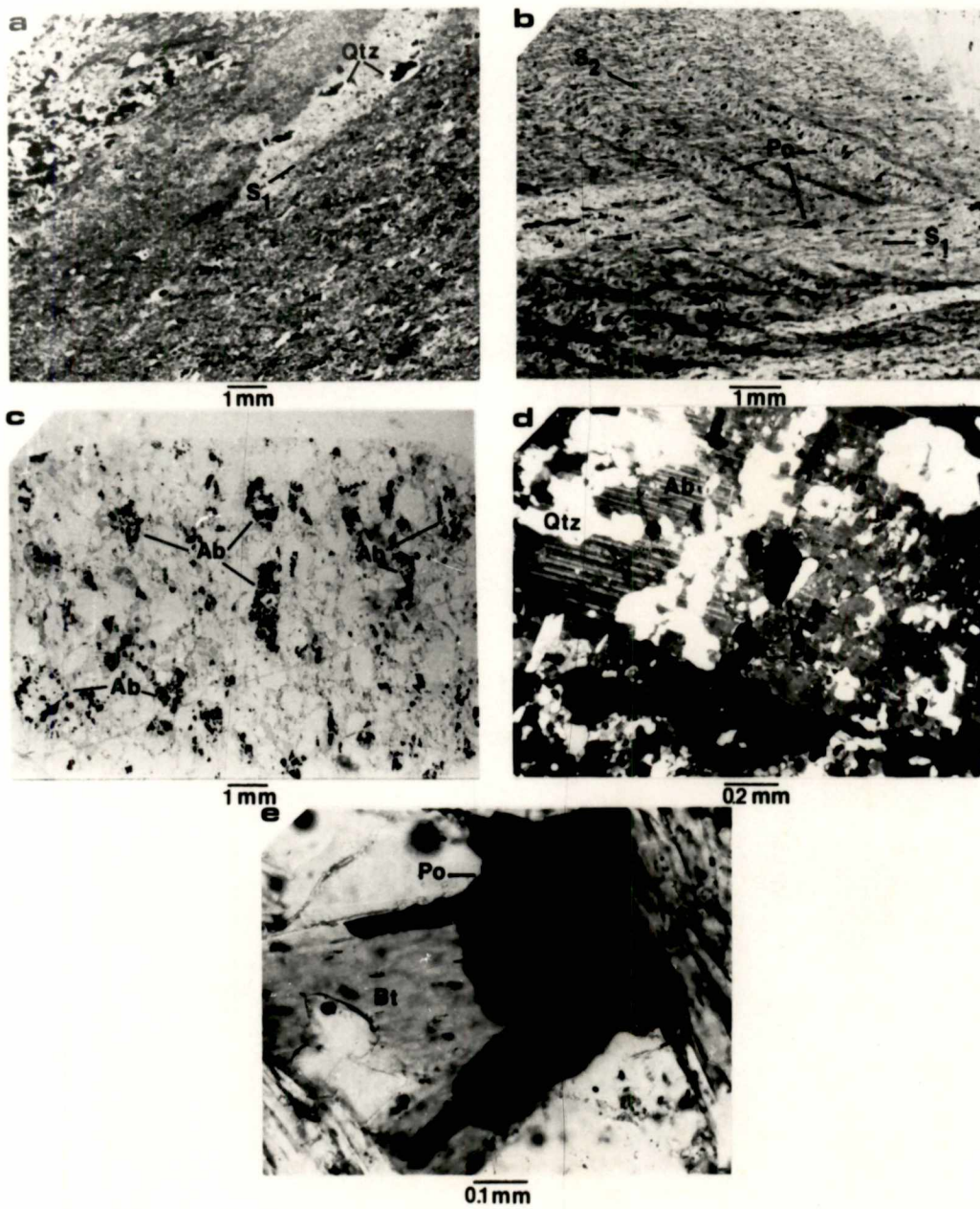


Figure 10

Samples from the biotite through staurolite zone which have differentiation crenulation cleavage show a preference for the pyrrhotite to be contained in the quartz-rich laminae (Figure 10b). The micaceous layers have ilmenite grains but very seldom sulfide grains. This indicates that sulfides are stable with quartz during metamorphism or that both phases are mobilized contemporaneously during the formation of differentiation cleavage.

In samples from the garnet zone, pyrrhotite commonly surrounds and invades detrital potassium feldspar and albite grains (Figure 10c). Albite displays a poikiloblastic intergrowth with quartz. Pyrrhotite extends into these quartz areas and inclusions of pyrrhotite and quartz in the albite have similar shapes (Figure 10d). The relationship between K-feldspar and pyrrhotite is similar to the albite-pyrrhotite association described above. The replacement type texture of pyrrhotite is not as prominent in the K-feldspar although quartz in the feldspar is embayed by pyrrhotite.

The pyrrhotite-feldspar texture is difficult to explain as no breakdown reaction for feldspar can be devised to explain the association with pyrrhotite. Possibly, the feldspar underwent supergene alteration during sedimentation which produced voids. These voids could have been filled with quartz and iron sulfides during diagenesis. Occasionally, feldspar grains in rocks from the chlorite

and biotite zones show alteration to ankerite. The resulting texture is very similar to the pyrrhotite-feldspar texture described above and suggests that iron sulfides could have replaced iron-bearing ankerite rather than the feldspars during metamorphism.

In the metasedimentary rocks of the Ducktown area, a change in the Fe-Ti-O phase with increasing metamorphic grade was first noted in an electron microprobe study by Holcombe (1973). This change, from rutile (chlorite grade) to ilmenite (biotite-garnet-staurolite grades) was also observed in this study. Samples from the biotite zone contain both rutile and ilmenite. Rutile shows ragged margins suggesting breakdown with increasing metamorphism and ilmenite becomes more prevalent with increasing grade. Visual observation suggests that samples with high sulfide content have low ilmenite content, and low sulfide-bearing samples display a higher ilmenite content. This has also been observed in some metasedimentary terranes of Japan (Banno and Kanehira, 1961). The inverse correlation between ilmenite and iron sulfides may reflect sedimentary and diagenetic factors as detrital rutile (ilmenite precursor) is more prominent in the finer-grained lithologies whereas sulfides are concentrated in the coarser-grained lithologies.

Ferro-magnesian silicates from the garnet and staurolite zones are partially replaced by pyrrhotite in several samples

(Figure 10e, p. 38). This phenomenon has been noted by others (Chinner, 1960; Fullagar et al., 1967; George, 1969). and is not an uncommon occurrence in other areas of the world. It might indicate that during and after the metamorphic formation of these ferro-magnesian silicates, sulfur reacted with these silicate minerals to produce iron sulfides and magnesium enriched silicates (Mallio and Gheith, 1972; Tso et al., 1979).

CHAPTER V

INTERPRETATION OF ANALYTICAL RESULTS

Modal Analysis

The results of the modal analysis for sulfides are summarized in Table 1. All samples with greater than 0.1% sulfide content (visual estimate) were analyzed. Evaluation of the modal data with respect to metamorphic control of sulfide content or phases requires two assumptions:

(1) that syngenetic sulfide content of all formations is relatively uniform over wide areas; and (2) pyrite is the predominant syngenetic sulfide phase (95% of total sulfide).

Studies by Hale (1974), Mohr (1972), and Poppelreiter (1980) concerning the Great Smoky Group north of the Ducktown area and by Weiner and Merschat (1978) south of the study area suggest that sulfide constituents are prominent over a wide area. Formations along strike to north and south exhibit a similar sulfide content to that observed in this study. In light of this, the first of the above assumptions appears reasonable; however it must be noted that local variations in the protolith may be present.

Many studies have shown that during sedimentation and diagenesis pyrite is the ubiquitous iron sulfide phase in

Table 1. Modal Analysis of Representative Samples from the Various Metamorphic Zones, Ducktown Mining District.

Sample	%Py	%Po	Py + Po	$\frac{\text{Py}^*}{\text{Py} + \text{Po}}$
<u>Chlorite Zone</u>				
1a	0.22 (3)	0.45 (11)	0.67 (11)	0.26 (3)
1b ③	7.02 (38)	4.61 (25)	11.63 (45)	0.60 (36)
1c ④	3.88 (22)	3.58 (22)	7.46 (31)	0.52 (20)
1d	1.80 (12)	5.64 (29)	7.44 (31)	0.18 (6)
1e	0.00	0.47 (11)	0.47 (11)	0.00
1q	0.87 (7)	0.00	0.87 (7)	1.00
1r	0.00	0.44 (11)	0.44 (11)	0.00
1v	0.58 (5)	1.58 (15)	2.16 (16)	0.21 (3)
1w ③	1.26 (9)	0.00	1.26 (9)	1.00
2b	0.84 (9)	2.76 (19)	3.60 (21)	0.13 (3)
2d ③	3.25 (9)	1.33 (14)	4.58 (24)	0.63 (19)
<u>Biotite Zone</u>				
3b	0.22 (3)	2.85 (19)	3.07 (19)	0.05 (1)
3c	0.45 (5)	3.38 (21)	3.83 (22)	0.09 (2)
4b	1.85 (12)	0.00	1.85 (12)	1.00
4c	0.21 (3)	5.61 (29)	5.82 (29)	0.03 (1)
4d	0.54 (5)	0.00	0.54 (5)	1.00
5a	0.00	0.76 (12)	0.76 (12)	0.00
5b	0.00	1.09 (13)	1.09 (13)	0.00
6b	0.00	2.50 (18)	2.50 (18)	0.00
6c	0.00	2.90 (19)	2.90 (19)	0.00
7a	0.19 (3)	1.15 (14)	1.34 (14)	0.10 (1)
7e	0.23 (3)	0.66 (12)	0.89 (12)	0.20 (3)
<u>Garnet Zone</u>				
7f	0.00	0.39 (11)	0.39 (11)	0.00
8a	0.00	2.06 (17)	2.06 (17)	0.00
8b	0.00	0.98 (13)	0.98 (13)	0.00
9a	1.42 (10)	1.52 (15)	2.94 (18)	0.48 (10)
9b	0.00	1.16 (14)	1.16 (14)	0.00
9c	0.00	1.14 (14)	1.14 (14)	0.00
9d	0.00	0.63 (12)	0.63 (12)	0.00
9f	0.00	2.30 (17)	2.30 (17)	0.00
9g ③	0.00	5.51 (28)	5.51 (28)	0.00
9h	0.00	1.50 (15)	1.50 (15)	0.00
<u>Staurolite Zone</u>				
H14,1311	0.00	0.61 (12)	0.61 (12)	0.00
H14,1371 ④	0.00	0.62 (12)	0.62 (12)	0.00
B750,2354	0.00	0.88 (13)	0.88 (13)	0.00
B750,2355	0.00	0.86 (13)	0.86 (13)	0.00
B750,2398	0.00	3.20 (20)	3.20 (20)	0.00
15a	0.00	0.66 (12)	0.66 (12)	0.00
15b	0.00	1.21 (14)	1.21 (14)	0.00
15e	0.00	1.30 (14)	1.30 (14)	0.00
16a ③ **	2.55 (15)	0.00	2.55 (15)	0.00
16b ③	0.00	0.60 (12)	0.60 (12)	0.00
17	0.00	1.17 (14)	1.17 (14)	0.00

○ - Number of replicate analyses.

() - Error in least units cited.

*Molar.

**Figure 16a represents fracture filling sulfide and is not included in the subsequent discussion.

sedimentary rocks (e.g., Berner et al., 1979). Reviews of the occurrence of pyrrhotite in sedimentary rocks conclude that while pyrrhotite is observed in marine sedimentary rocks, it is rare (Kaplan et al., 1963). Studies of the Great Smoky Group by Carpenter (1974) suggest that in low grade metamorphic rocks, pyrite is the only iron sulfide phase. Thus, the assumption that pyrite is the ubiquitous, unmetamorphosed iron sulfide phase seems justified.

In the Ducktown area, pyrrhotite is a common phase in all metamorphic zones. In order to delineate any reaction relationship between pyrite and pyrrhotite with respect to metamorphic grade, the molar ratios of pyrite/(pyrite + pyrrhotite) were calculated from modal data and plotted as a function of metamorphic grade (Ferry, 1981). This plot (Figure 11) shows a wide variation in pyrite/(pyrite + pyrrhotite) ratio, but the ratio does appear to decrease with increasing metamorphic grade. The average ratio for each metamorphic grade delineates the decrease more readily. This suggests that one or more reactions convert pyrite to pyrrhotite during progressive metamorphism.

To discern any variation of sulfide content with metamorphism, the sulfide content of each sample was plotted with respect to metamorphic grade (Figure 12). Samples from each zone display a wide range in sulfide content, as

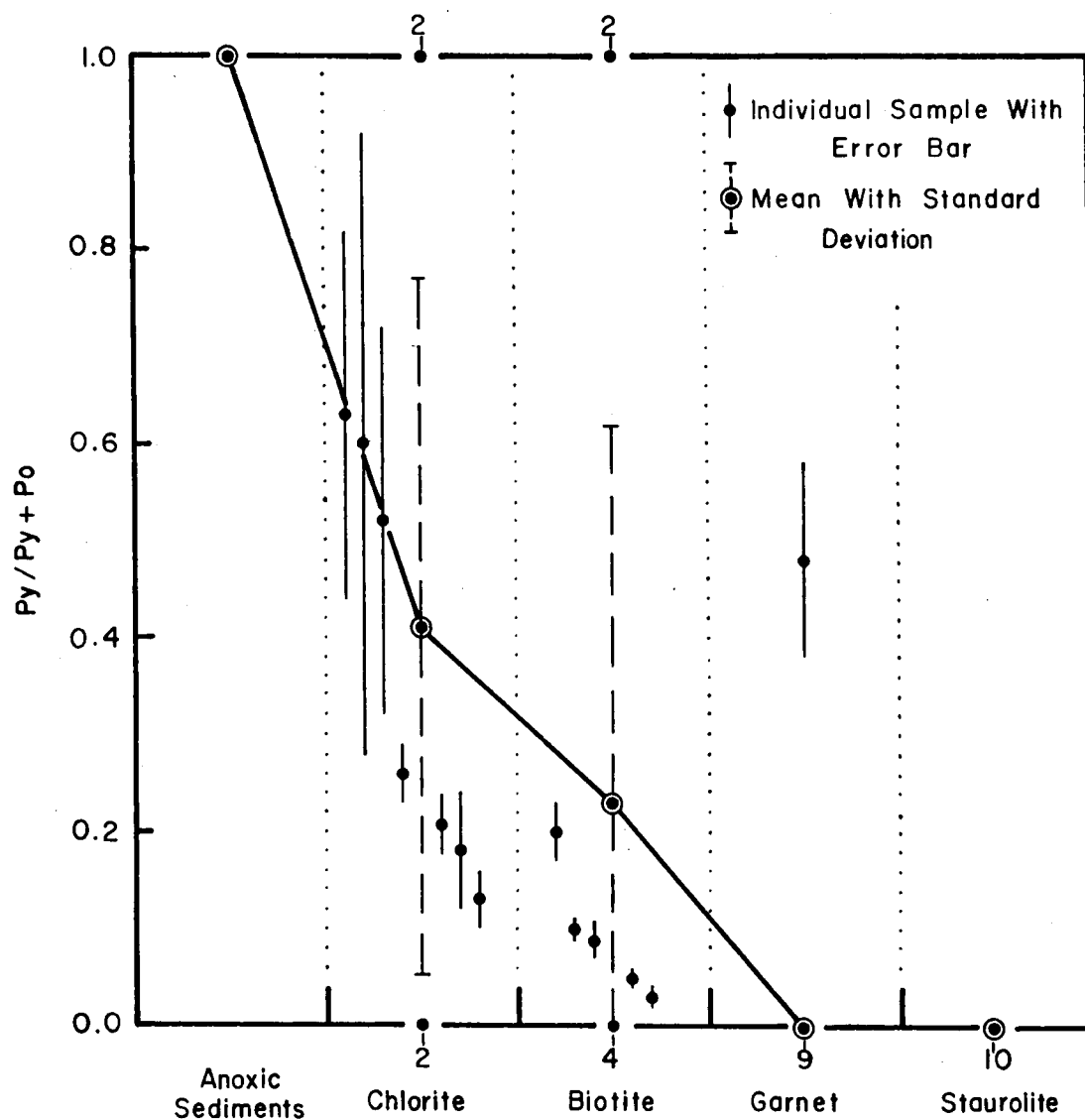


Figure 11. Variation in molar pyrite/(pyrite + pyrrhotite) ratio in metasedimentary rocks of the Ducktown area as a function of increasing grade of metamorphism. Small numbers identify the number of samples that plot at the same value, if more than one. See Appendix B for calculation of errors for individual samples.

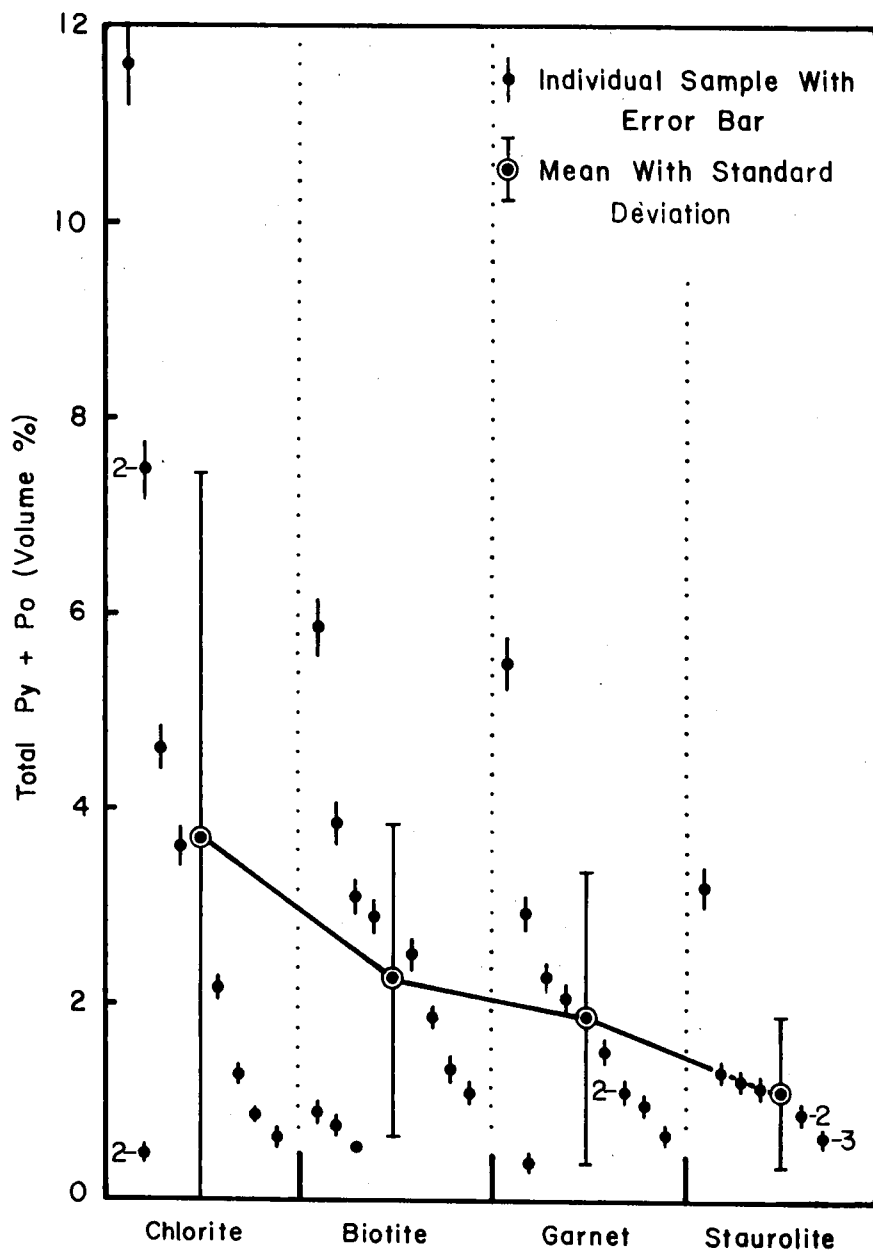


Figure 12. Variation in total sulfide content (pyrite + pyrrhotite) in metasedimentary rocks of the Ducktown area as a function of increasing grade of metamorphism. Small numbers identify the number of samples that plot at the same value, if more than one.

expressed by the large standard deviation. However, the overall trend is a decrease in sulfide content with increasing metamorphic grade. This becomes more apparent when the average for each grade is plotted. A decrease is seen from 3.7% average sulfide content in chlorite grade to 1.11% average sulfide content in staurolite grade samples. The statistical significance of differences in average Py + Po between the metamorphic zones was assessed using Student's t-test (Leabo, 1972). Differences were taken as significant if they occurred at a > 95% confidence level. Average Py + Po contents are significantly less in the staurolite zone than in the chlorite and biotite zones.

Two interpretations can be proposed to explain this decrease in sulfide content: (1) it delineates increasing syngenetic sulfide formation during the deposition of the Great Smoky Group; or (2) it reflects mobilization of sulfide constituents during metamorphism.

To test between these two interpretations, sulfide content of formations below the staurolite grade are compared with these same formations within the staurolite zone (Figure 13). If the decrease in sulfide content is a product of sedimentation, then the average sulfide content for each formation should be relatively similar regardless of the metamorphic grade. Results from Figure 13

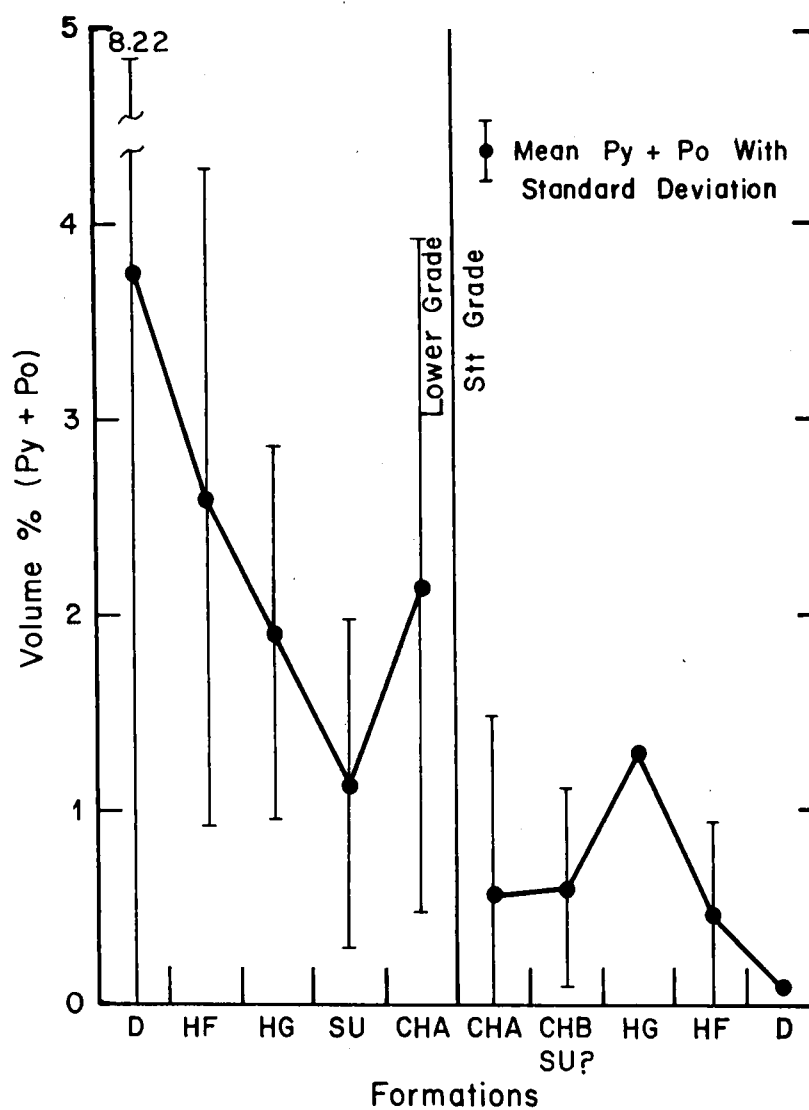


Figure 13. Comparison of average pyrite + pyrrhotite content (in percent) of formations from below the staurolite zone versus the same formations within the staurolite zone, Ducktown area.

indicate that most formations have a large variation of sulfide content as expressed by the large standard deviations. However, the average sulfide content in formations from the staurolite zone is 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. This decrease in sulfide content in the staurolite zone formations suggests that the variation in sulfide content is related to metamorphic mobilization of sulfide constituents rather than sedimentation-diagenesis. However, variation of sulfide content in the local protolith cannot be categorically denied.

If the decrease in sulfide content occurs during metamorphism, as suggested by Figure 13, there are two possible hypotheses to explain this decrease: (1) removal of sulfide constituents from the host rocks by some process; or (2) dispersion of sulfides in sulfide-rich horizons into sulfide-poor horizons (i.e., homogenization). In an effort to characterize which of the two processes may have been prevalent during metamorphism, the average sulfide content of metagreywacke, metasandstones, and metaconglomerates was plotted (Figure 14) from the chlorite-biotite zones versus the same lithologies within the staurolite zones. If the decrease in sulfide content is caused by a dispersive

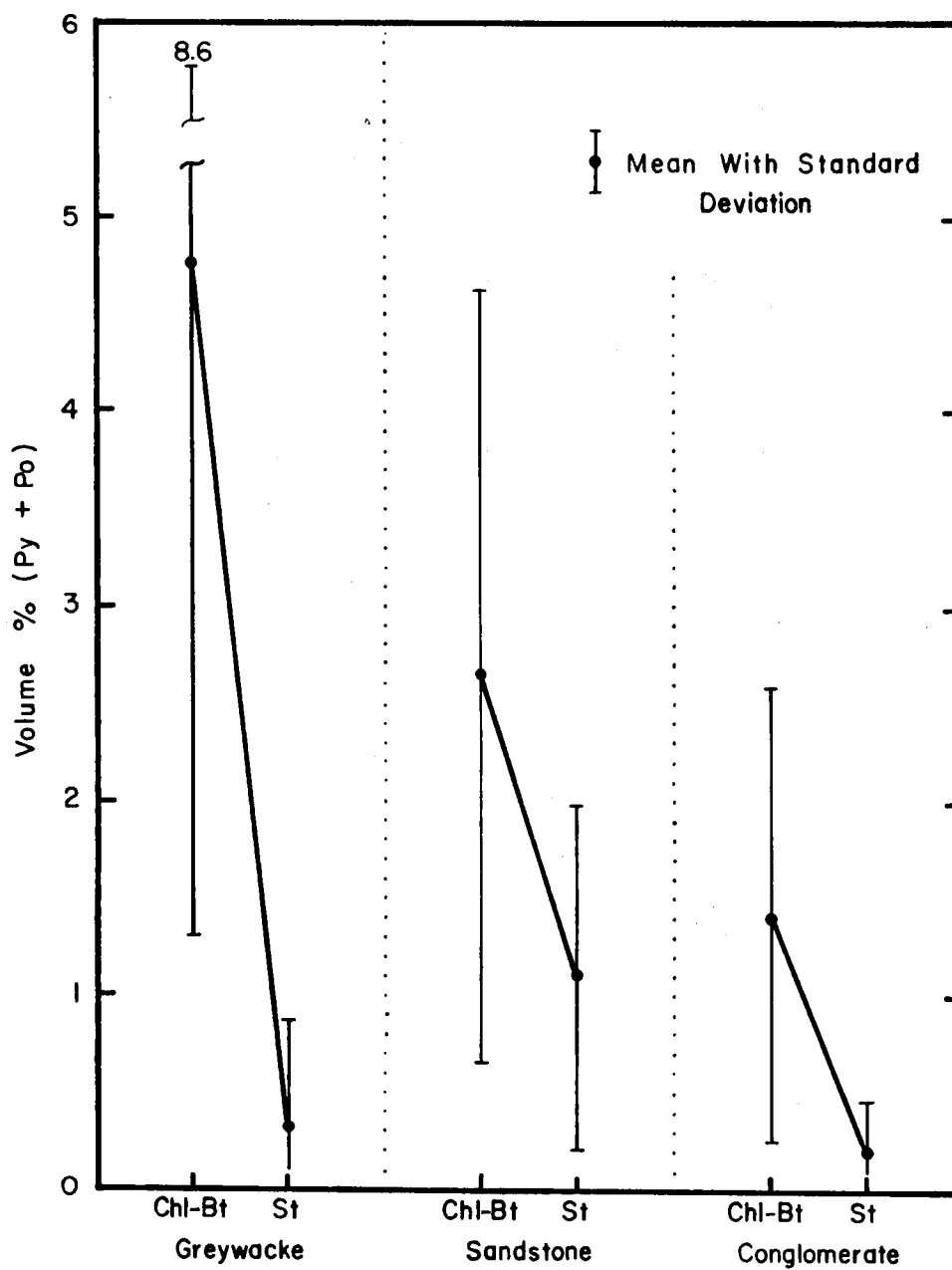


Figure 14. Comparison of the mean total sulfide content in metagreywackes, metasandstones, and metaconglomerates in chlorite-biotite zones versus staurolite zone, Ducktown area.

process, at least one of the lithologies should not display a decrease in sulfide content. If the decrease is caused by removal of sulfide constituents from the host rocks all lithologies should show a decrease in sulfide content.

Results from Figure 14 show possible decreases in sulfide content in all three lithologies. A Student's t-test of the decrease in sample means shows that in all lithologies the differences were significant at > 99% confidence limit. The conclusion is that the decrease in sulfide content is probably caused by removal of sulfide constituents from these rocks rather than by dispersion of sulfide constituents within these rocks.

Whole-Rock Chemical Analysis

Results for whole-rock chemical analysis are shown in Table 2. The large variation in whole-rock chemistry of these samples is a reflection of the wide diversity of sedimentary lithologies in the area. Using the results of the whole-rock chemical analysis, samples were plotted, with respect to lithologic type on a $Al + Fe + Ti$ versus $Ca + Mg$ (millimoles/100 mg) diagram and on a Al_2O_3 versus SiO_2 (weight %) diagram. Results are shown in Figures 15 and 16, respectively. These diagrams were constructed to determine chemically similar samples for Pearson correlation coefficient analyses and to possibly distinguish lithologic type based on the results of whole-rock chemical analysis.

Table 2. Whole-Rock Chemical Data for Representative Samples, Ducktown Mining District.

	Chlorite Zone				Biotite Zone				
	1a	1b	2d	3a	4d	4b	4c	4a	
SiO ₂	66.77(178)	61.93(187)	61.71(190)	66.20(140)	85.87(77)	51.97(297)	66.20(140)	81.19(26)	67.83(122)
TiO ₂	1.10(15)	0.93(12)	0.78(9)	2.59(40)	0.21(0)	1.05(14)	0.88(11)	0.41(3)	1.22(17)
Al ₂ O ₃	18.92(35)	17.72(54)	21.69(10)	17.31(61)	6.01(244)	17.78(53)	16.91(67)	9.34(190)	16.60(73)
Fe ₂ O ₃ *	7.44(83)	10.07(70)	4.44(99)	5.79(92)	0.39(10)	7.39(84)	4.51(2)	0.01(134)	5.10(95)
MnO	0.05(0)	0.11(3)	0.61(27)	0.04(0)	0.05(0)	0.30(12)	0.04(0)	0.02(1)	0.04(0)
MgO	2.15(19)	2.14(19)	1.50(17)	1.50(17)	0.33(13)	3.66(36)	1.23(16)	0.09(5)	1.39(17)
CaO**	0.59	0.92	0.72	0.90	0.51	5.75	0.79	0.33	0.86
K ₂ O	3.19(1)	2.35(3)	6.15(6)	4.57(3)	0.54(6)	5.26(4)	5.39(4)	1.71(4)	5.50(4)
P ₂ O ₅	0.11(22)	0.07(23)	0.07(23)	0.3(21)	0.42(21)	0.21(22)	0.22(22)	0.19(22)	0.18(22)
Sum	96.23	96.24	97.98	99.20	94.33	93.37	96.17	93.29	98.72
S***	3.73(19) ^a	5.95(19) ^a	1.58(13)	<0.10	0.29(3)	1.15(19) ^a	1.97(19) ^a	<0.10	0.57(5)
	Biotite Zone				Garnet Zone				
	6a	7a	8a	8b	9a	9b	9g	9h	
SiO ₂	56.15(251)	79.52(12)	62.86(180)	70.29(95)	62.00(186)	77.30(17)	73.61(58)	63.40(171)	74.38(49)
TiO ₂	1.09(15)	0.48(4)	0.80(10)	0.72(8)	0.87(11)	0.54(5)	0.56(6)	0.92(12)	0.57(6)
Al ₂ O ₃	23.02(31)	11.29(160)	17.52(60)	12.70(136)	19.29(29)	9.62(185)	10.01(179)	19.99(134)	10.44(172)
Fe ₂ O ₃ *	9.90(71)	1.80(112)	7.87(80)	1.92(111)	5.97(91)	3.02(106)	1.54(113)	7.33(85)	2.80(107)
MnO	0.05(0)	0.02(1)	0.09(2)	0.29(12)	0.13(4)	0.38(16)	0.29(12)	0.11(3)	0.23(9)
MgO	2.58(20)	0.34(13)	1.55(17)	0.48(13)	1.67(17)	0.07(12)	0.19(13)	1.60(84)	0.57(24)
CaO**	1.12	0.36	1.41	4.01	1.64	1.91	5.18	1.56	1.24
K ₂ O	6.55(7)	2.52(2)	4.09(1)	1.17(5)	4.75(3)	0.42(6)	0.42(6)	5.09(4)	0.92(5)
P ₂ O ₅	0.50(20)	0.28(21)	0.30(21)	0.33(21)	0.28(21)	0.37(21)	0.28(21)	0.20(22)	0.25(22)
Sum	100.96	96.61	96.49	91.91	96.60	93.63	92.08	100.20	91.40
S***	<0.10	0.51(7)	0.80(7)	0.38(5)	1.48(19) ^a	0.45(5)	2.01(19) ^a	0.59(6)	0.25(5)
	Staurolite Zone								
	10a	10b	H14,1311	H14,1371	B750,2355	B750,2398	11a	E1900,2765	
SiO ₂	40.98(419)	47.32(349)	75.97(32)	80.40(17)	64.99(153)	56.55(247)	78.80(30)	75.14(41)	54.20(273)
TiO ₂	1.19(16)	1.21(17)	0.72(8)	9.82(1)	1.04(14)	1.01(34)	0.93(12)	1.04(14)	1.21(17)
Al ₂ O ₃	20.66(7)	21.83(12)	11.14(161)	9.12(202)	13.82(117)	18.75(38)	10.31(174)	12.02(147)	26.50(88)
Fe ₂ O ₃ *	23.54(2)	19.54(22)	2.95(114)	3.63(103)	8.09(80)	11.03(65)	2.63(108)	3.78(102)	8.44(78)
MnO	0.54(24)	0.46(20)	0.09(2)	0.11(3)	0.11(3)	0.11(3)	0.05(0)	0.05(0)	0.09(2)
MgO	6.05(32)	3.23(23)	1.69(18)	1.07(15)	3.76(24)	3.77(24)	0.42(13)	0.94(15)	1.76(18)
CaO**	0.52	0.63	0.98	0.57	1.03	1.20	0.33	0.44	1.06
K ₂ O	1.80(4)	3.46(0)	2.64(2)	1.82(3)	2.28(2)	4.20(2)	2.51(3)	2.70(2)	7.76(9)
P ₂ O ₅	0.07(23)	0.10(22)	0.23(22)	0.25(22)	0.25(22)	0.25(22)	0.18(22)	0.36(21)	0.18(22)
Sum	95.35	97.78	96.41	97.79	95.37	96.87	96.16	96.47	101.20
S***	<0.01	<0.01	0.24(5)	0.24(5)	0.34(5)	1.12(19) ^a	<0.10	<0.10	<0.10
	Staurolite Zone								
	14a	15b	15c	15a	16a	16b	17	18a	
SiO ₂	78.39(5)	58.27(228)	54.06(274)	59.07(219)	45.65(368)	68.72(112)	62.36(183)	72.77(67)	
TiO ₂	0.60(6)	1.05(14)	1.31(18)	1.24(17)	1.25(17)	0.70(8)	0.92(12)	1.00(13)	
Al ₂ O ₃	9.82(182)	17.75(54)	22.71(26)	19.67(23)	26.61(89)	13.74(119)	18.96(34)	13.57(121)	
Fe ₂ O ₃	2.23(110)	11.29(64)	13.23(54)	11.52(63)	11.51(63)	4.95(96)	7.91(81)	4.95(96)	
MnO	0.04(0)	0.09(2)	0.15(5)	0.25(10)	0.15(5)	0.07(1)	0.05(0)	0.07(1)	
MgO	0.50(14)	3.28(23)	2.83(21)	2.45(20)	2.77(22)	1.51(17)	2.77(19)	0.96(15)	
CaO**	2.53	1.66	1.80	1.62	3.29	1.23	1.42	0.75	
K ₂ O	3.56(0)	4.39(2)	5.38(4)	4.48(2)	6.45(7)	1.62(4)	5.93(5)	3.24(0)	
P ₂ O ₅	0.56(20)	0.30(21)	0.31(21)	0.21(22)	1.11(17)	0.12(22)	0.25(22)	0.21(22)	
Sum	98.23	98.08	101.78	100.51	98.79	92.66	100.57	97.52	
S***	0.14(1)	0.47(5)	0.10(1)	0.26(5)	1.38(8)	0.23(5)	0.46(6)	<0.10	

*All Fe as Fe₂O₃.**Absolute error is $\pm 3\%$ for CaO.

***S computed from modal analysis.

() Absolute error in least units cited.

^aLECO titration analysis for S values.

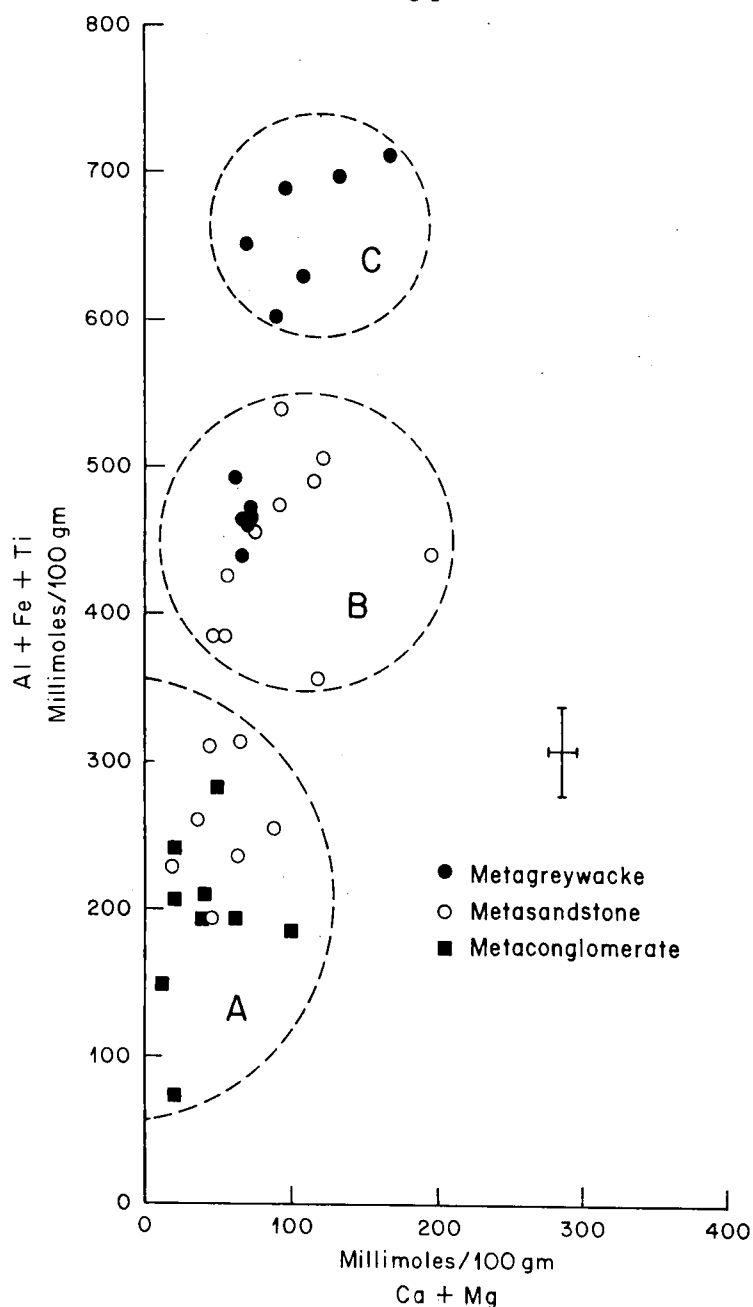


Figure 15. Plot of Al + Fe + Ti versus Ca + Mg (millimoles/100mg) allowing the grouping of metasedimentary rocks based on Al, Fe, Ti, Ca, and Mg contents. Error bars represent the largest calculated absolute error for (Al + Fe + Ti) and (Ca + Mg).

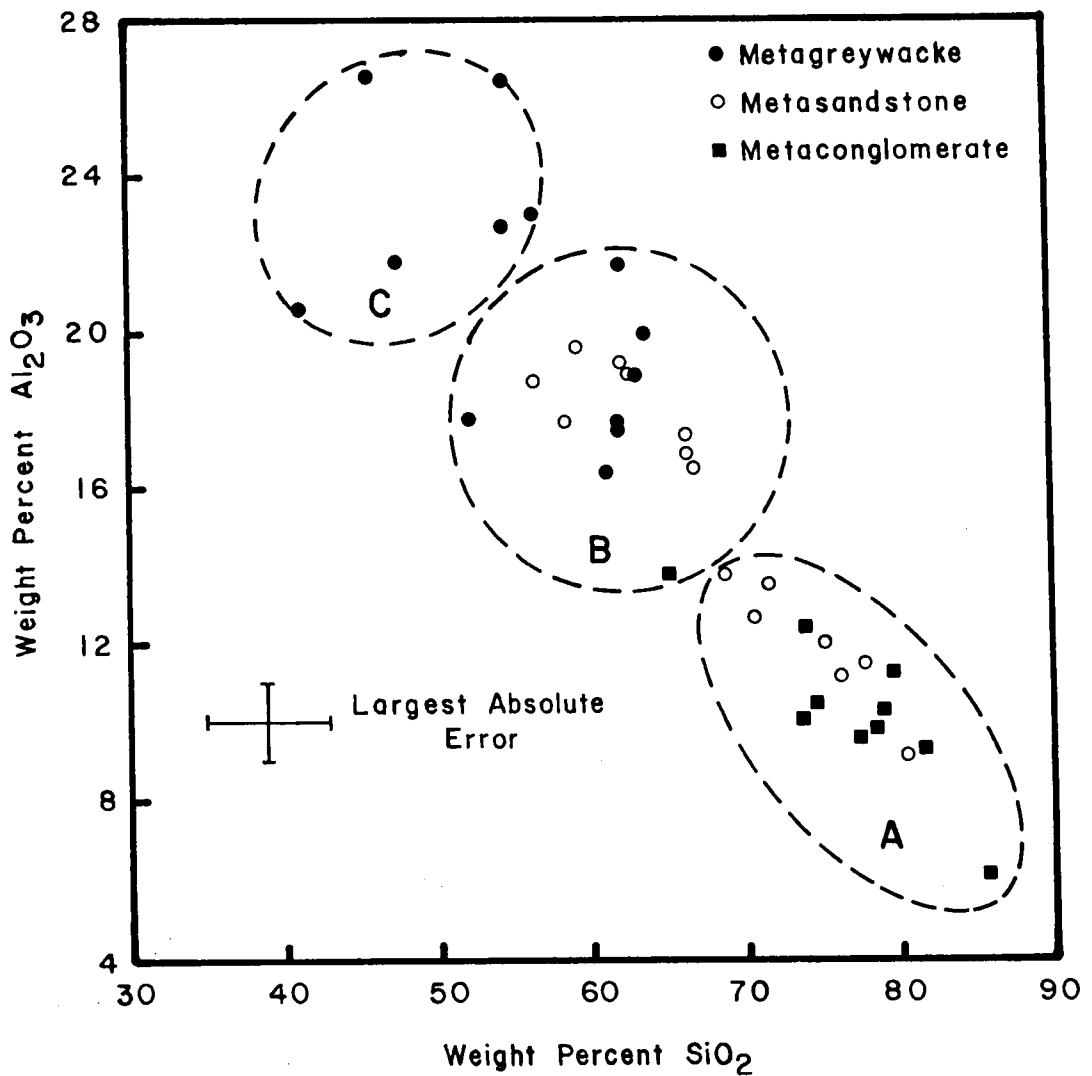


Figure 16. Plot of Al_2O_3 versus SiO_2 (wt. %) allowing grouping of metasedimentary rocks based on Al_2O_3 and SiO_2 contents. Error bars represent the largest measured absolute error for Al_2O_3 and SiO_2 .

Figure 15 shows a pronounced change in the Al + Fe + Ti content of samples with respect to lithologic type. Metaconglomerates and coarse-grained metasandstones contain the lowest amount of Al + Fe + Ti content. As the grain size of these samples decreases from metasandstone to meta-greywackes (shales, mudstones, phyllites) there is a corresponding increase in Al + Fe + Ti content. However, the overlaps of these lithologic types with each other does not allow the discernment of specific lithologies based on the Al + Fe + Ti/Ca + Mg plot, except on a broad scale. Results of Figure 15 also show that the range in Ca + Mg content of analyzed samples is relatively small compared to the Al + Fe + Ti and that these samples probably do not contain a significant carbonate component.

The lithologic trends in Figure 16 are similar to those in Figure 15. In Figure 16, the coarse-grained sediments have high SiO₂ contents with corresponding low Al₂O₃ contents. Generally, as the grain size of a sample decreases, the SiO₂ content decreases and the Al₂O₃ content increases. The overlaps of lithologic types in Figure 16 discourage the classification of samples into specific lithologies based on their SiO₂ and Al₂O₃ contents. However, the results of Figures 15 and 16 allow the discrimination of three chemically similar groups (Type A, B, C) based on Si, Al, Fe, and Ti contents. Type A rocks contain less

than 340 millimoles/100 mg of Al + Fe + Ti, have a SiO_2 content which ranges from 65 to 86 weight% (wt.%), and have a Al_2O_3 content from 6 to 13.75 wt.%. Type B samples have Al + Fe + Ti content between 360-450 millimoles/100 mg. These rocks contain 13.8-21.7 wt.% Al_2O_3 and 56.5-68 wt.% SiO_2 . Samples with a Al + Fe + Ti content above 600 millimoles/100 mg, a SiO_2 content less than 56.2 wt.%, and a Al_2O_3 content above 20.6 wt.% are classified as Type C rocks.

Consideration of the major oxide contents between Type A, B, and C samples shows that the difference in other elements besides Si, Al, Ti, and Fe supports this classification. Specifically, the average MnO , K_2O , and MgO contents systematically increase between samples from Type A to Type C while the average CaO and P_2O_5 contents do not show any appreciable differences between the three groups.

Correlation coefficients. The correlation coefficients, r , for (X, Y) pairs of elemental data for samples in the Ducktown area were determined for the least squares linear regression of those pairs. Modal data for S content was used where available. Table 3 shows the correlation coefficients of all analyzed elements versus S for all samples, for the three lithologic types (metagreywacke, metasandstone, and metaconglomerate), and for the three chemically similar

Table 3. Correlation Coefficients of All Elemental Analyses (XRF) with Sulfur.*

	Msd ^a S	Mgk ^b S	Mss ^c S	Mcg ^d S	A ^e S	B ^f S	C ^g S
SiO ₂	-0.08	0.38	-0.38	0.03	-0.14	-0.03	-0.26
TiO ₂	-0.15	-0.44	-0.22	-0.21	-0.27	-0.23	0.27
Al ₂ O ₃	0.09	-0.31	0.41	-0.17	-0.14	0.13	0.65
Fe ₂ O ₃	-0.06	-0.35	0.14	-0.23	-0.28	0.02	-0.31
MnO	0.12	-0.04	-0.10	0.55	0.51	-0.08	-0.29
MgO	-0.05	-0.29	0.15	-0.25	-0.33	-0.09	-0.20
CaO	0.26	0.07	0.01	0.79	0.73	-0.17	0.92
K ₂ O	-0.02	-0.23	0.44	-0.40	-0.50	-0.49	0.34
P ₂ O ₅	-0.10	-0.04	-0.08	-0.18	0.05	-0.70	0.94

^aMetasedimentary rocks, 38 samples.

^bMetagreywackes, 13 samples.

^cMetasandstones, 16 samples.

^dMetaconglomerates, 9 samples.

^eType A metasedimentary rocks, 16 samples.

^fType B metasedimentary rocks, 16 samples.

^gType C metasedimentary rocks, 6 samples.

*Sulfur values computed from modal data. All other elements were determined by XRF.

groups from Figures 15 and 16, pp. 54-55 (type A, B, C). The correlation coefficients matrix for all elemental pairs is given in Appendix A. Results are considered significant if they correlate above 0.90. The results of the correlation coefficients matrix show that S does not correlate with any of the measured elements in any group with the exception of CaO and P_2O_5 in type C rocks. If sulfide content is controlled by any of the major elements it cannot be discerned using whole rock analysis. In the case of type C rocks, all samples but one (16A) have a sulfide content which is below the minimum detectable limit of the modal analysis technique. In order to satisfy certain parameters of the correlation coefficients matrix program, samples with any visible sulfides under 160 $\times$ magnification (reflected light) were assigned a value of 0.10% S. Those samples with no visible sulfides were assigned a value of 0.01% S. The correlation of S with CaO and P_2O_5 is considered to be coincidental and does not appear to have any significance. The lack of correlation between S and Fe_2O_3 indicates that a considerable portion of total iron is distributed between ferro-magnesian silicates, titanium-oxide phases, and possibly carbonates.

The observation that sulfides are associated with quartz-rich layers and lamellae (Chapter IV) is not supported by the SiO_2 versus S correlation coefficients.

However, since bulk chemical analyses include both quartz-rich and mica-rich domains, the correlation of quartz and sulfides would not be discerned. Also, since Si is found in most other minerals besides quartz, bulk chemistry would probably not be able to distinguish this association.

Aluminum normalized atomic ratios. In order to compare the composition of metamorphic rocks from different zones, some basis for comparison must be established. Previous studies (e.g., Thompson, 1975; Ferry, 1983) have used a constant aluminum reference frame based on the small solubility of Al in aqueous fluids. This small solubility implies relatively little mass transport of aluminum during metamorphic and hydrothermal events. This aluminum-based reference frame was therefore used in this study to delineate any movement of analyzed elements with respect to metamorphic grade. The ratios of the atomic concentration of major elements to that of Al were calculated for each analyzed sample. These ratios were averaged for all samples from each zone and plotted in Figure 17. The Ca to Al ratio was not calculated for any sample due to the large inherent error of CaO analyses. Sulfur content was computed from modal data. Figure 17 shows that there is no systematic change of Si/Al, Ti/Al, Fe/Al, Mg/Al, K/Al, Mn/Al, P/Al, or S/Al with increasing grade of metamorphism.

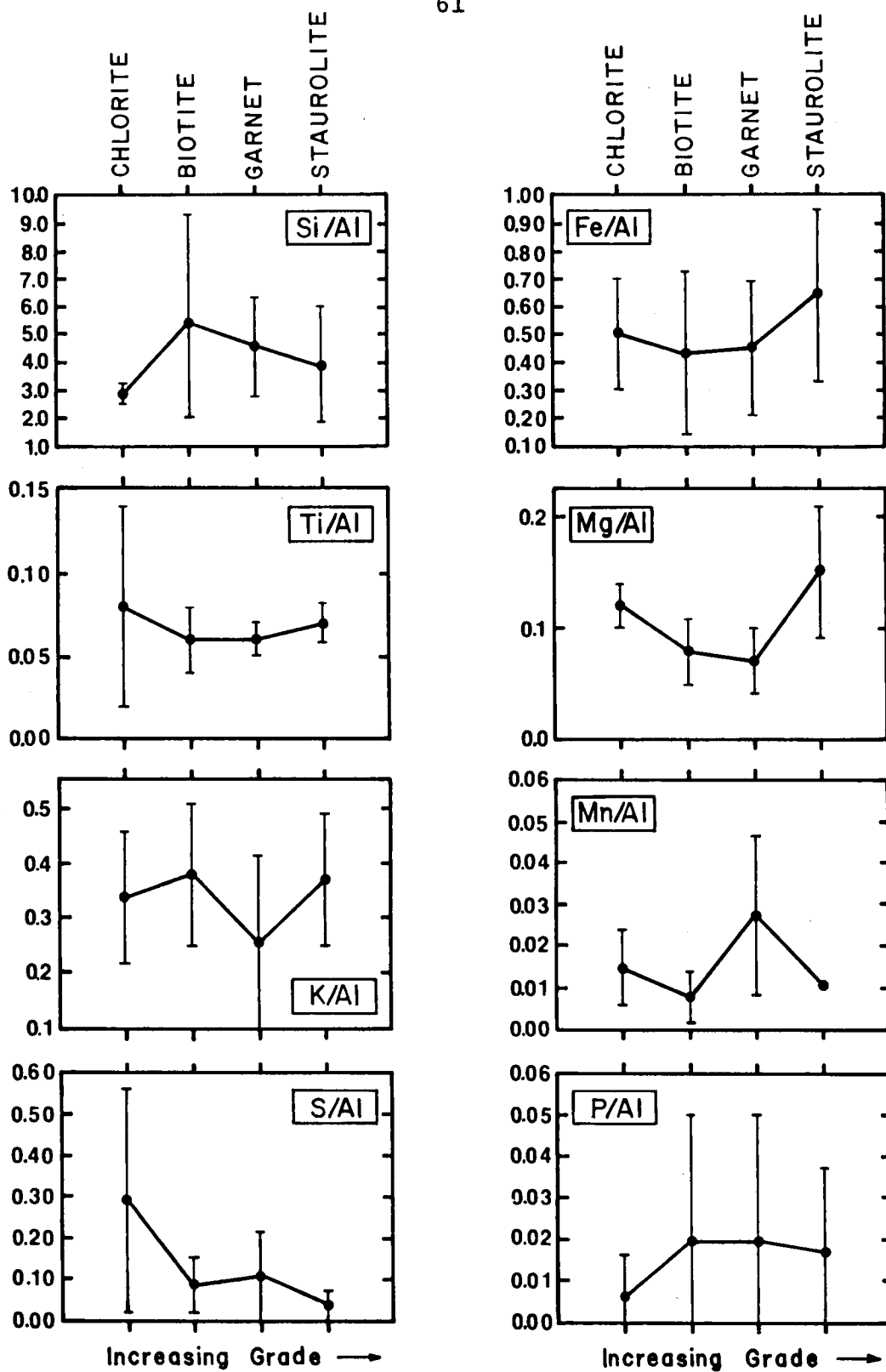


Figure 17. Average aluminum normalized atomic ratios for metasedimentary rocks in each metamorphic zone.

The statistical significance of differences in average ratios between metamorphic grades was assessed using the Student's t-test (at the 98% confidence level). Average Si/Al, Fe/Al, Ti/Al, Mg/Al, K/Al, Mn/Al, S/Al, and P/Al in the biotite, garnet, and staurolite zones are not different from corresponding values in the chlorite zone at more than a 95% confidence level. If little or no transport of aluminum occurs during metamorphism, the lack of significant differences of ratios between metamorphic zones indicates that mass transport of the above elements did not occur during metamorphism. Although there is no evidence for mass transport of the above elements it cannot necessarily be inferred from the data that these elements were absolutely immobile during metamorphism. Since the standard deviations average approximately 50% or greater of the mean in each zone, mass transport could occur if it was limited to less than approximately 50% of the amount of the element initially present within the rocks. Consequently, the large standard deviations do not allow the discrimination of small scale mass transport of the measured elements. Large scale mass transport during metamorphism (> 50% relative to the original amount) did not occur.

The lack of a significant decrease in means of the S/Al ratio with increasing metamorphism does not support

the decrease of sulfide content with increasing metamorphism as defined by modal data. However, the standard deviations of the ratios, which average 97% relative to the means, would not discriminate even large scale mass transport of sulfur during metamorphism. The S/Al ratios, in this case, cannot be used to support or repudiate the change in sulfide content which was delineated in Figure 12, p. 47.

CHAPTER VI

DISCUSSION

Any interpretation of data obtained in this study must account for several features: (1) the transition of pyrite to pyrrhotite with progressive metamorphism; (2) the decrease in sulfide content with increasing metamorphic grade; and (3) the association of sulfides with quartz-rich layers and lamellae. The above must also be evaluated with regard to the genesis of the Ducktown massive sulfide deposits.

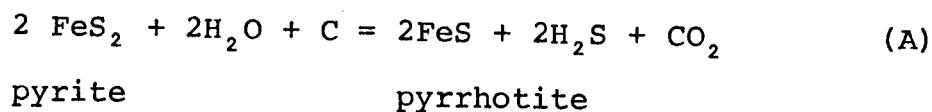
The transition of pyrite to pyrrhotite with increasing metamorphic grade observed in this study has also been noted in other studies (Kanehira, Banno, and Nishida, 1964; Guidotti, 1967; Thompson and Norton, 1968; Mohr, 1972; Holcombe, 1973; Carpenter, 1974; Nesbitt, 1979; Nesbitt and Kelly, 1980). These studies show that during prograde metamorphism, the formation of pyrrhotite from pyrite may be a relatively common occurrence in Precambrian massive sulfide deposits and metasedimentary rocks.

Experimental studies by Toulmin and Barton (1964) demonstrated that with increasing temperature, fS_2 and fO_2 vary together and that the presence of graphite restricts fO_2 and fS_2 to values within the stability field of pyrrhotite. Lambert (1973) showed that pyrite with carbonaceous

material and water decomposed at approximately 355°C to form pyrrhotite with the concomitant liberation of S.

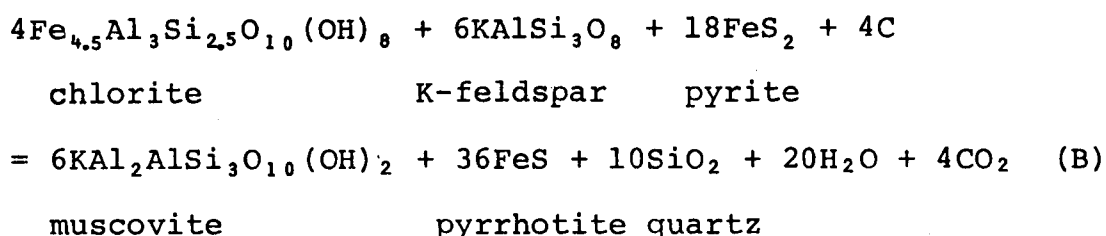
It appears in many instances that pyrite is not a stable phase during progressive metamorphism. The decrease in fO_2 and fS_2 with increasing metamorphism causes pyrrhotite to become the stable iron-sulfide phase (Taylor, 1970). This loss of pyrite with the formation of pyrrhotite can be represented by several different reactions which could occur during metamorphism. Since Figure 11, p. 46, documents that the change from pyrite to pyrrhotite occurs between the chlorite and garnet zones, the reactions considered are for the transition from chlorite to biotite zones and from biotite to garnet zones.

An example of a reaction which could occur in both the chlorite and biotite zones for an open-system with respect to sulfur may be represented by the reaction:

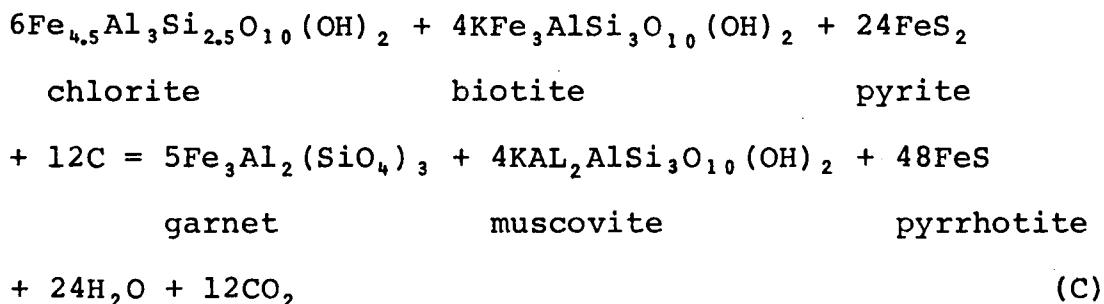


Consequences of reaction (A) are : (1) exactly one mole of pyrrhotite forms for every mole of pyrite consumed; and (2) whole rock sulfur contents decrease as the reaction progresses. Reactions of type (A) have been proposed by Ferry (1981).

Reactions which represent progressive metamorphism from chlorite to biotite zone and biotite to garnet zones in a closed-system with respect to sulfur are shown below by reactions (B) and (C), respectively. To simplify the system, ideal compositions for silicate and sulfide phases have been used (Labotka, per. comm., 1983).



and



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. It must be noted that reactions (A), (B), and (C) probably represent an oversimplification of a more complex system.

The above reactions, in conjunction with the modal data on sulfide content (Table 1, p. 44), can be used to test whether an open or closed system was operating during progressive metamorphism. For simplicity, it is assumed that pyrite reacts to form troilite (FeS). Also, the change in one mole of pyrite to one mole of troilite is accompanied by a 25% reduction in volume (Mason and Berry, 1968). In Figure 18, the average sulfide content and average pyrrhotite content is plotted with respect to metamorphic grade. Note that the difference between the mean pyrrhotite and mean pyrite plus pyrrhotite contents represents the mean pyrite content. Figure 18 shows that the transition from the chlorite to the biotite zone is accompanied by an 81% reduction in average pyrite content whereas the change from biotite to garnet zone is associated with a 100% reduction in average pyrite content. The 0.14% pyrite content in the garnet zone is a reflection of one anomalous sample (9a) which contains pyrite. Since the other samples from the garnet zone only contain pyrrhotite, sample 9a is not considered to be a representative sample of the garnet zone.

Given the volumetric changes in the transition of pyrite to pyrrhotite and the percent differences in pyrite content between metamorphic zones, the theoretical change in percent sulfide content was calculated using reactions (A),

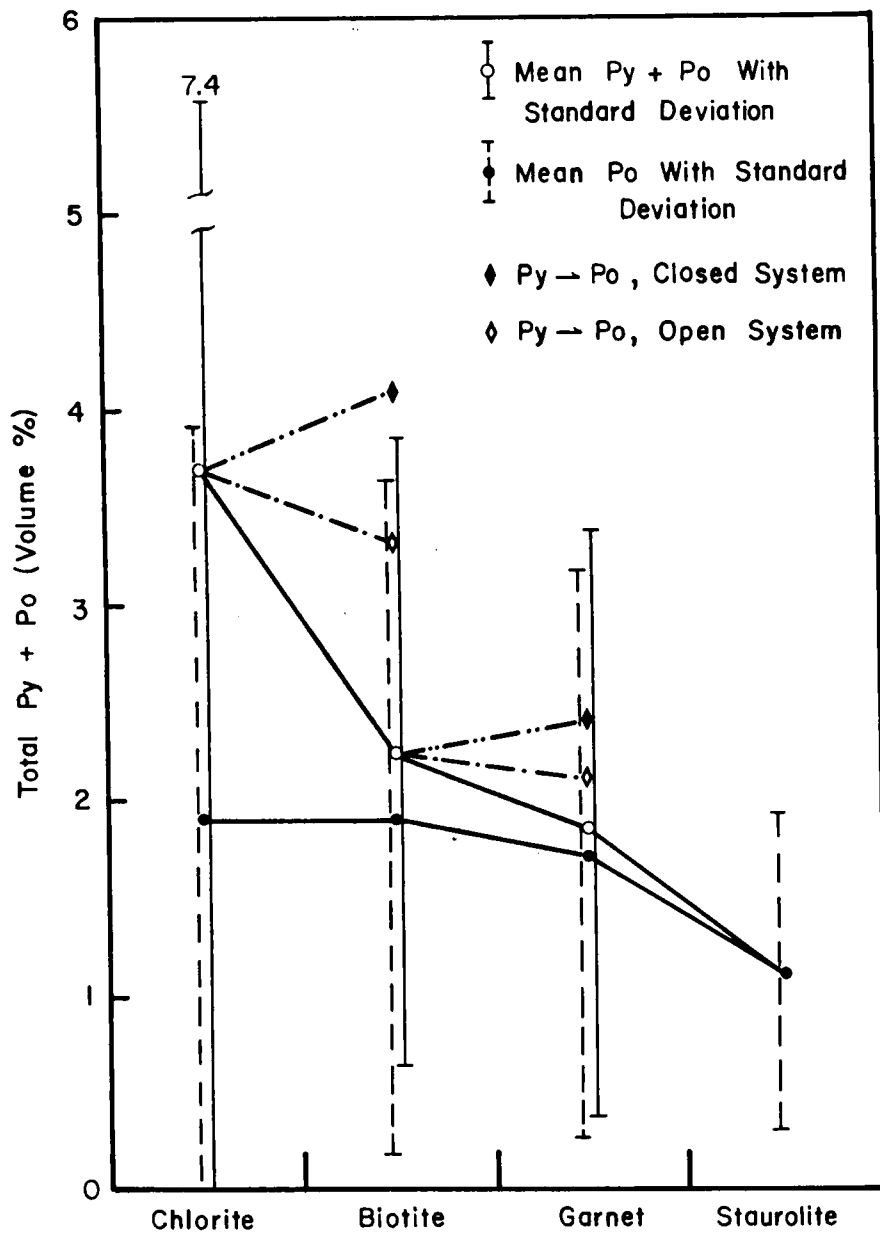


Figure 18. Comparison of mean pyrite and pyrrhotite contents in metasedimentary rocks of the Ducktown area for specific metamorphic zones and the calculated changes in sulfide content derived from open and closed metamorphic reaction systems.

(B), and (C). If the metamorphic system was closed to sulfur, a reaction of type (B) or (C) should show an increase in average sulfide content from the chlorite zone to the garnet zone. However, if the metamorphic system was open to sulfur (reaction A) the average sulfide content should decrease from the chlorite to the garnet zone. Results from Figure 18 suggest that the change 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 a reaction of pyrite to pyrrhotite in an open system.

Metamorphic Mobilization of Sulfide Constituents

The decrease in sulfide content from the chlorite to the garnet zone can be explained by a desulfidation type reaction (e.g., A) with excess sulfur produced in the reaction being removed from the rocks. However, since all pyrite is essentially transformed to pyrrhotite by garnet grade conditions, the above arguments will not explain the decrease in sulfide content from the garnet

zone to the staurolite zone. The association of pyrrhotite with quartz-rich domains of differentiated S_1 and S_2 cleavages suggests a possible mechanism explaining the decrease in sulfide content; specifically, the removal of sulfide constituents in the formation of differentiated cleavages.

Studies concerning the formation of cleavages in metamorphic terranes have provided evidence of small and large scale mobilization of original sedimentary components. Stephens et al. (1979) concluded that the differentiation into micaceous layers and quartz layers of metamorphosed sediments in Clunes, Australia, required the removal of Si, Na, Mn, Ca, and other components from the micaceous areas, concentrating the phyllosilicates and titanium oxide phases. The micaceous layers acted as channelways for pore fluid migration. The consequence of this was removal of material out of the system, causing substantial volume loss of the initial rock.

Williams (1972) in a similar study of flysch deposits in Australia concluded that the formation of differentiated cleavage was produced by the selective removal of quartz from domains rich in layered silicates. This was accomplished by fluid migration along movement zones and resulted in large scale mobilization of at least quartz over hundreds of meters or kilometers.

Glasson and Keays (1978) studied the Clunes area of Australia to determine if large scale movement of gold and sulfides during the development of differentiated cleavage could account for the genesis of associated gold bearing veins. They concluded that approximately 70 percent of the original sulfide content along with minor gold was removed from the micaceous domains during prehnite-pumpellyite grade metamorphism.

With regard to the Ducktown area, Holcombe (1973) studied the development of differentiated cleavage in the Ocoee Gorge and across the Ducktown area. These cleavages were prominently developed in the biotite through staurolite metamorphic zones. Results were similar to other studies; differentiated cleavage is produced by the selective removal of quartz, calcite, feldspar, and possibly sulfides from micaceous areas by fluid migration. This study indicates that the material removed from the micaceous domains could be the source for the numerous quartz, calcite, and sulfide veins in the area and could also supply additional sulfide material to existing ore bodies in the area.

It is suggested that the results of the present study, the change of pyrite to pyrrhotite and decrease in sulfide content related to metamorphic grade along with the association of pyrrhotite to quartz-rich domains of

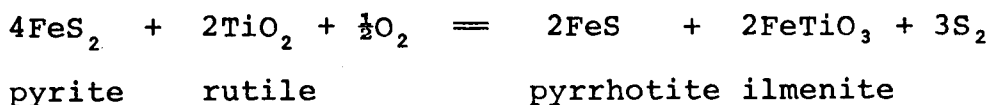
differentiated cleavages, indicate interrelated processes of sulfide mobilization over large distances (kilometers).

It is envisioned that with the onset of metamorphism and deformation during the Taconic orogeny, syngenetic pyrite became unstable and pyrrhotite with H_2S was produced in a type A reaction. In conjunction with the breakdown of pyrite, the formation of differentiated cleavages began by expulsion of connate/pore fluids and was continued by the formation of water during metamorphic mineral reactions (Williams, 1972). This expulsion of fluids was along preferred domains within the host rocks which exhibited a slight preferred orientation of detrital and diagenetic micaceous minerals. The preferential fluid migration along these micaceous domains removed quartz, feldspars, calcite, iron-sulfides, and H_2S concentrating the phyllosilicates and titanium oxide phases. The iron-sulfides removed by this process includes syngenetic pyrite along with H_2S and possibly pyrrhotite produced by the breakdown of pyrite.

Quartz-rich domains exhibited a small amount of recrystallization and addition of quartz from the micaceous domains by diffusion processes. Pyrite within these quartz-rich domains was converted to pyrrhotite and H_2S . Through time, the H_2S fluid migrated by diffusion processes to the micaceous domains and was removed from the system.

The effectiveness of sulfide and H_2S removal was controlled predominantly by the degree of metamorphism. Staurolite zone samples exhibit pervasive well-developed, differentiated cleavage and consequently low sulfide content, the sulfide found only in quartz-rich domains. The chlorite through garnet zone samples display decreases in sulfide content produced by the volumetric decrease in the transition of pyrite to pyrrhotite in a type (A) reaction as well as by removal of sulfides and H_2S in the development of differentiated cleavage.

The change of pyrite to pyrrhotite and the change of rutile to ilmenite suggests decreasing fS_2 with increasing metamorphism. The transition of rutile in the chlorite zone to ilmenite in the biotite through staurolite zone may be indirectly related to the development of differentiated cleavages. Also, the dissolution of iron-sulfides in cleavage development provides a ready source of Fe for a reaction of:



The above processes is complicated by metamorphic and structural complexities, variations in lithologic type, and local (B) reactions. The development of differentiated cleavages during both the F_1 and F_2 events suggests that this

process existed during the Taconic and possibly Acadian orogenies. However, pyrrhotite is more commonly seen in S_1 quartz domains indicating that the above process may have been more prevalent during the F_1 event.

The removal of this material in the development of cleavages provides a source for the numerous veins within the study area as suggested by Holcombe (1973). However the degree of removal from the system suggests that more material was removed than can be accounted for in these veins. In light of this, the presence of the Ducktown massive sulfide bodies within the staurolite zone offers some interesting possibilities as to where these sulfide constituents may have been localized.

Metamorphic Mobilization As An Ore Forming Process

Hypotheses concerning the genesis of the Ducktown massive sulfide bodies can be broadly categorized into two types: (1) a syngenetic formation with no addition of sulfide material during metamorphism; and (2) syngenetic formation with the addition of sulfide material during metamorphism. The major controversy is centered around the formation of the iron-poor, chloritic alteration zone surrounding the ore bodies (e.g., Brown, 1961; Tung, 1968).

Studies by Kalliokoski (1965), Kinkel et al. (1965), Vokes (1969), Salotti (1969) and Addy (1973) show that

major portions of the ore display the same metamorphic features as the country rocks, implying the existence of ore prior to metamorphism. Studies by Nesbitt (1979, 1982) and Nesbitt and Kelly (1980) suggest that the alteration zone is the result of sulfidation of the country rocks during metamorphism; the sulfur supplied by: (1) enrichment during premetamorphic emplacement of the ore; or (2) the breakdown of pyrite to pyrrhotite with generation of excess sulfur. The implication is that sulfur was not added to the ore bodies during metamorphism.

However, results of an oxygen, carbon, and hydrogen isotope study of the ore bodies and country rocks by Addy (1973) and Addy and Ypma (1977), suggests that the country rocks and ore bodies behaved as an open system during metamorphism. They imply that sulfide constituents were supplied to the ore bodies through shear zones, resulting in the alteration of the country rocks by sulfidation processes.

Holcombe (1973) showed that a large area, which contains a number of these ore bodies, has many features of a shear zone. Also, shearing within the ore bodies has been noted by Emmons and Laney (1926), Ross (1936), Kinkel et al. (1965), Magee (1968), Addy (1973), and others.

A major shear zone in the Ducktown area provides a ready escape route for the circulating metamorphic fluids within the country rocks. Results of this study support the interpretation of Addy and Ypma (1977) of an open, convective system operating during the Taconic and Acadian events. The material removed during the development of differentiated cleavage could have been mobilized to these shear zones. The result is the addition of sulfide and siliceous material to existing ore bodies and formation of an alteration zone of iron-poor silicates.

In order to determine if a significant amount of sulfur could be added to the Ducktown deposits in the development of differentiated cleavage, calculations were performed based on the data of this study. On the assumption that 0.5% of sulfur by volume was removed from a volume of metasedimentary rocks, $3.2 \text{ km} \times 6.4 \text{ km} \times 1.6 \text{ km}$ (the volume of metasedimentary rocks which contain all known ore deposits), the above process could add approximately 37 million tons of sulfur to the Ducktown deposits. If only 0.01% sulfur was removed in this process and localized into one area the resulting 7.4 millions tons of sulfur would produce a substantial ore deposit by itself.

CHAPTER VII

SUMMARY

Metasedimentary rocks from the Great Smoky Group were examined to determine the distribution of sulfide phases and the association of sulfide, oxide, and silicate minerals under metamorphic regimes. These data have been evaluated with respect to the genesis of the Ducktown massive sulfide deposits. The results are listed below.

1. With increasing metamorphic grade, pyrrhotite replaces pyrite as the stable sulfide phase (Carpenter, 1974).

2. Sulfides are associated with quartz-rich domains of differentiated cleavages.

3. Average sulfide content decreases in relation to increasing metamorphic grade. This is caused by the development of differentiated cleavages and the volumetric decrease in the transition of pyrite to pyrrhotite in an open metamorphic system.

4. Rutile is replaced by ilmenite as the stable Fe-Ti-O phase above the chlorite grade.

The data suggest that large scale migration of sulfide constituents does occur during the metamorphic development of differentiated cleavages. The migration of sulfide constituents indicates that the country rocks surrounding the Ducktown massive sulfide deposits was an open system

during metamorphism and could be responsible for addition of sulfides to these deposits. The application of this study to exploration remains uncertain and must be evaluated with studies in similar terranes which do not contain significant sulfide mineralization.

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APPENDICES

APPENDIX A

X-RAY FLUORESCENCE METHODS

Preparation Procedure

1. A slab was prepared from each sample, cut perpendicular to bedding or major foliation (if bedding was not discernible) using a Felkner Diamond Saw. A polished thin section was prepared from each sample for petrographic study.
2. Side pieces produced during slabbing of representative samples were cleaned and placed in a jaw crusher which was set at an aperture of 1/4".
3. The crusher was cleaned before and after each use with soap and water and dried thoroughly.
4. The sample was then placed into a tungsten-carbide rotary mill and ground to a fine powder.
5. The resulting powder was dried at 100°C for three hours.
6. Each sample was then split to produce a 1 gm. sample. This was mixed with 2 gms. of $\text{Li}(\text{BO}_3)_3$ (a flux) and 0.5 gms. NH_4NO_3 .
7. The resulting mixture was fused in a carbon crucible at 1100°C for 10 minutes.
8. The fused sample was mixed with boric acid to produce a total sample weight of 3.25 gms., then ground in a tungsten-carbide rotary mill for 45 seconds.

9. A pressed pellet was made for each sample using a boric acid backing. The exact procedure is described in Wheeler (1979).

Run Conditions

Major element oxides

Normalization presets: 400 SEC.

Concentration Units: %

Analysis condition:

Memory size: 16K
 Kilivolts: 10.0
 Current: 100
 Standard preset: 400 sec
 Unknown preset: 400 sec
 Energy range: 0-10 KeV
 Filter: 2, OP
 Anode: RH

Regions of interest:

<u>Region Name</u>	<u>Peak Region</u>
MgO	1.17-1.33
Al ₂ O ₃	1.42-1.56
SiO ₂	1.65-1.83
P ₂ O ₅	1.92-2.09
K ₂ O	3.22-3.41
CaO	3.59-3.79
TiO ₂	4.41-4.60
MnO	5.80-5.99
Fe ₂ O ₃	6.29-6.51

Matrix correction procedures are those described by Hasler and Kemp (1957). Table A-1 lists results of duplicate analyses (XRF) of five standards run as unknowns. Analyses of these standards was used to determine systematic errors in XRF analyses. Table A-2 lists the weight percent error

Table A-1. Bulk Chemical (XRF) Analyses of Five Standards Run As Unknown.^a

	NIM GRANITE		NIM SYENITE		GSP-1		G-2		BCR-1	
	Standard	XRF	Standard	XRF	Standard	XRF	Standard	XRF	Standard	XRF
SiO ₂	75.59	75.55 (0.65) ^c	63.72	63.55 (0.61)	67.27	65.98 (0.62)	69.19	66.40 (0.64)	54.48	51.69 (0.52)
Al ₂ O ₃	12.08	11.10 (0.25)	17.33	17.13 (0.18)	15.11	13.81 (0.30)	15.34	13.82 (0.28)	13.65	12.49 (0.27)
Fe ₂ O ₃ ^b	2.02	2.56 (0.02)	1.40	3.35 (0.02)	4.33	5.72 (0.03)	2.76	3.30 (0.03)	13.50	13.89 (0.06)
MgO	0.10	0.22 (0.01)	0.48	0.90 (0.04)	0.95	1.13 (0.05)	0.78	0.55 (0.02)	3.28	3.43 (0.06)
CaO	0.80	1.33 (0.01)	0.70	3.57 (0.02)	2.03	5.04 (0.02)	1.98	2.67 (0.03)	6.95	6.43 (0.04)
K ₂ O	4.98	5.10 (0.01)	15.34	15.61 (0.03)	5.48	5.42 (0.02)	4.51	4.50 (0.01)	1.68	1.68 (0.00)
TiO ₂	0.0009	0.07 (0.01)	0.0004	0.08 (0.01)	0.69	0.60 (0.02)	0.53	0.49 (0.02)	2.23	1.89 (0.03)
S	0.0003	0.03 (0.01)	0.0001	0.17 (0.01)	0.06	0.10 (0.01)	0.02	0.02 (0.04)	0.03	0.04 (0.01)
MnO	0.0002	0.03 (0.0)	0.0001	0.02 (0.01)	0.04	0.04 (0.01)	0.03	0.04 (0.0)	0.17	0.11 (0.03)
P ₂ O ₅	0.0002	0.29 (0.0)	0.13	0.41 (0.1)	0.28	0.54 (0.0)	0.14	0.36 (0.1)	0.36	0.47 (0.2)
TOTALS	95.57	96.28	99.10	104.79	96.24	98.38	95.28	92.15	96.33	92.12

^a Mean of two analyses.^b Total Fe calculated as Fe₂O₃.^c Units in () represent one standard deviation of replicate analyses in terms of least units cited.

Table A-2. Error of XRF Analyses of Five Standards
 (Calculated from Published Values: Flanigan
 et al., 1976; Russell et al., 1972).

	NIN-G	NIM-SY	GSP-1	G-2	BCR-1
SiO ₂ *	0.04	0.17	1.29	2.79	2.79
TiO ₂	-	-	0.09	0.04	0.34
Al ₂ O ₃	1.02	0.20	1.30	1.52	1.16
Fe ₂ O ₃	0.54	1.95	1.39	0.54	0.39
MnO	-	-	0.00	0.01	0.06
MgO	0.12	0.42	0.18	0.23	0.15
CaO	0.53	2.87	3.01	0.69	0.52
K ₂ O	0.12	0.27	0.06	0.01	0.00
P ₂ O ₅	0.29	0.28	0.26	0.22	0.11
S	-	-	0.04	0.00	0.01

*Weight Percent.

between XRF analyses of standards and the published values for these standards (Flanigan et al., 1976; Russel et al., 1972). Several calibration curves for determining corrections for unknowns are shown in Figure A-1 (based on analyses of standards, Table A-1). Tables A-3 to A-9 list correlation coefficients for all elements analysed (Si, Ti, Fe, Al, Mn, Mg, Ca, K, P).

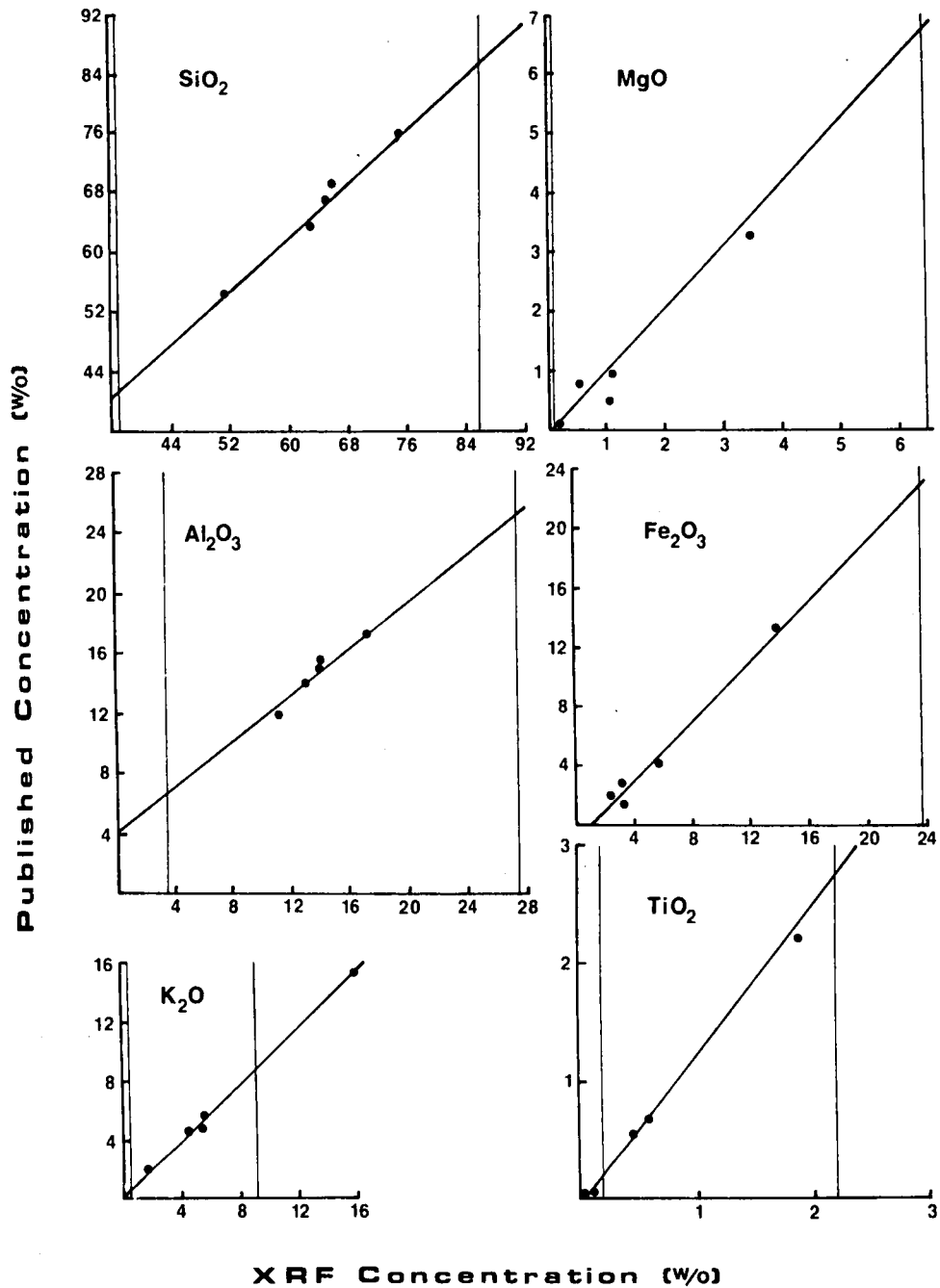


Figure A-1. Calibration curves of XRF analyses versus published data of SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, K₂O, and P₂O₅ for reduction of systematic errors in XRF analyses. Error bars represent absolute error of XRF analyses.

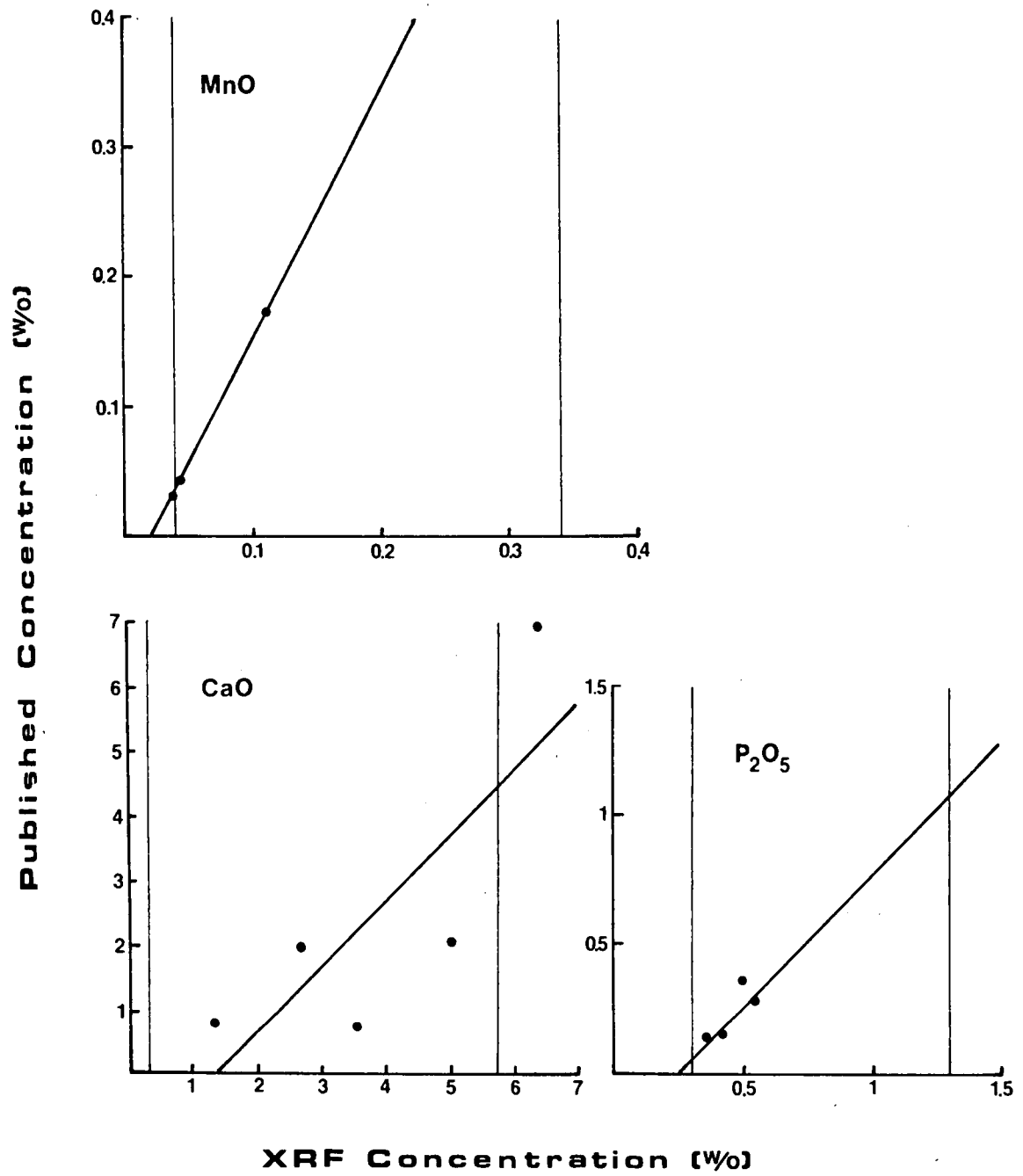


Figure A-1. (continued)

Table A-3. Correlation Coefficients of All Elemental Analyses (XRF) Metasedimentary Rocks, 38 Samples.

	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	K ₂ O	P ₂ O ₅
SiO ₂	-0.50	-0.91	-0.89	-0.40	-0.86	-0.23	-0.63	-0.15
TiO ₂		0.55	0.45	-0.05	0.42	-0.05	0.46	0.06
Al ₂ O ₃			0.73	0.22	0.68	0.09	0.81	0.18
Fe ₂ O ₃				0.43	0.86	-0.03	0.38	0.00
MnO					0.29	0.24	-0.09	-0.21
MgO						0.09	0.47	0.10
CaO							0.07	0.35
K ₂ O								0.33

Table A-4. Correlation Coefficients of All Elemental Analyses (XRF) Metagreywackes,
13 Samples.

	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	K ₂ O	P ₂ O ₅
SiO ₂	-0.72	-0.49	-0.77	-0.37	-0.83	-0.22	0.07	-0.30
TiO ₂		0.68	0.49	-0.18	0.49	0.13	0.08	0.29
Al ₂ O ₃			0.11	-0.11	0.05	-0.03	0.61	0.52
Fe ₂ O ₃				0.41	0.79	-0.25	-0.52	-0.06
MnO					0.48	-0.10	-0.22	-0.34
MgO						0.13	-0.45	-0.07
CaO							0.30	0.40
K ₂ O								0.47

Table A-5. Correlation Coefficients of All Elemental Analyses (XRF), Metasandstones,
16 Samples.

	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	K ₂ O	P ₂ O ₅
SiO ₂	-0.18	-0.92	-0.87	-0.18	-0.76	-0.31	-0.62	-0.03
TiO ₂		0.31	0.18	-0.23	0.04	-0.21	0.34	0.22
Al ₂ O ₃			0.74	0.04	0.55	0.18	0.82	-0.01
Fe ₂ O ₃				0.13	0.87	0.04	0.50	-0.01
MnO					0.01	0.79	-0.34	0.21
MgO						0.02	0.35	0.01
CaO							-0.18	0.31
K ₂ O								-0.04

Table A-6. Correlation Coefficients of All Elemental Analyses (XRF), Metaconglomerates,
9 Samples.

	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	K ₂ O	P ₂ O ₅
SiO ₂	-0.77	-0.97	-0.96	-0.10	-0.94	-0.35	-0.83	-0.69
TiO ₂		0.82	0.82	-0.08	0.71	0.12	0.78	0.35
Al ₂ O ₃			0.96	-0.08	0.95	0.17	0.91	0.66
Fe ₂ O ₃				0.02	0.96	0.17	0.88	0.73
MnO					-0.15	0.57	-0.42	-0.04
MgO						0.12	0.91	0.79
CaO							-0.01	0.29
K ₂ O								0.70

Table A-7. Correlation Coefficients of All Elemental Analyses (XRF), Metasedimentary Rocks, Type A, 16 Samples.

	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	K ₂ O	P ₂ O ₅
SiO ₂	-0.45	-0.86	-0.63	-0.34	-0.44	-0.45	-0.10	0.34
TiO ₂		0.66	0.65	-0.17	0.38	-0.18	0.57	-0.34
Al ₂ O ₃			0.69	-0.04	0.48	0.06	0.46	-0.46
Fe ₂ O ₃				-0.03	0.71	-0.15	0.43	-0.30
MnO					-0.29	0.69	-0.68	0.15
MgO						-0.22	0.41	-0.32
CaO							-0.38	0.31
K ₂ O								-0.03

Table A-8. Correlation Coefficients of All Elemental Analyses (XRF), Metasedimentary Rocks, Type B, 16 Samples.

	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	K ₂ O	P ₂ O ₅
SiO ₂	0.25	-0.28	-0.52	-0.39	-0.68	-0.74	-0.05	-0.04
TiO ₂		-0.15	-0.17	-0.31	-0.11	-0.07	-0.06	0.25
Al ₂ O ₃			-0.11	0.41	-0.21	0.01	0.47	-0.38
Fe ₂ O ₃				0.03	0.53	0.08	-0.40	0.20
MnO					0.05	0.21	0.35	-0.36
MgO						0.46	-0.31	0.15
CaO							0.20	0.15
K ₂ O								0.10

Table A-9. Correlation Coefficients of All Elemental Analyses (XRF), Metasedimentary Rocks, Type C, 6 Samples.

	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	K ₂ O	P ₂ O ₅
SiO ₂	-0.15	0.31	-0.80	-0.82	-0.80	0.01	0.75	0.00
TiO ₂		0.18	0.06	0.06	-0.07	0.45	-0.03	0.10
Al ₂ O ₃			-0.80	-0.70	-0.73	0.67	0.85	0.63
Fe ₂ O ₃				0.98	0.90	-0.48	-0.99	-0.49
MnO					0.83	-0.50	-0.95	-0.51
MgO						-0.37	-0.91	-0.33
CaO							0.48	0.93
K ₂ O								0.48

APPENDIX B

MODAL ANALYSIS TECHNIQUE

1. Thin sections were prepared of all samples.
2. Thin sections were placed in an enlarger and a photonegative was produced for each sample with a magnification of 5X.
3. A mylar grid was placed over the photonegative and sulfide grains and whole-rock outlines were traced onto the mylar. The grid was scaled at 0.1".
4. A Swift Automatic Tabulator, Unit A, was used to tabulate the area of the whole rock and sulfide area. Area estimates could discriminate at a $0.0125''^2$ level. Since pyrite and pyrrhotite are the predominant sulfide phases present, only these phases were tabulated. Other sulfide phases could not be determined (chalcopyrite, sphalerite, galena).
5. The percent pyrite and pyrrhotite was determined in relation to the ratio of sulfide area to thin section area of rock sample.
6. Precision was determined using a linear regression analyses of standard deviation of replicate analyses versus average sulfide content for the corresponding replicate analyses of representative samples (Figure B-1).
7. Modal analysis of samples with large sulfide grains and/or wide distribution of sulfides was performed using

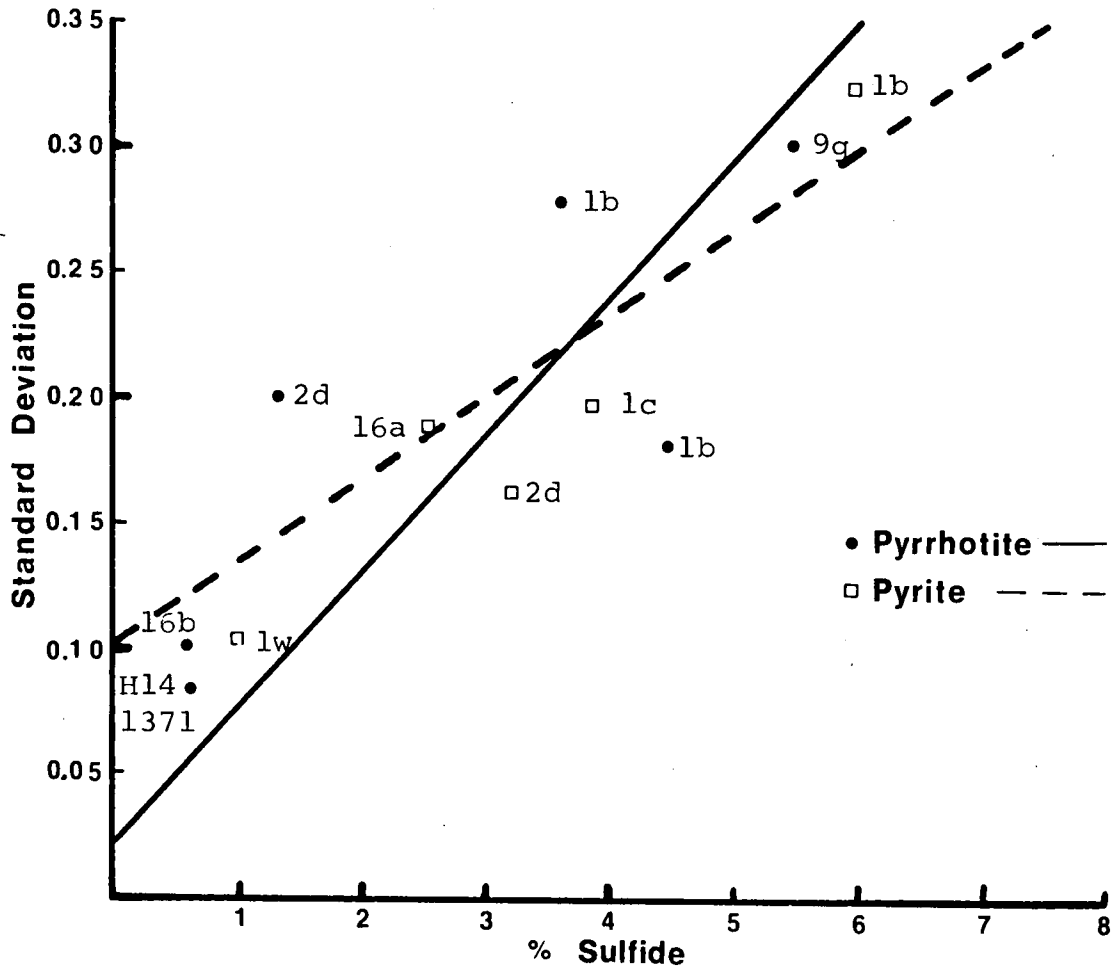


Figure B-1. Plot of one standard deviation of replicate analyses versus the average sulfide content for the corresponding replicate analyses. Data points have corresponding sample numbers. Lines represent the best fit line using a linear regression routine for computation of precision of modal analyses.

polished rock slabs. Sulfide grains and slab outline were traced onto a mylar grid (Fitch, 1959).

8. Percent sulfide was computed in relation to rock area.

9. Accuracy was determined by comparing results of modal analyses with the results (average of two analyses) of a Leco combustion furnace analysis of seven samples for sulfur content (courtesy of Brad Wheeler, EG&G ORTEC). USGS standard SGR-1 was run as an unknown for verifying accuracy of the Leco analyses. Results of SGR-1 analyses was <0.2% error from published values. Figure B-2 is a plot of calculated sulfur values determined from the modal data (Table 1, p. 44) versus results of sulfur analyses by Leco method. Figure B-3 is a plot of calculated sulfur values determined from results of typical point count analyses versus results of sulfur analyses by Leco method.

10. The standard deviation of Py + Po (Figures 12 and 18, pp. 47 and 68) was calculated using the equation (LeMaitre, 1982):

$$\sigma = \sqrt{a^2 + b^2} \quad \text{for } (A \pm a) + (B \pm b)$$

where A = Individual Py analysis

a = Estimated standard deviation of Py analysis

B = Individual Po analysis

b = Estimated standard deviation of Po analysis

σ = Standard deviation of (Py + Po)

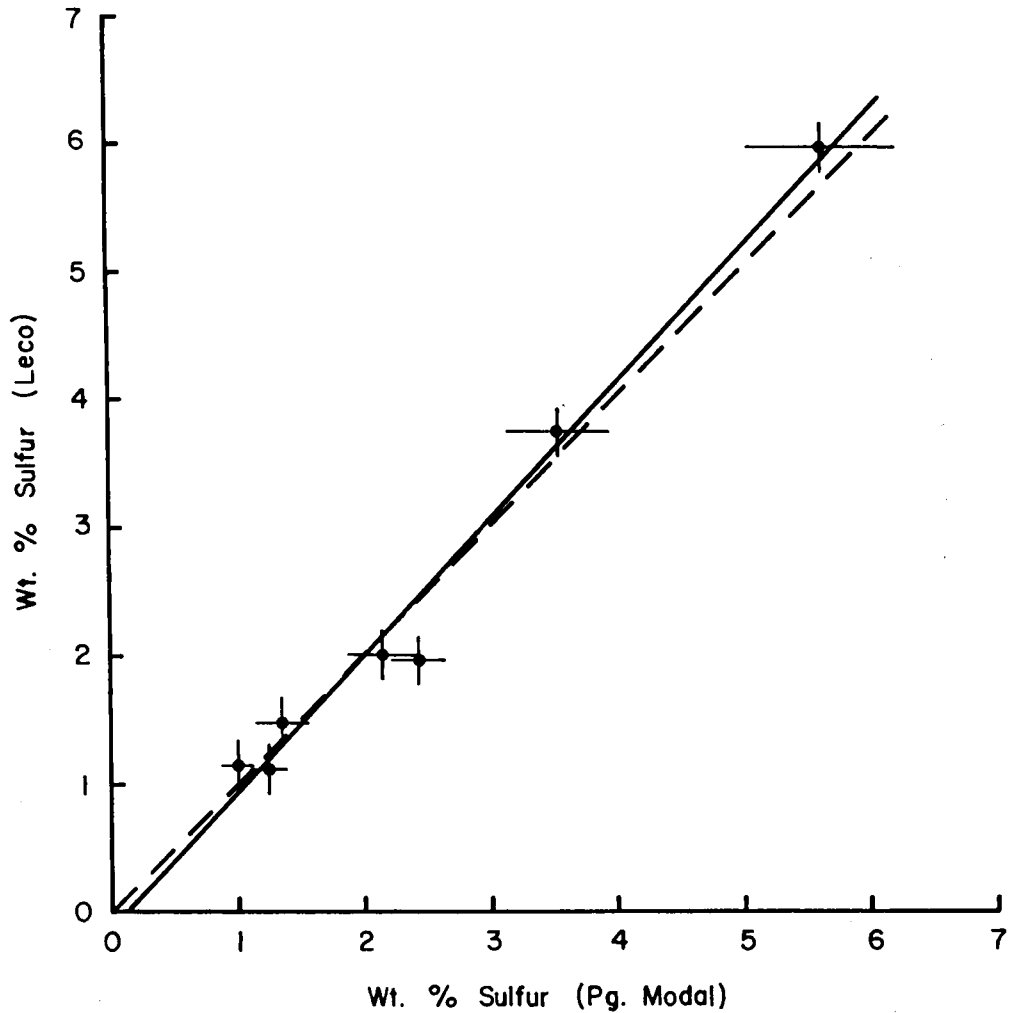


Figure B-2. Comparison of modal analysis results for sulfur versus Leco combustion furnace results for sulfur. Vertical and horizontal error bars represent two standard deviations. Dashed line represents a 1:1 correlation between results of both techniques. Solid line represents a "best fit" line determined by linear regression analysis.

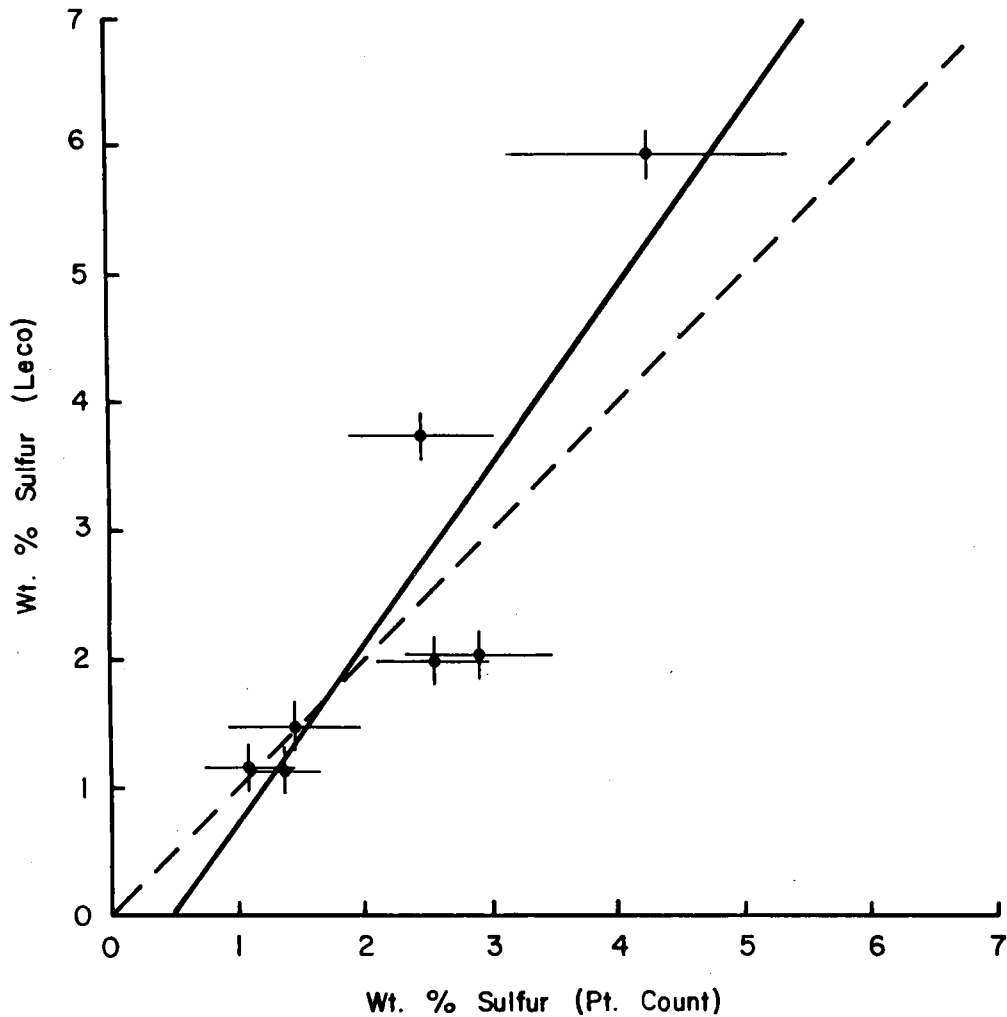


Figure B-3. Comparison of point count results for sulfur versus Leco combustion furnace results for sulfur. Vertical and horizontal error bars represent two standard deviations. Dashed line represents a 1:1 correlation between results of both methods. Solid line represents a "best fit" line determined by linear regression analysis.

11. The standard deviation of the ratio $P_y/(P_y + P_o)$ Figure 11, p. 46) was calculated using the equation (Young, 1962) :

$$\sigma = A/(A + B) \sqrt{2a^2 + b^2} \quad \text{for} \quad \frac{(A \pm a)}{(A \pm a) + (B \pm b)}$$

where A = Individual P_y analysis

a = Estimated standard deviation of P_y analysis

B = Individual P_o analysis

b = Estimated standard deviation of P_o analysis

σ = Standard deviation of $P_y/(P_y + P_o)$

APPENDIX C

MINERAL ASSEMBLAGES

The observed mineral assemblages for all specimens used in the investigation are tabulated in this appendix. These are listed in order, from the western to eastern edge of the study area. Drill core samples are prefixed by H14, B750, and E1900 which represent drill holes Hiwassee 14, Boyd 750, and Eureka 1900, respectively. Representative bulk chemistry is listed in Table 2, p. 53. Sample and drill hole location are shown in Figure 3, p. 7.

Table C-1 gives mineral assemblages of the Ducktown area of Tennessee. An X indicates phases that are present in any amount and are believed to have been present at the peak of metamorphism. A D represents detrital phases. A R signifies phases that are present and thought to be secondary or retrograde in origin. In the calcite column an A represents possible ankerite composition. In the graphite column a C represents carbonaceous material. Abbreviations used in the other column are:

ep—epidote

ccp—chalcopyrite

gn—galena

hem—hematite

sph—sphalerite

Table C-1. Mineral Assemblages of Ducktown Area, Tennessee.

Sample	Quartz	Plagioclase	K-Feldspar	Muscovite	Biotite	Chlorite	Garnet	Staurolite	Calcite	Sphene	Zircon	Apatite	Pyrite	Pyrrhotite	Magnetite	Ilmenite	Rutile	Graphite	Tourmaline	Other
DT-1A	X	D		X		X			A	X			X	X			D	C	D	ccp,gn,sph
DT-1B	X	D		X		X			A	X	D			X				C		
DT-1B	X	D		X		X			A		D		X	X	X		D	C		ccp,sph,hem
DT-1C	X	D		X		X			A	X	D		X	X			D	C	D	
DT-1D	X	D		X		X			X					X				C		
DT-1E	X	D		X		X			X		D			X				C		
DT-1F	X	D		X		X			X		D			X				C		
DT-1G	X	D		X		X			X		D									
DT-1H	X	D		X					X		D									
DT-1K	X	D	D	X					X		D									
DT-1L	X	D		X					X		D			X						
DT-1S	X	D	D	X					X		D		X	X						
DT-1T	X	D	D	X					X		D			X						
DT-1V	X			X		X			X					X			D	C		
DT-2A	X	D		X		X			X	X	D			X		D		X		
DT-3	X	D		X		X			X		D	D			X	D		X	D	hem
DT-4D	X	D	D	X					A		D		X	X						
DT-4B	X	X		X		X			A	X			X			D		C		
DT-4C	X	X		X					A			D	R	X				C		sph
DT-4A	X	X		X							D				X			C		
DT-5A	X	X		X					A					X				G	D	
DT-5B	X			X	X				X	X	D				X	X		X		
DT-6A	X			X	X	X					D							X		
DT-6C	X			X					A					R				C		
DT-7A	X			X					X		X		X	X				C		
DT-7D	X	D		X							D	D		X			D	C		
D-27a	X	X		X	X				X					X				C		
D-32	X	X		X	X	X								X						
DT-8A	X	D	D	X	X	X				X	X			X		X		C	D	ep
DT-8B	X		D	X		X	X		X	X	X			X		X				
DT-9A	X	X		X	X		X						X	X		X		X		
DT-9J	X	X		X	X	X	X						X	X		X		X		
DT-9E	X	X		X		X				X	X			X		X		C		

Table C-1. (continued)

Sample	Quartz	Plagioclase	K-Feldspar	Muscovite	Biotite	Chlorite	Garnet	Staurolite	Calcite	Sphene	Zircon	Apatite	Pyrite	Pyrrhotite	Magnetite	Ilmenite	Rutile	Graphite	Tourmaline	Other
DT-9B	X	D	D	X	X	X	X			X	X	X		X						
DT-9F	X			X	X		X							X				X		
DT-9G	X	X			X	X	X				X			X		X		X		
DT-9H	X	X		X	X	X	X							X		X		C		
DT-9I	X	X		X	X		X			X				X		X		X		
DT-9D	X				X	X	X					X		X						
DT-9C	X			X	X	X	X			X				X						
E-40	X	X		X					X	X						X				
H14,1311	X	X		X	X					X	X			X		X				
H14,1371	X			X	X	R	X				X			X		X				
H14,1406	X	X		X	X	X			X				X	X		X				
H14,1560	X	X		X		X										X				
DT-10C	X			X		X										X				
DT-10A	X			X		X	X									X				
DT-10B	X			X		X	X									X				
DT-10D	X			X		X	X			X										
DT-10E	X			X		X	X									X				
DT-10F	X			X		X	X									X				
DT-10C	X			X		X				X						X				
B750,2146	X			X	X	X				X				X		X		X		
B750,2354	X	X		X	X	X				X				X		X		X		
B750,2355	X	X		X	X	X	X				X	X		X		X				
B750,2398	X	X		X	X	X	X			X				X		X				
DT-11A	X	X		X	X					X						X				
DT-11B	X	X		X		R				X		X				X				
DT-11C	X	X		X	X											X				
E1900,2760	X			X	X		X					X		X						
E1900,2765	X	X		X	X		X			X		X				X				
DT-12A	X		X	X	X						X									
DT-12A	X	X		X	X											X				
DT-12B	X	D	D	X	X					X	X									
DT-12C	X	X	X	X	X					X						X				
DT-12D	X	X		X						X	X									
DT-12E	X	X		X	X					X						X				

Table C-1. (continued)

Sample	Quartz	Plagioclase	K-Feldspar	Muscovite	Biotite	Chlorite	Garnet	Staurolite	Calcite	Sphene	Zircon	Apatite	Pyrite	Pyrrhotite	Magnetite	Ilmenite	Rutile	Graphite	Tourmaline	Other
DT-12F	X	X		X	X						X									
DT-12G	X			X	X					X									X	
DT-12H	X	X		X	X					X										
DT-13A	X			X	X	X	X				X	X				X			X	
DT-14A	X			X	X				X	X						X				
DT-14B	X	X		X	X	X	X			X				X				X		
DT-15B	X			X	X	X	X									X		X	X	
DT-15C	X	X		X	X	X	X				X			X		X			X	
DT-15A	X	X		X	X	R	X				X			X		X			X	
DT-15E	X	X		X	X	R								X					X	
DT-16A	X			X		R	X						R			X				
DT-16B	X			X		R	X			X	X			X						sph
DT-17	X	X		X	X					X	X			X		X			X	
DT-18A	X	X		X	X						X					X				
DT-19	X			X	X	R	X	X		X	X					X			X	

VITA

Gary Runyon was born in Midland, Michigan, on September 8, 1950. He attended elementary schools in that city and was graduated from Midland High School in June 1968. In September 1968 he entered Delta College and continued at this facility until May 1970. In September 1970 he entered Michigan State University and in December 1972 he received a Bachelor of Science degree in geology. In the fall of 1983 he accepted employment with Northrup Services, Inc., as an assistant researcher of lunar geology at NASA's Johnson Space Center, Houston, Texas. In September 1976 Gary accepted a teaching assistantship at The University of Tennessee, Knoxville, and began study towards a master's degree in geology. Prior to completion of a master's degree he was employed as an exploration geologist by the Getty Mining Company in Knoxville, Tennessee. This position was terminated in September 1982 due to the world-wide recession. In September 1982 Gary reentered the Graduate School of The University of Tennessee, Knoxville, on a full-time basis. He was awarded a Master of Science degree in geology in August 1983.