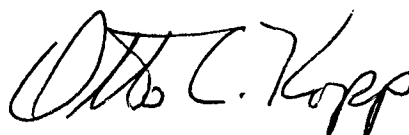


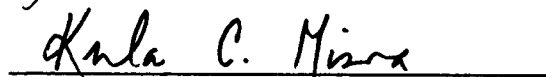
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A PETROGRAPHIC AND GEOCHEMICAL STUDY OF COEXISTING
LIMESTONES AND DOLOSTONES FROM THE MASCOT-JEFFERSON CITY
ZINC DISTRICT, EAST TENNESSEE, AND THE RIGHT FORK AREA,
CENTRAL TENNESSEE

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Thomas Bradford Crattie

December 1985

This thesis is dedicated, with love,
to my family.

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ABSTRACT

Since sphalerite is often associated with the medium to coarsely crystalline dolostones of the Upper Knox Group in East and Central Tennessee, this lithology has been investigated extensively. Past explanations for the formation of these dolostones include replacement of limestone during interaction with ore fluids, groundwater migrating through the Kingsport paleoaquifer, mixed freshwater and seawater during early diagenesis, and hypersaline brines.

The present study employs a controlled sampling method, standard petrographic techniques, cathodoluminescence petrography, and X-ray fluorescence analysis to investigate the origin of limestones and dolostones adjacent to mineralized areas. The samples came from the Coy mine, Mascot-Jefferson City district, East Tennessee, and core from the Right Fork area, Central Tennessee.

Three major lithologies were found in East Tennessee. Limestones are micrites and biointrapelsparites which are interpreted as having formed subtidally. Xenotopic-hypidiotopic, medium- to coarse-grained dolostones (X-H,MCd) replaced limestones after lithification, and in some cases, after silicification. The X-H,MCd were formed in two stages. During the first, zoned, subhedral rhombs (visible only with cathodoluminescence) were precipitated. During the second, anhedral, nonzoned dolomite crystals replaced

the remaining chert or micritic matrix using previous rhombs as nucleation sites. Dolomitization was accompanied by an increase in K, Fe, Mn, Sr, and Br, and a decrease in Cl. Xenotopic, fine-grained dolostones (X,Fd) were probably formed penecontemporaneously with sedimentation in an intertidal to supratidal environment and were later neomorphosed under reducing conditions.

In Central Tennessee, three major lithologies were also found. Limestones and X,Fd are similar to those from East Tennessee. Idiomatic-hypidiomatic, fine- to coarse-grained dolostones (I-H,FCd) are composed of mosaics of subhedral zoned rhombs (cloudy centers, clear rims). Elemental concentrations are generally similar to those of X,Fd, but Br/Cl ratios are lower in the I-H,FCd. The I-H,FCd are interpreted as having formed during early, near-surface diagenesis.

Petrographic and elemental evidence suggest formation of the X-H,MCd of East Tennessee in a stable reducing (burial) environment by interaction of limestone or chert with hypersaline brines. Whether these brines were basinal or evaporative in origin is a matter of speculation.

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CHAPTER I

INTRODUCTION

Although the degree to which ore solutions may have affected host carbonates in the Tennessee zinc districts has been investigated extensively, conflicting conclusions have been reached. A major aspect of this controversy has been the question of mode of origin of the medium to coarsely crystalline Knox dolostones.

Earlier studies (Hill, 1969; West, 1974) reflect the opinion of mine geologists that introduction of ore fluids caused recrystallization and replacement of limestone wall rock. This "recrystalline" dolostone is described by West (1974) as being composed of zoned dolomite crystals with euhedral centers, or of rhombs with clear rims and cloudy, anhedral centers when limestone is partially replaced. West also notes that patches of white gangue dolomite grade into country rock, which indicates a replacement origin. Snyder (1975), while discounting dolomitization by ore solutions, is more vague about the origin of coarse-grained dolostones (0.62-1.00 mm). He suggests an "orthochemical" or "metasomatic" replacement of limestone or recrystallization of fine-grained dolostone to produce uniform euhedral to subhedral dolomite crystals with sharp, interlocking grain boundaries. Partial replacement, according to Snyder,

formed zoned euhedral rhombs. Sphalerite precipitation was associated with a later phase of dolomite introduction along partings and breccia fillings (gangue). Harris (1971) proposes that medium to coarsely crystalline dolostones formed when limestone reacted with groundwater from the paleoaquifer in the Kingsport Formation. Magnesium, according to Harris's model, was provided by erosion of the overlying Mascot Dolomite.

More recently, several workers have suggested that replacement of limestone occurred in a meteoric-marine water mixing zone, producing coarser-grained dolostones (0.06-1.00 mm) early in diagenesis, before lithification (Churnet, 1979; Churnet and Misra, 1983). As evidence of such early replacement, Churnet and Misra (1983) cite low Na (according to Land, 1973) and Sr concentrations; increase of Fe toward the rims of individual dolomite crystals; lack of correlation between Sr and Fe and between Sr and Mn; sharp contacts between dolomite crystals and low-Mg calcite cement; and facies relationships between fine-grained dolostones and coarser-grained dolostones (both of which are regionally extensive). Their evidence against involvement of ore solutions in dolomitization includes similarity of coarser-grained dolostones associated with sphalerite to those far removed from ore deposits; proximity to mineralized zones of limestones that are not altered to dolostone; replacement of

limestone by sphalerite; and abundance of coarser-grained dolostones in an unmineralized section. Moss (1982) used evidence similar to that cited by Churnet and Misra to suggest slightly different conclusions. According to Moss, high Na values (after Veizer et al., 1977) indicate stabilization of medium- (0.20-0.60 mm) and coarse-grained (0.60-0.80 mm) dolostones in solutions "considerably more saline than marine water," but Sr and Mn concentrations suggest meteoric diagenesis in an open system. Interestingly, Moss notes that breccia matrix dolomite is "characterized by high Mn, Fe, and Na suggestive of a continentally derived brine under reducing conditions."

Other dolomite research in the Tennessee zinc districts has concentrated almost exclusively on gangue or white, coarsely crystalline dolomite, which is recognized as a breccia cement and fracture-filling phase. Although coarsely crystalline dolomite and gangue dolomite have been equated in other areas (Dunsmore, 1973; Radke and Mathis, 1981; Gregg, 1984), the two have been considered discrete in terms of type and origin by workers in the Tennessee zinc districts. Ebers and Kopp (1979) describe six major cathodoluminescent zones in the Mascot-Jefferson City district. Zones 3 and 4 are generally restricted to dolomitized limestone; precipitation of sphalerite was coeval with dolomite zones 3d to 5. Ebers (1976) notes the difference between

gangue zonation and that of small (0.10-0.25 mm) euhedral rhombs in partially replaced limestone. Larsen (1978) found calcite to be the dominant gangue mineral in the Elmwood district of Central Tennessee. He also describes three generations of calcite, the first zoned (three zones), the other two unzoned and similar to the calcites II and III of Ferguson (1981). The latter worker studied dolomite and calcite gangue in the Right Fork area of Central Tennessee and found five types of gangue: dolomite I, a saddle dolomite exhibiting undulatory extinction and five zones trending generally from dull red to bright red to nonluminescent; dolomite II, rhombs enclosed in restricted spaces with zonation similar to that of dolomite I, but showing no undulatory extinction; calcite I, a cement similar in zonation to dolomites I and II, but distinguished by characteristic shades of orange; calcite II, a cement composed of unzoned, anhedral, cavity-filling crystals; and calcite III, a cement similar to calcite II, but characterized by irregular surface textures. Sphalerite precipitation began with Ferguson's zone 3 and Larsen's zone 5, both of which showed signs of dissolution prior to mineralization. The two zones are thought to be equivalent.

Each of the previous studies has concentrated on one mode of formation for coarsely crystalline dolostones. The models have often been influenced by prevailing attitudes in

the literature--from dolomitization by mineralizing fluids (Hill, 1969; West, 1974) to schizohaline (Folk and Land, 1974) or Dorag-type (Badiozamani, 1973) dolomitization. The present study recognizes that dolomitization is probably a very lengthy, complex process and that no one model can be used to explain the formation of dolostones whose crystals or grains vary in morphology and whose chemical constituents differ even subtly (Land, 1980; Zenger and Dunham, 1980; Gregg and Sibley, 1984). It should be emphasized, too, that the upper Knox dolostones were not "born yesterday." After their initial deposition, they were reexposed during development of the Middle Ordovician unconformity, buried quite deeply, impregnated with large amounts of sphalerite and gangue minerals, involved in lengthy episodes of regional compression and thrusting, and exposed at the surface again after millions of years of burial. Comparison with Holocene analogues must be made with extreme caution. Several workers have recently emphasized the importance of mesogenetic (late diagenetic burial) dolomitization (Mattes and Mountjoy, 1980; Zenger, 1983; Gregg and Sibley, 1984). Zenger (1983) lists several factors that favor burial dolomitization, including higher temperatures that reduce "the proportion of hydrated Mg ions," thus increasing reaction rates; greater stability and time in the burial environment; low sulfate content in most subsurface brines

(Baker and Kastner, 1981); and Mg:Ca ratios within the stability field of dolomite (Usdowski, 1968).

With the above in mind, the following objectives were set for the present study:

1. To describe and differentiate limestones and dolostone types on the basis of petrographic and cathodoluminescent characteristics and elemental concentrations.
2. To suggest modes of origin for dolostone types.
3. If possible, to relate dolomite morphology and geochemistry to a model for sphalerite mineralization.

Locations and Stratigraphy

The Mascot-Jefferson City zinc district is located approximately 16 km northeast of Knoxville, Tennessee, in the Valley and Ridge physiographic province (Fig. 1). The Right Fork area is located 40 km northeast of Elmwood, Tennessee, on the northeast flank of the Nashville Dome (Interior Lowlands physiographic province, Ferguson, 1981). The two areas are presently 200 km apart, but the palinspastic distance was much greater.

Major ore bodies occur in the Kingsport (East Tennessee) and Mascot (Central Tennessee) Formations, the upper two formations of the Knox Group (Fig. 2). A deep and regionally extensive erosional surface cuts the top of the

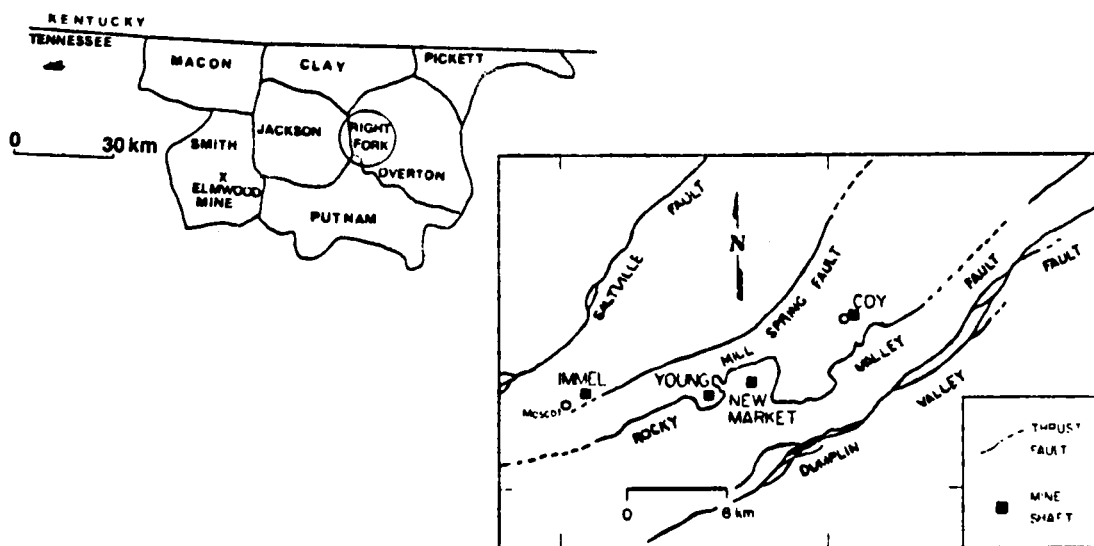
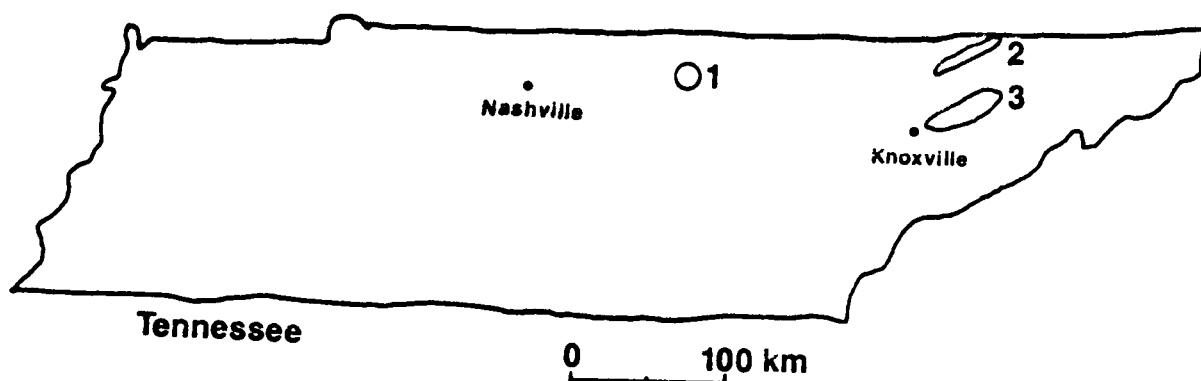


Figure 1. Map of Tennessee showing the Right Fork area (1), the Copper Ridge District (2), and the Mascot-Jefferson City District (3). (From Ferguson, 1981. Inset of Mascot-Jefferson City District from Taylor et al., 1983.)

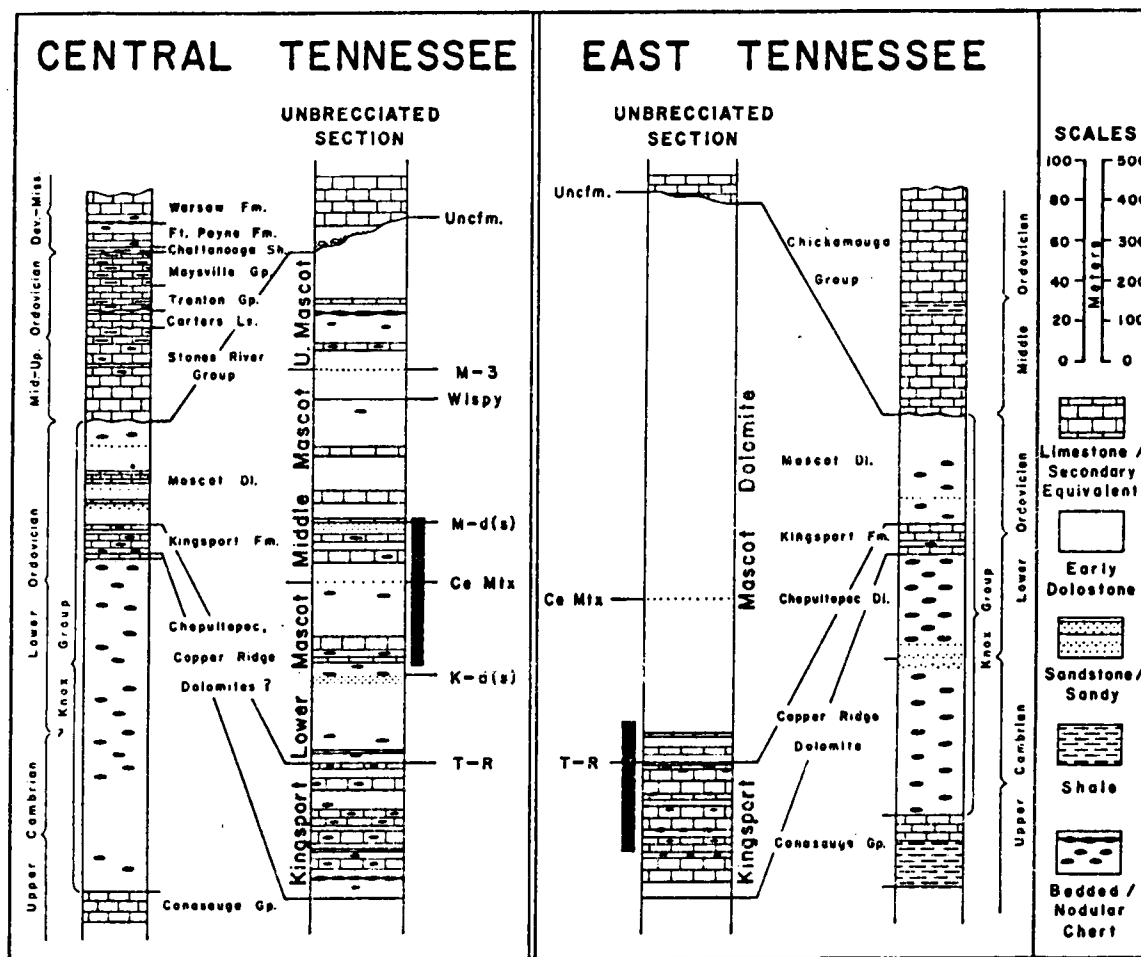


Figure 2. Stratigraphic columns of the Upper Knox Group in Central and East Tennessee (from Kyle, 1983).

Mascot and is unconformably overlaid by the Middle Ordovician Chickamauga Group (Harris, 1971). The Kingsport is predominantly limestone (or an "equivalent") in East Tennessee, but limestone and fine-grained dolostone occur in approximately equal proportions in Central Tennessee (Kyle, 1983). Mine geologists have divided the Kingsport into four stratigraphic units: the U, T, S, and R beds (Crawford and Hoagland, 1968). The Mascot Dolomite comprises mostly fine-grained dolostones and shales in East Tennessee, but there are many limestone interbeds in Central Tennessee. In East Tennessee, Knox strata dip at 10°, to 40°, southeast; in Central Tennessee, they are essentially horizontal (Kyle, 1983).

The Knox Group has been described as having been deposited in a marine peritidal environment (Sandrock, 1973; Snyder, 1975; Churnet et al., 1982) as "part of a thick sequence of epicontinental basin sediments that accumulated between the North American craton and the Appalachian orogenic belt" (Taylor et al., 1983, after Shanmugam and Walker, 1980).

Ore Occurrence

Ore-grade mineralization is found in the lower 20 m of the Mascot and in the upper 50 m of the Kingsport in the Mascot-Jefferson City zinc district (Kyle, 1983). Stratigraphically, the ore deposits are lower in the northeastern

part of the district (U bed) than in the southwest (R bed). The S bed is a good producer throughout the district (Crawford and Hoagland, 1968). In Central Tennessee, sphalerite is concentrated in a 60-m interval of the Middle Mascot (Kyle, 1983).

Ore is associated with breccia bodies that progress laterally from rubble breccia at the center to crackle breccia at the margins of the bodies (McCormick et al., 1971). These breccias can be divided into early, relatively undeveloped and unmineralized breccias and later, more extensive breccias that host sphalerite and gangue minerals (Churnet, 1979; Kyle, 1983). Some mineralized late breccia systems in Central Tennessee extend 60 m above the Knox unconformity (Kyle, 1983; Hoagland, 1976). Early, fine-rock matrix breccia is prevalent in the upper 150 m of the Mascot. Kyle (1983) suggests that the formation of early breccia was directly related to post-Knox erosion and that collapse breccias developed much later due to loading of fine-grained dolostone beds by Middle Ordovician sediments. Ore deposition in this case would have begun well into the Middle Ordovician (Caless et al., 1983). Kyle cites the absence of bleached rims (which are common in early breccia fragments) as evidence that late breccias formed after the period of oxidation related to subaerial exposure. Other workers (Churnet, 1979; Churnet and Misra, 1983) have

suggested that early breccias were formed during deposition of the upper Knox and that some early breccia bodies were later enlarged by ore solutions introduced before post-Knox erosion. Intimate association of sphalerite with coarser-grained dolostones (interpreted as early diagenetic by Churnet) is offered in support of this view. Moss (1982), however, points out that the Copper Ridge district contains no units coarse enough to produce coarse-rock matrix by synsedimentary erosion and deposition.

Ore-grade mineralization occurs principally along the "limestone edge" of the breccia bodies, while the centers of the bodies contain mostly dolomite gangue (McCormick et al., 1971). Taylor et al. (1983) found that fluid-inclusion data are similar for late vug-filling mineralization and earlier stages, which suggests precipitation from similar solutions.

Sample Collection

The sampling method was designed to investigate subtle chemical and petrographic differences between limestone and dolostone lithologies as mineralized breccia bodies are approached. A controlled sampling method was used because of the possible effects of proximity to specific ore structures and the importance of bedding surfaces "in controlling the transfer of underground solutions and the formation of karst cavities" (Sass-Gutkiewicz et al., 1982).

Forty-one samples were collected from the Coy mine in the northeastern portion of the Mascot-Jefferson City zinc district. The samples were taken from four stopes (Fig. 3) within a stratigraphic range of approximately 115 ft, from the U bed to the Kingsport-Mascot contact (Fig. 4). Paired samples were taken from areas 10 cm on either side of well-established contacts involving coarser-grained dolostone and limestone, coarser-grained dolostone and fine-grained dolostone, or fine-grained dolostone and limestone. These lithologies should have experienced similar conditions of temperature and pressure during most of their existence, as well as exposure to formation waters and/or ore solutions. It is realized, however, that individual beds might differ in porosity and permeability.

In Central Tennessee, seven drill cores, each approximately 1000 ft apart, were sampled along two well-established marker beds (the Ma shale and the Md sand, Fig. 2). The drill holes were located in a zigzag pattern that traversed areas thought to be barren, partially mineralized areas, and ore zones (Fig. 5). Twenty-eight samples (fourteen pairs) were obtained from the drill holes. These samples were to be used so that trace-element and petrographic variations could be compared with Mascot-Jefferson City district lithologies some 200 km to the east.

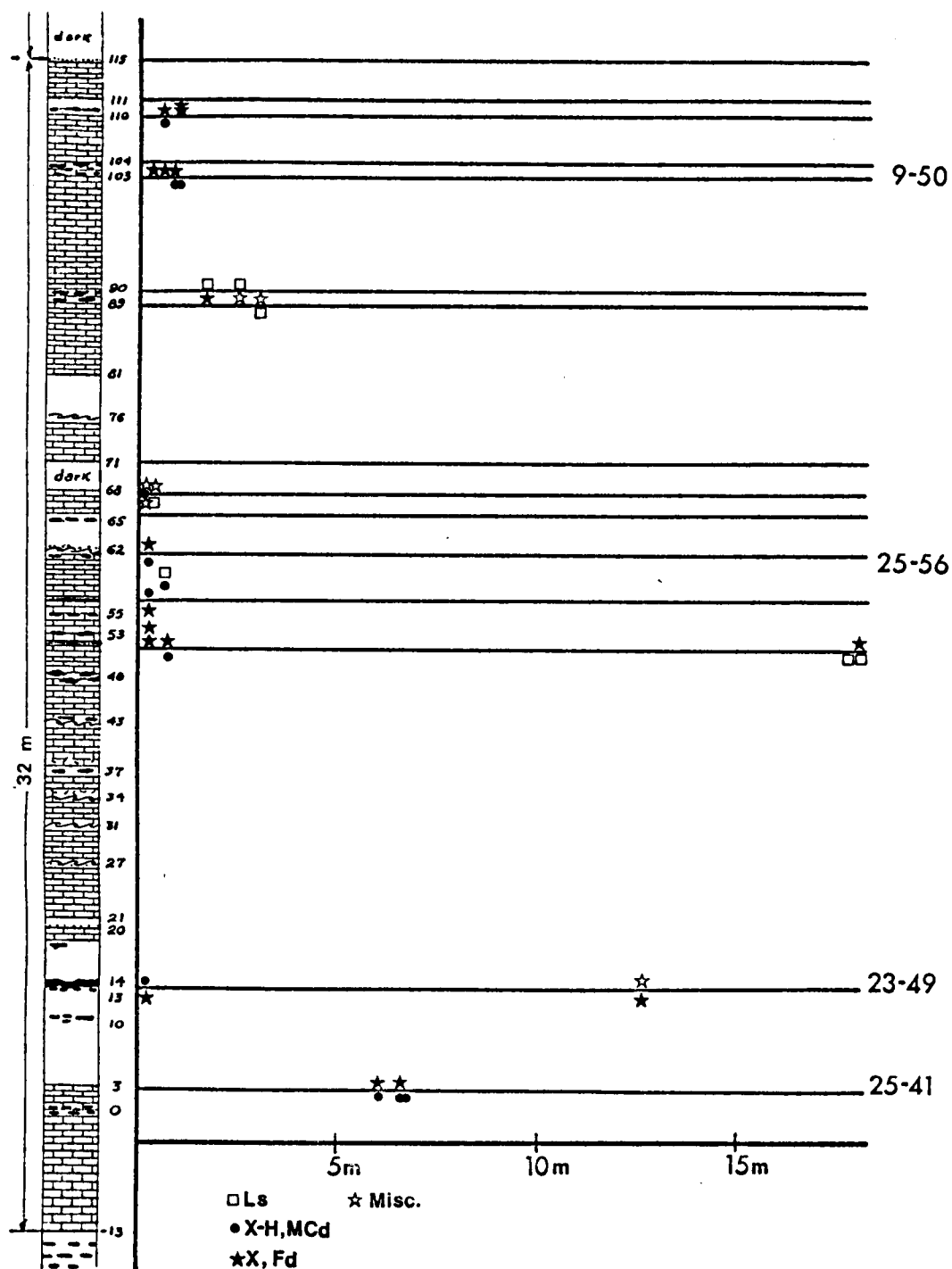


Figure 4. Stratigraphic sample locations in the Coy mine showing distance from mineralized areas. Mineralization is represented by the heavy vertical line at the left.

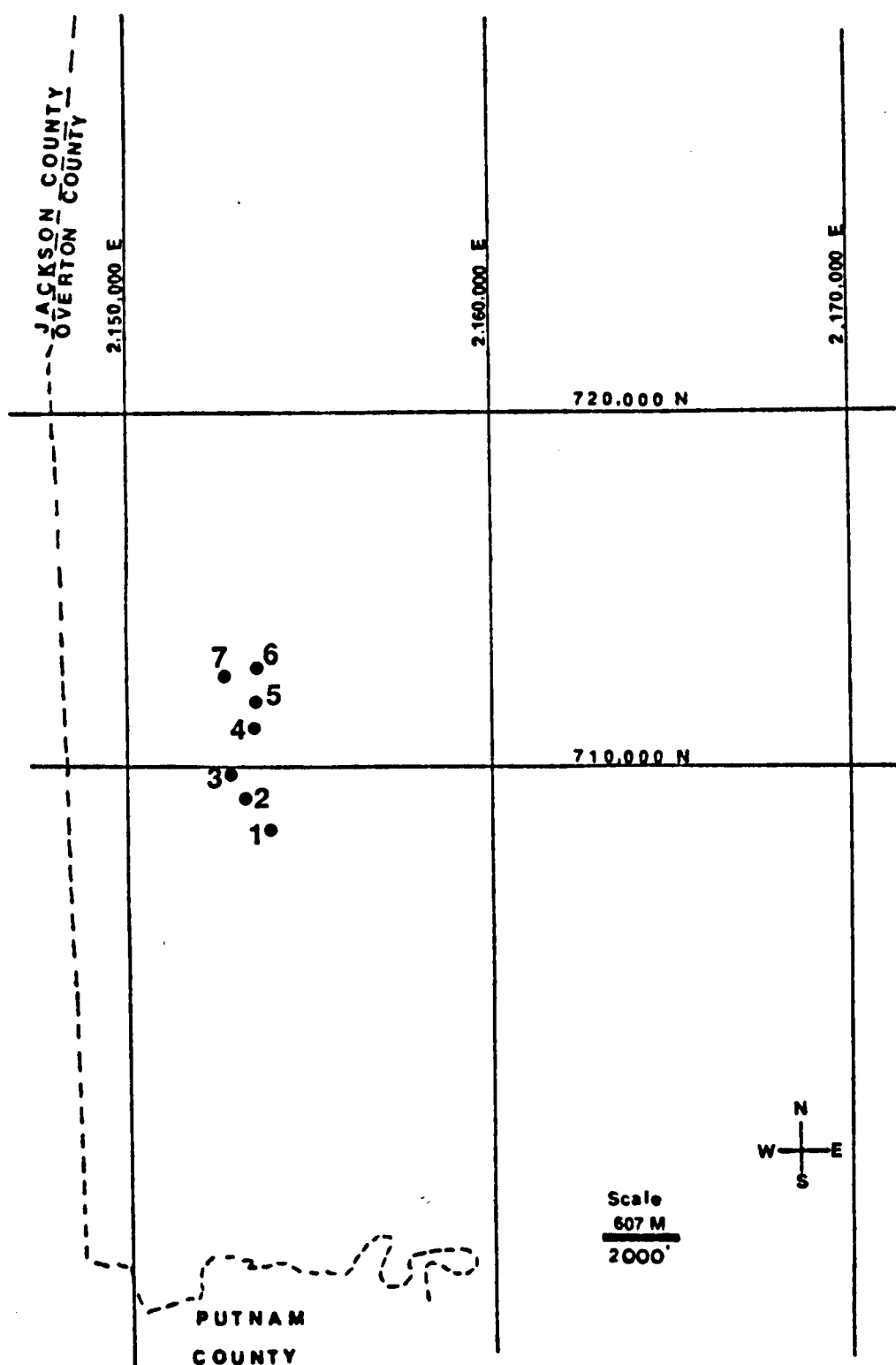


Figure 5. Locations of drill holes that were sampled in the Right Fork area (modified from Ferguson, 1981).

CHAPTER II

PETROGRAPHY

Introduction

Forty-one thin sections were made from samples collected in the Coy mine, and 28 were made from Right Fork-area core samples. The locations of samples taken from the Coy mine are shown in Figure 4 (p. 14) in relation to mineralized breccia bodies (distances from the breccia bodies are approximate). Thin sections were examined by means of standard petrographic techniques and cathodoluminescence microscopy. Lithologic descriptions of individual thin sections are given in Appendix A.

Textural terms used to describe fabrics of limestones and dolostones in the present study have been employed in previous studies of the Tennessee zinc districts (Snyder, 1975; Churnet, 1979; Ferguson, 1981; Moss, 1982). Limestones are described in accordance with the classification system of Folk (1959). The terminology of Friedman (1965) is used to describe dolomite textures. Idiotopic, hypidiotopic, and xenotopic refer to fabrics composed largely of euhedral, subhedral, and anhedral crystals or grains, respectively. A fabric in which larger cement crystals enclose smaller grains or crystals is poikilotopic. Porphyrotopic refers to textures in which larger

crystals are enclosed in a finer-grained matrix. Gregg and Sibley (1984) have proposed a system for the classification of dolomites that is a modification of Friedman's work. Central to their classification scheme is the idea of a "critical roughening temperature" (CRT) below which faceted crystals and euhedral to subhedral crystal mosaics are produced. Above the CRT (estimated to be 50°C for dolomite), nonfaceted crystals and hypidiotopic to xenotopic crystal mosaics result. Therefore, according to Gregg and Sibley, more idiotopic dolomites are primarily produced by near-surface processes (occasionally above the CRT "if growth-inhibiting effects of the solution or impurities stabilize crystal faces"), and more xenotopic dolomites are most commonly produced by replacement of limestone or neomorphic recrystallization of dolomite after burial and above the CRT. Gregg and Sibley's ideas are discussed in the present study, but their classification system is not used per se because it is still undergoing critical review.

Grain size has often been used to classify dolostones in the zinc districts, and similar origins have been inferred for dolostones in specific grain-size groupings (Snyder, 1975; Churnet, 1979; Moss, 1982). This practice stems from the use of the terms primary (fine-grained) and recrystalline (coarse-grained), coined by miners (West, 1974). Primary dolostones were thought to have had an

early sedimentary origin, whereas coarsely crystalline dolostones were considered to have originated from interaction of wall rock with mineralizing fluids. Churnet (1979), however, concludes that coarser-grained dolostones had been formed in a meteoric-seawater mixing zone.

Moss's (1982) grain-size classification is used here because it offers a middle range of grain sizes. The grain-size divisions are as follows: very fine (0.03 mm), fine (0.03 to 0.20 mm), medium (0.20 to 0.60 mm), coarse (0.60 to 0.80 mm), and very coarse (0.80 mm).

Cathodoluminescence Microscopy

Thin sections were also examined by means of cathodoluminescence. The colors and intensities (bright, dull, nonluminescent) vary with type of mineral, applied voltage, beam focus, and concentrations of activating and inhibiting ions within the crystal lattice. In calcite and dolomite, manganese is thought to be the primary activator and iron is the primary inhibitor (Schulman et al., 1947; Sommer, 1972; Frank et al., 1982). Experimentally determined relationships between degrees of luminescence and Fe and Mn concentrations are given in Appendix B.

Mn concentrations greater than approximately 75 ppm appear to be necessary for the onset of luminescence. Fe concentrations between 10,000 and 15,000 ppm effectively

quench luminescence in most cases, regardless of Mn concentrations. Frank et al. (1982) suggest that as the Fe:Mn ratio increases, intensity of luminescence decreases until only dull luminescence ensues at $\text{Fe:Mn} > 2$; however, Pierson (1981) and Fairchild (1983) found bright luminescence at Fe:Mn ratios as high as 10 and 5, respectively. To explain these varied results, Fairchild (1983) proposes a difference in luminescent behavior among different suites of rocks. Pierson (1977) suggests that Fe and Mn substitute for Mg in the dolomite crystal lattice. The resulting bands of color represent three-dimensional zones within a crystal. These zones, which are homogeneous in intensity and color of luminescence, imply homogeneity of Mn and Fe concentrations (Oglesby, 1976; Frank et al., 1982). Kopp (personal communication, 1984) notes that the chemical states of Fe and Mn, as well as their positions in the carbonate lattices, exert a strong influence on their activating and quenching properties.

A model proposed by Oglesby (1976) and Carpenter and Oglesby (1976) attempts to explain the formation of these zones. According to that model, a luminescent zone in calcite or dolomite "represents a period of time during which the pe, pH, and, in environment IV (Figure 6), total sulfur in the pore water were essentially constant." Thus a change in luminescent zonation indicates a change in

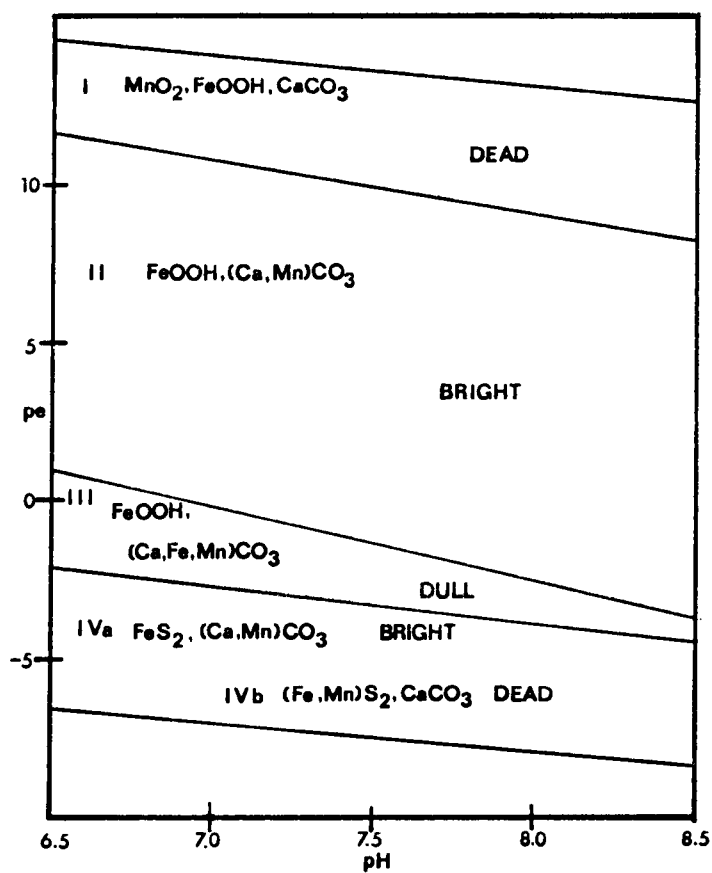


Figure 6. Mineral assemblages, calcite composition, and cathodoluminescence as a function of pH and pe (from Frank et al., 1982).

pore-water chemistry. Environment I is oxidizing, which prevents Mn and Fe from entering the crystal lattice (these elements enter the calcite or dolomite lattice more easily when in a reduced state) and results in a nonluminescent zone. Environment II is more reducing, and Mn is able to enter the lattice. Luminescent intensity is generally bright, but the degree of brightness may depend on the amount of available Mn. With increasing reduction, Fe can enter the lattice and dull luminescence results (environment III). In environment IVa, Fe reacts with H_2S and pyrite is precipitated, effectively removing Fe and producing a bright zone. Higher concentrations of H_2S (environment IVb) cause removal of Mn from the pore water, and a carbonate showing little or no luminescence is precipitated. The presence of accessory iron oxides or sulfides may allow distinction between environments II and IVa and environments I and IVb.

Carpenter and Oglesby's model must be used with some caution. Although they state the Fe and Mn concentrations (10^{-7} m) used to calculate their boundaries, they do not state the S or CO_3 concentrations. Also, their calculations were made assuming a temperature of $25^\circ C$. Oglesby (1976) mentions that an increase in temperature from $25^\circ C$ to $50^\circ C$ (still below the temperatures at which many MVT deposits were formed) lowers each boundary in Figure 6 by

approximately three pe units, but preserves the relative geometry of the phase diagram. The pH values in the diagram range from 6.5 to 8.5, corresponding to the pH range found in most groundwaters. No attempt was made to correct the pH values for higher temperatures.

Grover and Read (1983) apply Carpenter and Oglesby's model to some burial-related cements found in Middle Ordovician carbonates in Virginia. They interpret a non-luminescent-bright-dull cementation pattern as being associated with increasingly reducing conditions accompanying burial. Zoned cements in peritidal beds formed in vadose to shallow phreatic environments. These cements are pendant and pore-rimming and commonly occur with crystal silt. Zoned cements in subtidal facies, according to Grover and Read, formed in shallow to deeper burial regimes. Meteoric water is proposed to have fallen directly upon tidal flats or to have traveled through paleoaquifers from tectonic highlands to the southeast. Peritidal facies to the northwest, separated from southeastward uplands by a developing shale basin, have only dull, nonzoned cements, which suggests cementation in a reducing environment exclusively. Deeper-burial dull calcite and ferroan dolomite cements are proposed to have formed at 75° to 135°C from fluids derived from basinal shales. Because they formed in oxidizing conditions,

according to Grover and Read, nonluminescent cements can be used to map regional paleoaquifer systems. Such interpretations should be made with caution, however, because these cements can originate under a range of pH and Eh conditions, as noted by Carpenter and Oglesby (1976).

Xenotopic, Fine-Grained Dolostones (X,Fd)

Specimens of this lithology were found in both East and Central Tennessee. These dolostones have a xenotopic fabric of grains and rhombs 0.03 to 0.20 mm in the longest dimension (Fig. 7). There is very little intergranular porosity, clay and pyrite (parallel to bedding or randomly distributed) being the dominant interstitial materials. This type of dolostone forms the major lithology of the Mascot Dolomite in the Mascot-Jefferson City district and occurs as marker beds (110, 103, 89, 76, 68, 62, and T beds) in the Kingsport Formation (Fig. 4, p. 14). In the Right Fork area of Central Tennessee, very fine-grained dolostones (dolomicrite: grain size 0.03 mm) were found as frequently as fine-grained dolostones, but this may be a result of limited sampling along the Ma shale and Md sand marker beds. In the Right Fork area, X,Fd contain a higher percentage of clastics (as rounded quartz grains) than do those in the Mascot-Jefferson City district.

X,Fd are mottled by what appears to be dolomicrite. On rare occasions, subhedral rhombs were found. These

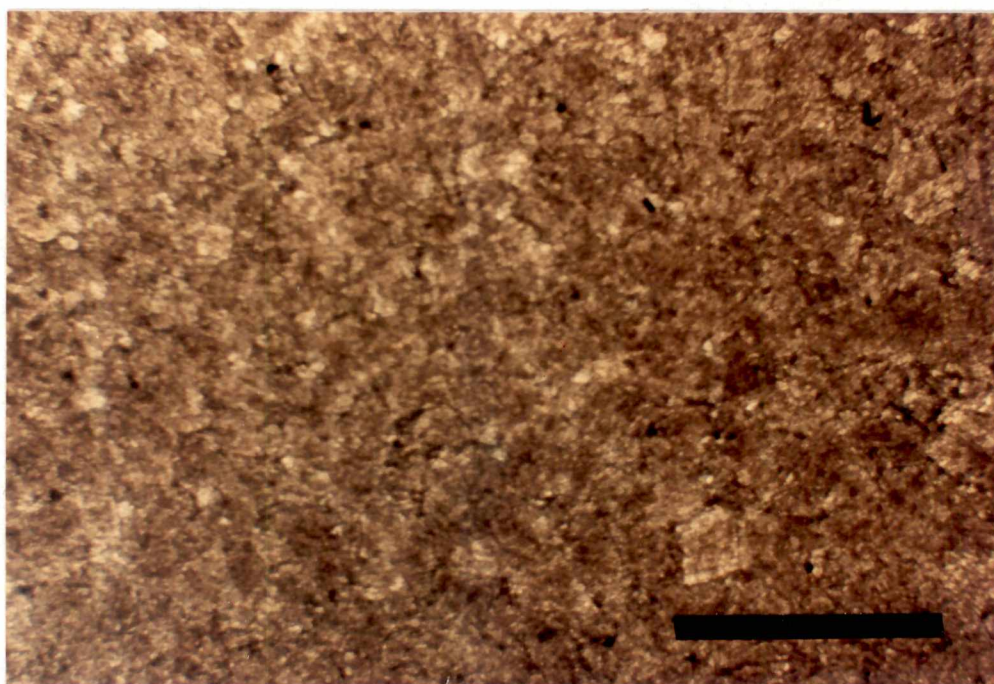


Figure 7. Photomicrograph of X,Fd from the Right Fork area (sample MD3A, transmitted light). Scale bar represents 1 mm.

rhombs are both unzoned and zoned, having micritic-looking (opaque) centers and clear rims. Clearer grains and crystals are found in "healed" microfractures (Zenger, 1983); these relatively clear grains are often enlarged. In the Mascot-Jefferson City district, fractures are filled by white sparry dolomite for the most part, but in the Right Fork area of Central Tennessee, the majority of fractures are lined with texturally unzoned dolomite euhedra and filled with coarse, blocky calcite. These relationships have also been observed by Ebers (1976) and Ferguson (1981). Coarse calcite fills bedding-parallel voids in X,Fd as well.

Previous studies in the East Tennessee zinc districts (Crawford and Hoagland, 1968; West, 1974; Snyder, 1975; Churnet, 1979; Moss, 1982) have suggested that the origin of X,Fd was penecontemporaneous with sedimentation or occurred during early diagenesis in a peritidal (intertidal to supratidal) environment. Cryptalgal laminae, rare mudcracks and birdseyes, and sparse fauna (as ghost fossils) are cited as evidence of this mode of formation. The presence of chert and possibly early gypsum (indicated by nodular vugs with length-slow chalcedony) suggests elevated salinities. Grain sizes coarser than those of present-day peritidal analogues (typically 0.005 to 0.020 mm) and stoichiometric Ca:Mg molar ratios are

attributed to the effects of aggradational neomorphism in the presence of fresh water (Churnet, 1979). Zenger (1972) notes the neomorphic grain-size increase of Paleozoic supratidal dolostones (0.04 to 0.20 mm). Gregg and Sibley (1984) suggest that the very fine grain size and non-stoichiometry of modern dolomites associated with evaporitic environments make them "particularly susceptible to neomorphic recrystallization." X,Fd of East and Central Tennessee usually show nonzoned, dull red luminescence (Fig. 8) suggesting neomorphism in a reducing environment (Grover and Read, 1983).

A Holocene analogue for penecontemporaneous supratidal dolomitization in a hypersaline hydrologic regime is the sabkha environment in the Persian Gulf (Illing et al., 1965). Less arid analogues include the dolomite supratidal crusts of Andros Island in the Bahamas (Shinn et al., 1969) and the Coorong coastal plain of Australia (von der Borch et al., 1964). However, Zenger and Dunham (1980) emphasize that the areal extent of these Holocene dolomites is relatively small.

Idiotopic-Hypidiotopic, Fine- to Coarse-Grained Dolostones (I-H,Fcd)

Among the samples collected for the present study, this lithotype is found almost exclusively in Central Tennessee. Four samples from the Coy mine (C9A, C9C, C10B,

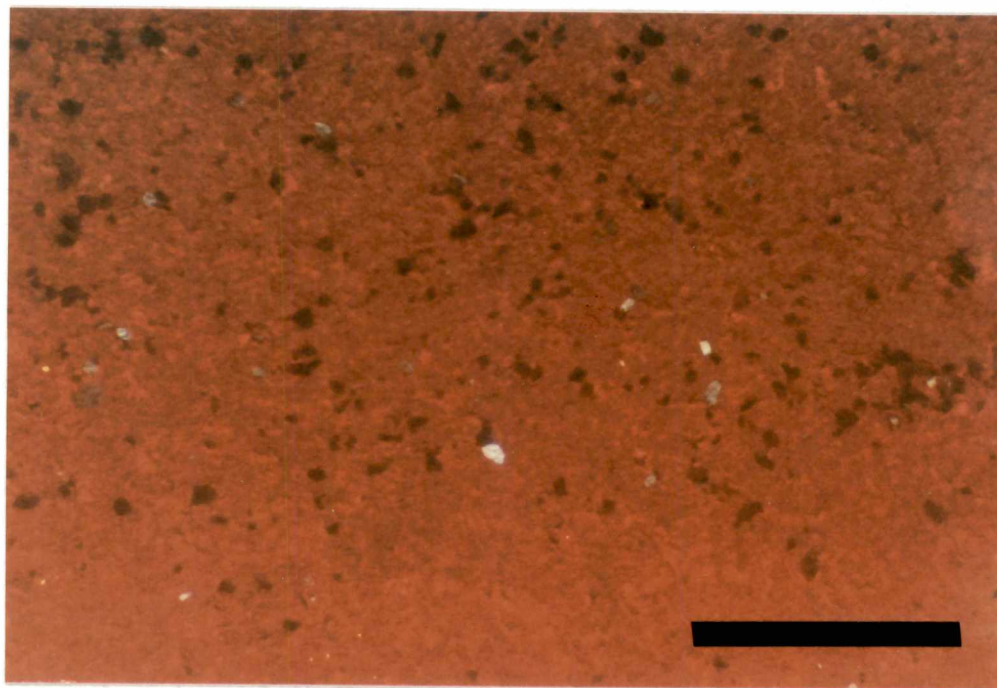


Figure 8. Photomicrograph of X,Fd from the Right Fork area (sample MD3A, with cathodoluminescence, Kodacolor print, ASA 400). Scale bar represents 1 mm.

C21B) have a fabric of subhedral, texturally zoned rhombs similar to that of I-H,FCd. However, the matrix between the rhombs has been replaced by dull orange-red, nonzoned (CL) dolomite (discussed in the section on X-H,MCd). Three samples (C9C, C10B, C21B) contain pockets and lenses of gangue dolomite that are underlaid by mottled areas where gangue "invades" the wall rock. I-H,FCd fabric consists of fine- to coarse-grained subhedral rhombs that are texturally unzoned and zoned (opaque centers and clear rims, Fig. 9). The rhombs, which are typically characterized by intermediate (0.30 to 0.60 mm) grain size, often appear to "float" in a matrix of micrite or clay. Extinction is sharp.

The cloudy centers of I-H,FCd from Central Tennessee luminesce a medium orange-red (micrite luminesces in various shades of orange), and the clear rims show thin alternating zones of a brighter orange and medium orange-red similar to the luminescence of the rhomb center (Fig. 10). One sample from the Coy mine (C21B) has relatively bright orange-red centers and nonluminescent rims. The other (C9A), taken from a clay seam below the 68-71 bed, has rhombs that are characterized by nonluminescent centers and thin bright zones (Fig. 11). Luminescent characteristics of I-H,FCd suggest near-surface diagenesis (Frank et al., 1982; Grover and Read, 1983). A periodic

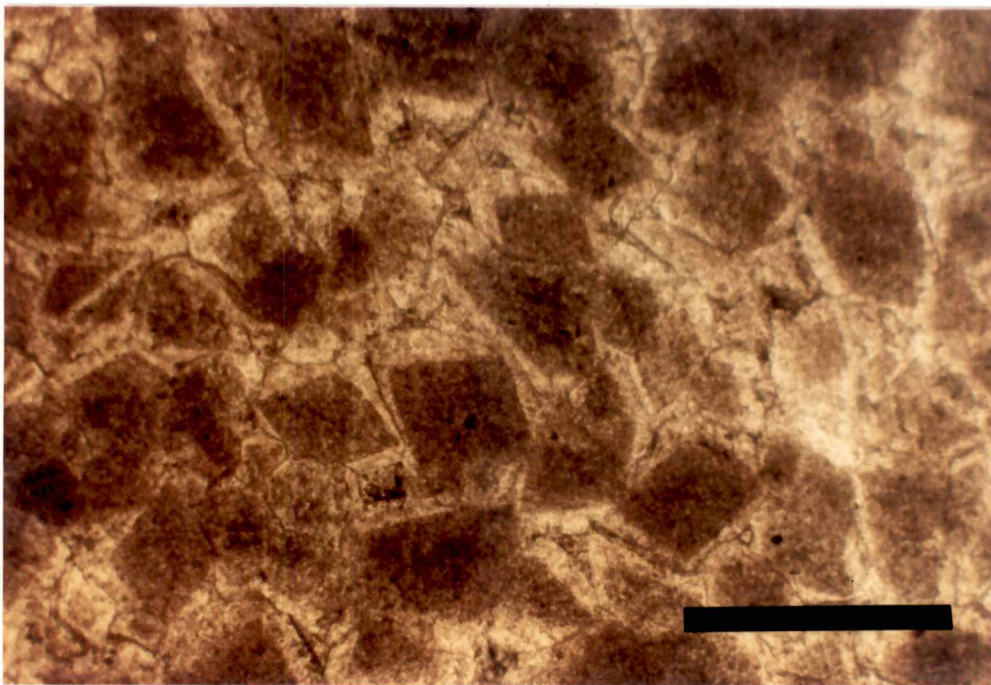


Figure 9. Photomicrograph of I-H, FCd from the Right Fork area (sample MD7B, transmitted light). Scale bar represents 1 mm.

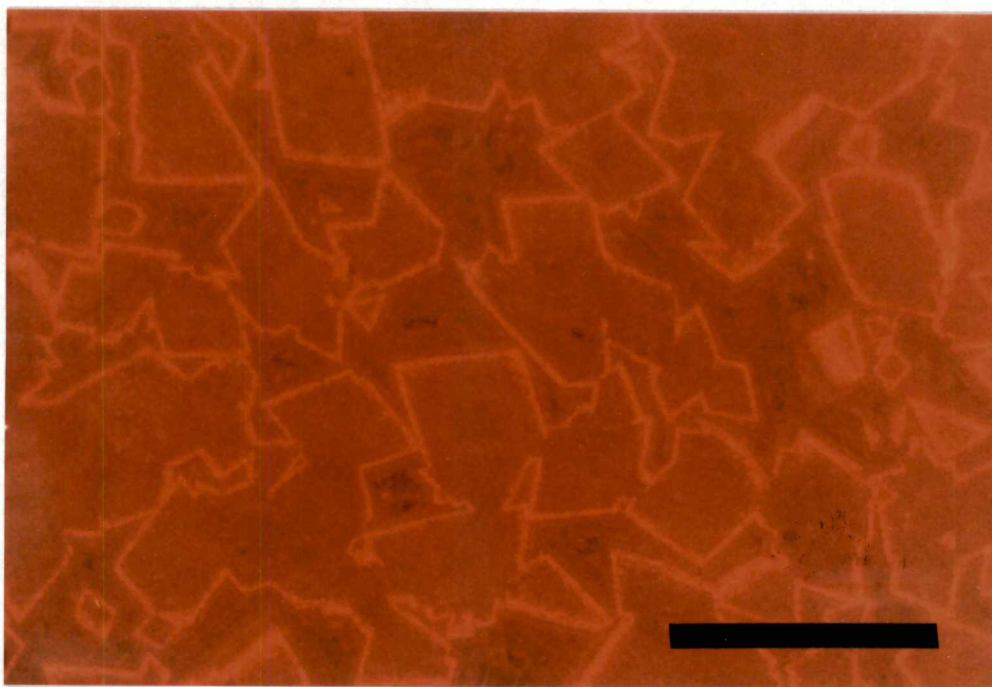


Figure 10. Photomicrograph of I-H, FCd from the Right Fork area (sample MD7B, with cathodoluminescence, Kodacolor print, ASA 400). Scale bar represents 1 mm.

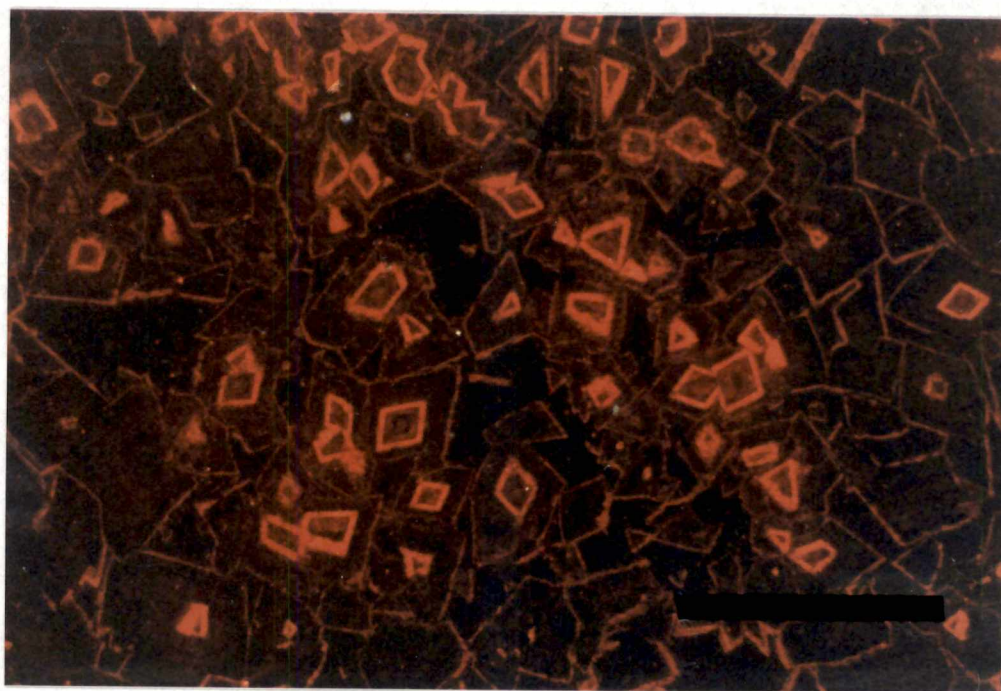


Figure 11. Photomicrograph of I-H, FCd rhombs from a clay seam in the Coy mine (sample C9A, with cathodoluminescence, Kodacolor print, ASA 400). Scale bar represents 1 mm.

influx of oxygenated waters would result in nonluminescent zones, and subsequent stagnation of pore waters would result in the entrance of Mn into the crystal lattice to produce a bright zone.

I-H,FCd are most similar to dolostones considered to have formed in meteoric-seawater mixing or schizohaline environments. Churnet (1979) and Moss (1982) have suggested such origins for medium- and coarse-grained dolostones in the Copper Ridge district. The literature yields almost identical descriptions of these near-surface dolomites (zoned, in these descriptions, refers to textural zonation): (1) zoned euhedral rhombs up to 0.5 mm, micritic matrix, dense xenotopic mosaics above 40 percent dolomitization (Middle Jurassic of Israel; Katz, 1971); (2) euhedral limpid crystals, zoned rhombs 0.05 to 0.10 mm, coarse sparry calcite (Upper Carboniferous, Permian of Norway; Folk and Siedlecka, 1974); (3) anhedral grains to euhedral rhombs, up to 0.25 mm, zoned (dark centers, clear rims) or limpid (Eocene of Egypt; Land et al., 1975); (4) subhedral to euhedral rhombs 0.01 to 0.08 mm, commonly zoned (opaque centers, clear rims), dissolved centers (Eocene of Florida; Randazzo and Hickey, 1978). Saller (1984) has reported limpid and cloudy-centered rhombs in subsurface dolostones of the Enewetak atoll. He suggests that these dolostones formed by replacement of calcite during reaction with cold seawater 900 m below the surface.

Xenotopic-Hypidiotopic, Medium- to Coarse-Grained Dolostones (X-H,MCd)

This lithotype was found almost exclusively in East Tennessee (only one sample, MA3A, came from the Right Fork area). Crystals are usually medium- to coarse-grained, but very coarse-grained (>0.80) crystals do occur. The most common fabric consists of a mosaic of anhedral and subhedral crystals. Often very thin stylolites form the boundaries between crystals. This fabric should not be confused with that of more rounded, enlarged X,Fd crystals. Occasionally X-H,MCd crystals are spear-shaped (curved, with serrated edges). In partially dolomitized limestones, rhombs have serrated edges. It appears that the X-H,MCd of the present study differ in texture from coarser-grained dolostones described in previous studies of the Tennessee zinc districts.

In transmitted light, crystals exhibit arcuate cleavages (Churnet, 1979; Radke and Mathis, 1980) and have a turbid (not limpid) appearance (Fig. 12). In their study of "saddle" dolomites, Radke and Mathis (1980) attributed turbidity to an abundance of inclusions, both fluid and solid (calcite, quartz). This turbidity reflects the replacement nature of the dolomite and argues against formation in a mixing zone. Turbidity implies interaction with saline fluids (Radke and Mathis, 1980; Choquette, 1971). Dolomites described as having formed in mixing

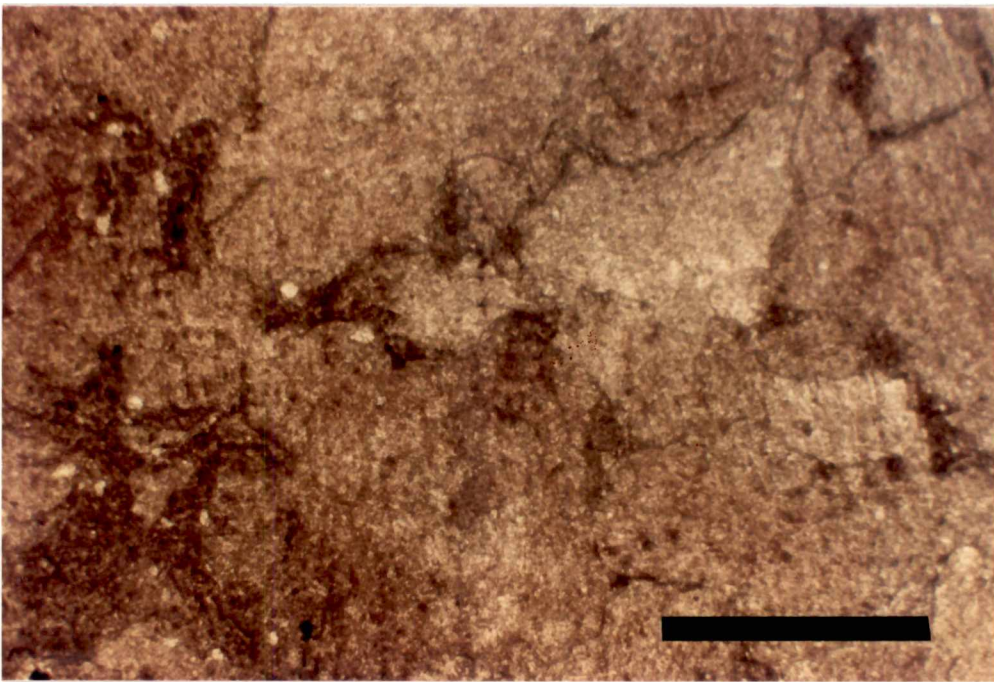


Figure 12. Photomicrograph of X-H, MCd in chert matrix from the Coy mine (sample C20B, transmitted light). Scale bar represents 1 mm.

zones are most often limpid or zoned, with cloudy centers and clear rims. X-H,MCd crystals show sweeping extinction with crossed nicols.

In partially dolomitized limestones, X-H,MCd crystals grow across both micrite and sparry calcite cement (Fig. 13), which suggests replacement of limestone after cementation and lithification. X-H,MCd crystals also overgrow fractures (Fig. 14), an indication of postcompactional dolomitization (Saller, 1984). When the matrix is composed of chert, several interesting relationships can be observed. First, dolomoldic textures (seen most clearly with the gypsum plate in) mimic fine-grained euhedral rhombs. Second, when X-H,MCd crystals go to extinction, their poikilotopic nature is more evident; in fact, the dolomite can hardly be discerned from the chert matrix (Fig. 15). These textures indicate replacement of limestone and early dolomite by chert, and subsequent replacement by X-H,MCd. Completely dolomitized rocks have a xenotopic-hypidiotopic fabric with small amounts of interstitial chert or clay.

In transmitted light with crossed nicols, X-H,MCd, whether they appear as anhedral mosaics, spear-shaped crystals, or serrated rhombs, are similar to mesogenetic (burial) dolomites reported by workers in other areas. Similarities include crystal shape, sweeping extinction,

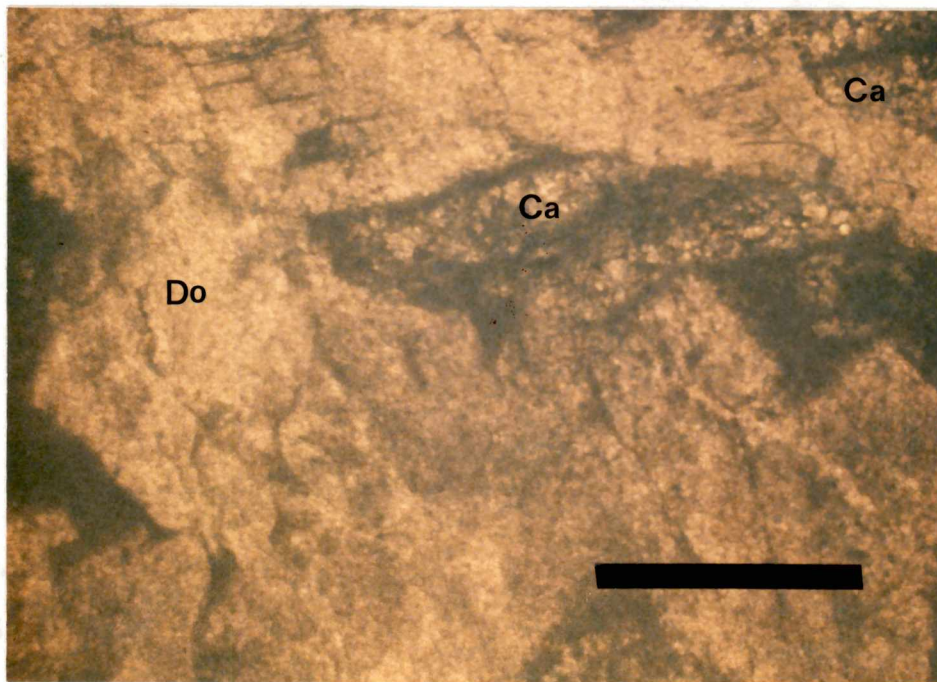


Figure 13. Photomicrograph of X-H, MCd (Do) growing across sparry calcite-filled Hedstroemia pores (Ca) in partially dolomitized limestone (sample C2B, transmitted light, print from Ektachrome slide, ASA 400). Scale bar represents 1 mm.

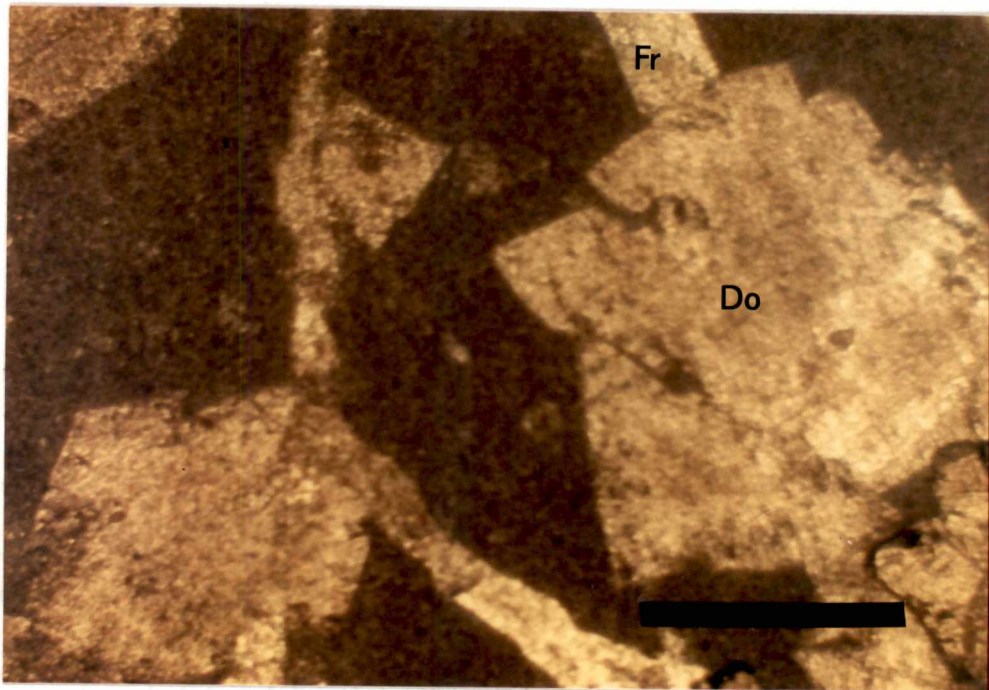


Figure 14. Photomicrograph of X-H, MCd crystals overgrowing fractures (Fr) in partially dolomitized limestone (sample C13B, transmitted light). With cathodoluminescence, fractures are nonluminescent and bright orange; dolomite is dull red. Scale bar represents 1 mm.

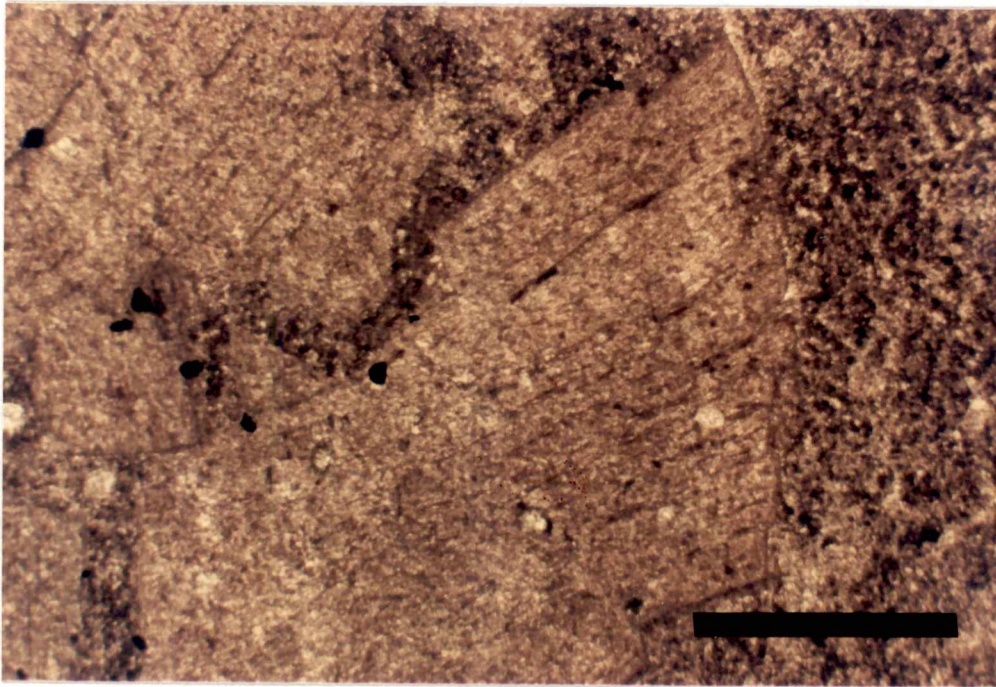


Figure 15. Photomicrograph of spear-shaped X-H, MCd in chert matrix showing its replacement nature (sample C16A, transmitted light). Note chert and pyrite poikilotopically enclosed by X-H, MCd. Scale bar represents 1 mm.

turbidity, arcuate cleavages, and very coarse crystallinity. Alternative terms for this dolomite type include replacement "saddle" dolomite (Devonian of Pine Point, Canada; Dunsmore, 1973; Radke and Mathis, 1980), late diagenetic burial dolomite (Devonian of California; Zenger, 1983), and xenotopic dolomite (Permian of Texas, Ordovician of Michigan; Gregg and Sibley, 1984).

In previous studies of the Tennessee zinc districts, a fairly strict distinction has been drawn between X-H,MCd and gangue dolomite, which is considered a breccia cement or fracture-filling phase. West (1974) and Moss (1982) both comment upon the limited replacement nature of gangue dolomite. Several workers in other areas (Dunsmore, 1973; Radke and Mathis, 1980; Radke, 1982) have proposed that replacement "saddle" dolomite, which has textures similar to those of X-H,MCd of the present study, shares basically the same origin with void-filling "saddle" dolomite (late ferroan dolomite of Choquette, 1971; white sparry dolomite of Beales, 1971; baroque dolomite of Folk and Assareto, 1974; gangue dolomite of Ebers and Kopp, 1979). Both types of dolomite are associated with sulfide mineralization and hydrocarbon occurrences in several areas. Evidence from the present study, especially the cathodoluminescent petrography, suggests that X-H,MCd and gangue dolomite differ in origin.

In transmitted plane polarized light and with crossed nicols, gangue dolomite resembles X-H,MCd. Both are coarsely crystalline, have arcuate cleavages, and exhibit sweeping extinction. When cathodoluminescence is used, however, it appears that X-H,MCd and gangue dolomite have experienced rather different growth histories. Luminescent zonation in gangue dolomites of the Mascot-Jefferson City district is thoroughly examined in Ebers (1976) and Ebers and Kopp (1979). These workers describe six luminescent zones ranging from "very dark red" to "very bright red." The same zonation sequence in gangue dolomites was found throughout the district, from the U bed of the Kingsport Formation to the lower Mascot Dolomite. The formation of each zone was interpreted as being essentially time-correlative (that is, synchronous) throughout the district. Sphalerite was precipitated during the deposition of zones 3d through 5, a sequence proceeding from "bright medium red" through "dark red" to "bright red." Zone 3 probably formed in Oglesby's environment IV (Fig. 6, p. 20). This is a reducing environment that contains ample H_2S to form pyrite, removing Fe from solution and producing a bright zone. Ebers (1976, Fig. 24) notes that pyrite is disseminated throughout zone 3.

Zonation in X-H,MCd is quite different from that in gangue. In some samples (C6A, C9C), gangue zones 5 and 6

can be seen "invading" X-H,MCd wall rock. In general, the luminescent signatures of the X-H,MCd are nonluminescent rhomb cores, the dull nature of luminescence, and the existence of rather thick zones if rhombs are present. In what appears to be a xenotopic fabric (anhedral mosaic) in transmitted light (Fig. 12, p. 34), zoned rhombs with curved crystal faces (Fig. 16) are visible with cathodoluminescence. The xenotopic appearance results from subsequent dolomitization of the matrix. Essentially the same zonation sequence is found in some samples from above the 89-90 bed (Fig. 4, p. 14), below the 110-111 bed, and above the T bed. The zonation sequence consists of a rhomb with a nonluminescent center (in many cases with brighter orange areas within, especially along cleavage traces), followed by a medium bright orange-red zone, a thin dull red zone, and another medium bright orange-red zone (Fig. 16; Fig. 17). The matrix between the rhombs has been replaced by nonzoned dull red or orange-red xenotopic dolomite crystals. A zonation pattern similar to that just described but lacking the rhomb's nonluminescent center is also seen in samples from the 68-71 bed (C10B) and the U bed (C22A). The zonation pattern suggests at least two periods of dolomitization. During the first period, sub-hedral zoned rhombs were precipitated, which implies changing pore-water chemistry. During the second,

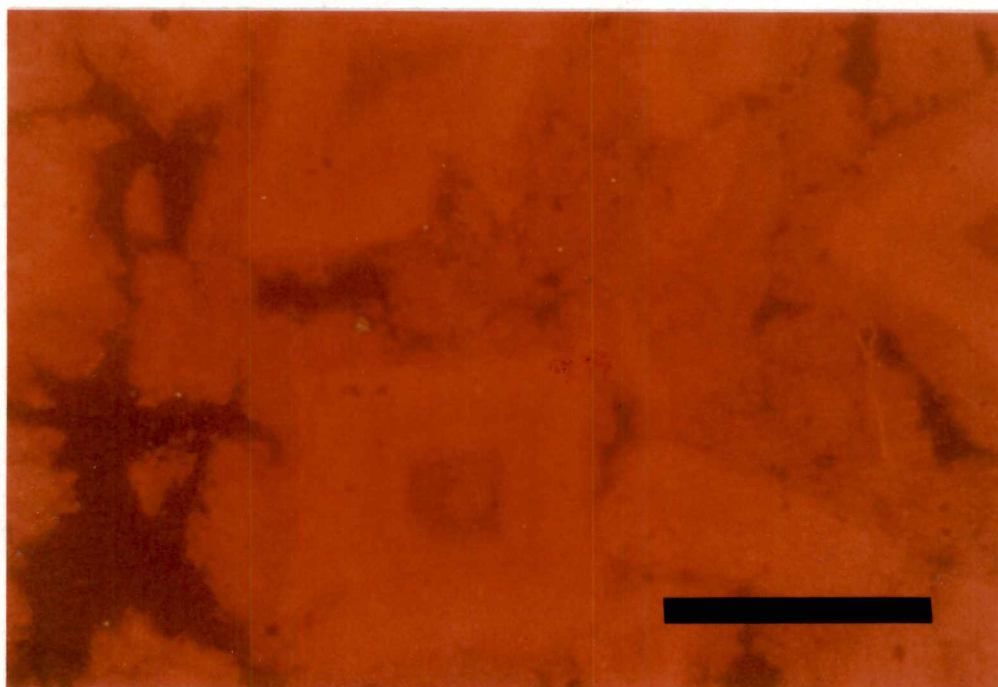


Figure 16. Photomicrograph of X-H, MCd from the Coy mine showing two stages of dolomitization, subhedral and anhedral (sample C20B, with cathodoluminescence, Kodacolor print, ASA 400). Scale bar represents 1 mm.

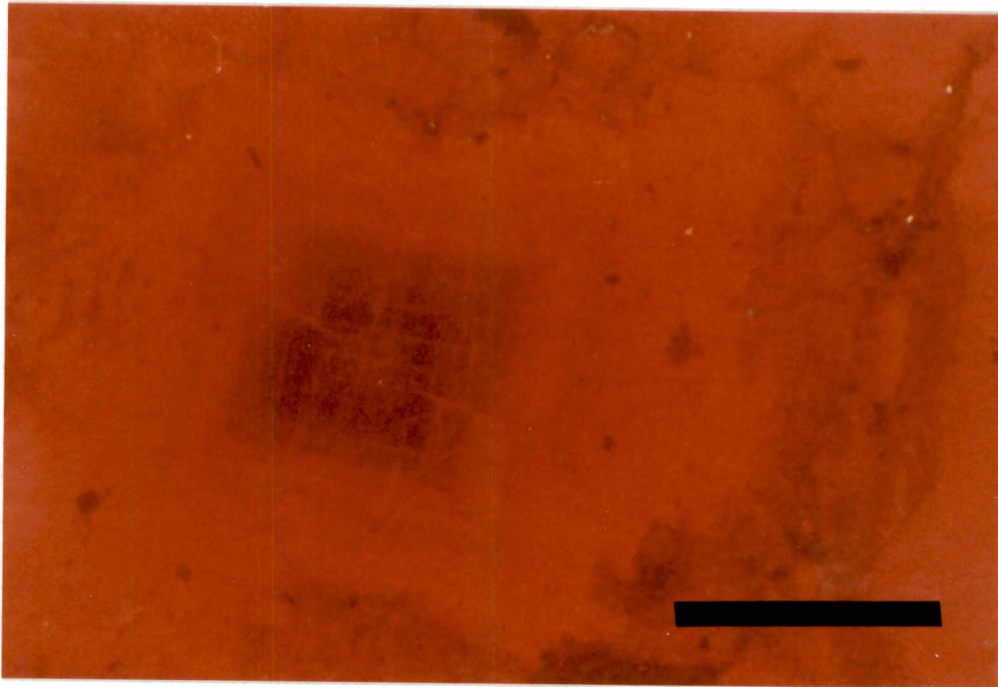


Figure 17. Photomicrograph of X-H, MCd from the Coy mine showing zonation similar to that of Figure 16 (sample C6A, with cathodoluminescence, Kodacolor print, ASA 400). Sample C6A was located approximately 30 m above sample C20B. Scale bar represents 1 mm.

anhedral, nonzoned crystals formed, using the subhedral crystals as nucleation centers. It is doubtful that the anhedral boundaries of these crystals are due to compromised growth, because some of the anhedral boundaries abut chert matrix. Gregg and Sibley (1984) suggest that euhedral and subhedral crystals grow below a critical roughening temperature (estimated at 50°C for dolomite) and that anhedral crystals grow above this temperature. They further propose that these temperatures are related to depth of burial.

Another zonation sequence was found in subhedral serrated rhombs from two samples of partially dolomitized limestones (C10A and C13B, Fig. 14, p. 37) and from a completely dolomitized rock (C11A) containing sphalerite. These samples were located near the R bed-S bed contact (Fig. 4, p. 14). Dolomite in the partially dolomitized samples appears to be related to stylolites, and in all three samples the dolomite crosscuts late-stage, calcite-filled microfractures (Fig. 14). The luminescent color of these dolomite crystals is redder and less orange than that of dolomite crystals forming anhedral mosaics, and the luminescent zones vary more subtly in color and intensity.

Both zonation patterns are substantially different from those found in the gangue dolomites. A general dull luminescence in X-H,MCd suggests a high Fe:Mn ratio,

possibly indicating precipitation in a reducing environment similar to Carpenter and Oglesby's (1976) environment III (Fig. 6, p. 20). Thicker zones and rather subtle alternations in intensity (as well as absence of nonluminescence, except at rhomb cores) suggest burial conditions under which pore waters were not subject to frequent flushing (Grover and Read, 1983).

Limestones

Limestone lithologies observed in the present study are similar to those described by previous workers (Sandrock, 1973; Snyder, 1975; Churnet, 1979), which were interpreted as having been deposited in intertidal and shallow subtidal environments. These environments are represented by two basic lithotypes: (1) micrite (or microspar), usually characterized by burrows, birdseyes, and bedding-parallel laminae of possible algal origin, and (2) intrapelmicrites or intrapelsparites, marked by varying abundances and types of fossil allochems. Churnet (1979) lists fossil allochems found in the Copper Ridge district, in decreasing order of abundance, as trilobites, gastropods, ostracodes, brachiopods, pelmatozoans, and sponges. In the present study, a large intact specimen of the algae Hedstroemia sp. was noted in sample C2B. Equant sparry calcite cement fills interallochem pore space, suggesting precipitation in the freshwater phreatic or mixing-zone

environments (Longman, 1980). This cement also fills Hedstroemia pores, which are delineated by unbroken micritic envelopes indicative of early cementation. No marine fibrous cements (Bathurst, 1975; Longman, 1980) were noted.

Limestones have been replaced by dolomite to varying degrees. Samples C18 and C19 (Fig. 4, p. 14) are unaltered biomicrites located approximately 18 m from a nonmineralized breccia body. The only dolomite present in these samples consists of a few small unzoned rhombs. (Completely altered limestones were discussed in the sections on I-H,FCD and X-H,MCd. The original features of these limestones have been obliterated.) Partially altered limestones are potentially useful because they offer clues to conditions of limestone replacement by dolomite. Two locations in the Coy mine represent two possible ways in which the limestones were altered. The lithotypes at these locations are similar to those found elsewhere in the Coy mine.

At stope 9-50, 648 level (Fig. 4, p. 14), three samples were taken from the R bed, above the 89-90 X,Fd bed. The samples were located approximately 3, 2, and 1 m from a mineralized breccia body. Sample C1A, furthest from the breccia, consists of relatively unaltered micrite and intrapelsparite, with some disseminated sphalerite.

Dolomite is present as a few small (0.37 mm) unzoned rhombs. Closer to the breccia body, samples C2B (biomicrite) and C3B (microspar) are increasingly altered. Both are extensively dolomitized with X-H,MCd, which occurs as anhedral crystals and serrated rhombs. This dolomite replaces interallochem sparry calcite cement as well as micrite, indicating dolomitization after lithification of the limestone (Mattes and Mountjoy, 1980). In C3B, sphalerite is disseminated in a discontinuous band surrounding a chert fragment. There is an increase in the abundance of dolomite as the chert and sphalerite are approached. These relationships suggest that late-stage dolomitization, silicification, and sphalerite mineralization are related.

Samples C10A and C13B are from stope 25-56, level 381. Sample C10A is a biointrapelmicrite from the R bed (below the 68-71 X,Fd), and C13B is a biopelmicrite from the S bed (below the 62-65 X,Fd). Both have been partially replaced by coarse, spear-shaped crystals and serrated rhombs that appear to be related to stylolitization. Dolomite grows across stylolites and is consumed by them, which implies growth roughly contemporaneous with stylolite formation (Churnet, 1979). This dolomite replaces micrite as well as fossil allochems. Luminescent zonation in these samples has been discussed in the section on X-H,MCd.

Summary

1. As suggested by previous workers, X,Fd were probably deposited in intertidal to supratidal environments. Dull red luminescence and rare bright rims suggest neomorphism under reducing conditions, with occasional influxes of meteoric water in more porous rocks.

2. I-H,FCd (in this study, found almost exclusively in Central Tennessee) are most similar petrographically to dolomites reported in near-surface meteoric-seawater mixing or schizohaline environments. Thin bright zones and non-luminescing zones suggest "frequent" flushing of pore solutions by oxygenated meteoric waters.

3. X-H,MCd (in this study, found exclusively in East Tennessee) exhibit textures to those described by various authors as characterizing mesogenetic or burial dolomites. The X-H,MCd differ texturally from coarser-grained dolostones described in previous studies of the Tennessee zinc districts. Cathodoluminescent evidence suggests two distinct periods of dolomitization. During the first, zoned rhombs were precipitated--rhombs differing from those expected in near-surface, diagenetic environments. With crossed nicols, the rhombs exhibit sweeping extinction and appear to be a single crystal with later nonzoned anhedral dolomite. With cathodoluminescence, the rhombs show rather thick, dull zones with no dramatic changes in intensity.

These properties suggest precipitation in a stable reducing environment, possibly phreatic, possibly deeper connate. During the second period of dolomitization, anhedral crystals were precipitated. These crystals are dull and nonzoned with luminescence. X-H,MCd grow across stylolites and fractures and crosscut bedding. These features imply dolomitization after lithification. The intimate association of X-H,MCd, chert, and sphalerite in sample C3B suggests a possible relationship in modes of formation of these three phases. Although X-H,MCd and gangue dolomite are similar in appearance in transmitted light and with crossed nicols, their luminescent signatures differ.

4. Initially limestones were deposited in an intertidal to shallow subtidal environment. Replacement by chert and X-H,MCd took place after compaction and cementation by sparry calcite.

CHAPTER III

ELEMENTAL CONCENTRATIONS

Sample preparation procedures are outlined in Appendix C. Seventy-four whole-rock analyses were performed at EG&G ORTEC, Oak Ridge, by X-ray fluorescence spectrometry and with reference to nine NBS standards (Appendix D, Table 8). Standard error, counting error, analyses results, and duplicate results for some samples are given in Appendix D, Tables 9-11. Although data for 13 elements were obtained, discussion of such elements as S, P, and Ti is limited. Elemental concentrations in the present study are somewhat higher than those determined by means of atomic absorption spectrometry because the present analyses were performed on whole-rock samples. Approximate insoluble-residue influence can be inferred by plotting various elements against Al and calculating their correlation coefficients (Bein and Land, 1982). In the following discussion, an element's concentration does not vary systematically with Al (clay) content unless such variation is specified.

Elemental concentrations are discussed and compared with values (Table 1) from other studies of the East Tennessee zinc districts (data from Central Tennessee are limited). Concentrations are also compared with values from

TABLE 1. Average Fe, Mn, and Sr Values (ppm) from Studies of Tennessee Zinc Districts

Lithology	Present Study	Moss (1982)	Snyder (1975)	West (1974)
		<u>Fe</u>		
Limestones	1216 ± 1000	228 ± 104 6627 ± 825	464 ± 330	277 ± 150
X, Fd	3768 ± 830	1644 ± 604 7604 ± 1533	3651 ± 1061	1382 ± 246
X-H, MCd	5043 ± 766	2006 ± 504 8760	3687 ± 552	1956 ± 790
		<u>Mn</u>		
Limestones	165 ± 211	23 ± 10 86 ± 32	60 ± 21	301 ± 179
X, Fd	320 ± 82	169 ± 10	420 ± 315	164 ± 55
X-H, MCd	740 ± 157	162 ± 53	514 ± 242	412 ± 160
		<u>Sr</u>		
Limestones	211 ± 42	275 ± 68		188 ± 42
X, Fd	154 ± 45	81 ± 16		38 ± 21
X-H, MCd	130 ± 13	170 ± 28		52 ± 43

Snyder (1975) and the present study conducted in the Mascot-Jefferson City district. Those of West (1974) and Moss (1982) are from the Copper Ridge district.

Weber's (1964) survey study of 300 dolostones. Elemental concentrations should be compared with caution, since values can vary both within a particular rock and regionally. Also, the X-H,MCd of the present study appear to differ texturally from coarser-grained dolostones of previous studies.

The present discussion is divided by element, location (Central and East Tennessee), and lithology. Lithologies in East Tennessee, as described in Chapter II, comprise limestones; xenotopic, fine-grained dolostones (X,Fd); and xenotopic-hypidiotopic, medium- to coarse-grained dolostones (X-H,MCd). The occurrence of idiotopic-hypidiotopic, fine- to coarse-grained dolostones (I-H,FCd) is limited to four samples, one of which has a clay matrix (C9A). Three samples (C9C, C10B, C21B) are composed of I-H,FCd and white sparry (gangue) dolomite. The components are in close proximity and were difficult to separate during sample preparation. These samples appear to represent rocks that were more completely replaced by subhedral rhombs during the first stage of dolomitization, described in Chapter II. Later dull, nonzoned dolomite, however, is present as well. Because of its alternating areas of white sparry dolomite and dolomitic wall rock, this lithotype has been termed "zebroid" dolomite by other workers (Beales and Hardy, 1980; Zenger, 1983) and is mentioned elsewhere in relation to

lead-zinc deposits. The relatively infrequent occurrence of I-H,FCd and, in one sample, its occurrence in clay limit discussion of this lithology in the present study.

Lithologies in Central Tennessee are limestones; X,Fd; and I-H,FCd. One sample (MA3A) of X-H,MCd was taken from the Right Fork cores.

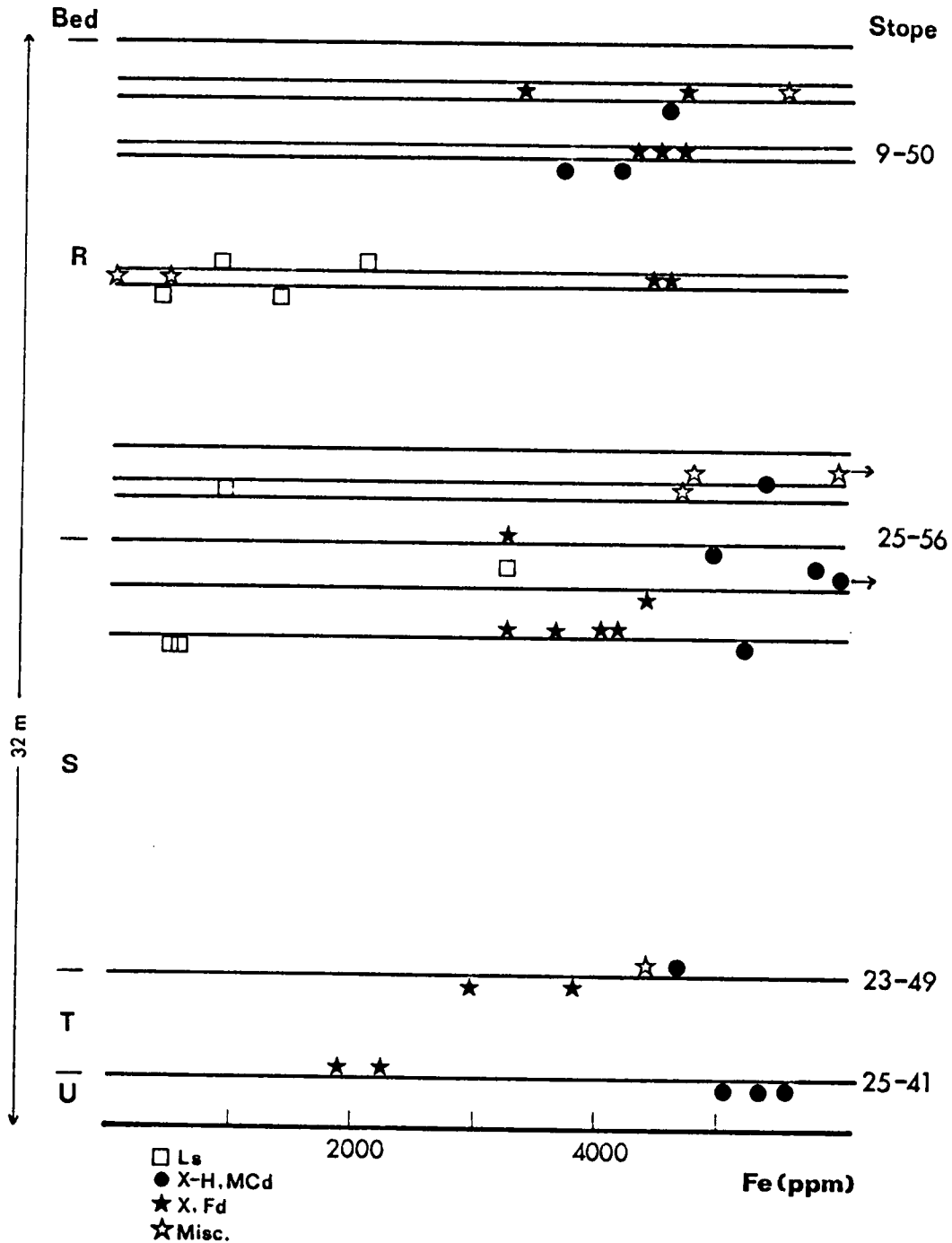
Iron

East Tennessee. When compared with those reported in previous studies of the East Tennessee zinc districts, Fe concentrations of the present study are generally greater (Table 1). In limestones, the reason for these higher Fe values is probably partial dolomitization of certain limestone samples, as noted in the petrography section. Even though X-H,MCd often contain no Al (clay), their Fe values are higher than those of any other lithology.

The X,Fd values of the present study are similar to those of Snyder's fine-grained dolostones from the Coy mine (3768 and 3651 ppm, respectively) but are higher than those found by West (1974) in the Copper Ridge district (1382 ppm). Moss (1982), also working in the Copper Ridge district, perceived a bimodal distribution of Fe in this lithology (1644 and 7604 ppm). In the present study, X,Fd show roughly similar Fe concentrations in individual locations and at similar stratigraphic levels, but the values

vary more widely from level to level (Fig. 18). This pattern suggests a facies control of the Fe distribution and/or neomorphism in similar solutions (Bein and Land, 1982; Gregg and Sibley, 1984).

The average Fe concentration of X-H,MCd (5043 ppm) is higher than those of Snyder's and West's coarse-grained dolostones (3687 ppm and 1956 ppm, respectively). The values for X-H,MCd of the present study fall between the bimodal values for Moss's coarse-grained dolostones (2006 and 8760 ppm). Fe concentrations in X-H,MCd of the present study are fairly consistent (usually between 4000 and 6000 ppm). Since Fe substitutes for Ca and Mg most readily in the reduced state (Oglesby, 1975; Frank et al., 1982), it is likely that these high concentrations of Fe are due to long-term equilibration in a burial environment. Other workers have commented that ferroan dolomites result from "late" alteration by saline formation waters in a reducing environment (Land, 1980; Moss, 1982). Mixing-zone dolomites, on the other hand, "should be nonferroan, reflecting typically oxidizing conditions" (McHargue and Price, 1982). Other workers agree that with increased burial, stagnation and organic depletion of oxygen decrease the redox potential of aquifer waters (Grover and Read, 1983; Heckel, 1983). According to Wong and Oldershaw (1981), "Most formational waters below the vadose/phreatic interface are likely to be reducing."



Central Tennessee. The average Fe concentrations in X,Fd and I-H,FCd are similar (2086 and 2145 ppm, respectively). The values are comparable to those of Weber's (1964) AP "primary" (2700 ppm) and S4,S5 "secondary" (2100, 2000 ppm) dolostones.

Manganese

"Distribution coefficient" (D) is a term that refers to the ratio of the solubility products of two pure solids, such as CaCO_3 and MnCO_3 , that can be considered as composing a solid solution (Morel, 1983). If $D > 1$ for a particular trace element, then that element is preferentially concentrated in the solid phase (Pingitore, 1978). If $D = 1$, the trace element is concentrated equally in the solid and the liquid phases. If $D < 1$, the trace element is preferentially concentrated in the liquid. The trace element may be enriched in the solid phase by autoenrichment, the increase of a trace element as a result of a decrease in the major element in an open system, and by alloenrichment, the increase of a trace element due to an external supply of that element. "Autodepletion" denotes the loss of a trace element ($D < 1$) from a diagenetic site due to high water flow. "Allodepletion" refers to the loss of a trace element when a liquid containing low concentrations of the element enters the diagenetic area. After equilibration, the chemistries of limestones and dolostones are subject to

change during dissolution/cement precipitation and recrystallization (Pingitore, 1978). Although the Mn partition coefficient for dolomite is not known, it is thought to be greater than unity (Pingitore, 1978; Land, 1980), which means that Mn would be concentrated in the solid phase during diagenesis. Mn concentrations in that phase are thought to be controlled primarily by Eh conditions (Oglesby, 1976; Brand and Veizer, 1980; Moss, 1982), with Mn entering the crystal under reducing conditions. Modern oceans are reservoirs of Mn (Degens, 1965; Land et al., 1975), as are meteoric waters (Turekian, 1976; Churnet, 1979) and oil-field brines (Rittenhouse et al., 1969).

East Tennessee. The average Mn concentrations determined in the present study are compared with those of other studies of Tennessee zinc districts in Table 1 (p. 51). Unaltered limestones contain no detectable Mn. Mn values for X,Fd, and X-H,MCd are higher in the Coy mine (Synder, 1975, and the present study) than at the two locations in the Copper Ridge district (West, 1974; Moss, 1982). The average Mn concentration of X-H,MCd is especially high (740 ppm), but it is within the range of Weber's (1964) M3 "argillaceous" dolostones (640 ppm).

Figure 19 illustrates the variation in Mn concentrations with stratigraphic level. In general, Mn concentrations follow the same pattern as concentrations of Fe--that

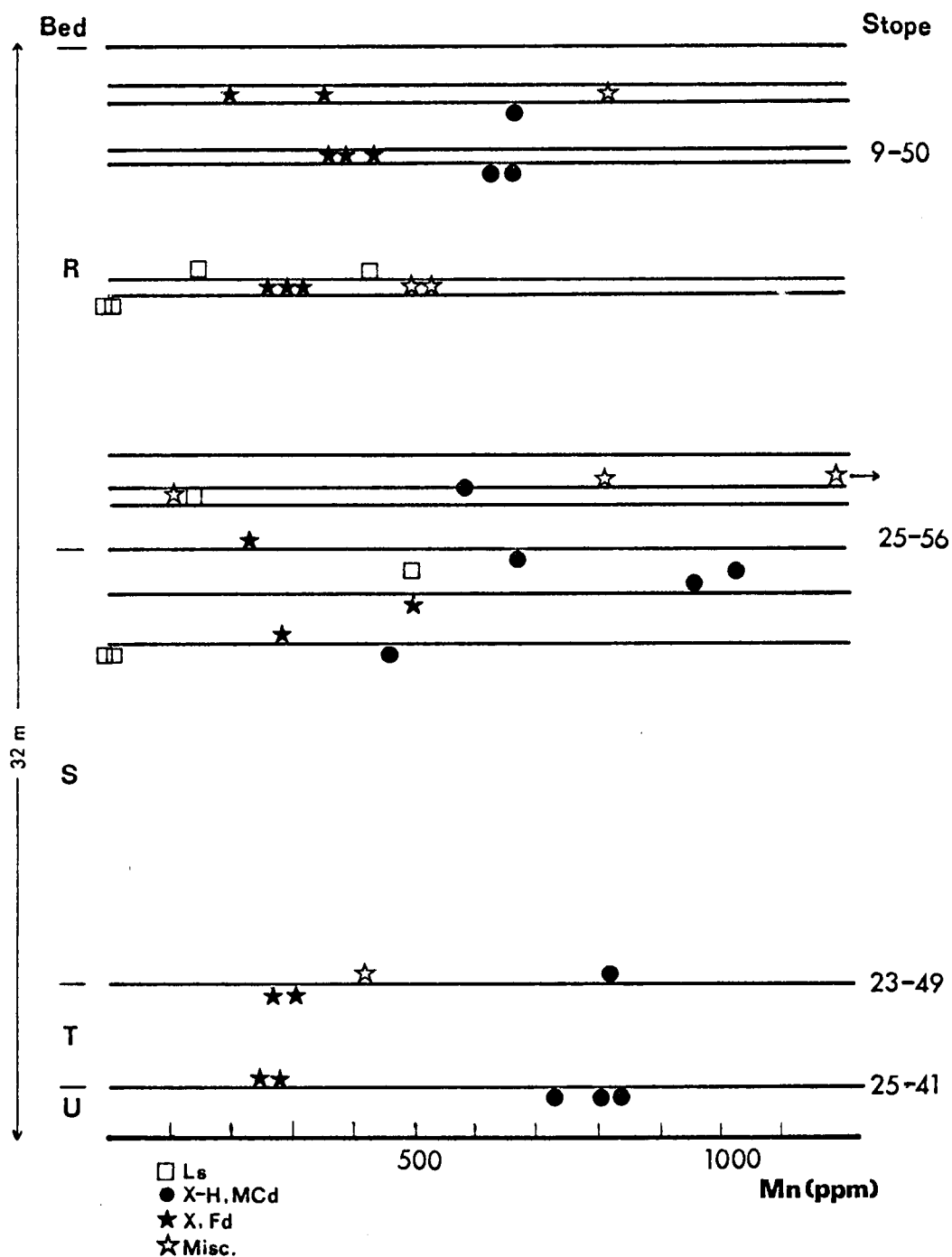


Figure 19. Variation of Mn concentration with stratigraphic level among samples taken from the Coy mine.

is, $X-H, MCd > X, FD > Ls$; however, two samples of partially dolomitized limestone contain higher Mn concentrations than most of X, Fd . X, Fd show very little variation in Mn, even through a vertical distance of approximately 35 m and a horizontal distance of 1200 m. Most samples have concentrations between 250 and 450 ppm. The pattern suggests either remarkably stable depositional and diagenetic conditions or neomorphism of X, Fd over a long period of time and in a rather stable reducing environment. The average Mn concentration for $X-H, MCd$ is approximately double that for X, Fd , and the individual values are considerably more variable.

Central Tennessee. Limestones contain very low Mn concentrations, comparable to those of East Tennessee undolomitized limestones of the present study (Appendix D, Table 8). $I-H, FCd$ and X, Fd have average Mn concentrations that are fairly similar (231 and 215 ppm, respectively). Mn values vary little in either lithology, but the concentrations for $I-H, FCd$ are more variable. As with X, Fd of East Tennessee, this pattern suggests either extremely stable depositional and diagenetic environments or fairly steady reducing conditions in a burial environment.

Strontium

Sr concentrations in Recent calcitic sediments average from 1000 to 1200 ppm (Badiozamani, 1973). This average

decreases to 400 to 700 ppm in ancient limestones (Kinsman, 1969; Land et al., 1975). Kinsman and Holland (1969) suggest that the concentration of Sr in a solid phase is determined by the ratio of Sr to Ca in the solution and by the temperature "at which the sediment was deposited." Presumably the temperature at which subsequent recrystallization episodes took place would also determine the ultimate Sr concentration in the solid. Badiozamani (1973) found that the Sr concentration in calcite is inversely proportional to the degree of supersaturation of the solution with respect to calcite. Thus low Sr concentrations such as those found in ancient limestones and dolostones can result from diagenetic equilibration with calcite-supersaturated solutions or with solutions, such as meteoric water, that contain much less Sr than does seawater.

Churnet (1979) and Moss (1982) use this reasoning to explain Sr distribution in some limestones and dolostones in the Copper Ridge district. Their belief that Sr depletion is primarily attributable to equilibration with meteoric waters is predicated on Kinsman's (1969) $D_{\text{calcite}}^{\text{Sr}}$ of 0.14 at 25°C. The $D_{\text{calcite}}^{\text{Sr}}$ is considerably lower at higher temperatures (0.08 at 100°C, Kinsman, 1969; 0.055 at 40°C, 0.058 at 94°C, Katz et al., 1972; 0.025 at 250°C, Katz and Mathews, 1977), but Churnet noted that temperatures above 100°C "are not attained in normal sedimentary environments or during

most stages of diagenesis." This statement does not take into account the fact that elevated homogenization temperatures (82° to 149°C, Roedder, 1971; 100° to 120°C, Taylor et al., 1983) have been reported for fluid inclusions in gangue and ore minerals from the Tennessee zinc districts. Hydrocarbons are a common constituent of Knox dolostones in the Tennessee zinc districts, including those of the present study (Larry Landau, 1984, personal communication). The presence of hydrocarbons suggests the minimum temperature of 115°C that is required for petroleum formation (Collins, 1975). Conodont coloration indices (Harris, 1979) for Lower and Middle Ordovician carbonates in East Tennessee indicate minimum temperatures of 60° to 140°C. Even if these higher temperatures are ignored, it is likely that the $D_{\text{dolomite}}^{\text{Sr}}$ is lower than Kinsman's 0.14. Land (1980) concludes from a study of Sr-depleted chalk altered during marine burial diagenesis in the absence of meteoric water and at a normal geothermal gradient that it is "quite possible that the effective $D_{\text{dolomite}}^{\text{Sr}}$ for replacement dolomitization is . . . very much lower than 0.07." Since distribution coefficients for Sr into calcite or dolomite are probably quite low, equilibration with meteoric water is not required to explain Sr depletion in the limestones and dolostones of the Kingsport Formation.

East Tennessee. Average Sr concentrations in the carbonate rocks of the present study are greater than those of West (1974), as shown in Table 1 (p. 51). Average concentrations for limestones (211 ppm) and for X-H,MCd (131 ppm) are slightly less than those of Moss (1982): 275 and 170 ppm, respectively. X,Fd of the present study have a greater average Sr content (154 ppm) than the fine-grained dolostones of Moss (92 ppm). This may be partly due to additional Sr content in clays, since Sr correlates well with Al in this lithology. Average Sr concentrations of the present study are similar to those of Weber's (1964) primary (174 ppm) and secondary (187 ppm) dolostones.

Central Tennessee. The average Sr concentration of X,Fd (254 ppm) is greater than that of X,Fd from the Coy mine, suggesting a lesser degree of diagenetic stabilization (Veizer et al., 1978; Churnet, 1979). Both X,Fd and I-H,FCd (235 ppm) have even higher Sr values than the Coy mine limestones. Right Fork limestones show an average Sr concentration of 320 ppm.

Potassium

K is found in lattice sites, fluid inclusions, and clays in limestones and dolostones (Bein and Land, 1982). Suggested sources of K include the following:

1. Seawater concentrated by evaporation (Carpenter et al., 1974).

2. Adsorption from seawater onto the surface of clays (Schmidt, 1973; McHargue and Price, 1983). However, when smectite is converted to illite, Si, Mg, Ca, and various base metals are released into solution and K enters the clay. Carpenter et al. (1974) have suggested that smectite-illite conversion is an "important mechanism for the origin of metal-rich brines in sedimentary basins," but the process would also deplete K from such brines. Haynes and Kesler (1983) have noted a "significant population" of fluid inclusions in sphalerite and dolomite from the Mascot-Jefferson City district, with "higher K content than most modern basinal brines."

3. Concentration by marine algae (McHargue and Price, 1983). K is stored within the cells of organisms rather than in intercellular fluid and is therefore retained during decay (Weaver, 1967). Vinogradov (1963) found that the ash of some marine algae contains 20 to 40 percent K_2O .

East Tennessee. Average K concentration is highest in X-H, MCd (9976 ppm, Appendix D, Table 10). Limestones have an average concentration of 2448 ppm, and X, Fd contain 5053 ppm. Only X, Fd show a good correlation between K and Al, so it is probable that most of the K in this lithotype is contained in clay. Weber (1964) found K concentrations of 6550 ppm in 135 primary dolostones and 3970 ppm in 94 secondary dolostones.

Central Tennessee. Average K concentrations in X,Fd and I-H,FCd are 4593 and 3754 ppm, respectively. These values are similar to those for X,Fd in East Tennessee.

Silicon

East Tennessee. In carbonate lithologies of the present study, Si (as SiO_2) occurs in chert, detrital quartz grains, or clays. The limestones contain quartz primarily as detrital quartz and chert that is commonly associated with partial dolomitization. This is supported by a strong negative correlation between Si and Ca. In X,Fd, Si is found mostly in detrital quartz grains and in clay in concentrations of 10^3 to 10^4 ppm. X-H,MCd are relatively rich (10^4 to 10^5 ppm) in Si, which occurs primarily in interstitial chert and in chert nodules. As mentioned in Chapter II, small dolomite rhombs, as well as the original calcitic sediment, appear to have been replaced by chert. The large amount of Si needed for replacement could have come from several possible sources:

1. Dissolved sponge spicules. Sponges are a common fauna in the upper Knox Group (Churnet, 1979).
2. Saline formation waters that may be supersaturated with respect to quartz. Carpenter and Miller (1969) and McHargue and Price (1983) suggest that clay minerals control the amount of silica in formation waters.

In fact, chert nodules, often associated with the dolostone lithologies of the present study, might be related to dolomitization. Baker and Kastner (1981) found that the formation of chert is a two-step process. First, amorphous silica is transformed to opal-CT, depressing the Mg content of pore solutions. Baker and Kastner's experiments suggest that "about four times as much Mg is available on exchange sites of solid silica as is dissolved in pore waters." In the siliceous sediments of the Northern Pacific, the conversion of biogenous silica to opal-CT begins 600 m below the sea floor (Tucker, 1983). The formation of chert is not necessarily an "early" phenomenon. It is possible that some dolomite of the present study, especially X-H,MCd that contain abundant interstitial chert, formed during the transformation of opal-CT to chert.

Central Tennessee. In X,Fd and I-H,FCd, detrital quartz grains and clays contain most of the Si. Concentrations are in the 10^3 - to 10^4 -ppm range (Appendix D, Table 11), with the exception of a few samples that contain a large component of detrital quartz (Md sand). It is possible that proximity to continental environments, suggested by abundant detrital quartz grains, accounts for the elevated concentrations of K and other elements (such as Br) in X,FD as a result of the evaporation of seawater.

Bromine and Chlorine

Several workers (Rittenhouse, 1967; Carpenter et al., 1974) have suggested that natural waters can be characterized by their Br:Cl or Br:total dissolved solids (TDS) ratios. Rittenhouse (1967) divides natural waters into five groups on the basis of their Br:TDS ratios. These groups are presented in Figure 20. Group I waters have Br and TDS concentrations approximating those of seawater (65 ppm Br) or of seawater diluted with water of low TDS or Br concentrations. Group II waters show Br contents greater than that of seawater, possibly as an effect of decomposed organic matter during early diagenesis or from concentrations by semipermeable shale membranes. Group III waters have TDS greater than that of seawater, but Br concentrations are lower. These waters may have originated from the dissolution of halite. Group IV waters show TDS lower than that of seawater, but the concentrations of Br are less than would be expected in seawater diluted with waters of low TDS and Br concentrations. Group V waters have both Br and TDS concentrations greater than those of seawater. These waters are described as bitterns formed from seawater evaporated past the point of halite deposition.

Interpretations of the mode of formation of these waters are based upon the assumption that during calcium carbonate and gypsum deposition, little Br is lost. When

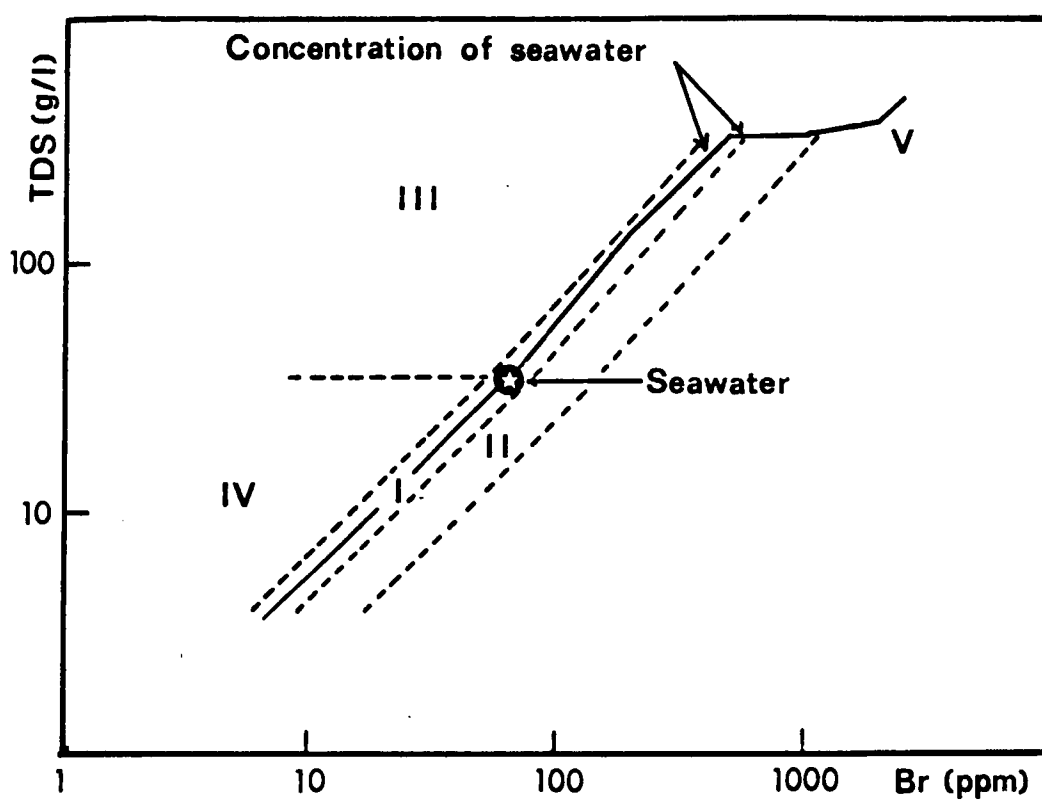


Figure 20. Five groups of natural waters based upon bromine and total dissolved solids (TDS) content (modified from Rittenhouse, 1967).

halite is precipitated, the substitution of Br for Cl in the crystals is restricted by the large ionic radius of Br. Br concentration in the evolved brine is near 550 ppm at the onset of halite deposition and may exceed 1000 ppm. Analyses from 20 modern evaporite sequences show that Br concentrations in halite typically fall between 30 and 80 ppm and rarely exceed 200 ppm (Herrmann and Knake, 1973; Panno et al., 1983).

Panno et al. (1983) suggest an origin for brines involved in lead/zinc mineralization of the Buick Mine in the Viburnum Trend, based upon Br:Cl ratios of dolostone wall rock and salinities of fluid inclusions. They found that the Br:Cl ratio increased from approximately 0.0035 (that of seawater) at a distance of 750 ft from the ore body to 0.0094 immediately adjacent to the ore body. They interpret their results as indicating that the ore solutions were brines formed by evaporation of seawater past the point of halite deposition (Rittenhouse's Group V). Other workers (Rittenhouse, 1967; Collins, 1975; Graf, 1982) have noted that such highly saline waters can form by interaction with shales and long-term equilibration with country rock. Bromine enrichment in subsurface brines can also occur by subsurface leaching of bioconcentrated Br or anion exchange (Cl for Br) on clays (Kozin, 1960; Collins, 1975).

Panno et al. found a good correlation between Br and Cl in dolostones adjacent to the Buick ore body. They interpret Br:Cl ratios in the rocks as reflecting the Br:Cl ratio of the ore-forming solutions. In dolostones of the present study, there is a negative correlation for Br and Cl. Therefore, the Br and estimated total dissolved solids for dolostones of the present study cannot be plotted on Figure 20.

East Tennessee. Br concentrations in the present study range between 2 and 13 ppm (Appendix D, Table 8) in X,Fd (average 7 ppm) and between 3 and 10 ppm in X-H,MCd (average 7 ppm). The limestones are generally devoid of Br, with the exception of two partially dolomitized samples. Two samples (C1B, C2A, Appendix D, Table 8) containing chert breccia fragments have extremely high Br concentrations (36 and 51 ppm, respectively).

Cl concentrations in limestones range from 347 ppm in partially dolomitized samples to 2669 ppm in relatively "pure" micrites (average 1900 ppm). X,Fd Cl concentrations are between 40 and 1028 ppm (average 434 ppm), and those for X-H,MCd average 256 ppm and range from 0 to 1128 ppm in a sample that contains relict micrite.

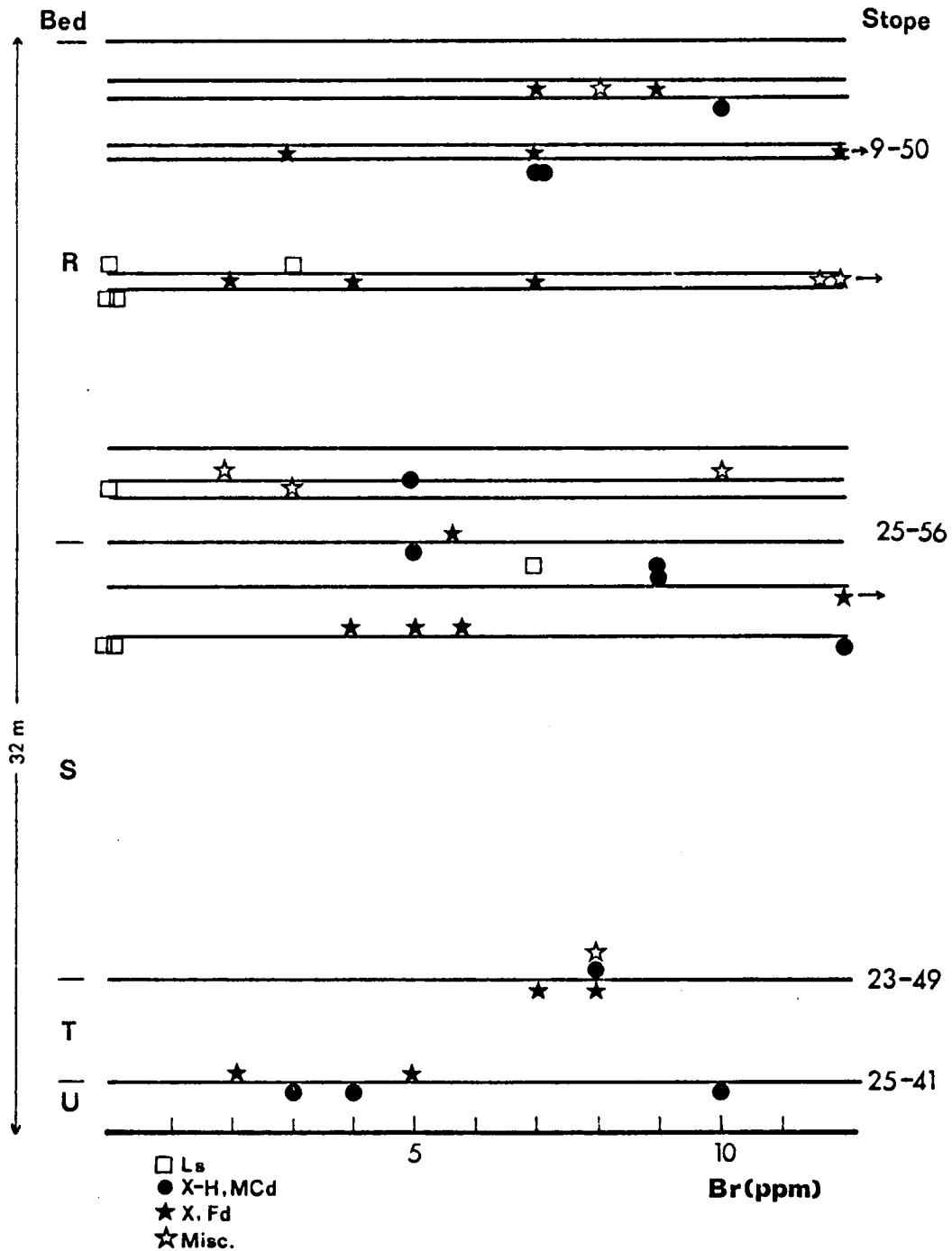
Panno et al. (1983) found Br and Cl concentration ranges of 4 to 7 ppm and 500 to 1000 ppm, respectively,

proximal to the Buick ore body. These values were determined by whole-rock neutron-activation analysis and XRF spectrometry. Panno et al. attribute halide enrichment to an increase in abundance of fluid inclusions adjacent to ore. Correlation coefficients for Br-Cl and Br-Al in the present study are neither significantly positive nor negative, so the amount of Br contained in clays, in the carbonate lattice, or in fluid inclusions cannot be discussed accurately. However, Churnet and Misra (1981) concluded that Cl concentrations in dolostones of the Copper Ridge district could not be explained by the presence of NaCl fluid inclusions (Moss, 1982). Element-element plots for Br and Cl do reveal several possible explanations of their concentrations. Limestones are usually devoid of Br and characterized by high Cl concentrations, so their Br:Cl ratios are essentially nil. Partially dolomitized limestones have Br:Cl ratios slightly higher than that of seawater (0.0035). The Br:Cl ratios of X,Fd vary between 0.0058 and 0.0488, and those of X-H,MCd range from 0.0080 in a sample with relict micrite to "infinity" (no detectable Cl) in dense, anhedral dolomite mosaics. A plot of Br:Cl vs. Cl in Figure 21 illustrates these relationships. The diminution or absence of Cl in X-H,MCd is not fully understood; however, it might be due to the extreme solubility of the Cl ion or to complexing of Cl with base-metal ions.

X-H,MCd were located adjacent to breccia bodies and mineralized areas, in contrast to limestones, which were 3 to 18 m from mineralized areas. Haynes (1984, personal communication) has noted the increase of Br:Cl ratios in fluid inclusions of dolomite gangue "directly associated with ZnS (i.e., in stages 3d to 5 in the cathodoluminescent sequence of Ebers and Kopp)." Location of X-H,MCd by means of extremely high Br:Cl ratios may prove to be a good prospecting method, especially if core samples are used. Br:Cl ratios from nonmineralized country rock need to be determined to test this hypothesis.

Diagrams of Br and Cl variations with stratigraphic level (Figs. 22 and 23) show the similarity of Br and Cl values in some paired samples and at similar stratigraphic levels. Comparable values for paired X-H,MCd and X,Fd suggest epigenetic influence, since it is doubtful that the same diagenetic pore fluid would exist for supratidal and subtidal facies.

Central Tennessee. As in East Tennessee, limestones usually show no Br above detection limits. Br concentrations vary between 2 and 14 ppm (average 7 ppm) for X,Fd and between 0 and 6 ppm (average 5 ppm) for I-H,FCd. One sample containing chert breccia fragments (MA7A2) shows a very high Br concentration (32 ppm). Limestones have Cl concentrations in the 2000-ppm range. Cl concentrations in X,Fd



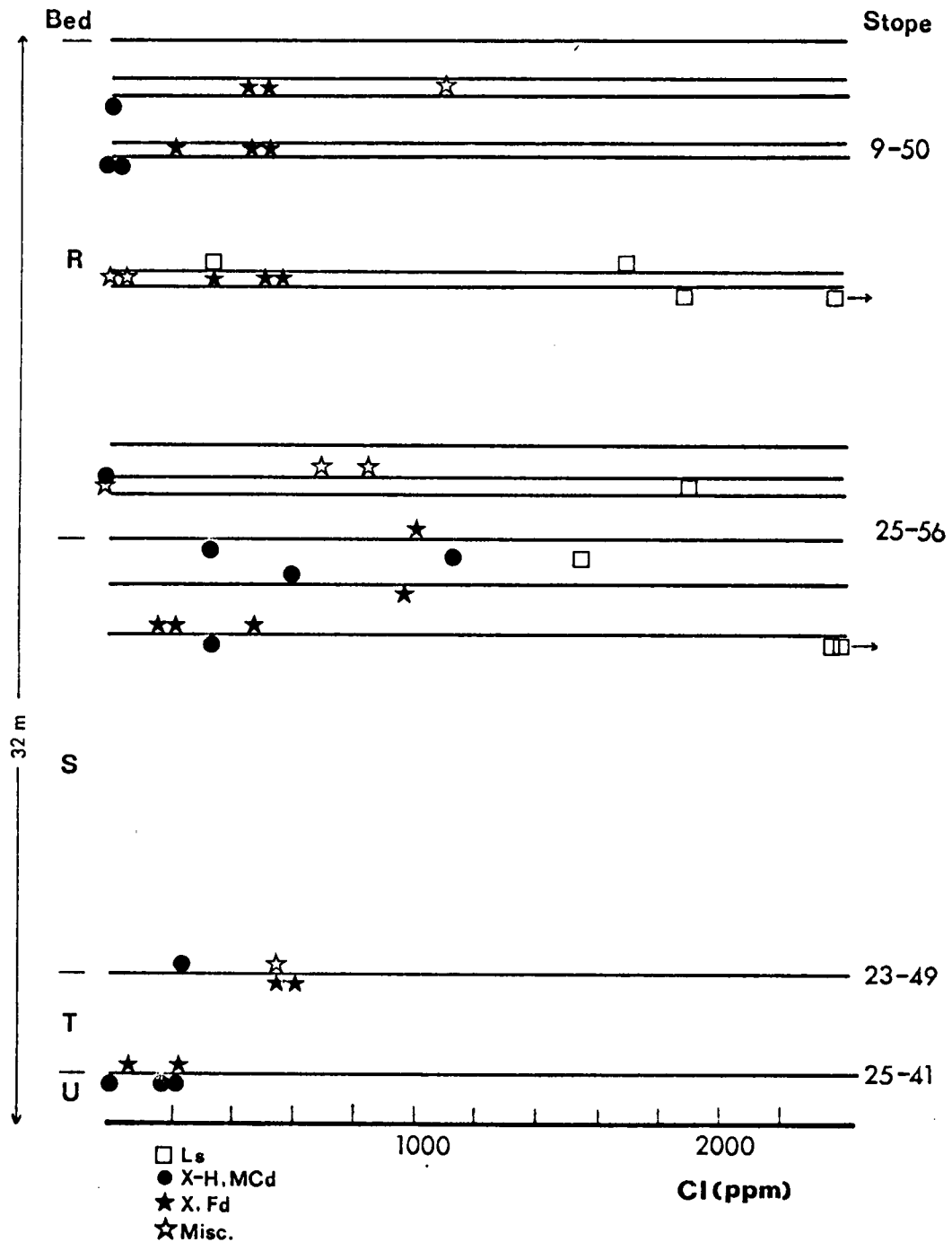


Figure 23. Variation of Cl concentration with stratigraphic level among samples taken from the Coy mine.

range from 0 to 483 ppm (average 164 ppm) and are usually lower than those in X,Fd of East Tennessee. I-H,FCd show Cl values ranging from 222 to 640 ppm (average 392 ppm).

A plot of Br:Cl vs. Cl (Fig. 24) reveals a trend similar to that in lithologies of the Coy mine. There is a general decrease in Br with increasing Cl. Very high Br and low Cl concentrations occur in dolomicrites and in samples containing abundant detrital quartz. Br:Cl ratios range from 0.0083 to 0.0444 in X,Fd and from 0 to 0.0225 in I-H,FCD. These ratios, especially in X,Fd, vary systematically from borehole to borehole at the levels of both the Ma shale and the Md sand. It is possible that the areas characterized by elevated Br:Cl ratios were paleotopographic highs that, being infrequently flooded, retained the high Br levels of an evaporative brine (Long and Gudramovics, 1983).

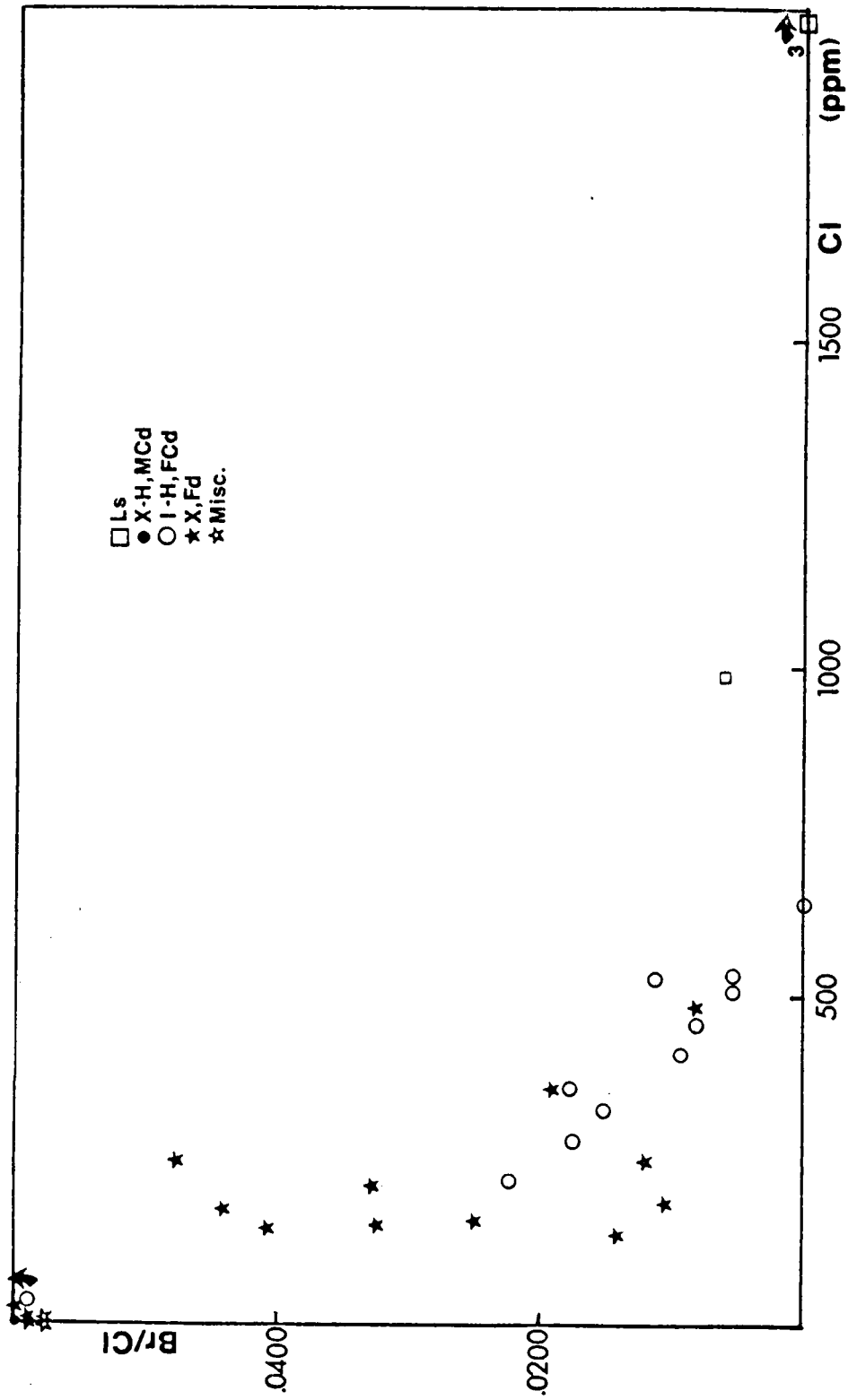


Figure 24. Plot of Br/Cl vs. Cl for the various lithologies from the Right Fork area.

CHAPTER IV

ELEMENTAL CORRELATIONS

Correlation coefficients (Tables 2-6) are considered highly significant if they are greater than 0.85 or less than -0.85, and weakly significant if they are greater than 0.70 or less than -0.70. A strong positive correlation between elements suggests either that the elements were introduced by the same solution and were taken into the dolomite or calcite crystal lattice at relatively similar rates or that both elements are contained in a particular noncarbonate phase, such as pyrite or clay minerals, that influences the overall composition of the samples. A strong negative correlation suggests that the two elements have dissimilar partition coefficients; hence, one element would be preferentially concentrated in solution and the other would be concentrated in the solid (Veizer, 1978; Churnet, 1979). Another interpretation is that the two elements were introduced into the rock at different times by different solutions.

Elemental correlations for the various lithologies of East and Central Tennessee are discussed separately. Correlation coefficients for limestones of Central Tennessee will not be discussed because the sample number is small (4).

TABLE 4. Correlation Coefficients for X,Fd (n=17) from the Coy Mine, Mascot-Jefferson City District

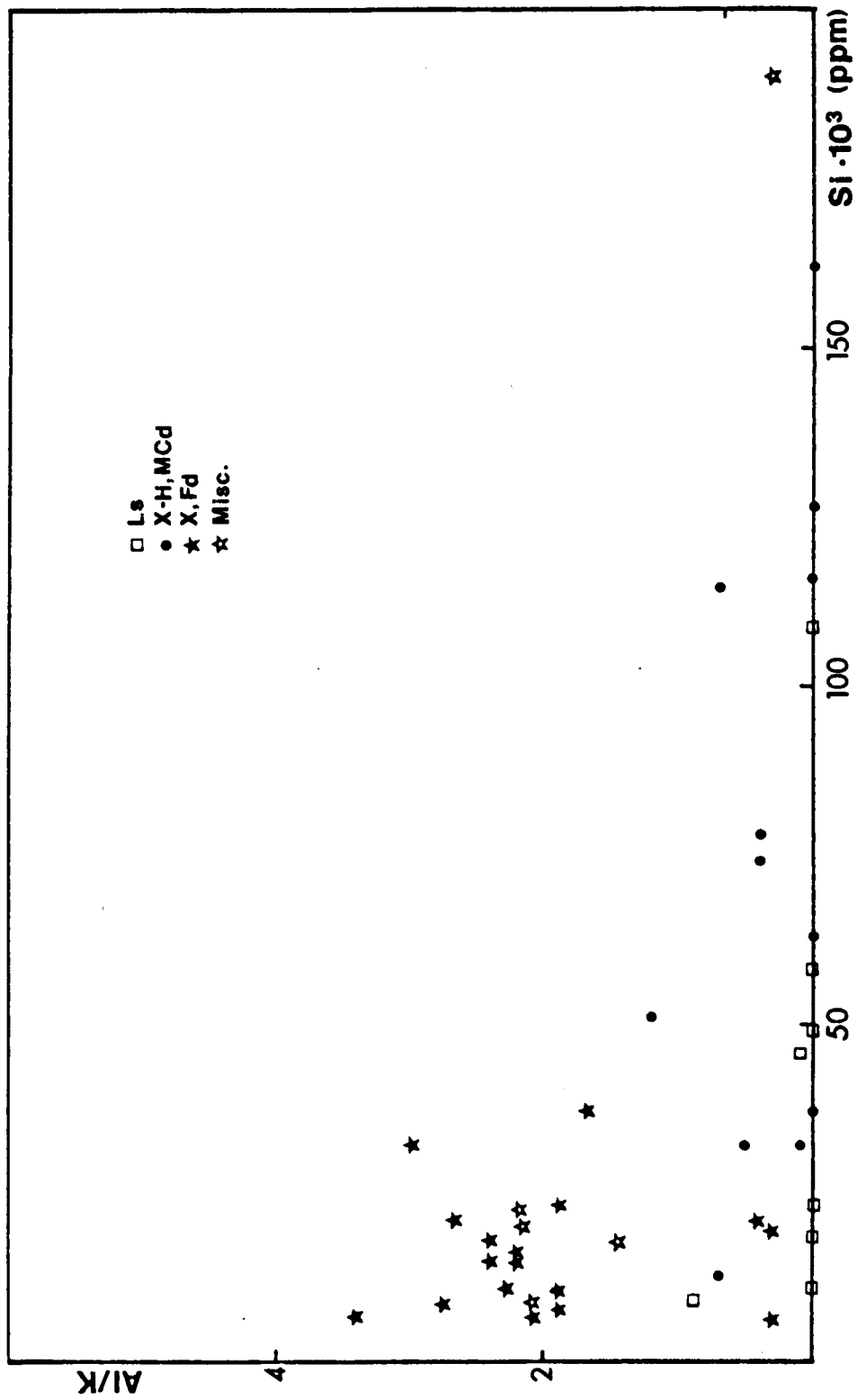
	Mg	Si	Al	K	Fe	Mn	Sr	Br	Cl	S	Ti	P
Ca	-0.26	-0.46	-0.02	0.04	-0.22	-0.07	0.26	-0.05	0.54	0.42	0.32	-0.06
Mg		<u>-0.73</u>	-0.65	-0.69	0.00	0.14	<u>-0.92</u>	-0.40	<u>-0.72</u>	-0.53	0.23	-0.43
Si			0.58	0.58	0.14	-0.05	0.67	0.44	0.28	0.20	-0.48	0.35
Al				<u>0.82</u>	-0.20	-0.27	<u>0.74</u>	0.04	0.30	0.34	0.21	0.47
K					-0.21	-0.30	<u>0.71</u>	0.09	0.28	0.14	0.00	0.33
Fe						0.63	-0.21	0.43	0.31	-0.29	-0.28	0.31
Mn							-0.31	0.61	0.31	-0.24	-0.12	0.03
Sr								0.29	0.53	0.61	-0.04	0.26
Br									0.57	0.28	-0.28	0.16
Cl										0.48	-0.22	0.46
S											0.07	0.27
Ti												-0.24

East Tennessee

Limestones. It is assumed that Al is associated with clays. The only element that correlates well with Al is Ti (Table 2). Presumably this element is also concentrated in clays. Si does not correlate well with Al because Si occurs in detrital quartz and chert as well as in clays. Figure 25 shows the relative concentrations of Al and Si in the various lithologies. Positive correlations exist between Si and P and between Si and S, perhaps as a result of the addition of these elements under reducing conditions.

A positive correlation exists between Ca and Sr (Table 2, Fig. 26), which suggests that this element was present in calcite in the original limestone. Such a relationship for Sr has been documented by various workers (Kinsman, 1969; Veizer et al., 1978; Churnet, 1979). A strong negative relationship exists for Ca-Mg, Ca-Mn, and Ca-P, and there are weak negative correlations for Ca-Si, Ca-Fe, and Mg-Sr. These negative correlations may reflect partial replacement of limestone by dolomite and chert, probably in a reducing (burial) environment.

The relationships between Ca, Mg, Br, and Cl are very interesting. Ca shows an excellent positive correlation with Cl, which confirms the concentration of Cl in the original limestone. Mg correlates well with Br, which suggests its introduction with dolomitization. Fe, Mn, and



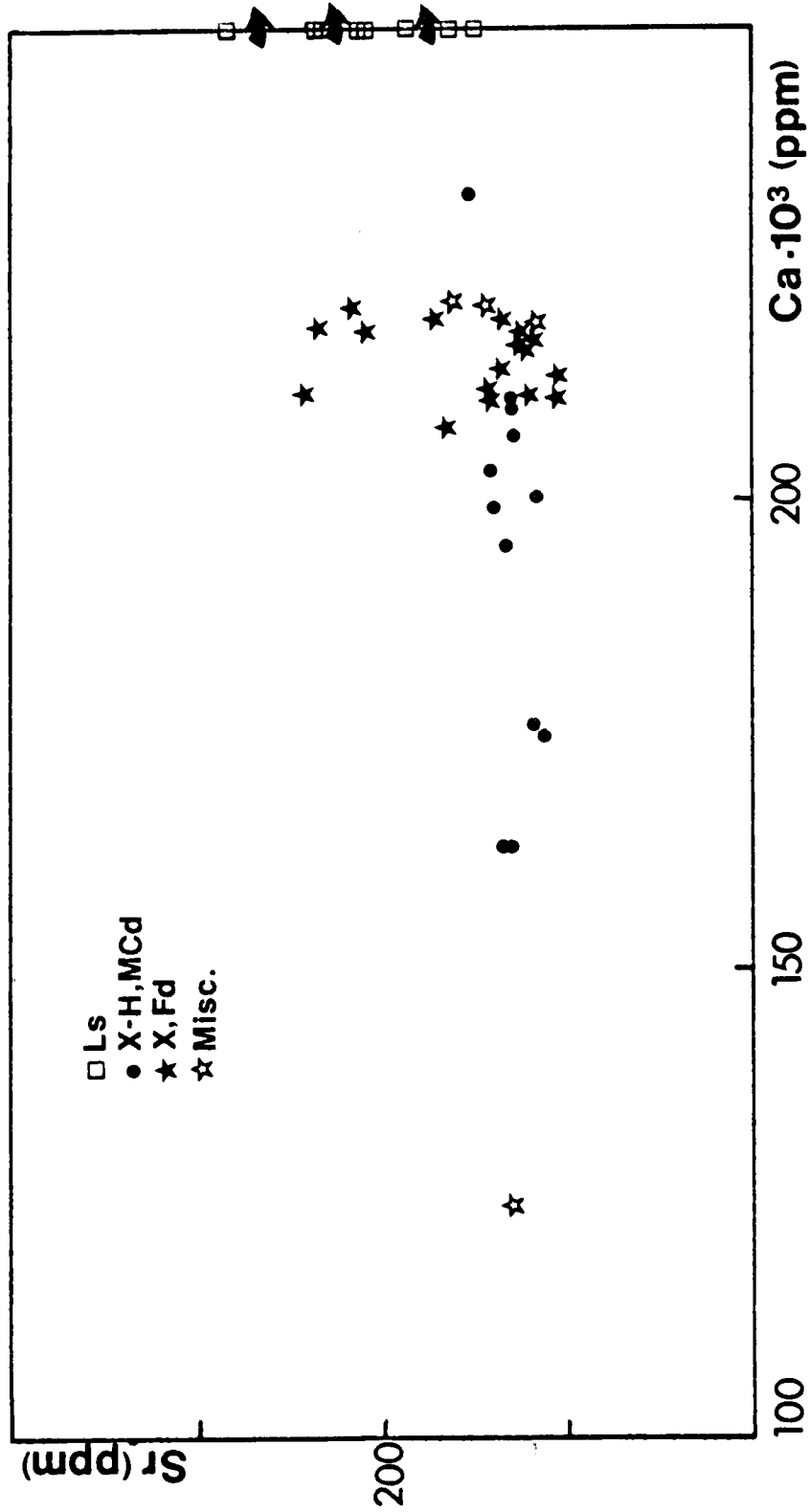


Figure 26. Plot of Sr vs. Ca for the various lithologies from the Coy mine.

Br also correlate positively (Cl correlates negatively with Mg and Mn).

The following conclusions are based upon the above interelement correlations:

1. Depositional, diagenetic, and epigenetic conditions influenced elemental compositions in the limestones. Sr and Cl were concentrated in calcite of the original limestone, and Fe, Mn, and Br were introduced during dolomitization. Figure 27 illustrates the positive correlation between Mn and Fe in limestones. P and S were precipitated with chert, which replaced limestone.

2. The relationship between Br:Cl ratios and Cl concentrations is shown in Figure 21 (p. 71). It can be seen that only two limestones (both partially dolomitized) contain detectable Br. Cl concentration decreases in the partially dolomitized limestones. Panno et al. (1983) documented an increase in Br:Cl ratios in dolostones proximal to the Buick ore body, but they did not mention a concomitant decrease in Cl. These workers, however, gave no values for limestones, nor did they describe dolostone types. Their concentration values are most similar to those of X,Fd of the present study. As discussed in the section on Br and Cl concentrations, this decrease in Cl could be due to the great solubility of the Cl ion. Although Br and Cl behave similarly in solution, Br concentration in a brine

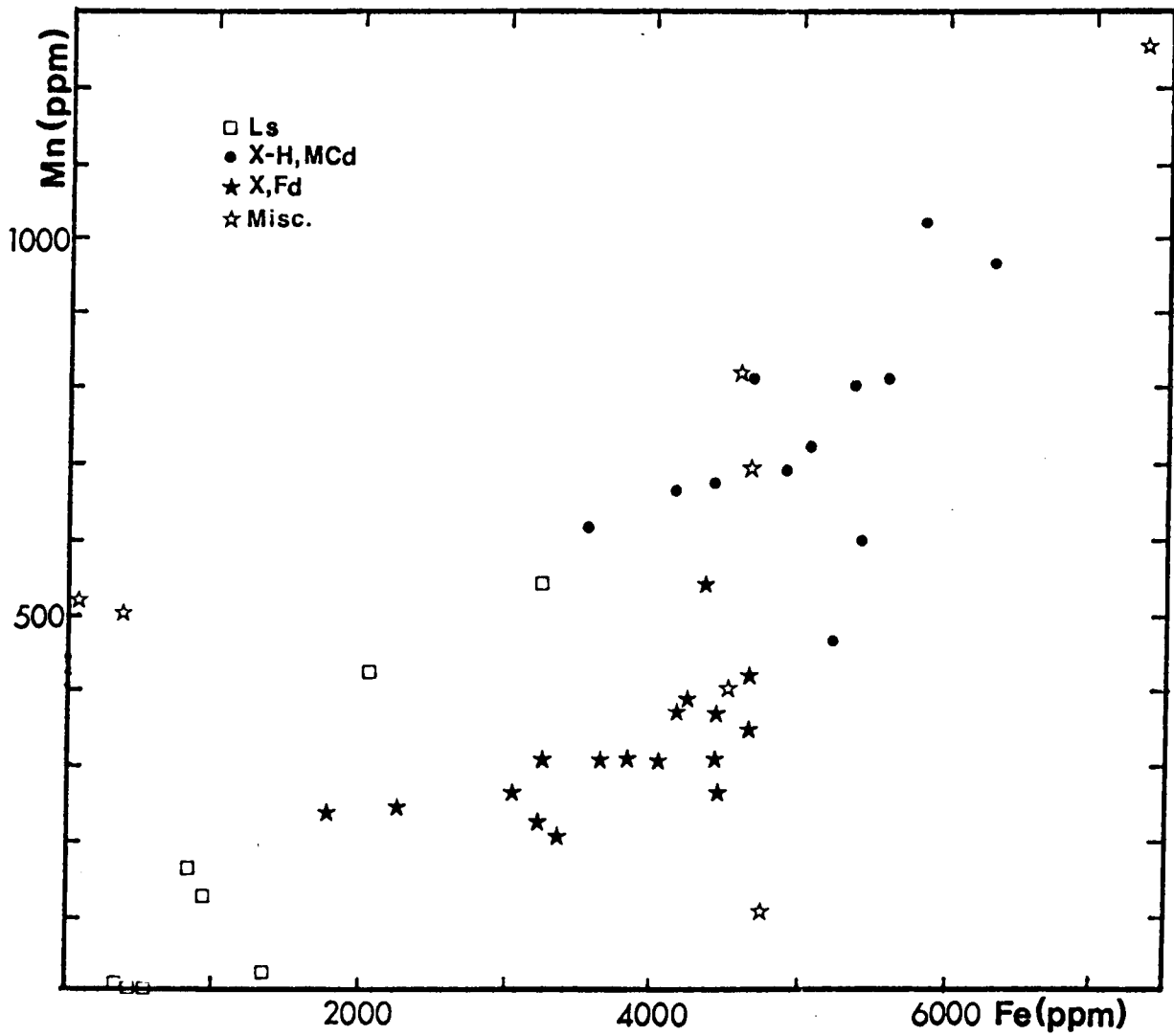


Figure 27. Plot of Mn vs. Fe for the various lithologies from the Coy mine.

increases exponentially in relation to Cl concentration as seawater evaporates (Collins, 1975). Thus much more Br would be available in an evaporative brine than in seawater. This is often true of oil-field brines as well (Collins, 1975).

X-H,MCd. Ca, Sr, and Cl are positively correlated as in the limestones (Table 3, Fig. 26, pp. 80, 86). However, such elements as Fe and Mn, which correlate negatively with Ca in the limestones, show strong positive correlations with Ca in X-H,MCd. This reversal seems odd, since Fe and Mn were probably introduced initially during dolomitization of the limestones. In addition, Mn correlates positively with Cl and Sr in X-H,MCd (Fe correlates more weakly with Sr and Cl). Si and P correlate positively as in the limestones, and both show negative correlations with Ca. These results suggest the following conclusions:

1. Completely dolomitized rocks (X-H,MCd) were ultimately affected by solutions that differed in some ways from those present at the onset of dolomitization. However, the data in Figure 27 suggest that the Mn:Fe ratios of the solutions remained roughly constant throughout the dolomitization process.

2. These solutions were not simply a mixture of fresh water and seawater, because one would expect an antipathetic relationship between Mn and Fe and Sr in such a case (Veizer

et al., 1978; Churnet, 1979; Brand and Veizer, 1980; Churnet and Misra, 1983). As Figures 28 and 29 show, such a negative relationship does exist in the case of limestones and X,Fd, both of which appear to be "primary," or nearly so. X-H,MCd, however, show well-documented increases in Sr with higher Mn and Fe concentrations. Such additional Sr may have come from the dissolution of such evaporite minerals as strontianite and celestite. Further, mixing-zone dolomites should be "nonferroan, reflecting typically oxidizing conditions" (McHargue and Price, 1982).

3. The positive relationships between Ca, Fe, Mn, Sr, and Cl in X-H,MCd--a reversal of trends found in the limestones--might be due to the following: (a) "late" alteration of dolostones in a stable, reducing environment by saline formation waters whose Mg:Ca ratios were lowered by dolomitization (Katz, 1971; Land, 1980; Moss, 1982); (b) interaction with Na-Ca-Cl brines that were either expressed from clays during montmorillonite-illite conversion at depth, thus releasing Si, Fe, Mg, Ca, and Na (McHargue and Price, 1982), or formed by dissolution of evaporite minerals (Land and Prezbindowski, 1981) that subsequently traveled updip to form ferroan dolomites in a reducing environment; or (c) progressive pressure solution of limestone host rock, accompanied by an increase in Ca activity of pore waters (Wong and Oldershaw, 1981).

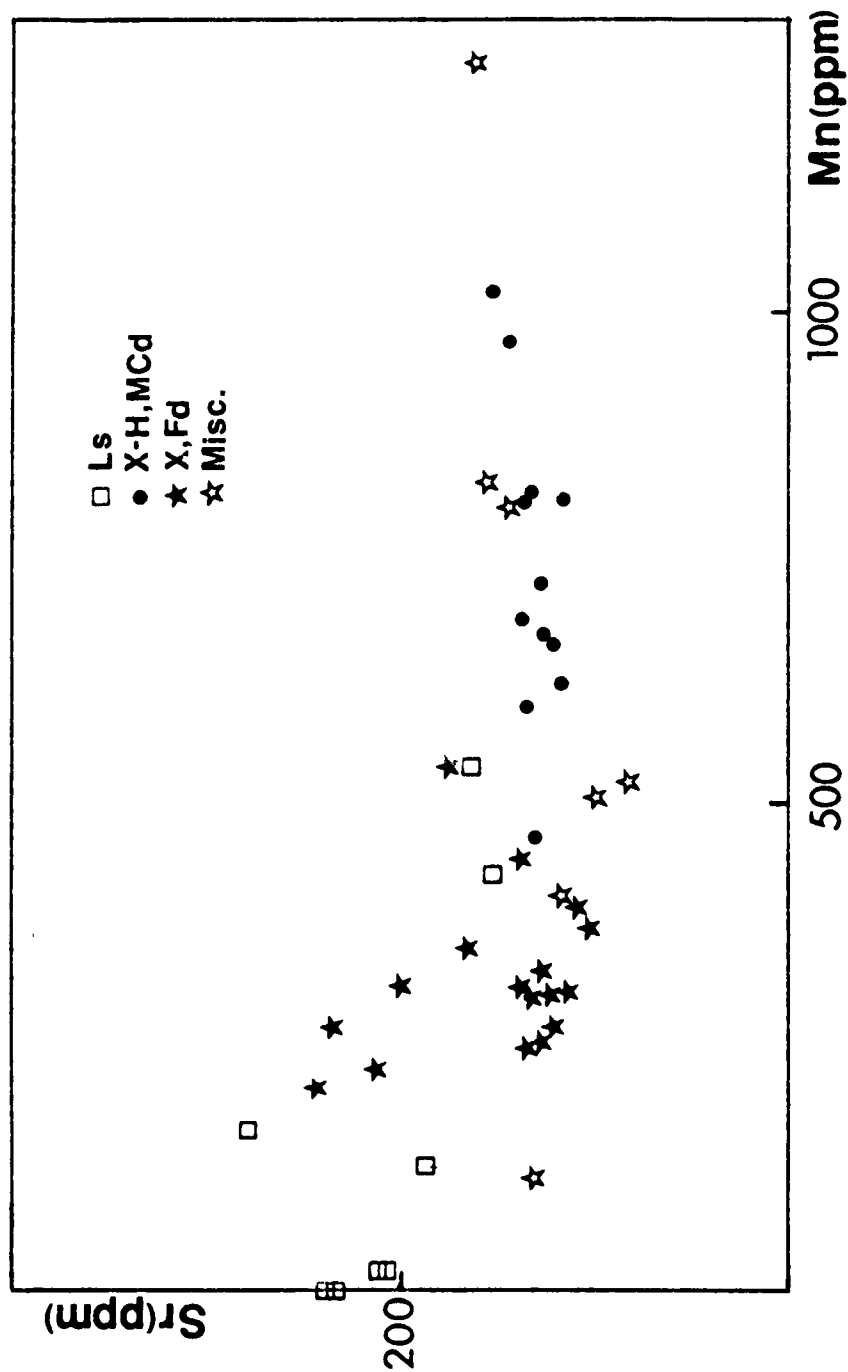


Figure 28. Plot of Sr vs. Mn for the various lithologies from the Coy mine.

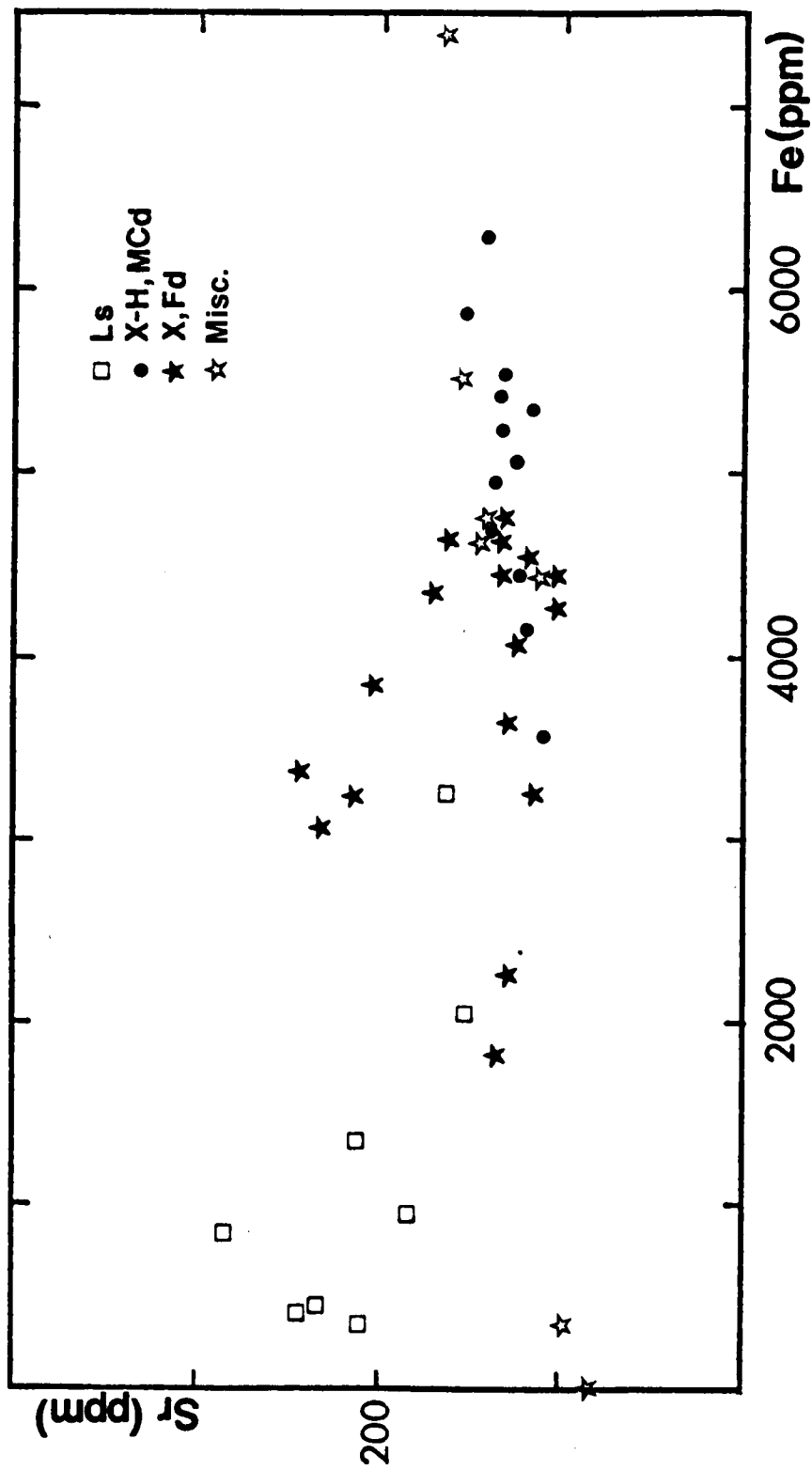


Figure 29. Plot of Sr vs. Fe for the various lithologies from the Coy mine.

4. It appears from data in Figure 27 that X-H,MCd represent a fairly direct replacement product of the limestones. However, petrographic evidence and negative correlations for Ca-Si, Ca-P, Si-Mn, and Si-Fe suggest that some of X-H,MCd replaced chert, which originally replaced limestone. Figure 25 (p. 85) illustrates the high concentrations of Si in X-H,MCd.

X,FD. Formation of X,FD, as discussed in Chapter II, was probably penecontemporaneous with sedimentation or early diagenesis. Interstitial clay occurs in every sample of X,FD, and the only significant positive correlations are those between Al, K, and Sr (Table 4, Fig. 25, pp. 81, 85). Therefore it is assumed that these elements are concentrated in clay. It is interesting to note that the three "zebroid" dolostones plot with X,FD in Figures 25 (p. 85) and 26 (p. 86).

As in the limestones, Mg correlates negatively with Sr and Cl, suggesting the presence of the latter two elements in the original calcitic sediments and their loss during neomorphism. Mg also shows a negative correlation with Si, as did Ca in the limestones and X-H,MCd. This correlation in X,FD may reflect the replacement of dolomitic sediment by chert or the "competition" for space with clay (Mg shows weaker negative correlations for Al and K).

Conclusions regarding X,Fd and made on the basis of correlation coefficients are limited:

1. K, Al, and Sr are concentrated in clays.
2. Mg seems to have been introduced during dolomitization of a former calcitic sediment, as indicated by negative correlations with Sr and Cl.

Central Tennessee

X,Fd. Correlation coefficients for X,Fd of Central Tennessee may be more revealing than those for X,Fd of East Tennessee. The positive correlations for Ca-Cl and Al-Ti (Table 5, p. 82) and the negative correlation for Ca-Si have been reported in discussion of the lithologies of East Tennessee.

Positive correlations also exist for K-Si and Br-Si. These correlations cannot be attributed to the elements' concentration in clays because Si shows only a weak negative correlation to Al and the correlation of Br with Al is strongly negative. Si in X,Fd occurs most often in detrital quartz grains, which suggests proximity to a continental environment. It is possible that Br and K were concentrated in dolostones that formed on paleotopographic highs flooded only infrequently (Long and Gudramovics, 1983).

I-H,FCd. As previously discussed, strongly positive correlations for Ca-Cl and Br-Mg and negative correlations

for Ca-Mg and Mg-Cl (Table 6, p. 83) are related to dolomitization (with an increase of Br) of a calcitic phase (containing Cl). In this lithology, Br and Cl actually show a marked negative correlation.

Elements associated with clays are reflected by positive correlations for Fe-Al, Fe-K, Fe-P, Al-S, S-P, S-K, K-P, Si-P, and K-Si. Negative correlations for Al-Cl, Si-Ti, and Mn-S suggest that Cl, Ti, and Mn are not concentrated in clays (this may account for the weak negative correlation between Mn and Fe). Fe also correlates well with S, which indicates the presence of pyrite.

Examination of correlation coefficients for I-H,FCd suggest the following conclusions:

1. Dolomitization of an originally calcitic sediment also resulted in an increase in Br and a decrease in Cl. The increase in Br suggests dolomitization by a hypersaline brine.
2. The poor correlation for Mn and Fe can be explained by the presence of Fe in clay minerals and in pyrite.

Summary

1. Limestones that are partially dolomitized to X-H,MC dolomite are enriched in Fe, Mn, and Br relative to unaltered limestones. Most limestones have no detectable Br, and Cl concentrations in partially dolomitized limestones are lower than those in relatively "pure" limestones.

Br:Cl ratios in these partially dolomitized limestones are slightly higher than that of seawater (0.0035). Positive correlations for Mg-Fe, Mg-Mn, Mg-Br, Ca-Cl, and Ca-Sr (Table 2, p. 79) clearly indicate the preference of these elements for calcitic or dolomitic fractions of the rock during the early stages of dolomitization. Negative correlations for Ca-Si and Si-Cl reflect replacement of limestone by chert.

2. X,Fd of East and Central Tennessee show rather similar concentrations of certain elements: 9105 and 9691 ppm Al, 4216 and 4593 ppm K, and 7 and 7 ppm Br, respectively. Higher Fe and Mn concentrations and lower Sr concentration in the East Tennessee sample suggest a greater degree of diagenetic or epigenetic alteration. In East Tennessee X,Fd, correlation coefficients link K and Sr with clay content. A negative correlation for Mg-Cl reflects the loss of Cl upon dolomitization or neomorphism. In Central Tennessee X,Fd, positive correlations for K-Si and Br-Si might suggest more intense evaporative conditions for samples with high detrital quartz content (those closer to continental environments or located on paleotopographic highs).

3. I-H,FCd (from Central Tennessee exclusively) show concentration ranges for the various elements that are similar to those of X,Fd of Central Tennessee, which

suggests that both dolostone types formed in similar environments. Correlation coefficients indicate an increase in Br and a decrease in Cl with dolomitization.

4. X-H,MCd of East Tennessee are replacement products of limestones and chert. Average concentrations of Si, K, Fe, Mn, and Br are generally higher in X-H,MCd than in the other lithotypes studied. There was no detectable Cl in several samples. Surprisingly, in view of the fact that X-H,MCd replace limestones, positive correlations for Ca-Fe, Ca-Mn, Mn-Sr, and Mn-Cl occur. These correlations are the reverse of those found in partially dolomitized limestones. The strong negative correlation for Ca-Si and the high Si concentrations reflect extensive replacement of limestone by chert. It is possible that positive correlations for Ca-Fe and Ca-Mn result from a decrease in the Mg:Ca ratio of fluids involved in the process of dolomitization. It is also possible that later stages of dolomitization took place in the presence of Ca-rich brines. The positive correlation for Mn-Sr (and the weak positive correlation for Fe-Sr) suggest the involvement of waters other than meteoric and sea, since Sr is generally thought to decrease in rocks equilibrated with meteoric waters.

CHAPTER V

DISCUSSION AND CONCLUSIONS

Since ore is most often found in the presence of coarser-grained dolostones (X-H,MCd of the present study), they have received much attention. Earlier workers in the Tennessee zinc districts agree that coarser-grained dolostones are a replacement product of limestones, but the method of replacement is elusive. Proposed models of dolomitization include the following:

1. Interaction with groundwaters traveling through the Kingsport paleoaquifer (Harris, 1971).
2. Alteration by mineralizing fluids (West, 1974).
3. Early diagenetic (prelithification) formation in a meteoric-seawater mixing zone (Churnet, 1979).
4. Interaction with hypersaline formation waters in a reducing environment and subsequent equilibration with meteoric water (Moss, 1982).

It is thought by the author that the X-H,MCd of the present study differ in origin from or represent further alteration of dolostones described in previous studies. The X-H,MCd seem to have a limited areal extent (proximal to ore bodies) while the coarser-grained dolostones of previous studies have a regional extent.

Replacement of sparry calcite interallochem cement and of micrite suggests dolomitization of the limestone after

cementation or lithification (Mattes and Mountjoy, 1980). X-H,MCd also grow across stylolites and fractures and cross-cut bedding. Chemical and cathodoluminescent evidence indicates two (possibly lengthy) periods of dolomitization. During the earlier period, subhedral zoned rhombs were produced. This process resulted in varying degrees of dolomitization of the limestones. Strong positive correlations for Mg-Fe and Mg-Mn, as well as high values of Fe and Mn, suggest reducing conditions accompanying increased burial (Carpenter and Oglesby, 1975; Grover and Read, 1983). Generally dull luminescent signatures and thick zones with nondramatic alternations of intensity also suggest precipitation in a reducing environment. Nonluminescent zones are absent in X-H,MCd (with the exception of rhomb cores), as are thin bright zones. Since nonluminescent and bright zones are thought to be indicative of periodic influxes of oxygenated meteoric water and subsequent stagnation (which are typical of near-surface conditions), it is probable that the zoned dolomites formed in phreatic or deeper connate environments (Oglesby and Carpenter, 1975; Grover and Read, 1983). Because zoning in dolomite crystals is typical of a mixing environment, the fresh-water component could have been groundwater that migrated through the Kingsport paleo-aquifer (Harris, 1971). The similarity of luminescent zonation patterns in some dolomites from different levels and

different areas supports this model. Gregg and Sibley (1984) suggest that such subhedral (and euhedral) rhombs form at temperatures below 50°C, which suggests shallow burial conditions.

During a later period of dolomitization, anhedral nonzoned dolomite crystals were produced. It is doubtful that these crystals attained their anhedral and rather corroded appearance from growth along compromise boundaries, because some of the crystals abut chert matrix. Compromise growth in dolomites observed elsewhere produces straighter crystal edges. Nonzoned (with cathodoluminescence), dull orange-red crystals are indicative of dolomites formed in a stable reducing environment (Frank et al., 1982; Grover and Read, 1983), which suggests deeper burial. Gregg and Sibley (1984) propose that anhedral dolomite crystals are precipitated above a critical roughening temperature of 50°C, another indication of deeper burial.

In more fully dolomitized rocks of the present study, some correlations are the reverse of those that hold true for partially dolomitized limestones. Ca-Fe and Ca-Mn show good positive correlations. These correlations might result from an increase in the Ca:Mg ratio of the earlier dolomitizing fluid or of the presence of Ca-rich connate brines (Land and Prezbindowski, 1983). Sr correlates positively with Mn and Fe, the reverse of correlations found in

limestones and dolostones stabilized in a meteoric-seawater mixing zone. It is possible either that this increase in Sr accompanies the late-stage increase in Ca or that more Sr becomes available through the dissolution of such evaporite minerals as strontianite or celestite, as suggested by Collins (1975). Sr is also enriched in subsurface brines (up to 3500 mg/l) in comparison with seawater (8 mg/l, Collins, 1975). Haynes (1984, personal communication) found Sr in fluid inclusions (from the Mascot-Jefferson City district) that also contained Br. Rarely did he find Sr in samples devoid of Br.

High Br:Cl ratios for X-H,MCd suggest interaction with hypersaline brines (Panno et al., 1983). Moss (1982) reached the same conclusion using Na concentrations in the Copper Ridge district. Limestones contain the highest concentrations of Cl, but they have no detectable Br unless they are partially dolomitized. Br:Cl ratios for partially dolomitized limestones are slightly higher than that of seawater. X,Fd and X-H,MCd show similar average Br concentrations. In fact, some paired samples of X,Fd and X-H,MCd have the same Br value, which suggests influence by the same solution. Since one lithotype (X,Fd) is presumed to have been deposited in an arid supratidal environment and the other in a subtidal one, it is likely that the solutions responsible for the dolomitization were not depositional or

early diagenetic pore fluids. High Br concentrations seem to occur in samples that contain a good deal of chert. Low Cl concentrations in X-H, MCd (some contain no detectable Cl) could perhaps be due to multiple recrystallization episodes in the presence of waters with an increasing fresh-water content (groundwaters or circulating meteoric waters traveling through the paleoaquifer and out into the rock via bedding planes (Sass-Gutkiewicz, 1982) and/or microfractures and stylolites (McHargue and Price, 1982; Zenger, 1983). A greater proportion of fresh water would be expected with the passage of time (Barnes, 1979; Hanor, 1979). Isotopic evidence suggests that meteoric waters are the dominant source of water in deep saline brines (Hanor, 1979). Graf (1982) notes that dolomitization generates concentrated Cl brines rich in Ca. Cl is a highly soluble ion that may be concentrated in subsurface brines by evaporation of seawater, concentration of dissolved solids in marine pore fluids, or leaching of Cl from mineral lattices or grain surfaces (Berry, 1967; Graf, 1982). Since Br behaves much as Cl does (Collins, 1975), it is likely that the Br concentration of the solution or solutions that affected X-H, MCd was much higher than that of seawater. Also, comparatively more Br would remain in the rock because of its larger ionic radius.

Some workers have commented on the petrographic similarities and intimate occurrence of coarser-grained

dolostones and "saddle" dolomites (Radke and Mathis, 1980; Gregg and Sibley, 1984). Buchbinder et al. (1984), studying carbonate lithologies on the coastal plain of Israel, found that "saddle" dolomites and coarser-grained dolostones (similar to X-H,MCd of the present study) have identical isotopic values with the same stratigraphic and geographic variations. They interpret this evidence as indicating effects from subsequent circulating fluids, coprecipitation from a low-temperature meteoric-water-influenced solution, or coprecipitation from higher-temperature saline solutions. In this case, even the isotopic evidence is equivocal.

Since "saddle" dolomites are recognized as having filled voids before, during, and after sulfide deposition in the Tennessee zinc districts (Ebers and Kopp, 1979; Churnet, 1979), the luminescent signatures of X-H,MCd were examined for similarities. No luminescent similarities were found, which could indicate that they precipitated from different solutions or that precipitation in a void produces zonal patterns different from those that result from replacement.

In conclusion, X-H,MCd appear to have been formed in the presence of--or finally affected by--mixed hypersaline brines and fresh water (circulating meteoric water or groundwater) in a reducing environment (phreatic and/or deeper connate). Whether these solutions were evaporative brines that were refluxed through karstic caverns (Beales

and Hardy, 1980) or deeper waters, similar to oilfield brines, that were expelled from compacting Sevier Basin shales to travel updip through the Knox paleoaquifer (Hoagland, 1976; Taylor et al., 1983; Grover and Read, 1983) is still a matter of speculation.

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APPENDIXES

APPENDIX A

Lithologic Descriptions

C1A. Ls. Stope 9-50, below 89-90 bed. Micrite at bottom with equally spaced bedding-parallel stylolites. Vertical calcite-filled burrows terminated along stylolites. Intrapelsparite at top of slide, few small unzoned, limpid dolomite rhombs in micrite and intraclasts. Very small amount of sphalerite at top.

C1B. Chert. Stope 9-50, in 89-90 bed. Elongate, rectangular, parallel X,Fd breccia fragments in crackle-brecciated chert. Numerous microfractures filled with dolomite and/or quartz. Many small dolomite rhombs scattered throughout chert.

C2A. Chert. Stope 9-50, in 89-90 bed. Chert, numerous microfractures filled with dolomite and quartz. At top, X,Fd separated from chert by stylolite. Vugs filled with megaquartz, chalcedony, and baroque dolomite.

C2B. Ls. Stope 9-50, above 89-90 bed. Biomicrite, partially dolomitized. Large intact Hedstroemia sp., pores filled with sparry calcite. Sparry calcite and micrite replaced by dolomite (0.5-1.5 mm), spear shapes, anhedral crystals, arcuate cleavages, sweeping extinction. Few unzoned rhombs of dolomite with sharp extinction.

C3A. X,Fd. Stope 9-50, in 89-90 bed. Bedded, "micritic" mottling. Bedding-perpendicular stylolites and "healed" microfractures. At bed partings, X,Fd grains

enlarged and slightly clearer. Horizontal vein filled with gangue, gradational contact with X,Fd. Ghost trilobites, one fairly well preserved.

C3B. Ls. Stope 9-50, above 89-90 bed. Microspar, partially dolomitized and replaced by sphalerite. Dolomite is mostly spear-shaped or anhedral, ≥ 0.85 mm, sweeping extinction, arcuate cleavages, poikilotopic, often terminated by stylolites. Irregular contacts between dolomite and sphalerite and between chert and sphalerite. Some zoned (cloudy centers) rhombs, sharp extinction. Voids filled with chalcedony and gangue.

C3C. X,Fd. Stope 9-50, above 89-90 bed. Sphal. Cht. Gangue. Top of slide is sphalerite (replacive) in mostly irregular contact with poikilotopic X-H,MCd and microspar. Below sphalerite is "rind" of gangue dolomite in gradational contact with X,Fd and chert. Sphalerite contains inclusions of X,MCd and a few small rhombs. Megaquartz void-fill in chert.

C4A. X-H,MCd. Stope 9-50, below 103-104 bed. Dolomite (0.75-1.5 mm), anhedral, spear-shaped, poikilotopic, in chert matrix. Thin stylolites along crystal boundaries. Vertical "healed" microfractures pass through matrix as well as through dolomite. Large rounded chert fragment in stylolitic contact with X,MCd and containing gangue dolomite.

C4B. X,Fd. Stope 9-50, in 103-104 bed. Abundant quartz grains. Gangue dolomite in vugs connected by vertical microfractures to gangue dolomite and sphalerite at bottom of slide. Scattered pyrite.

C5A. X,Fd. Stope 9-50, in 103-104 bed. Bedded. Abundant quartz grains. Fractures crosscut vugs containing gangue dolomite and chert.

C5B. X,Fd. Stope 9-50, in 103-104 bed. Bedded. Similar to C5A.

C6A. X-H,MCd. Stope 9-50, below 110-111 bed. Anhedral mosaic, poikilotopic, chert matrix. Dolomite exhibits arcuate cleavages and sweeping extinction, stylolitic crystal boundaries. Numerous microfractures.

C6B. X,Fd, in 110-111 bed. Crackle brecciated. Abundant quartz grains. X,MCd at bottom of slide. Gangue dolomite-filled fractures. Some larger quartz grains appear corroded.

C7. X,Fd. Stope 9-50, in 110-111 bed. Bedded. Abundant large (0.75 mm) quartz grains, pressure-solved at rims, some exhibit sweeping extinction. Enlarged X,Fd at bottom of thin section (now medium- and coarse-grained), sweeping extinction.

C8. X,Fd. Stope 9-50, in 110-111 bed. Bedded. Dolomitic shale seam at bottom of thin section. Linear area of enlarged (medium-grained) crystals parallel to bedding, 1 cm

above clay seam. Enlarged crystals exhibit sweeping extinction. Much interstitial clay and pyrite.

C9A. I-H,FCd. Stope 25-56, below 68-71 bed. Euhedral and subhedral rhombs (0.18-0.5 mm), zoned (cloudy centers) and unzoned, sharp extinction. Rhombs "float" in a clay matrix.

C9B. X-H,MCd. Stope 25-56, below 68-71 bed. Anhedra crystals, spear-shaped dolomite (up to 1.25 mm) in clay matrix. Dolomite exhibits arcuate cleavages and sweeping extinction. A few small (0.25 mm) subhedral zoned (cloudy centers) rhombs appear to be related to clay seams. Sphalerite and chert replacing X,MCd at top of slide.

C9C. "Zebroid" dolomite (Zenger, 1983). Stope 25-56, 68-71 bed. Subhedral, zoned (cloudy centers) rhombs. There seems to be a progression from fine-grained dolomite in a clay seam, to subhedral zoned medium-grained rhombs, to pockets of gangue dolomite (up to 3.00 mm). Medium- and coarse-grained dolomite show sweeping extinction. Interstitial clay.

C10A. Ls. Stope 25-56, below 68-71 bed. Top of slide is biomicrite, bottom is intrapelsparite. Between the two lithotypes is X-H,MCd that appears to be related to stylolites. X-H,MCd crystals are anhedra, spear-shaped, and serrated rhombs. Dolomite replaces some trilobite fragments as well as micrite. Some sphalerite associated with stylolites and X-H,MCd.

C10B. "Zebroid" dolomite (Zenger, 1983). Stope 25-56, in 68-71 bed. Progression from fine-grained dolomite in clay seam, to I-H,FCd (subhedral zoned rhombs), to pockets of gangue dolomite. Interstitial clay. Similar to C9C.

C11A. X-H,MCd. Stope 25-56, below 62-65 bed. Xenotopic to hypidiotopic fabrics, rhombs generally unzoned (in transmitted light). Grain size varies from fine to coarse (0.13 to 0.75 mm). Coarser grains show sweeping extinction and arcuate cleavages. Abundance of coarser rhombs and matrix increases toward sphalerite at top of slide. Sphalerite poikilotopically encloses pyrite and dolomite, and is intersected by microfractures. Dolomite crystals grow across and are offset by calcite-filled microfractures.

C11B. X,Fd. Stope 25-56, in 62-65 bed. Area of gangue dolomite at bottom of slide, stylolitic contact with X,Fd. Oblique and vertical stylolites. One stylolite has "opened up" and contains chert and medium-grained dolomite rhombs (zoned with thin dark rim, transmitted light). Numerous vertical "healed" microfractures, often offset along stylolites.

C12A. X,Fd. Stope 25-56, in 52-56 bed. Abundant pyrite.

C12B. X-H,MCd. Stope 25-56, above 52-56 bed. Anhedral and spear-shaped crystals, arcuate cleavages, sweeping extinction, poikilotopic. Abundant interstitial clay and clay seams.

C13A. X-H,MCd. Stope 25-56, below 62-65 bed. Arcuate cleavages and sweeping extinction. Can see "relict" micrite. X-H,MCd occurs as serrated rhombs, spear-shapes, and anhedral crystals. Dolomite grows across trilobite fragments as well as micrite. Bedding-perpendicular stylolites contain pyrite.

C13B. Ls. Stope 25-56, below 62-65 bed. Biopel-micrite, extensively dolomitized by X-H,MCd occurring as serrated subhedral rhombs (average 0.75 mm), some zoned with cloudy centers. Dolomite crystals are associated with stylolites and numerous microfractures emanating from stylolites.

C14. X,Fd. Stope 25-56, from 52-56 bed. Angular X,Fd fragments and gangue (rubble breccia) in dolomitic "silt." Abundant pyrite.

C15. X,Fd. Stope 25-56, from 52-56 bed. Similar to C14.

C16A. X,MCd; X,Fd. Stope 25-56, below 52-56 bed. X,Fd and chert breccia fragments in matrix of X-H,MCd and chert. X-H,MCd appears to be a replacement of chert. Some gangue dolomite vein-filling and sphalerite.

C16B. X,Vfd (dolomicrite). Stope 25-56, in 52-56 bed. Numerous microfractures, vertical, horizontal, and conjugate sets oblique to horizontal. Vugs filled with gangue dolomite. Abundant pyrite, nonbedded.

C17. X,Vfd (dolomicrite). Stope 25-56, in 52-56 bed. Vertical vein filled with gangue dolomite. Areas of enlarged crystals usually connected to "healed" microfractures. Abundant nonbedded pyrite.

C18. Ls. Stope 25-56, below 52-56 bed. Biomicrite with few trilobite fragments. Oblique sinuous, reddish-brown stylolites containing small unzoned dolomite rhombs and pyrite. Vertical, dolomite-filled microfractures emanate from stylolites.

C19. Ls. Stope 25-56, below 52-56 bed. Similar to C18. Abundant burrows and birdseyes.

C20A. X,Fd. Stope 23-49, in T bed. Oblique "healed" microfractures. Abundant nonbedded pyrite.

C20B. X-H,MCd. Stope 23-49, above T bed. Very coarse anhedral crystals (up to 2 mm), arcuate cleavages, sweeping extinction, stylolitic sutures. Chert matrix. Numerous microfractures and dolomitic clay seams.

C21A. X,Fd. Stope 23-49, in T bed. Bedded. Some subhedral, zoned rhombs. Vertical vein containing gangue dolomite, indistinct contact with X,Fd. Stylolites perpendicular and parallel to bedding. Abundant interstitial pyrite.

C21B. "Zebroid" dolomite (Zenger, 1983). Stope 23-49, above T bed. A mosaic of subhedral zoned (cloudy centers, clear rims) rhombs, medium grained (0.25-0.38 mm), sharp

extinction. Also xenotopic crystals (0.25-0.50 mm), non-zoned, weak undulatory extinction. Gangue dolomite in intimate contact with the I-H,FCd. Bedding-parallel and -perpendicular stylolites.

C22A. X-H,MCd. Stope 25-41, below T bed. Anhedral, sweeping extinction, arcuate cleavage, poikilotopic, some very coarse crystals (up to 2 mm). Sinuous stylolites containing pyrite.

C22B. X,Fd. Stope 25-41, bottom of T bed. "Pockets" of slightly enlarged grains (0.25-0.40 mm). Abundant interstitial pyrite.

C23A. X-H,MCd. Stope 25-41, below T bed. Anhedral crystals, arcuate cleavages, sweeping extinction, poikilotopic. Oblique and horizontal stylolites transect chert matrix as well as dolomite. Numerous microfractures.

C23B. X,Fd. Stope 25-41, bottom of T bed. "Pockets" of slightly enlarged grains. Interstitial clay and pyrite. Some quartz grains (0.30-0.50 mm).

Central Tennessee

MA1A. Ls. Biointrapelsparite, pelmatozoan and trilobite fragments. Abundant subrounded quartz grains (covering 50-60 percent of area at top of slide). Intraclasts must have been somewhat lithified before compaction because there is little embaying by quartz grains. Clay seams containing quartz and dolomite.

MA1B. X,VFd (dolomicrite). Bedded. Thin laminae of opaques and well-rounded quartz grains (0.05-0.38 mm). Bedding offset approximately 0.5 cm by mud crack filled with subhedral and anhedral unzoned dolomite (up to 0.5 mm). Larger crystals exhibit sweeping extinction.

MA2A. X,Fd. Laminae of opaques and subrounded quartz grains. Microfractures filled with coarse, blocky calcite. Abundant interstitial clay and pyrite.

MA2B. X,VFd (dolomicrite). Fractures lined with dolomite rhombs, unzoned, about 0.30 mm in long dimension, weakly sweeping extinction. Interior of fractures filled with coarse blocky calcite.

MA3A. X-H,MCd. "Jumbled" serrated rhombs and anhedral crystals in chert matrix. Rhombs are mostly unzoned, though some have cloudy centers. Dolomite crystals enclose quartz grains and large "framboids" of pyrite. Abundant pyrite.

MA3B. X,VFd (dolomicrite). Bedded. Oblique fracture at bottom of slide, lined with subhedral and anhedral dolomite crystals (exhibiting sweeping extinction). Center of fracture filled with coarse blocky calcite.

MA4A. X,Fd. A few zoned (cloudy centers) rhombs. Abundant interstitial pyrite and quartz grains (0.05-0.12 mm).

MA4B. I-H,FCd. At bottom of slide is oblique bed of medium-grained subhedral rhombs (zoned with cloudy centers).

Vertical vein of gangue dolomite that might be enlarged crystals (poikilotopically encloses quartz).

MA5A. Ls. Biopelmicrite, partially dolomitized. Fauna include trilobites and pelmatozoans. Dolomite is mostly coarse (0.50 to 1.00 mm), occurring along stylolites and microfractures. Dolomite occurs in two forms: (1) subhedral and anhedral rhombic forms, cloudy centers, and (2) anhedral crystals, unzoned, sweeping extinction. Abundant subrounded quartz grains, up to 0.50 mm, some enclosed in dolomite.

MA5B. X,VFd (dolomicrite). Bedded. Laminae of subrounded quartz grains.

MA6A. I-H,FCd. Subhedral and anhedral forms, some zoning (cloudy centers). Abundant interstitial clay and pyrite. Numerous vertical "healed" microfractures.

MA6B. I-H,FCd. Subhedral and anhedral forms, some zoning (cloudy centers). "Ghost" gastropods and relict micrite. Some coarse calcite spar filling pores. Abundant interstitial pyrite. Numerous vertical microfractures. Two stylolitic laminae containing fine-grained dolomite.

MA7A. Rubble breccia. Chert breccia fragments in matrix of I-H,FCd (mostly subhedral rhombs, zoned with cloudy centers, 0.37-0.68 mm). "Flowing" bed of X,Fd at center of slide. Chalcedony vug-fill. Also a spherical vug in chert breccia fragment filled with gangue dolomite. Very abundant pyrite.

MA7B. X,VFd (dolomicrite). Uniform.

MD1A. X,VFd (dolomicrite) and quartz. Quartz grains (0.07-0.55 mm), randomly distributed. Vein at top of slide, parallel to bedding, lined with limpid dolomite rhombs (about 0.15 mm), filled with coarse blocky calcite.

MD1B. X,VFd (dolomicrite) and quartz. Uniform.

MD2A. Ls. Pelsparite. Interallochem pores filled with blocky calcite. Dolomite is rare, limpid, fine (about 0.05 mm), and euhedral. Dolomitic clay seams at top and bottom of slide.

MD2B. X,VFd and quartz. Bedding looks disrupted and "intraclasts" delineated by quartz grains.

MD3A. X,VFd and quartz. At top of slide, separated by stylolite, is relatively unaltered pelsparite. At bottom, separated by stylolite, is gangue dolomite with some mega-quartz void-fill. Abundant interstitial pyrite.

MD3B. Ls. Pelsparite. Birdseyes and pores between peloids filled with sparry calcite.

MD4A. X,Fd and I-H,FCd. Left half of slide is uniform X,Fd. Right half is subhedral zoned (cloudy centers) rhombs, chert matrix, chert fragments, megaquartz void fill, and medium-grained anhedral crystals.

MD4B. X,Fd. Uniform. Interstitial pyrite and clay.

MD5A. I-H,FCd. Mostly zoned (cloudy centers) subhedral rhombs interspersed with irregular patches of anhedral crystals. Interstitial pyrite and clay.

MD5B. I-H,FCd. Subhedral zoned (cloudy centers) rhombs with irregular patches of anhedral crystals. Micritic matrix. Gastropods replaced by sparry calcite.

MD6A. I-H,FCd. Mostly subhedral zoned (cloudy centers) rhombs, 0.50-1.00 mm. Sharp extinction.

MD6B. X,Fd. Abundant quartz grains (0.05-0.12 mm) and interstitial pyrite. Also, pyrite along stylolitic surfaces. Vein filled with coarse blocky calcite.

MD7A. I-H,FCd. Fabric of zoned dolomite euhedra and subhedra. Interstitial pyrite. Vein of dolomite cut by vein containing coarse blocky calcite.

MD7B. I-H,FCd. Subhedral rhombs, zoned (cloudy centers). Many vertical microfractures. Larger fractures filled with coarse blocky calcite. Smaller fractures appear to be "healed" microfractures filled with dolomite.

APPENDIX B

TABLE 7. Variations in Intensity of Cathodoluminescence with Iron and Manganese Concentrations in Calcite and Dolomite (modified from Frank et al., 1982)

Reference	Mn (ppm)	Fe (ppm)	Fe/Mn	Luminescence	Mineral
Long and Agrell (1965)	10,000 1000	1000 10,000	0.1 10.0	Brightly luminescent Non-luminescent	calcite
Martin and Zeegers (1969)	360±70 140±30 30±20	- - -	- - -	le niveau supérieur le niveau moyen le niveau inférieur	calcite
Freeman (1971)	200 100 <100	trace trace trace	- - -	Luminescent Dull luminescence Non luminescence	calcite
Oglesby (1976)	864 1392±144 432±48 <240	<240 768±48 1056±96 <240	<0.28 0.55 2.4 -	Very bright Bright to very bright Dull Non-luminescent	calcite
George (1977)	8112 8880	2016 4656	0.25 0.52	Very bright Bright	calcite
Fox (1979)	2304 1824	384 3456	0.17 1.9	Bright Dull	calcite
Pierson (1981)	>80	<15,000	-	Produces luminescence	calcite dolomite
Churnet and Misra (1981)	1000-2400 400-1000	3700-8900 9600-9800	3.7-3.71 9.6-24.5	Bright red Dark red	dolomite
Grover and Read (1983)	>72 95 4200 440	<10,000 250 370 1000	- 2.6 0.09 2.27	Produces luminescence Non-luminescent Bright Dull	calcite
Fairchild (1983)	>72	<14,400	-	Produces luminescence	dolomite

APPENDIX C

Sample Preparation Procedures

1. Individual offcuts from Coy mine hand samples and split cores from the Right Fork area were placed on a thick pad of paper towels which rested on a steel anvil. Another thick batch of paper towels was placed over the sample and a rock hammer was used to break the sample. Care was taken so that the rock did not penetrate the towels. Pieces were selected from the interior of the rock and these were broken into pea-size pieces.

2. The pea-size pieces were examined under a binocular microscope for homogeneity. Pieces that contained gangue dolomite or paper towel slivers were discarded.

3. About 10 g of sample were placed in a clean Petri dish and each piece was sprayed with deionized water. The water was drained and each piece was sprayed again. The water was poured out and the sample was dried in an oven at 50°C for 15 minutes. The sample now was handled only with rubber gloves.

4. The 10 g of sample were placed in a tungsten carbide rotary swing mill with 5 ml of methanol and ground in a shatterbox for 6 minutes.

5. Three grams of sample (and boric acid for backing) were pressed at 15,000 lb (total load) to make a briquette which was stored in a desiccator until analyzed.

APPENDIX D

TABLE 8. Calibration Results in Weight Percent Using X-ray Fluorescence Spectrometry (TEPA)

Parameters	Al ₂ O ₃		SiO ₂		FeO ₂		FeO		CaO		TiO ₂		MgO ₂		MgO		Cr ₂ O ₃		B ₂ O ₃	
	List	Totals	List	Totals	List	Totals	List	Totals	List	Totals	List	Totals	List	Totals	List	Totals	List	Totals	List	Totals
Standard Error ^a	0.19		0.20		0.02		0.01		0.05		0.06		0.02		0.05		0.02		0.04	
Counting Error	0.09		0.03		0.009		0.01		0.004		0.02		0.002		0.005		0.001		0.0077	
Al ₂ O ₃	1.08	0.25	0.87	0.20	0.43	0.02	0.34	0.53	0.21	0.59	0.10	0.08	0.01	0.04	0.04	0.04	0.01	0.02	0.2378	0.0003
SiO ₂	20.58	0.53	19.53	0.65	0.63	0.04	0.54	0.65	0.21	30.14	0.25	0.03	0.04	0.04	0.04	0.04	0.01	0.16	0.2114	0.0003
FeO ₂	20.58	0.53	19.53	0.65	0.63	0.04	0.54	0.65	0.21	30.14	0.25	0.03	0.04	0.04	0.04	0.04	0.01	0.16	0.2114	0.0003
FeO	0.34	0.46	0.43	0.20	0.61	0.03	0.09	0.07	0.08	0.75	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.08	0.1398	0.0003
CaO	2.32	0.48	1.91	0.55	0.98	0.19	0.79	0.88	0.39	39.84	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.08	0.1398	0.0003
TiO ₂	2.32	0.48	1.91	0.55	0.98	0.19	0.79	0.88	0.39	39.84	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.08	0.1398	0.0003
MgO ₂	6.75	0.36	1.60	0.47	0.62	0.07	0.46	0.62	0.68	24.16	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.11	0.0840	0.0003
MgO	0.47	0.39	0.47	0.39	0.62	0.07	0.46	0.62	0.68	24.16	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.11	0.0840	0.0003
Cr ₂ O ₃	0.19	0.19	1.39	0.65	0.05	0.05	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.01	0.0003	0.0003
B ₂ O ₃	0.25	0.25	0.25	0.25	0.05	0.05	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.01	0.0003	0.0003
Standard Error ^a	0.19		0.20		0.02		0.01		0.05		0.06		0.02		0.05		0.02		0.04	
Counting Error	0.09		0.03		0.009		0.01		0.004		0.02		0.002		0.005		0.001		0.0077	

TABLE 9. Elemental Concentrations for Various Lithologies, Coy Mine, Mascot-Jefferson City District, East Tennessee

Sample	Wt. percent			ppm									
	CaO	MgO	SiO ₂	Al	K	Fe	Mn	Sr	Br	Cl	S	Ti	P
<u>Limestones</u>													
C1A1	46.72	0.94	10.81	312	5489	1360	28	214	ND	1953	848	ND	370
C1A2	51.64	0.46	4.89	ND	1465	361	15	212	ND	2519	2047	ND	289
C2B	46.33	2.51	10.57	ND	1306	851	166	281	ND	1715	297	ND	241
C3B	32.64	8.88	23.28	ND	1864	2064	434	152	2	347	3299	ND	709
C10A	45.30	1.95	12.33	ND	5154	985	134	189	ND	1925	1402	ND	395
C13B	39.69	9.49	3.94	ND	1556	3243	542	165	7	1581	423	ND	281
C18	53.92	0.57	1.89	1369	1516	443	ND	236	ND	2669	224	198	90
C19	53.98	0.48	2.39	ND	1234	419	ND	240	ND	2487	235	ND	215
Mean	45.91	3.17	9.35	210	2448	1216	165	211	1	1900	1097	25	324
S.D.	7.09	3.78	6.96	481	1789	1000	211	42	2	744	1102	70	182
<u>X-H, Mcd</u>													
C4A1	24.72	18.58	24.82	ND	9646	4114	670	120	7	ND	152	ND	531
C4A2	22.91	17.34	34.81	ND	9106	3569	624	114	7	ND	ND	ND	532
C6A	24.56	17.10	27.32	ND	13,344	4421	676	124	10	ND	18	ND	710
C9B*	22.93	16.87	24.73	28,521	38,328	5400	600	134	5	ND	ND	ND	736
C11A	27.90	17.47	16.00	3959	10,176	4901	690	139	5	354	726	ND	454
C12B	28.47	17.79	11.09	17,678	14,655	6300	969	143	9	597	252	ND	446
C13A	32.71	17.14	2.82	1066	1606	5862	1025	153	9	1128	204	402	308
C16A*	29.66	19.69	6.99	159	2977	5259	461	132	12	341	ND	ND	206
C20B	27.32	18.07	16.45	5289	13,017	4646	804	135	8	255	ND	ND	314
C22A1	29.39	20.18	6.47	ND	2000	5599	818	131	3	199	ND	ND	376
C22A2	28.98	20.36	0.04	ND	3210	5059	730	129	4	202	56	ND	206
C23A	28.16	19.81	13.50	ND	1646	5391	811	114	10	ND	ND	ND	295
Mean	27.31	18.37	15.42	4723	9976	5043	740	131	7	256	117	33	426
S.D.	2.97	1.31	10.71	9061	10,203	766	157	12	3	334	219	116	177

TABLE 9 (Continued)

Sample	Wt. Percent			ppm									
	CaO	MgO	SiO ₂	Al	K	Fe	Mn	Sr	Br	Cl	S	Ti	P
X, Fd													
C3A	30.71	20.48	1.40	3310	1562	4442	307	138	2	332	56	492	231
C3C	30.51	20.45	1.47	535	1577	4484	276	124	7	524	737	ND	330
C4B	29.75	20.36	4.52	1167	2853	4646	421	138	13	469	392	ND	198
C5A	29.58	20.34	4.27	971	2822	4255	396	106	7	236	168	ND	324
C5B	29.87	20.88	2.51	8417	3641	4476	378	103	3	495	370	ND	378
C6B	29.10	19.54	6.89	10,715	828	4667	358	168	9	472	779	ND	362
C8	29.74	17.74	7.81	20,200	11,763	3348	207	244	7	472	533	ND	407
C11B	30.86	17.87	5.08	12,749	6801	3271	230	218	6	1028	929	ND	330
C12A	30.77	19.08	3.33	10,849	4955	4379	543	172	13	998	556	232	333
C14	29.64	20.84	3.52	13,469	6139	3632	302	133	4	176	5	649	180
C15	29.60	20.68	3.39	13,648	5590	4057	304	129	6	200	272	332	414
C16B	30.36	20.52	1.77	9281	3345	4158	336	129	7	166	823	302	356
C17	30.50	20.62	1.55	8761	2603	3222	305	119	5	467	694	621	385
C20A	30.54	18.93	4.05	14,624	6118	3836	313	201	7	578	1141	611	323
C21A	30.54	18.85	4.50	16,559	6149	3049	274	236	8	598	1272	403	333
C22B	30.04	20.94	2.23	5763	2990	1857	241	137	2	41	424	84	192
C23B	30.27	21.01	1.79	3774	1941	2284	255	130	5	127	820	514	194
Mean	30.14	19.95	3.53	9105	4216	3768	320	154	7	434	587	249	310
S.D.	0.51	1.07	1.88	5832	2702	830	82	45	3	277	361	257	79
Miscellaneous**													
C7	33.02	16.05	4.04	5451	3791	5548	825	158	8	1105	211	ND	174
C9A	17.59	14.84	40.70	19,137	65,770	4729	115	132	3	ND	ND	ND	966
C9C	30.82	17.92	4.81	15,320	6960	4661	800	144	2	863	110	ND	302
C10B	30.92	18.16	4.31	12,327	5816	7308	1259	161	10	691	228	402	389
C21B	30.68	20.02	2.17	4886	2383	4492	403	118	8	573	92	429	225
C1B	13.58	7.56	78.38	ND	ND	358	511	100	36	ND	ND	ND	ND
C2A	9.94	2.60	92.45	ND	ND	ND	523	85	51	ND	ND	ND	958

*These samples were eliminated from correlation coefficient calculations because of inhomogeneities with sample.

**See lithologic descriptions, Appendix A.

TABLE 10. Elemental Concentrations for Various Lithologies, Right Fork Area, Central Tennessee

Sample	Wt. percent		SiO ₂	ppm						P			
	CaO	MgO		Al	K	Fe	Mn	Sr	Br		Cl	S	Ti
<u>Limestones</u>													
MA1A	41.35	1.20	21.91	ND	7431	2262	57	386	6	954	2001	ND	684
MA5A	50.68	2.23	3.04	ND	966	464	40	270	ND	2123	401	378	370
MD2A2	53.33	0.50	3.48	ND	1213	218	17	304	ND	2382	280	ND	174
MD3B	54.55	0.45	1.20	2985	1153	502	ND	318	ND	2538	500	105	455
Mean	49.98	1.10	7.41	746	2691	862	29	320	2	1999	797	121	421
S.D.	5.97	0.83	9.72	1492	3126	942	25	49	3	717	812	179	211
<u>I-H, FCD</u>													
MA4B1	29.15	20.43	6.85	4064	1586	1353	248	159	5	222	572	307	227
MA4B2	30.75	20.26	1.70	4755	3989	1448	255	148	10	52	763	ND	416
MA6A	29.17	19.59	8.04	13,196	7308	2904	222	179	5	285	1769	ND	548
MA6B	32.24	17.88	3.39	4327	2628	954	240	185	6	528	163	251	303
MD5A	30.71	18.37	6.40	9774	5182	3137	217	202	4	409	1634	168	440
MD5B	34.30	14.13	6.25	5883	3942	2051	190	226	ND	640	1210	ND	382
MD6A1	32.00	18.02	2.99	14,425	3576	1730	247	223	5	332	356	958	303
MD6A2	32.61	18.28	1.15	3911	1082	985	251	215	3	517	193	645	285
MD7A1	31.30	18.35	3.31	16,791	4699	3457	189	310	6	348	2610	246	527
MD7A2	32.53	16.79	3.08	13,563	4244	3899	198	468	3	509	3257	2355	467
MD7B	32.13	17.28	5.45	4220	3053	1682	281	272	4	466	650	129	466
Mean	31.54	18.13	4.42	8628	3754	2145	231	235	5	332	1198	460	397
S.D.	1.53	1.75	2.27	5003	1718	1031	30	91	2	166	1021	694	105

TABLE 10 (Continued)

Sample	Wt. percent			Al	K	Fe	Mn	ppm		Cl	S	Ti	P
	CaO	MgO	SiO ₂					Sr	Br				
<u>X, Fd</u>													
MA1B	30.90	19.09	2.80	20,195	3701	2659	217	296	3	248	1461	693	447
MA2A	30.76	18.42	4.32	21,341	5780	3807	220	262	2	140	2376	650	334
MA2B1	30.23	19.21	5.09	16,078	5487	2543	207	280	2	187	1495	353	410
MA3B	29.85	20.03	4.42	15,491	5419	3628	188	239	6	146	2523	370	454
MA4A	29.21	20.78	6.07	6006	3694	1365	229	135	6	ND	542	ND	325
MA5B	30.20	19.92	3.86	14,498	4558	1653	215	219	4	160	931	484	314
MA7A1	31.12	17.46	8.51	ND	2328	1520	188	362	8	44	1114	ND	242
MA7B	30.97	19.36	2.88	10,190	3440	1803	232	284	8	180	1188	483	239
MD1A	27.40	17.09	20.72	ND	5921	1397	236	379	14	ND	286	ND	662
MD1B	33.14	15.89	4.18	18,641	4175	1549	184	422	4	483	645	247	601
MD2B	29.37	18.18	10.65	ND	4150	1563	249	313	10	58	634	ND	463
MD3A	28.00	16.41	18.52	926	10,509	2196	202	189	13	ND	1099	ND	545
MD4A2	30.18	19.90	4.48	6503	3400	1282	235	172	7	211	653	159	247
MD4B	29.81	20.00	4.86	12,357	4910	1582	226	163	5	152	803	39	321
MD6B1	31.50	18.24	4.57	4591	3494	1376	207	172	7	360	499	ND	378
MD6B2	30.65	19.07	4.38	8078	3973	2513	211	182	12	248	1476	9	22
Mean	30.21	18.69	6.89	9681	4593	2086	215	254	7	164	1108	218	375
S.D.	1.35	1.40	5.36	7492	1825	810	19	85	4	133	641	253	157
<u>X-H, Mcd</u>													
MA3A1	22.92	16.48	36.52	ND	6800	4595	294	126	11	ND	3120	ND	854
<u>Miscellaneous*</u>													
MA7A2	20.60	9.00	58.20	ND	3149	3027	362	149	32	ND	1353	ND	889
MD4A1	24.25	17.69	31.76	ND	3860	860	295	142	13	ND	ND	ND	706

*See lithologic descriptions, Appendix A.

TABLE 11. Duplicate Analyses

Sample	Wt. percent			ppm								S	Ti	P
	CaO	MgO	SiO2	Al	K	Fe	Mn	Sr	Br	Cl				
<u>Limestones</u>														
Cl0A (1st)	45.30	1.95	12.33	ND	5134	985	134	189	ND	1925	1402	ND	395	
	45.15	1.76	12.13	ND	5175	982	109	202	ND	1778	1423	ND	432	
	45.21	1.88	12.26	ND	5158	985	122	196	ND	1758	1483	ND	503	
	45.24	1.89	12.41	ND	5202	1008	125	198	ND	1717	1464	ND	454	
ClA2 (1st)	51.64	0.46	4.89	ND	1465	361	15	212	ND	2519	2047	ND	289	
	51.47	0.46	4.86	ND	1472	376	32	219	ND	2477	2299	ND	307	
	51.47	0.40	4.79	ND	1489	386	27	218	ND	2454	2124	ND	447	
<u>X-H, Mcd</u>														
Cl6A (1st)	29.66	19.69	6.99	159	2977	5259	461	132	12	341	ND	ND	206	
	29.65	19.58	6.90	ND	2951	5215	486	137	8	270	ND	ND	273	
	29.60	19.71	7.01	ND	2920	5175	489	133	11	192	32	ND	354	
<u>X, Fd</u>														
Cl6B (1st)	30.36	20.52	1.77	9281	3345	4158	336	129	7	166	823	302	356	
	30.39	20.36	1.75	8361	3295	4130	340	131	5	154	867	542	309	
<u>Miscellaneous*</u>														
ClB (1st)	13.58	7.56	78.38	ND	ND	358	511	100	36	ND	ND	ND	932	
	13.57	7.23	77.75	ND	ND	317	466	105	35	ND	ND	ND	961	
	13.58	7.30	77.74	ND	ND	321	487	109	39	ND	ND	ND	856	
Cl0B (1st)	30.92	18.16	4.31	12,327	5816	7308	1259	161	10	691	228	402	389	
	31.03	17.96	4.27	11,904	5890	7311	1252	160	11	721	261	426	324	
	30.92	18.30	4.36	10,834	5823	7308	1275	167	8	684	250	268	435	

*See lithologic descriptions, Appendix A.

VITA

Thomas Bradford Crattie was born on February 22, 1952, in Memphis, Tennessee. He attended elementary schools throughout the South and went to high school in Paris, Tennessee. In 1972, Mr. Crattie was drafted into the U.S. Army and spent two years at Ft. Polk, Louisiana, and Ft. Ritchie, Maryland. Upon separation from the armed forces, he attended the University of Tennessee, Knoxville, and subsequently earned a Bachelor's degree in geology in 1979. He has worked as a copy editor with Academic Press in New York City and as an exploration geologist with the Getty Mining Company. Presently, Mr. Crattie is employed as an environmental geologist with the Tennessee Department of Health and Environment in Johnson City, Tennessee.