To the Graduate Council:

I am submitting herewith a thesis written by Roland Martin Larsen entitled "A Study of the Cathodoluminescent Properties and the Trace Element Distribution of the Gangue Calcite (and Other Phases) at the Elmwood Mine in Smith County, Tennessee." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Geology.

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A STUDY OF THE CATHODOLUMINESCENT PROPERTIES AND THE TRACE ELEMENT DISTRIBUTION OF THE GANGUE CALCITE (AND OTHER PHASES) AT THE ELMWOOD MINE IN SMITH COUNTY, TENNESSEE

A Thesis

Presented for the

Master of Science

Degree

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Roland Martin Larsen

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ABSTRACT

A study of the gangue calcite (and other phases) from the Elmwood area in Central Tennessee indicates that the application of cathodoluminescent analysis and trace element chemistry can be applied toward a better understanding of the paragenetic relationships that exist in Mississippi-Valley-type deposits.

Three generations of calcite have been identified on the basis of cathodoluminescent, textural and physical properties; an early zoned calcite and two post-sphalerite, unzoned calcites.

Observations on the early gangue calcite indicate that a regular cathodoluminescent zonation pattern can be traced within the mine and up to 10 miles (16 km) from the Elmwood deposit. This zonation consists of a series of light and dark orange cathodoluminescent bands that are thought to reflect minor changes in the physiochemical environment during deposition. There is an indication that the early (zoned) calcite and (zoned) dolomite were coprecipitates.

Information obtained in this study suggests that zone 2 in the calcite and dolomite developed simultaneously with early sphalerite deposition, i.e., the occurrence of sphalerite as inclusions in zone 2 with the apparent continued growth of zone 2 in the presence of sphalerite.

Comparison of the cathodoluminescent growth zones in calcite (and dolomite) suggests that there were periods when the geochemical parameters were comparable over large areas during the deposition of each sequential zone. It appears that the development of the Elmwood area gangue calcite (and less widespread dolomite and ore minerals) occurred on a relatively large scale (perhaps tens to hundreds of square miles). This may have been facilitated by extensive interconnected channel ways and fractures that could promote fluid movement where the conditions (pH, temperature, CO_2 pressure, total pressure, trace element composition and salinity) changed more or less synchronously with time. Petrographic observations indicate that these channel ways did not appear to have closed at any time during the deposition of the ore and gangue mineralization. Further, there is some evidence of dissolution and replacement with probable periods of non-deposition between ore and gangue depositional sequences.

The absence of compositional zoning in the last two (post-sphalerite) stages of calcite deposition indicates that the nature of the chemical environment which affected zoning did not fluctuate significantly from beginning to end of later calcite deposition. The amber color observed in the latest calcite is believed to be due to trace amounts of Fe, Mn and Yb.

The results of electron microprobe analysis on the zoned calcite indicates that at the low levels of concentration of Fe and Mn in the calcite it was only possible to obtain semiquantitative analysis with the EMP. However, these preliminary data indicate that the dark zones are higher in Fe and lower in Mn while the light zones are lower in Fe and slightly higher in Mn. The results for Zn (0.07%) remained more or less constant in both the light (zone 2) and dark (zone 1) zones. Analysis of the zoned dolomite indicates that the amount of Fe present in corresponding dark zones may be eight to ten times that of calcite.

X-ray fluorescence analysis of calcite gangue and host dolostone samples indicates that: (1) other elements (Y, Yb and Pb) may be enhancing luminescence in calcite and dolomite; (2) there are differences in the trace element content and distribution between the zoned calcite and host dolostone samples from the mine (mineralized) versus outlying ("unmineralized") core samples; (3) silicification appears to be more extensive in the area of the mine. Quantitative analyses on host dolostone from the mine area indicate that these samples are considerably more siliceous than the outlying ("unmineralized") core samples. Petrographic observations suggest that silica deposition had decreased substantially during the deposition of early, zoned calcite and dolomite. Further study revealed that quartz occurs

as inclusions in zone 2 and 3 of the zoned calcite and in the early sphalerite.

The results of the analytical work on the gangue calcite and host dolostone suggest that a geochemical halo may exist around the Elmwood deposit, i.e., possible evidence of alteration caused by the incoming Zn-S bearing solution(s).

The results of cathodoluminescent analysis are not yet conclusive since the lateral and vertical extent of the zonation has not been determined. However, there is an indication that this technique can be employed to study the paragenetic sequence and the parameters that have controlled the emplacement of sphalerite in the Elmwood area.

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CHAPTER I

INTRODUCTION

I. INTRODUCTION

The Knox Dolomite has produced zinc in Tennessee for over a century (Oder and Ricketts, 1961). Despite extensive research, several critical questions concerning the genesis of these deposits remain unanswered, i.e., the source of the metals and sulfur, the transportation mechanism, the nature of the physiochemical environment during the deposition of the coexisting phases and the age(s) of the mineralization. It is well known that there is a common association between gangue minerals and sulfide ore minerals. This relationship implies that the origin of the ore minerals must be closely tied to the origin of the gangue.

The gangue carbonates in the Tennessee zinc deposits frequently luminesce under electron bombardment (cathodoluminescence) (CL) as a series of light and dark bands (or zones) which reflect physiochemical changes that have occurred during crystal development. The study of this CL zonation may yield information concerning the nature of the geochemical environment prior to and after the introduction of the sphalerite.

CL petrography has been applied to the study of the dolomite gangue in several Mississippi Valley type deposits (Ebers, 1976) in eastern Tennessee. The application of this technique, in conjunction with analytical chemistry, can contribute towards a better understanding of the relationships that exist between the gangue dolomite and zinc mineralization (Ebers, 1976; Cobb, 1973).

The primary purpose of this investigation was to study the gangue calcite within the Knox Group in the Elmwood area in order to better understand the paragenetic relationships that exist. Cathodoluminescent petrography was used to determine if the gangue displayed a predictable pattern (zonation) from one locality to another within the mine and to compare these results to outlying "unmineralized" core samples up to 10 miles (16 km) from the mine. It was hoped that the pattern of CL zones observed in calcite within the mine would differ (in sequence, color and hue, and/or trace element content) when compared to outlying "unmineralized" core samples.[1]

II. LOCATION

The Elmwood mine is located in the northeast corner of the Central Basin section in the Interior Lowlands

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[1]Other phases were also studied with CL and analytical chemistry including host dolostone, dolomite, sphalerite, fluorite, galena and barite from the Elmwood area.

Physiographic Province, approximately 50 miles (80 km) east of Nashville near the community of Elmwood in Smith County, Tennessee (Figure 1; Callahan, 1977; DeGroot, 1973; Winslow and Hill, 1973).

The Central Basin is structurally a broad anticline (Nashville Dome) with dips away from the apex, seldom exceeding 50 feet per mile (Winslow and Hill, 1973). The deposit is situated on the northeast side of the Nashville Dome in an area of moderate topography (400-500 feet of relief) near the Eastern Highland Rim (Callahan, 1977; Winslow and Hill, 1973).

III. GEOLOGIC SETTING

The Elmwood deposit is located in the Knox Group which is not exposed (except for two crypto-explosive structures, the Flynn Creek and Wells Creek) in Central Tennessee. In the Elmwood area the Knox Group is overlain by 1,000-1,350 feet (335-410 m) of Middle-Upper Ordovician argillaceous, fossiliferous limestone (Figure 1; Callahan, 1977; Kyle, 1976). The Cambro-Ordovician Knox Group is composed of a sequence 3,000 feet (915 m) thick that includes five formations: Copper Ridge Dolomite, Chepultepec Dolomite, Kingsport Formation and the Mascot Dolomite (dolostone) (Figure 2; Kyle, 1976).

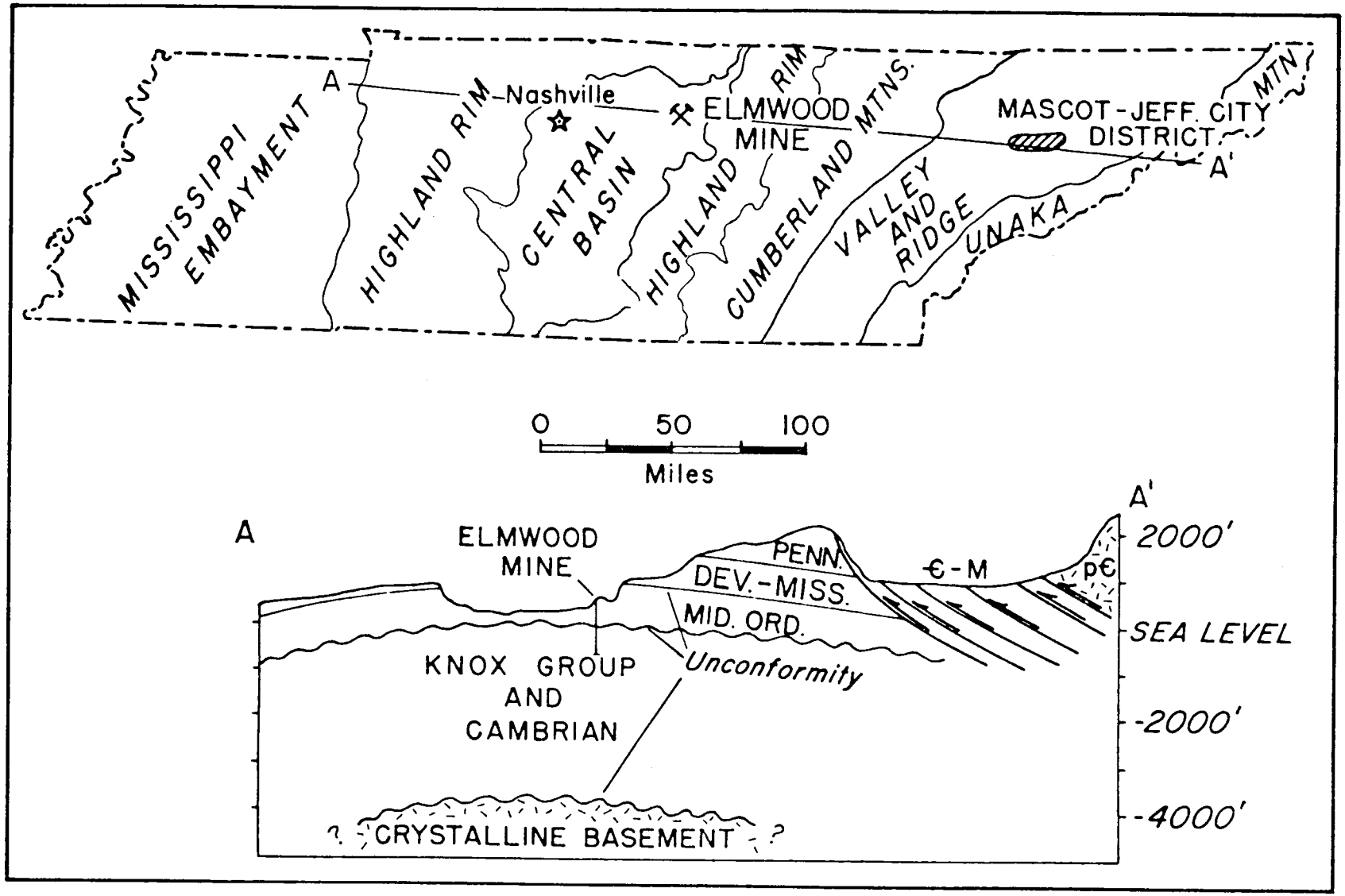


Figure 1. Geologic map and partial east-west vertical section—State of Tennessee (after Callahan, 1977).

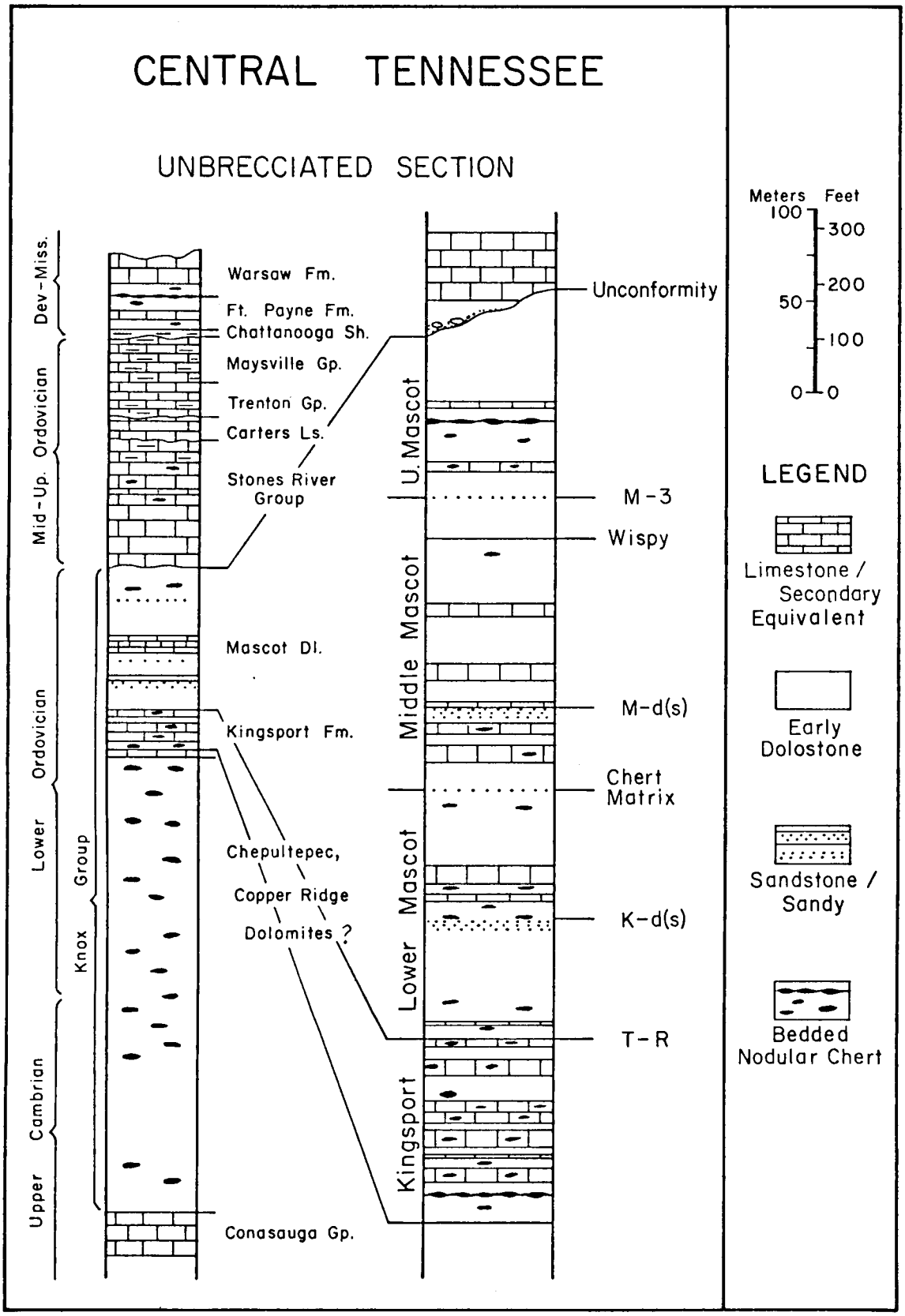


Figure 2. Generalized stratigraphic section of Central Tennessee Zinc District (after Kyle, 1976).

The Mascot Dolomite, which is the most extensively mineralized sequence in Central Tennessee, consists of finely crystalline dolomite, interbedded limestone units up to 40 feet thick, and medium to coarsely crystalline dolostone units termed "limestone equivalents" and quartz sandstone with dolomite cement. The Mascot ranges in thickness from 612-841 feet (187-256 m) (Stagg and Fischer, 1970; Kyle, 1976; Degroot, 1973). The upper portion of the Mascot experienced widespread erosion during pre-Chazayan time that resulted in the development of a large paleokarst system with as much as 125 feet of relief occurring on the erosional unconformity (Gilbert and Hoagland, 1970; Stagg and Fischer, 1970). Paleosinks are evidenced by brecca-filled dissolution zones that extend to depths in excess of 900 feet below the unconformity (Gilbert and Hoagland, 1970). The karstification is recognized as being similar to that observed in East Tennessee and is believed to be a factor in the localization of the zinc deposits (Gilbert and Hoagland, 1970).

Mineralization in Central Tennessee is localized primarily within the Mascot Dolomite (Winslow and Hill, 1973). A particularly favorable sequence within the Middle Mascot Dolomite, between the so-called M-1 and Chert Matrix markers, contains two thick limestone beds which are more frequently mineralized than the overlying and underlying zones and is

the interval under consideration in this study (Figure 3; Winslow and Hill, 1973; Kyle, 1976). This portion of the section has experienced extensive lateral and vertical brecciation which could have been the result of a regional aquifer system that developed in early Ordovician time when circulating ground water dissolved limestone units and extensive breccias were formed (Winslow and Hill, 1973). New Jersey Zinc Company geologists generally accept a theory that involves solutions migrating through fractures, dissolving the more soluble limestone units causing the collapse and brecciation of the overlying dolostone beds. Not all of these breccias are mineralized. The best mineralization occurs at the tops and outer edges of the breccia bodies (Winslow and Hill, 1973).

IV. MINERALIZATION

The mineralized interval (900-1,700 feet below the surface) in the Elmwood area contains a predominantly calcitic gangue (with locally significant quantities of sphalerite, fluorite, galena and barite) which cements dolostone breccia blocks (Anonymous, 1969; Winslow and Hill, 1973; Kyle, 1973). As of 1977, the ore grade at Elmwood averaged roughly 4% zinc with local zones that may run as high as 18% zinc (Callahan, 1977; Winslow and Hill, 1973). The spatial relationships of the mineralized zones (the ore

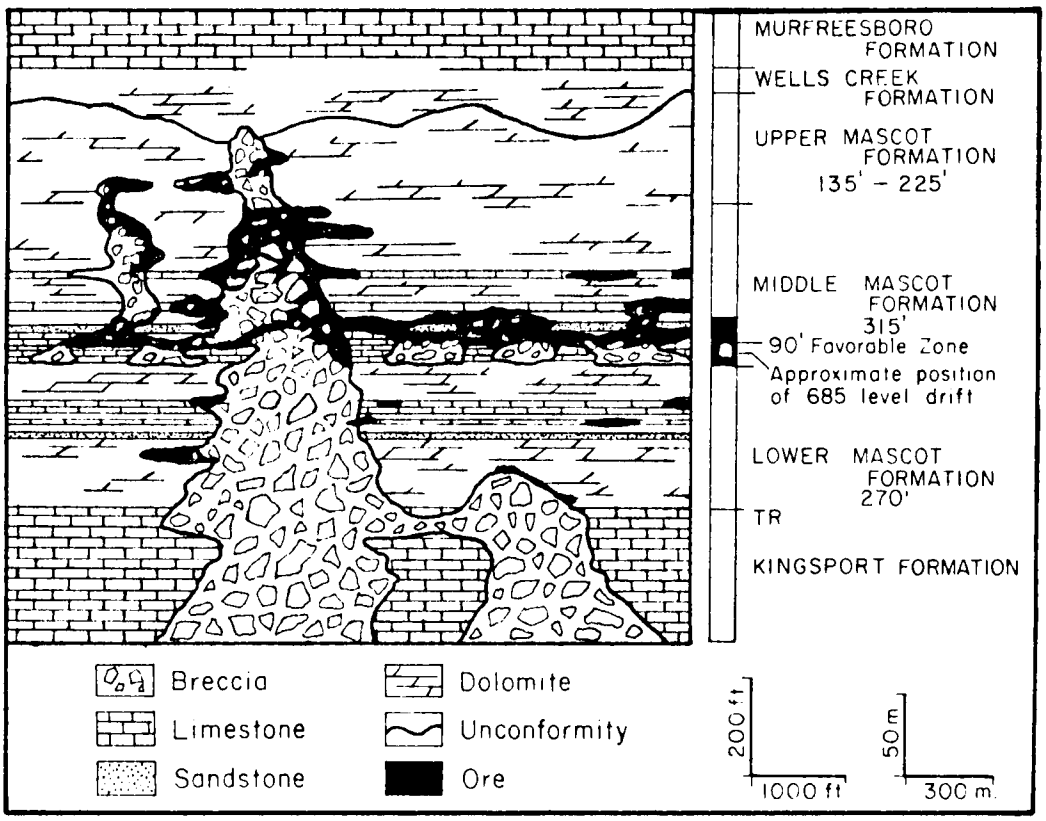


Figure 3. Interpretation of Knox geology in the Elmwood area (after Winslow and Hill, 1973).

is not uniformly distributed throughout the breccia structures) are such that there is as yet no sound basis for defining the distribution of ore between drill holes (Figure 3; Callahan, 1977; Winslow and Hill, 1973).

CHAPTER II

CATHODOLUMINESCENCE

I. INTRODUCTION

Luminescence includes several different phenomena in which a material gives off nonthermal radiation that is characteristic of that material (Marshall, 1973). Electron excited luminescence (cathodoluminescence)[1] occurs when the surface of the specimen is excited by an electron beam resulting in the emission of visible light (Sommers, 1973; Longini, 1949). The excitation of luminescence is due to impact ionization that results in electron shifts on the orbital level of either the atoms in the host lattice or impurity ions in the host (Kniseley and Laabs, 1973). The electrons are raised to metastable energy levels and trapped in luminescent centers that have an energy level close to the original orbital position. All excess energy is then emitted as light (Kniseley and Laabs, 1973; Longini, 1949).

Impurities are capable of enhancing or quenching CL in carbonates; for example, Fe^{+2} tends to quench, whereas Mn^{+2} enhances, CL in calcite (Medlin, 1963). Other elements

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[1]The process of converting cathode-ray energy into visible (includes light in the ultraviolet and infrared portions of the spectrum) light is called cathodoluminescence.

can act as activators (Pb^{+2}, Mg^{+2} and rare earth elements) and quenchers (Ni^{+2} and Co^{+2}) in calcite (Sipple and Glover, 1965; Oglesby, 1976). Ultraviolet radiation studies on calcite show that luminescence will increase to a maximum of 3.4% Mn and then decrease to zero at 17% Mn (Northrup, 1972). Meyers (1974) indicates that some natural, luminescent calcite contains more than 1,000 ppm Mn^{+2}. In addition to impurity content, luminescence (observed colors and intensities) is affected by several factors, the most important of which is the energy of the impinging electrons. Colors generally get brighter with increasing excitation potential.

The phenomena of cathodoluminescence in minerals has been investigated since the late 1870's (Long and Agrell, 1965). In the 1960's, geological applications of cathodoluminescence began to be expanded with the advent of the electron microprobe (Sipple and Glover, 1965). Due to the high initial and operating costs, a less expensive method to study cathodoluminescence was necessary. This need resulted in the development of the Luminoscope (Nuclide Corporation, Acton, Mass.), a device that consists of an electron source with a variable high voltage power supply and a vacuum chamber mounted on a conventional petrographic microscope (Sipple and Glover, 1965; Marshall, 1973; Ebers, 1976). This instrument has been applied successfully in the study of compositional zoning, fracture filling, exsolution,

intergrowths, recrystallization, attainment of equilibrium, skeletal structures, radiation and alteration halos[1] (Herzog, 1973). A Luminoscope was used to study the CL properties of the coexisting phases that are present in the Central Tennessee zinc district to ascertain if the gangue calcite luminesces in a sequence of zones as is the case with the gangue dolomite in the East Tennessee deposits (Ebers, 1976).

II. ZONATION

Cathodoluminescence in calcite and dolomite is frequently observed as a sequence of growth bands or zones (probably caused by varying amounts of activator and quencher ions) which are visible due to light and dark color variations (Sipple and Glover, 1965). Long and Agrell (1965) correlated the x-ray emissions of Fe^{+2} and Mn^{+2} with the intensity of CL for zoned carbonates and determined that zones displaying high intensity or bright colors contained 1.0% Mn^{+2} and 0.1% Fe^{+2} and the dark zones were reversed (0.1% Mn^{+2} and 1.0% Fe^{+2}).

Recent work by Oglesby (1976) on calcite and dolomite cements in the Upper Smackover Formation (Upper Jurassic) of Eastern Mississippi, indicated that CL zonation is the

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[1] In many instances the relationships that are observed with cathodoluminescence are not detectable with conventional petrography or could only be studied with detailed experiments.

result of changes in one or more variables, namely: trace elements (Fe, Mn and Mg), pE (redox potential), pH, and total sulfur content of the aqueous solution from which these cements were deposited. His model postulates that there is a relationship between the Fe^{+2} and Mn^{+2} content in CL zones in calcite and dolomite and the pE, pH and total sulfur in the pore water at the time these phases were precipitated. If a particular zone displays homogeneity in its CL characteristics, it can be inferred that the crystal was formed in equilibrium with the activities of the cations in the solution at the time of formation and that the Fe and Mn contents are homogeneous throughout the zone. Thus, the observed uniformity of the CL intensity and color in a particular zone of calcite and dolomite cements in the Upper Smackover Formation may be a reflection of the Fe^{+2} and Mn^{+2} distribution that disrupted the lattice of the crystal. Zonal boundaries are an indication that the character of the aqueous solution changed with time. Thus, variation in the CL properties and zoneal boundaries indicate that the character of the solution(s) changed gradually or spasmodically during crystal growth and that throughout this period each zone was probably in equilibrium with the solution at the time of deposition. If two sequences of zones exhibit similar colors and hues of color intensities and trace element chemistry, it can be presumed, as a first

assumption, that these zones were deposited during the same period under similar conditions and therefore are correlative.

III. CORRELATION

Petrographic applications of CL zonation in calcite and dolomite have been investigated by Smith and Stenstrom (1965), Sipple and Glover (1965), Freeman (1971), Meyers (1974), Ebers (1976) and Oglesby (1976). It is generally accepted that the physiochemical relationships that existed at the time of the formation of the crystal have not changed, i.e., solid state diffusion has not affected the zonal relationships (Oglesby, 1976). Correlation between individual samples within a measured section and from section to section ("cement stratigraphy" or "microstratigraphic correlation") must consider the following: zonal sequences (correlation of matched sets of zones), luminescent characteristics (color/hue, brightness and saturation) and relative thickness of luminescent zones (Oglesby, 1976; Ebers, 1976; Meyers, 1974). Based on observational criteria, CL (growth) zones always occur in the same order and gaps in the sequence are due to the nature of the thin section cut, nondeposition, differences in the rate of growth between two crystals during a particular period of development and dissolution (Oglesby, 1976; Ebers, 1976). The removal of zones through dissolution is a nonselective process that is revealed as an irregular

trace that may cross one or more zones and is generally easily detectable in thin section.

CHAPTER III

OTHER ANALYTICAL TECHNIQUES

I. SAMPLE SELECTION AND PREPARATION

Samples from the mine were collected from 11 locations in active stopes and along haulage ways which included 9 locations in the upper level and two from the lower level of the underground workings (Figure 4).

Seventeen diamond drill holes were also sampled in the Elmwood area (Figure 4). Sampling of the core was confined to the interval between the M-1 and Chert Matrix markers; it is believed that this interval roughly corresponds to the stratigraphic interval of the mine samples. Sampling of core was done in an irregular concentric pattern adjacent to the mine with the maximum distance from the mine being approximately 10 miles (16 km). Approximately 85% of the core samples were obtained from apparently "unmineralized" areas.

Thin sections were prepared from all of the samples and offcuts were retained for possible future use. Each thin section was observed with the Luminoscope and photographs were taken of critical areas. Polished sections consisting of zoned calcite, dolomite and sphalerite were prepared for use on the EMP and pressed pellets were used in XRF analyses.

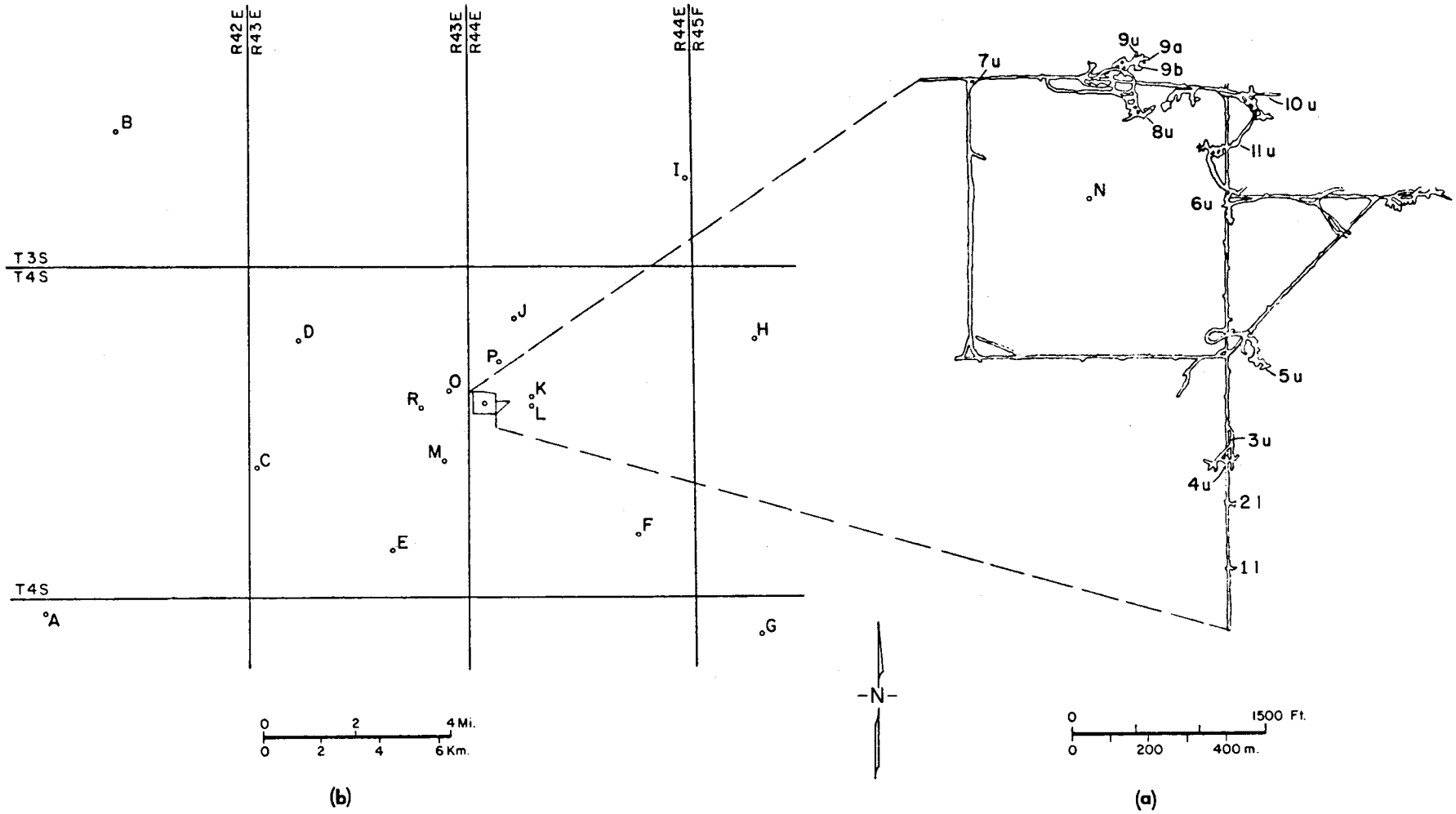


Figure 4. Sample locations of core (A-R) and mine samples (1-11) from the Elmwood mine and surrounding area. Map (a) represents a plan view of the underground workings prior to November, 1975, and map (b) represents a plan view of core sample locations (diamond drill holes), after New Jersey Zinc Company maps.

The reader is referred to Appendix E for details concerning the preparation of samples for analysis and information concerning the photographic technique.

II. ELECTRON MICROPROBE ANALYSIS

Cathodoluminescent observations on the gangue calcite and dolomite from the Elmwood mine and surrounding area indicate that these phases luminesce in a sequence of zones and that this pattern can be traced within the mine; this pattern was also observed in the outlying core samples. An automated M.A.C. 400S electron microprobe was used: (1) to analyze the zoned calcite and dolomite in order to determine if there were differences in the Fe, Mn and Zn content of corresponding light and dark zones in mine versus core samples; (2) to establish whether partitioning of Fe and Mn had occurred between the liquid and solid phases at the time of deposition of this apparent assemblage; and finally (3) to analyze sphalerite samples from the Elmwood mine and surrounding area for Fe, Mn, Cd, Zn and S for purposes of checking earlier work by Kyle (1973) and to determine if the dark inclusions in the sphalerite were caused by variations in the proportions of these elements.

The reader is referred to Appendix A for details concerning the operating conditions and standards that were used in the analyses.

III. X-RAY FLUORESCENT ANALYSIS

X-ray fluorescent analysis (XRF) was employed to analyze for Fe and Mn in calcite and to determine if other elements could be enhancing the observed CL in this phase. Na, Mg, Al, P, S, K, Ca, Ti, Mn, Fe and Sr in calcite and dolostone samples were determined quantitatively and qualitative results were obtained for calcite, host dolostone, sphalerite, fluorite, galena and barite from the Elmwood mine and surrounding area.

Initial XRF work on the calcite samples utilized a Norelco Universal Vacuum X-Ray Spectrograph at the University of Tennessee. Preliminary results indicate that there are detectable quantities of Fe, Mn, Sr, and Yb in the zoned calcite. A general increase in the Mn concentration was noted in the light luminescing zones, while Fe remained relatively constant for both light and dark zones. There is an indication that Yb is present in small quantities in the mine calcite samples. The reader is referred to Appendix B for details concerning the methods of study, operating conditions and the results of the preliminary work.

A TEFA model 6110 automated energy dispersive x-ray fluorescence analyzer (EDXRF) was used to obtain quantitative and qualitative data for zoned calcite, amber calcite and host dolostone as well as some qualitative determinations for sphalerite, galena, fluorite and barite samples.

Operating conditions and the analytical precision for quantitative calculations on calcite and host dolostone samples are presented in Table 8 (Appendix C). The utilization of seven carbonate standards used in this study were furnished by ORTEC Inc. and represent samples from the National Bureau of Standards and various cement companies from the U.S. and Canada.

All qualitative work was concerned with evaluating carbonates for elements not analyzed during the quantitative analyses as well as examining the trace element contents of sphalerite, galena, fluorite and barite. Samples were analyzed under different operating conditions. Spectra were retained for future use. The reader is referred to Appendix D for details concerning operating conditions and examples of selected spectra.

The procedures used for sample preparation were in accordance with TEFA analysis report "Analysis of Limestone and Dolomites by EDXRF" and are presented in Appendix E.

CHAPTER IV

RESULTS

I. CATHODOLUMINESCENCE

Calcite and Dolomite

The application of CL analysis has resulted in a better understanding of the paragenetic relationships that exist in the Elmwood area.

A study of thin sections from the Elmwood mine and surrounding area indicates that there are at least 3 generations of calcite. This is based upon CL, textural and physical properties. The earliest and by far the most abundant calcite is zoned (zones 1 through 3) and appears to have closely followed or was coprecipitated with dolomite (a zone to zone relationship between these phases tends to indicate that calcite and dolomite were deposited together). Zoned calcite (and less frequent dolomite) was observed in more than 60% of the samples. The later zones (2 and 3) may have been deposited (at least locally) during the initial stages of sphalerite deposition (see page 33). Some time after sphalerite deposition, a later, typically unzoned light brownish-orange calcite was deposited. This calcite is not common (observed in less than 10% of the samples). The third

and latest carbonate, an amber calcite, is an unzoned, medium-orangish brown luminescing phase.

The presence of 3 luminescent zones in the early gangue calcite and less ubiquitous dolomite necessitated standardizing the description of luminescent coloration between individual zones in a zonal sequence. Sommer (1972) was able to characterize CL and x-ray luminescence in the visible range of the spectrum for Mn^{+2} activated carbonate minerals. CL emissions varied from 590μm (yellow-orange) for calcite to 677μm (red) for magnesite. The color terminology presented in Table 1 has been adopted from the National Bureau of Standards Circular 553 (Kelly and Judd, 1955). This system utilizes three parameters, color/hue, brightness and saturation, to describe observed coloration. In order to reduce the number of variables that could affect the color designation, all observations were done within specific limits as suggested by Ebers (1976) and which are presented in Table 2.

Local variations in conditions within zone 1 are represented by two subzones 1a and 1b. Frequently, subzone 1b is missing; however, when present it occurs with either a transitional or sharp boundary with zone 1a. In some instances, all of these relationships can be observed in the same sample (Figures 5 and 6). Several other subzones (including a minor pyritic zone observed in only one specimen

TABLE 1

CATHODOLUMINESCENT ZONATION, COLOR DESIGNATION AND FREQUENCY OF ZONED CALCITE AND DOLOMITE AT THE ELMWOOD MINE AND SURROUNDING AREA

Zone	Color/Hue (Brightness)	Saturation[1]	Color Designation[2]	Frequency of Zones 60% of the Slides Contained Zoned Calcite (54 Out of 90)
Oldest				
1a Calcite	Dark Brown[3]	Blackish	Blackish Brown	Approx. 6% of the slides contained only zone 1a
Dolomite	Med.-Dark Red	Grayish	Med. Dk. Grayish Red	
1b Calcite	Medium Brown	Moderate	Med. Orangish Brown	Approx. 3-4% of the slides contained only zones 1a-1b
Dolomite	Medium Red	Light Grayish	Med. Light Grayish Red	
2 Calcite	Orange	Strong	Strong Brownish Orange	Approx. 20% of the slide contained zones 1(a&b)-2
Dolomite	Light Red	Strong	Strong-Brilliant Red	
Youngest				
3 Calcite	Med. Dk. Brown	Moderate	Mod. Dk. Orangish Brown	Approx. 70% of the slides contained zones 1(a&b)-3
Dolomite	Dk. Blackish Red	Blackish	Dk. Blackish Red	

[1]Saturation refers to the degree of difference in color/hue, i.e., the strongest colors are the brightest, whereas weak colors are deep, grayish or blackish.

[2]Color terminology from the National Bureau of Standards Circular 553 (Kelly and Judd, 1955).

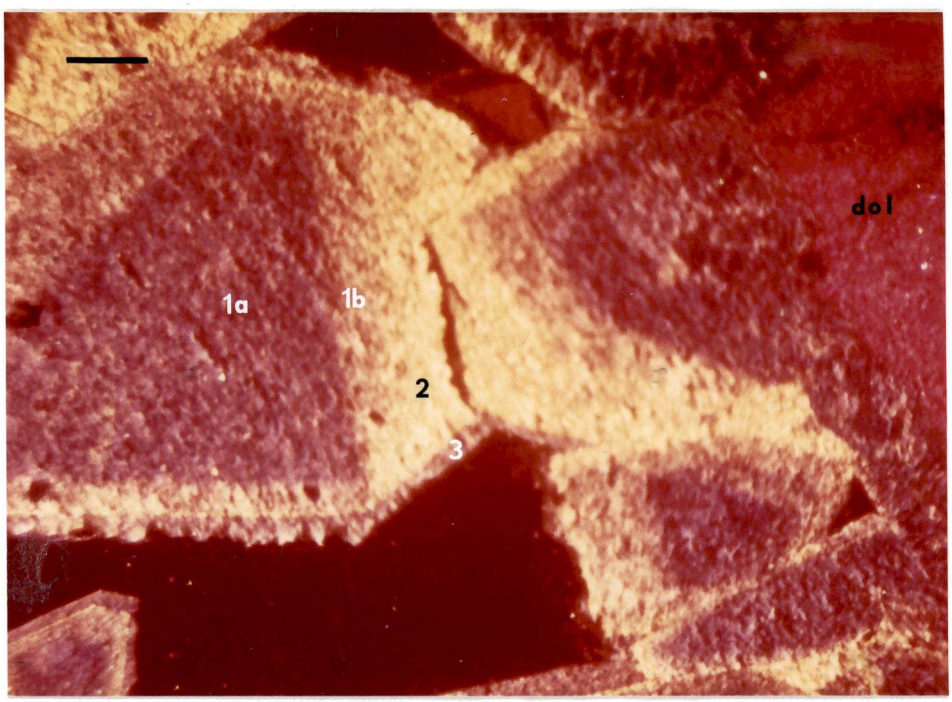
[3]Color/hue and saturation are dependent upon voltage used in exciting luminescence. Colors and saturation are brighter with increasing voltage, respectively. Observations were made in the range of 14-16 kv.

TABLE 2

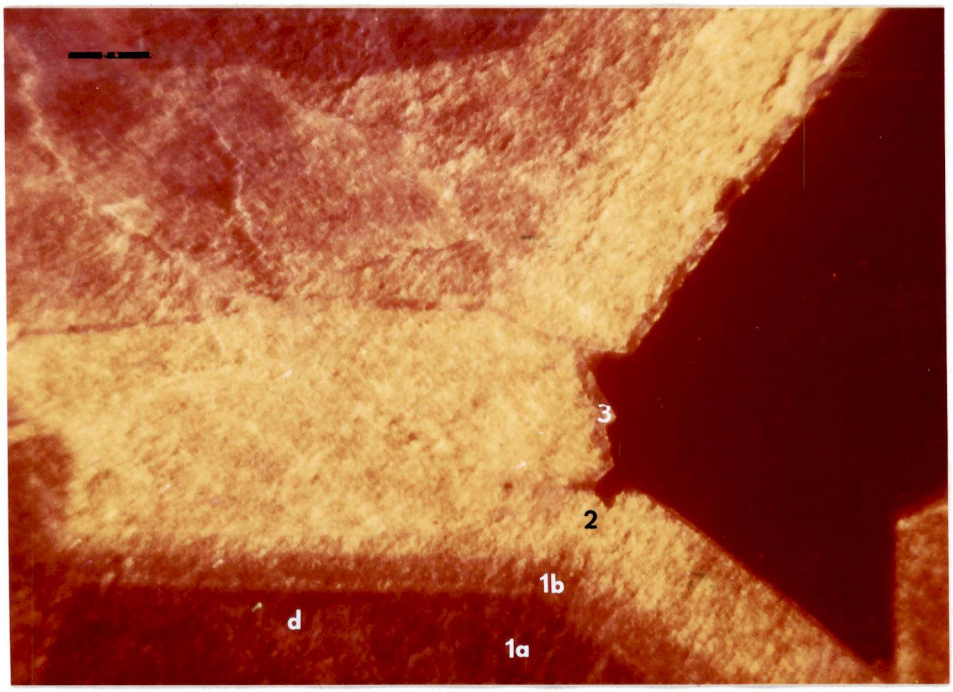
VARIABLES THAT AFFECT COLOR/HUE AND INTENSITY OF CATHODOLUMINESCENCE AND THE VARIABLE LIMITS OBSERVED IN THIS STUDY

Variables	Operational Limits
Applied KV and discharge currents of electron gun	14-16 KV/60 ma-.5 millamp
Degree of polish of thin section	400 mesh finish
Discoloration of vacuum chamber window	Light-medium yellow
Microscope characteristics	Bausch and Lomb 3-1/2 × obj., 5x ocular
Diameter of e^- beam	5 cm
Atmosphere	Vacuum (125-150 millitorr)
Light level in working area	Darkness

Modified after Eberts, 1976



(a)



(b)

Figure 5. Photomicrographs (ASA 160) of zoned calcite filling fractures. Zones 1-3 can be observed to have grown toward the center of a fracture (5a and 5b). In photo (a) calcite can be observed developing in open space on dolostone (dol). Note evidence of partial dissolution in zone 3. Photo (b), zone 1a, contains dolomite inclusions (d). Bar scale represents 5 mm. (a) Location 8 and (b) location 5.

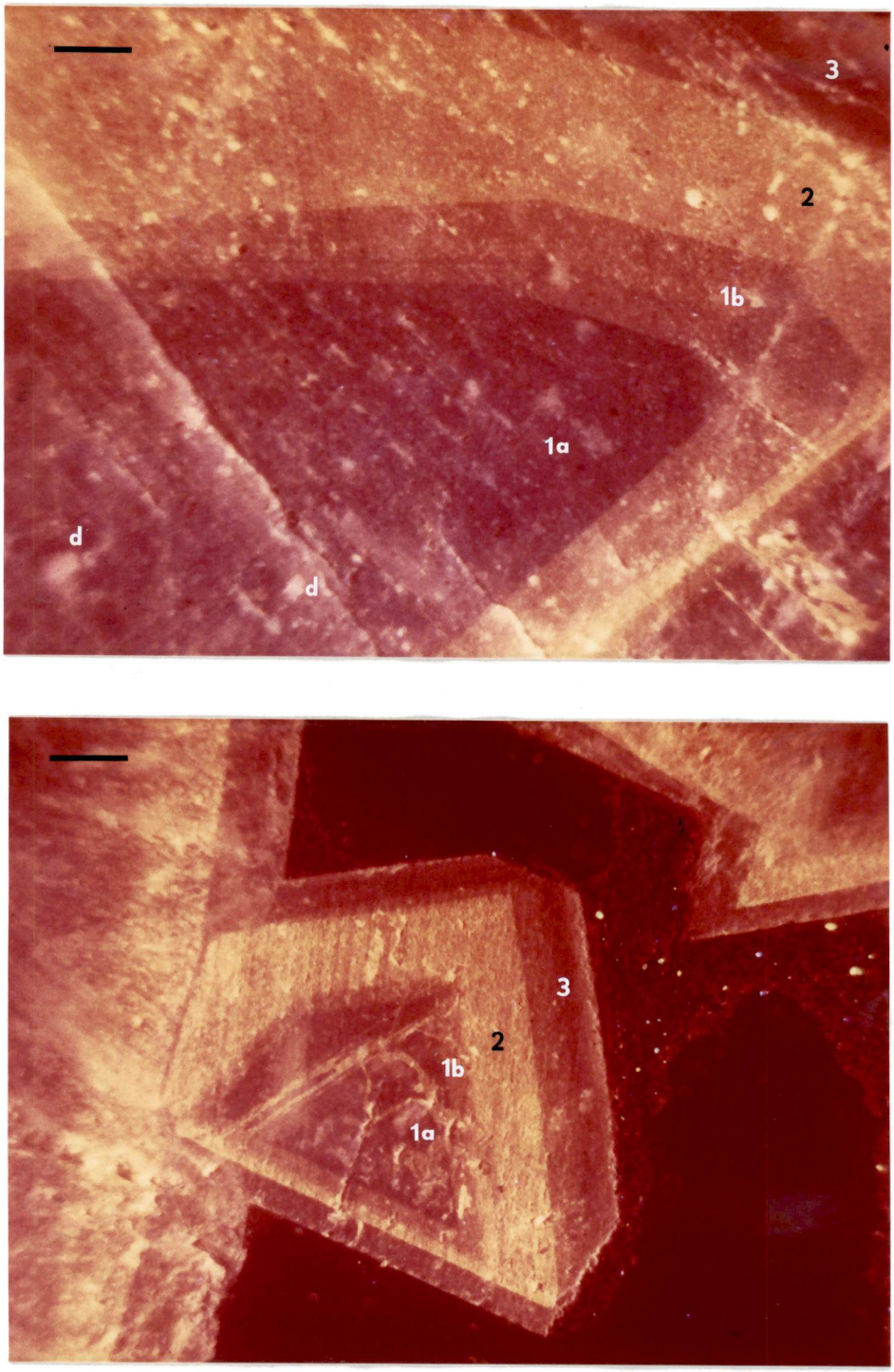


Figure 6. Photomicrographs (ASA 160) taken in cathodoluminescent light displaying zonation (zones 1-3) in calcite. Note dolomite inclusions (d) in zone la (upper photo). Bar scale represents 5 mm. (Location B).

from location 5) were noted in mine samples. These zones were very irregular and discontinuous and generally could not be traced for more than 10-15 mm on a slide.

Zone 1a, the oldest, is represented as a prominent, relatively wide, zone that forms the center or core of the calcite and dolomite crystals. In calcite this zone frequently contains dolomite inclusions (Figure 6). Approximately 6% (3 out of 54) of the slides that contain zoned calcite reveal only zone 1a. Calcite color designations for zone 1a can range from a blackish brown to a darkish brown. The corresponding zone in dolomite is a moderate-dark red.

Zone 1b in calcite and dolomite is transitional between zone 1 and 2, possibly due to a slight change in the solution chemistry. This zone is generally thinner than zone 1a and is the least conspicuous zone. Approximately 3-4% of the slides that contain zoned calcite reveal only zones 1a-1b. Color designations for the zone 1b calcite and dolomite are moderate-orangish brown and moderate-light grayish red, respectively.

Zone 2 is the most distinctive in terms of its relative thickness and coloration. Consequently, zone 2 is very useful for purposes of zonal correlation in calcite and dolomite. Approximately 20% of the slides that contain zoned calcite reveal only zones 1-2. Corresponding calcite and dolomite samples of zone 2 are strong brownish-orange and strong brilliant red, respectively.

Zone 3 represents a slight departure in terms of color/hue, brightness and saturation between the zoned calcite and dolomite. The luminescence observed in zone 3 of the calcite is slightly darker than zone 1a in color/hue, brightness and saturation. Zone 1a can be distinguished from zone 3 because zone 1a is confined to the center or core of the crystal. This inner zone (1a) is much thicker than zone 3 and commonly contains small (< 1-3 mm) dolomite inclusions. In dolomite, zone 3 is considerably darker than the corresponding calcite zone, indicating that perhaps there is a substantial increase in the amount of quencher (Fe^{+2}) ion available during the growth of this zone (see page 30). Corresponding calcite and dolomite of zone 3 are moderate orangish-brown and a dark blackish-red, respectively. Approximately 70% of the slides that contained zoned calcite and dolomite revealed zones 1, 2, and 3.

Zonal correlation can be attempted according to the criterion presented on page 14. This technique can be best applied to small fractures that have experienced open space filling (Figure 5, page 25).

Observations on the zoned calcite indicate that this consistent CL zonation pattern can be correlated (traced) throughout the sampled area; i.e., within the mine and up to 10 miles (16 km) from the deposit (compare Figures 5 and 6, pages 25 and 26 (taken from samples 10 miles apart)).

The CL pattern observed in the calcite is very similar to the rarer dolomite in terms of the number of zones, degree of saturation, brightness of individual zones and the relative thickness of corresponding zones (Figure 7). Thickness of cathodoluminescent zones can be attributed to the nature of the thin section cut. An apparent thickening or thinning of the zone(s) can also occur depending upon the size of the open space which was filled, e.g., the thickness of zones may be dependent upon the volume of fluid passing through a given size opening where small fractures contain thinner zones than corresponding zones in larger fractures (Cobb, 1973; Ebers, 1976). In specific instances equivalent zones (e.g., zones 2 and 3 of the calcite and dolomite) can be observed to be in contact with each other (Figure 7). This relationship tends to indicate that these phases were deposited simultaneously from the same solution. It is noteworthy that the zoned dolomite (and calcite) consistently occurs near dolostone fragments and can be observed growing from a dolostone substrate or as individual crystals near the host. A late stage, finely crystalline dolomite (apparently unrelated to the earlier zoned dolomite) can be observed cutting zoned calcite and sphalerite (Figure 8).

Mineralization is commonly associated with zoned calcite samples that display zones 2-3; however, this zonation is not always observed with mineralization. There is an

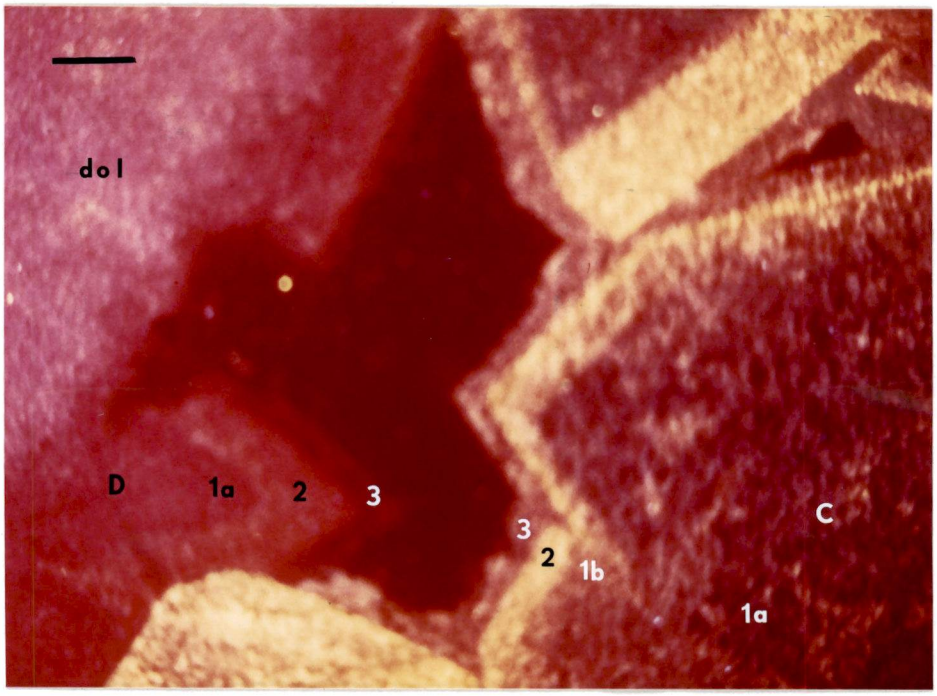
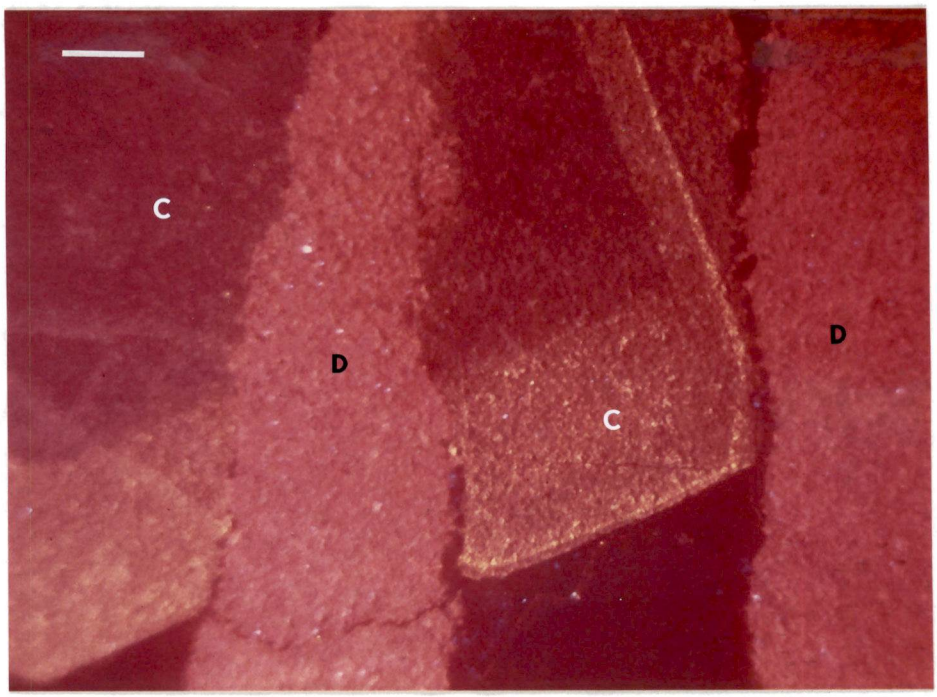
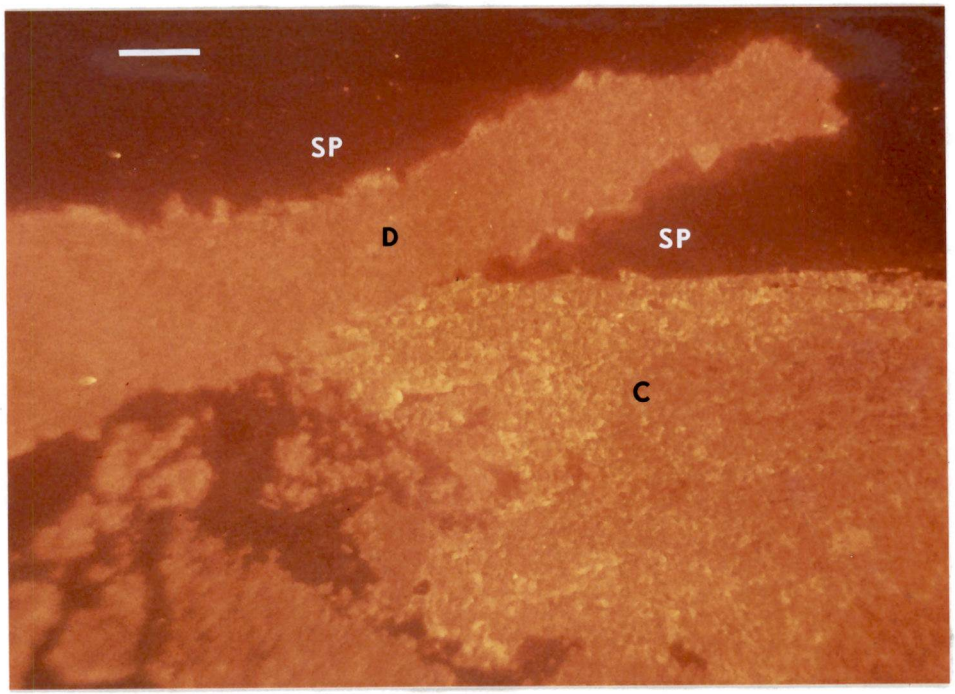


Figure 7. Photomicrograph (ASA 160) taken in cathodoluminescent light of zoned calcite (c) dolomite (D) displaying zones 1-3 and dolostone (dol). Bar scale represents 5 mm. (Location 11).



(a)



(b)

Figure 8. Photomicrographs (photo (a) ASA 160, photo (b) ASA 200) taken in cathodoluminescent light showing late, finely crystalline dolomite (D) cutting zoned calcite (C) in photo (a) and sphalerite in photo (b). Bar scale represents 5 mm. (Location 5).

indication that the latter zones (2 and 3 and dolomite) could be deposited (at least locally) in the presence of sphalerite or Zn-S bearing solution(s) (Figure 9). However, petrographic observations indicate that this phenomenon was not common (observed in only one instance from location H). The development of large euhedral crystals with sharp contacts (the absence of significant interaction between carbonates and sulfides) between calcite and sphalerite (and dolomite and sphalerite), in addition to the relative purity (only trace quantities of foreign ions) of these phases, suggests that the physiochemical environment of deposition of the sulfides was not significantly different from the physiochemical environment that deposited the early and late gangue carbonates. However, the existence of CL zonation in the early carbonates indicates that minor fluctuations in the physiochemical environment occurred prior to and possibly during sphalerite deposition.

There is evidence of local dissolution of zones prior to sphalerite deposition. Such dissolution is frequently confined to zone 3 as evidenced by irregular boundaries and corrosion within the zone (see page 25). In other instances a complete sequence has been partially dissolved and replaced by sphalerite (Figure 10). The study of the thin sections from the mine area and outlying core samples indicates that dissolution and replacement are relatively minor and are

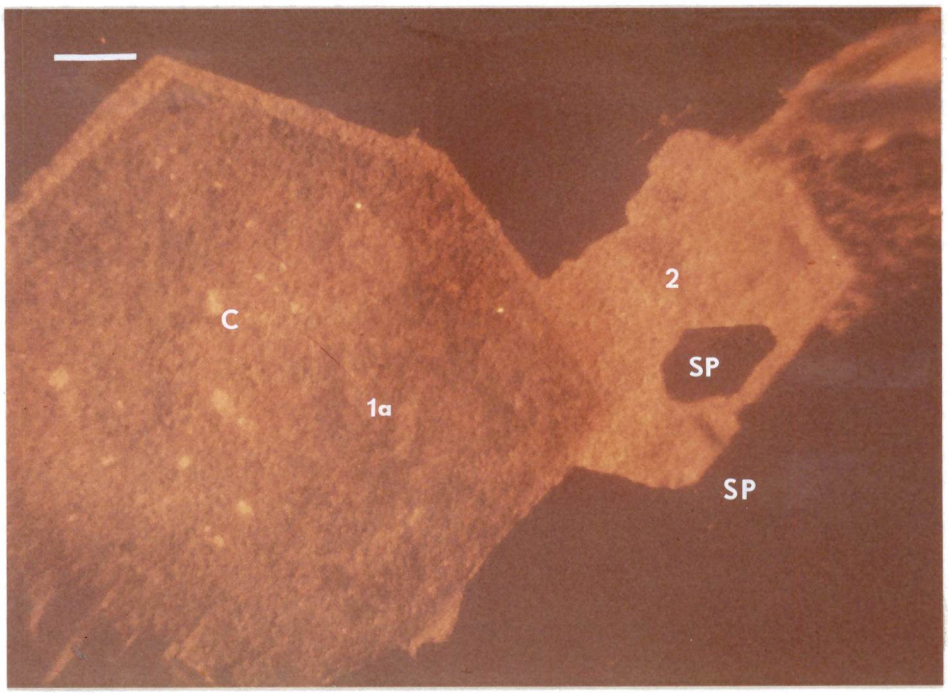


Figure 9. Photomicrograph (ASA 200) taken in cathodoluminescent light showing sphalerite (SP) inclusion within zone 2 of early zoned calcite. There is an indication that zone 2 was developing simultaneously with early sphalerite deposition. Bar scale represents 5 mm. (Location H).

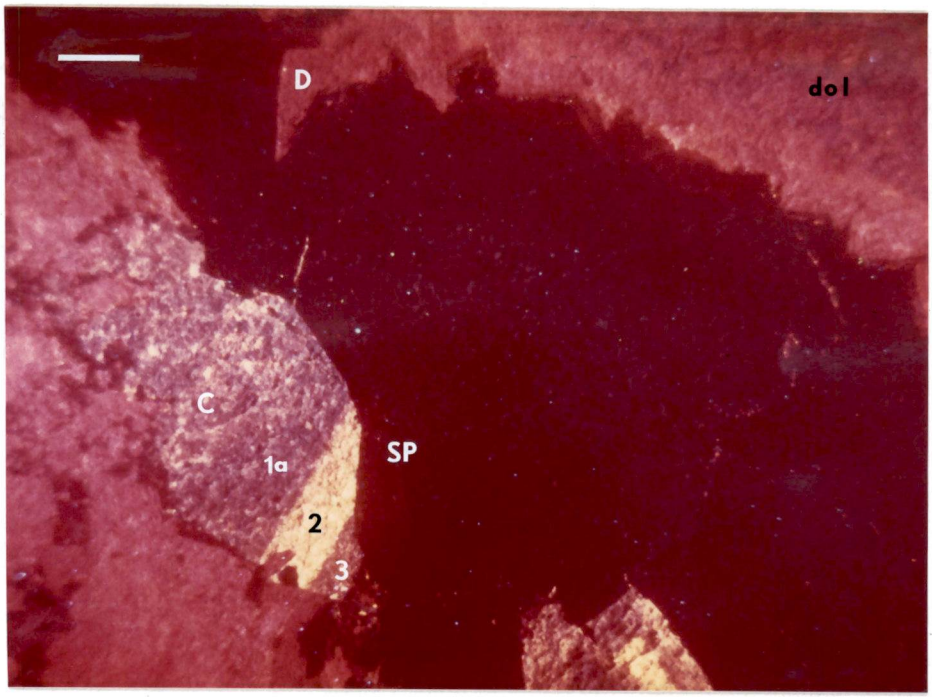


Figure 10. Photomicrograph (ASA 160) taken in cathodoluminescent light showing evidence of dissolution of calcite (C) zones 1-3 and subsequent sphalerite (SP) deposition. Note dolomite (d) growth on dolostone (dol) substrate. Bar scale represents 5 mm. (Location H).

confined to the area where calcite is in contact with sphalerite.

The second generation of calcite occurs as a coarse crystalline phase that is essentially unzoned except for small areas that reveal changes in color/hue and saturation (Figure 11).

The third generation (amber) calcite displays a massive texture that is very similar to the zoned calcite. This late phase revealed ill-defined nondescript zones or lineations that parallel the crystal boundaries; however, these zones are local and cannot be traced for any distance (Figure 12).

At this time it is not possible to determine what the relationships are between the second and third generations of calcite.

Host Dolostone

The Mascot Dolomite consists primarily of finely crystalline dolomite that luminesces a moderate pinkish red. The results of CL observations on mine dolostone samples revealed a predominance of medium grained dolomite that commonly contains disseminations of primary quartz (a light blue luminescing phase) (see page 40). Infrequently (especially in the area of the mine), the author has noted the presence of calcite occurring as remnants in the host dolostone (Figure 13). This phenomena may represent

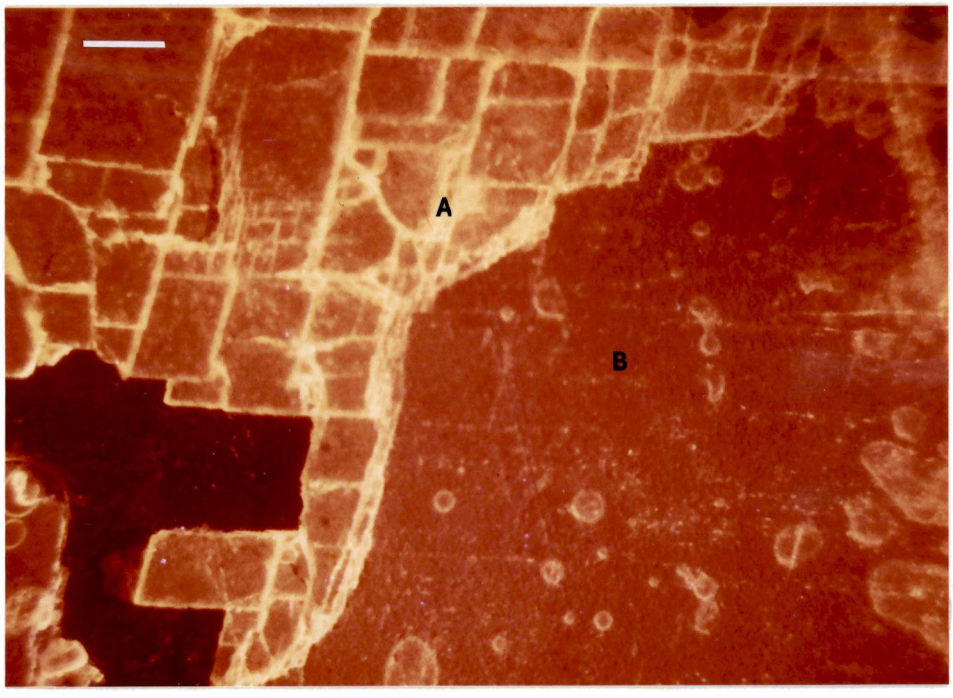


Figure 11. Photomicrograph (ASA 160) taken in cathodoluminescent light of the second generation of calcite (A) in contact with zone 1a of early zoned calcite (B). Bar scale represents 5 mm. (Location E).

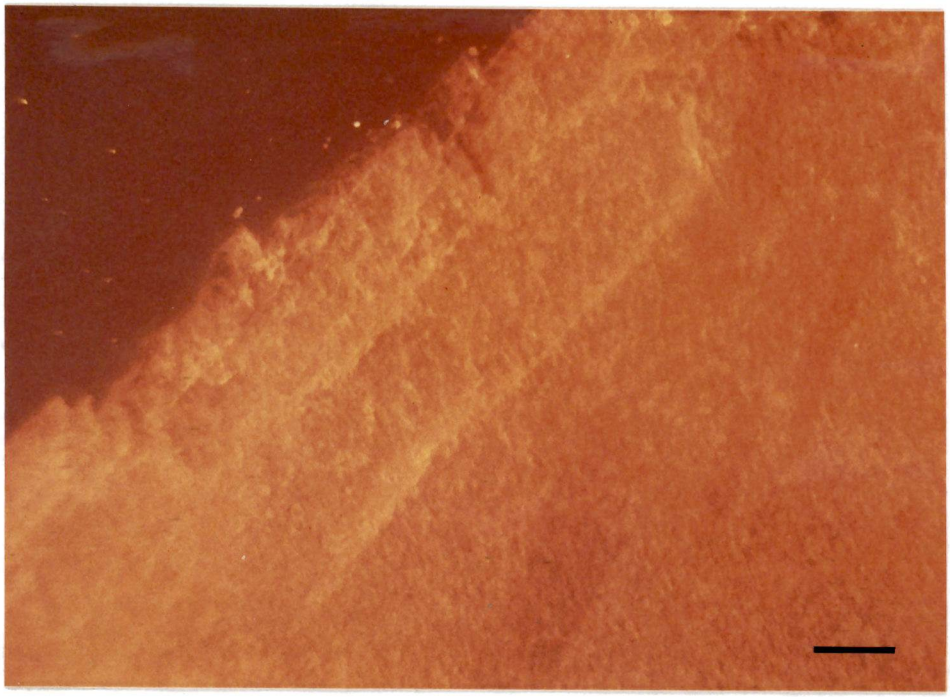


Figure 12. Photomicrograph (ASA 200) of the late amber calcite taken in cathodoluminescent light. Bar scale represents 5 mm. (Elmwood mine, exact location unknown.)

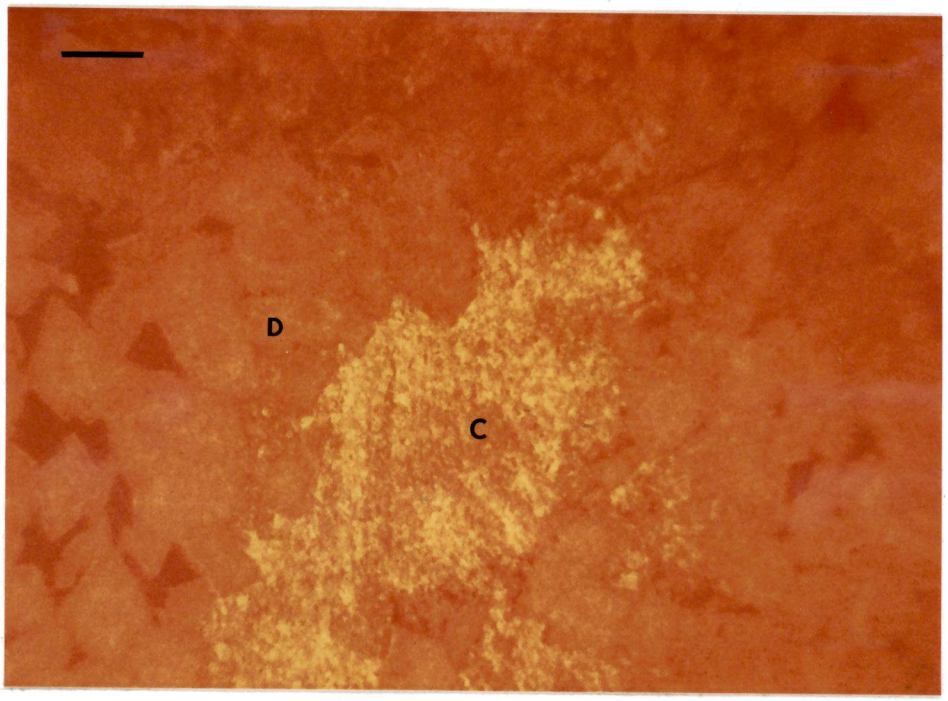


Figure 13. Photomicrograph (ASA 200) taken in cathodoluminescent light of dolostone sample revealing medium grained dolomite (D) with remnants of calcium carbonate (C). Bar scale represents 5 mm. (Location 1).

incomplete dolomitization of a limestone horizon or perhaps the calcite represents void or pores in the host that have been filled by calcium bearing solutions prior to or during the introduction of the sphalerite.

In the mine area, a substantial amount of nonluminescing quartz was observed in the host dolostone. This nonluminescing phase appears as nearly circular grains that may be detrital grains deposited at the same time as the host dolostone. There is evidence of overgrowth as well as irregular extinctions in this phase. In addition, silicification that lined fractures and breccia blocks in the sample area also was nonluminescent.

Fluorite

Fluorite at the Elmwood mine postdates the sphalerite and galena and occurs as coarse, pale blue-purple cubic crystals (up to 10 cm in diameter), that luminesce light-medium blue (Kyle, 1976).

There may have been some reaction between the host dolostone breccias and the incoming fluorite-forming solutions. This alteration is reflected in the host as a lightening or washing out of the colors as one approaches the contact between the dolostone and the fluorite (Figure 14). This may be due partially to the dominance of blue that in effect lightens the reds. The relationship of

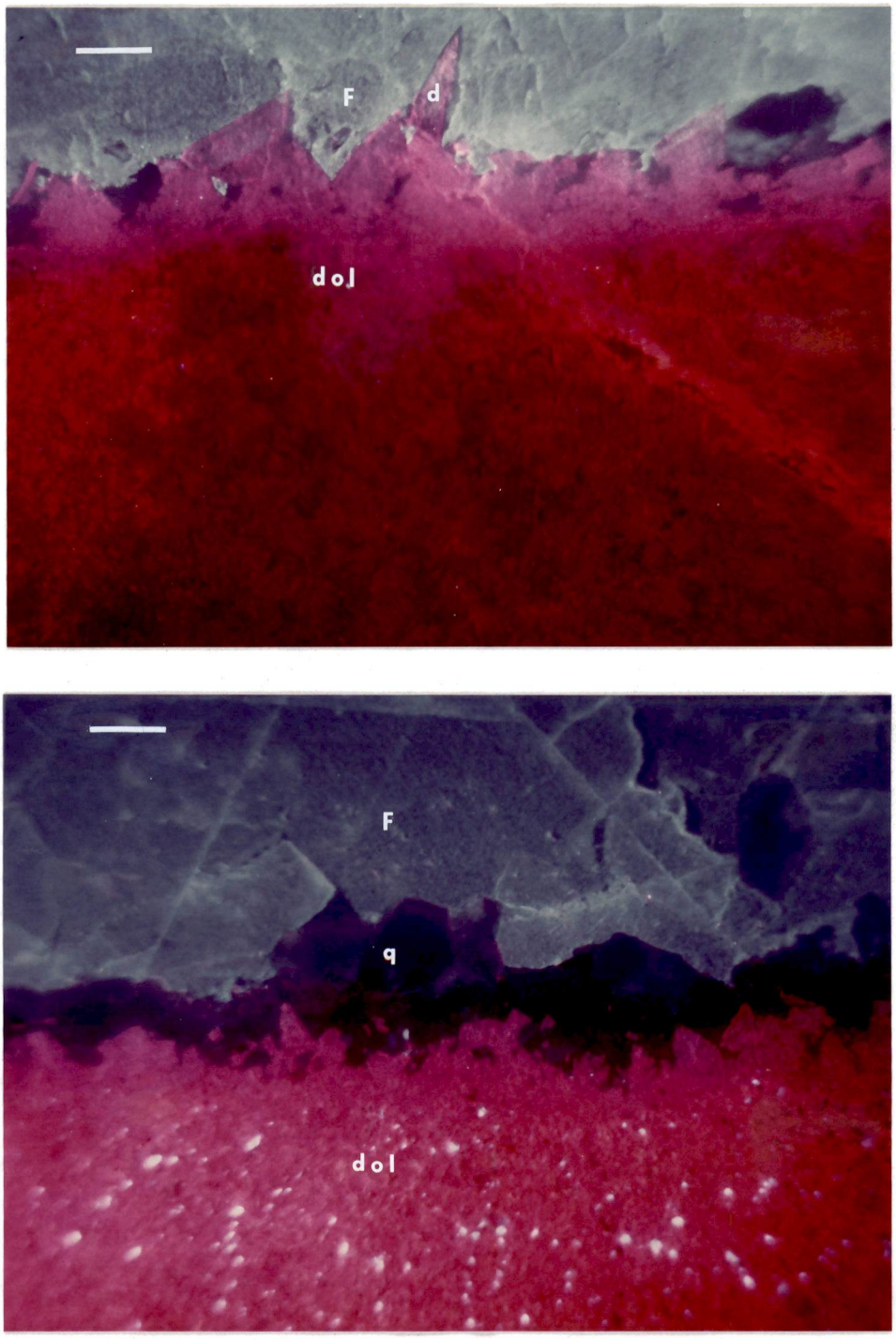


Figure 14. Photomicrographs (ASA 160) taken in cathodoluminescent light. Photograph (a) reveals fluorite (F) in contact with dolomite (d) growing on host dolostone (dol). Photo (b) shows fluorite (F) in contact with host dolostone (blue luminescing areas represent quartz. Note development of quartz (q) between dolomite and fluorite. Bar scale represents 5 mm. (Location (a) 8 and (b) 9).

the sphalerite to the fluorite is one of little or no reaction between these phases. Sphalerite can occur as well-developed inclusions in the fluorite (Figure 15).

II. NONLUMINESCING PHASES

Quartz

Euhedral nonluminescing quartz occurs commonly along fractures and on dolostone breccia fragments in the area of the mine. Based upon current study, it appears that this silicification was more extensive in the area of the mine. Quartz probably filled voids in the host, as well as lining fractures and dolostone breccia fragments. Kyle (1973) reported that silicification in the Elmwood area can be pervasive and is largely restricted to open space filling fractures, vugs and interstitial space. There is evidence of minor replacement of dolostone by silica rich solutions near dolostone breccia boundaries (Figure 16).

Observations indicate that quartz deposition occurred during calcite and early sphalerite deposition. Figure 17 represents photomicrographs of zoned calcite taken in transmitted light and with CL light revealing quartz inclusions that are confined primarily to zone 2. Note the absence of evidence for zonation when only transmitted light is used.

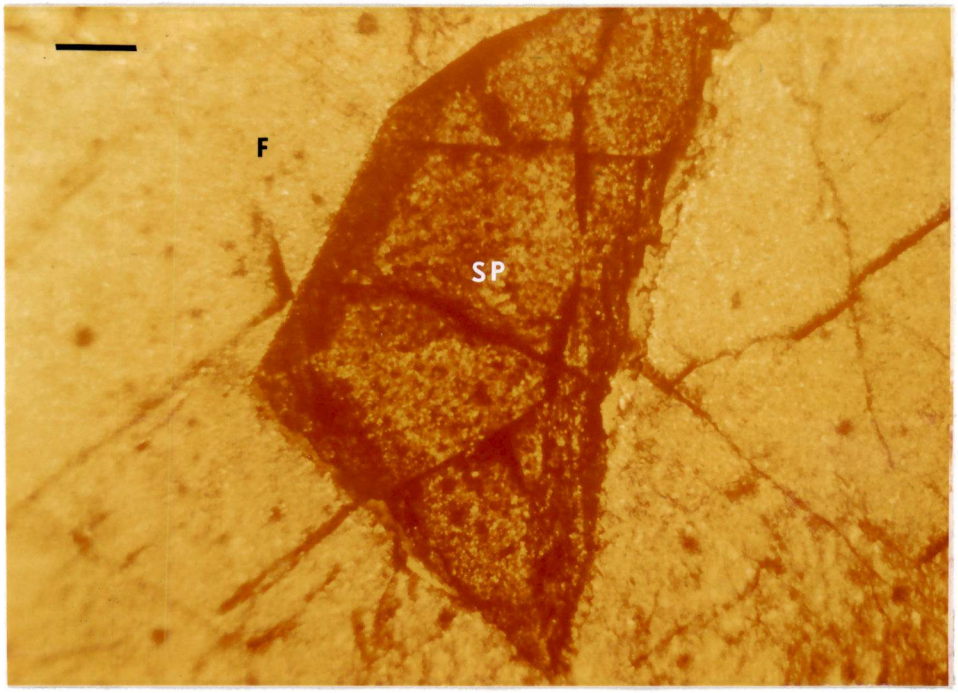


Figure 15. Photomicrograph (ASA 200) taken in transmitted light showing sphalerite inclusion (SP) in fluorite (F). Bar scale represents 5 mm. (Location 3).

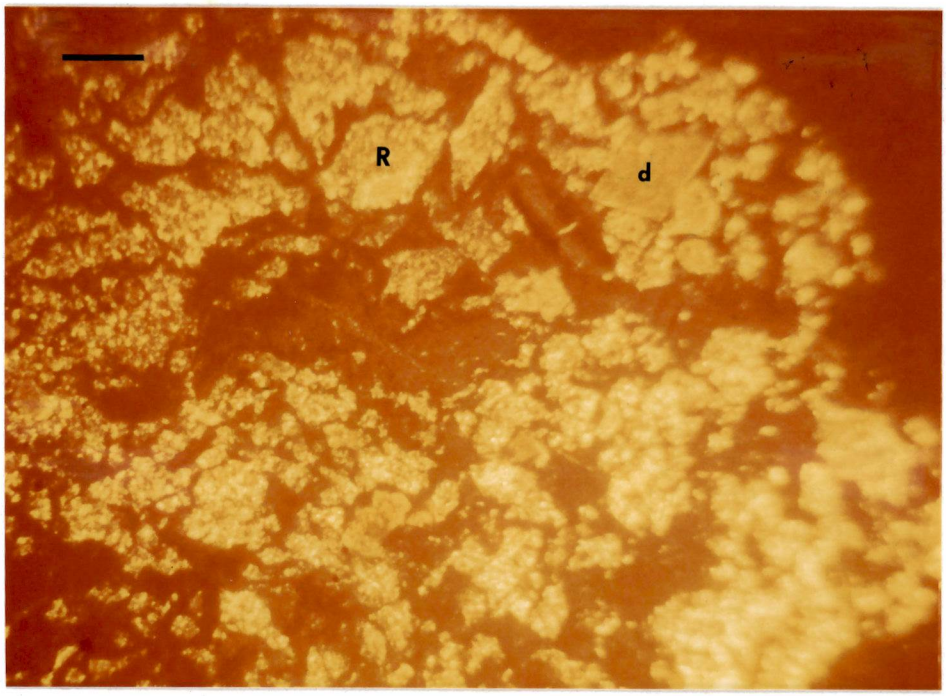


Figure 16. Photomicrograph (ASA 200) taken in transmitted light of quartz replacing dolomite (R) with an apparent still later stage of dolomite (d) deposition which replaces both early dolomite and mid-stage quartz. Bar represents 5 mm. (Location 7).

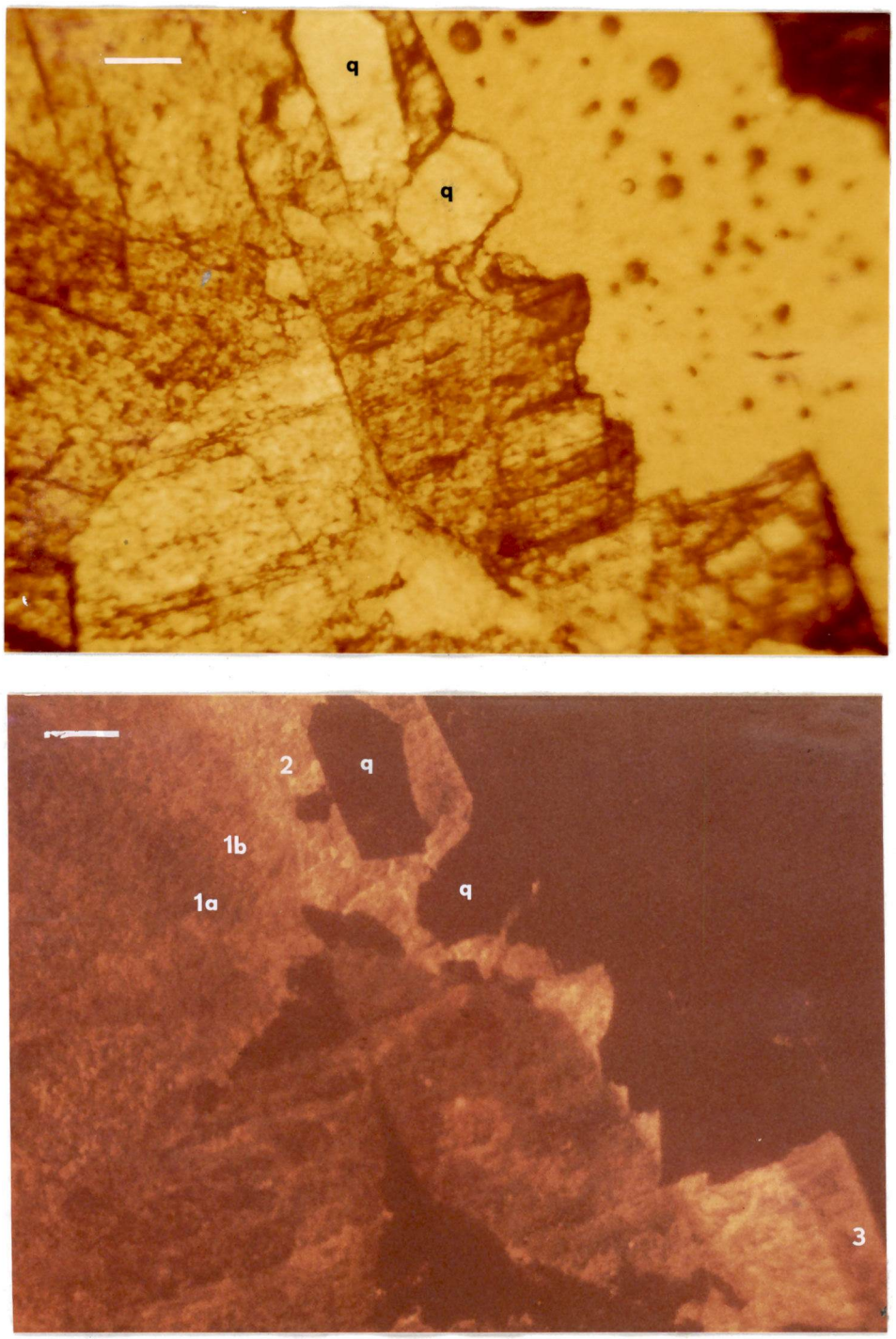


Figure 17. Photomicrographs (ASA 200) taken (upper in transmitted light and lower in cathodoluminescent light) of zoned calcite with quartz (q) inclusions which are confined primarily to zone 2 and 3. Bar scale represents 5 mm. (Location 4).

Sphalerite, Galena and Barite

Sphalerite (aside from minor luminescing inclusions), galena and barite does not luminesce. The few luminescing inclusions in sphalerite may be due to traces of unreplaced carbonates or a luminescing variety of sphalerite (Figure 18). There is some uncertainty as to the cause of some dark, nonluminescing inclusions (Figure 19). Chemical analyses (EMP) indicate that variations in the distribution of Fe, Mn, Cd and Zn is not the cause of these inclusions.

Sphalerite, galena and barite generally display sharp contacts with only minor alteration (dissolution and/or replacement) of calcite.

III. ELECTRON MICROPROBE ANALYSES

Calcite and Dolomite

Electron microprobe analyses (for Fe, Mn and Zn) were attempted on zoned calcite and dolomite from the Elmwood mine and vicinity. The trace amounts of these elements, i.e., usually <0.05%, made analyses difficult to perform. Most of the values were near the limits of detection (i.e., Fe 0.02%, Mn 0.02%, Zn 0.02%). However, these preliminary data indicate that the dark zones (zone 1) in the calcite are higher in Fe and lower in Mn while the light zones are lower in Fe and slightly higher in Mn. The dark zones (zone 3) in dolomite were observed to give values which were

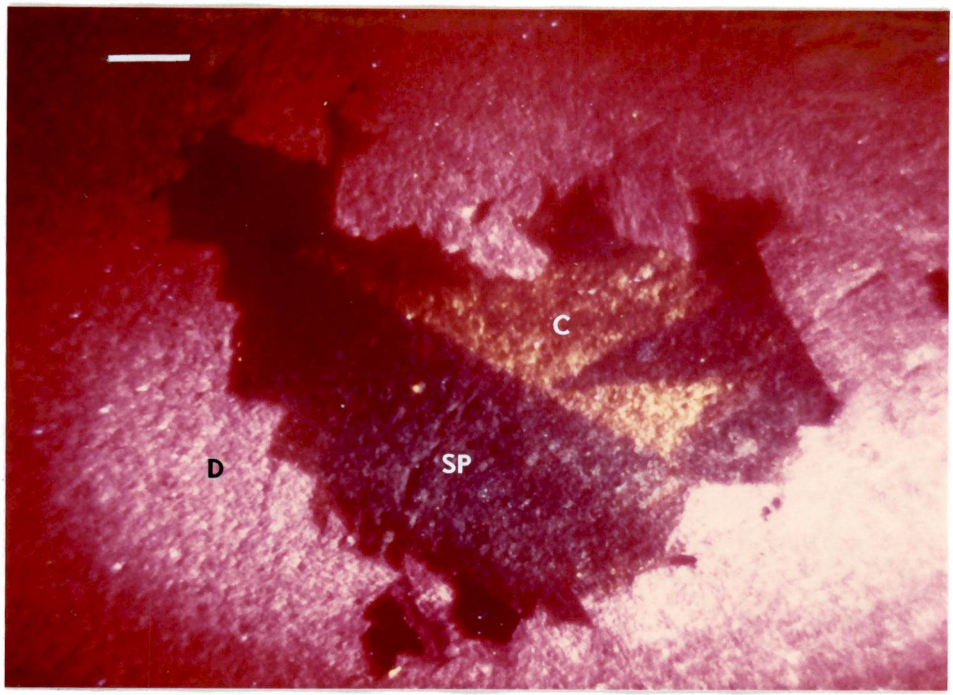


Figure 18. Photomicrograph (ASA 160) taken in cathodoluminescent light revealing luminescing inclusion in sphalerite (SP) which occurs as an inclusion in later dolomite (D). Note luminescing inclusion (C) in sphalerite. Bar scale represents 5 mm. (Location J).

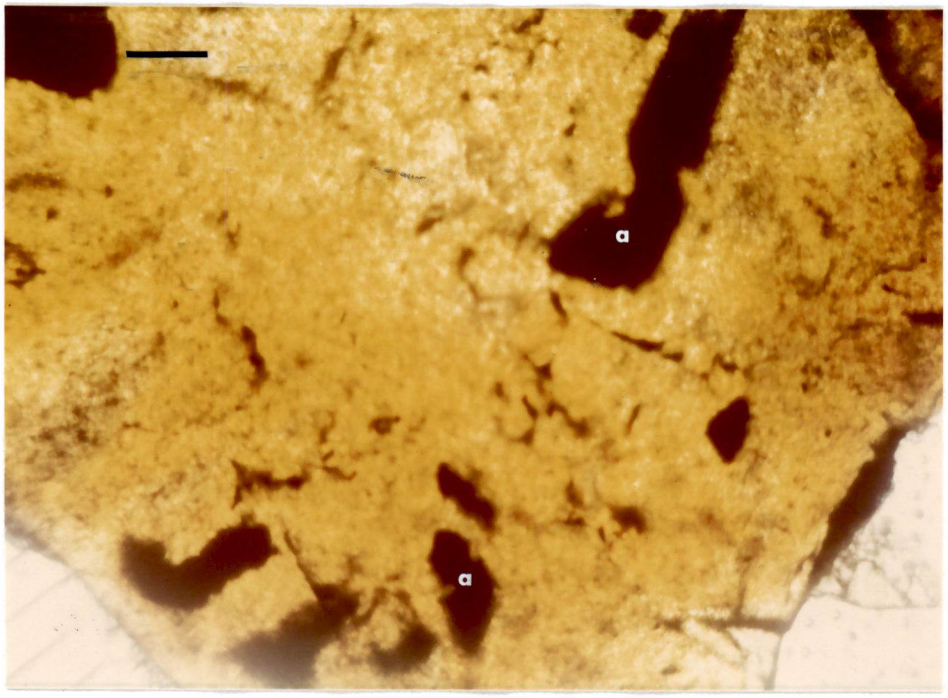


Figure 19. Photomicrograph (ASA 160) taken in transmitted light of sphalerite revealing dark, nonluminescing inclusions (a). Bar scale represents 5 mm. (Location 9).

judged to be realistic (Fe 0.3%, Mn <0.05% and Zn <0.05%). Light zones (zone 2) in dolomite commonly gave values that were slightly lower in Fe with small increases in Mn, while Zn remained generally constant at .07%.

At this time it is not possible to demonstrate that trace element partitioning of Fe and Mn has occurred between the solid and liquid phases during calcite and dolomite deposition. The results do indicate that dolomite has taken Fe into its structure at a much higher rate than calcite (8-10 to 1), while Mn and Zn appear to go into both phases with about equal ease.

Sphalerite

The results of quantitative analysis of the sphalerite samples from three different areas (EMP traverses across several dark inclusions representing 35 analyses, see Table 3) indicate that the Fe and Mn content of the sphalerite is relatively constant and that the dark inclusions are not due to the compositional variations in Zn, Fe, Mn and Cd.

IV. X-RAY FLUORESCENT ANALYSES

Calcite

EDXRF was utilized to obtain quantitative and qualitative determinations on several zoned calcite samples from the

TABLE 3

METAL CONTENT OF SPHALERITES FROM THE ELMWOOD MINE AND THE SURROUNDING AREA

Location	Fe	Mn	Cd	Zn
2	0.16-0.70	ND	0.19-0.82	65.58-66.45
9	0.23-0.38	ND	0.11-0.82	64.31-66.50
11	0.21-0.71	ND-0.09	0.65-1.64	64.09-66.21

ND = Not detected (i.e., <0.05%).

Elmwood mine and outlying core samples in addition to the amber calcite. The results of the quantitative and qualitative analyses (Table 4) indicate that:

1. The Fe^{+2} concentration[1] in the lighter zones is noticeably lower than in the darker zones while Mn^{+2} did not vary significantly. The Fe concentration in the zoned calcite samples is slightly higher than the values reported with EMP (1,200-2,000 ppm vs. 1,000-1,100 ppm) and the Mn concentration in the zoned calcite samples analyzed is similar to results reported by EMP (100-800 ppm vs. 100-500 ppm).
2. Results of the analyses of zoned calcite indicate that Mg, P, S and Sr are consistent in the calcite samples and Na, Al, Si, K and Ti were below the limits of detection (less than 1 ppm).

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[1]The results of XRF analyses for Fe are subject to contamination by other Fe bearing phases such as pyrite (FeS_2). In order to establish the relative purity of the calcite samples, an optical examination (200X) of several polished sections of zoned calcite samples was carried out. This evaluation revealed the presence of occasional pyrite and sphalerite grains ranging from 1-5 microns with infrequent grains up to 10μ in diameter. These observations indicate that the results for Fe_2O_3 (Table 4) may have been enhanced (contaminated) by the existence of trace amounts of pyrite. Corrections have been made in order to determine how much of the Fe would be in solid solution with calcite (see Table 4).

TABLE 4

RESULTS OF EDXRF QUANTITATIVE AND QUALITATIVE ANALYSIS OF SOME ELMWOOD SAMPLES

Sample	Location(s)[1]	NaO	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Mn_2O_3	Fe_2O_3	Fe Residual[2]	SrO	Qualitative Determinations
Calcite (zoned)	9,11	--	0.190(±0.023)[3]	--	--	0.085(±0.001)	0.054(±0.003)	--	54.274(±0.051)	--	0.010(±0.001)	0.142(±0.004)	0.088	0.022(±0.00)	
Calcite (zoned)	9,11	--	0.171(±0.023)	--	--	0.085(±0.001)	0.054(±0.003)	--	54.389(±0.051)	--	0.012(±0.001)	0.229(±0.004)	0.149	0.025(±0.00)	
Calcite (zoned)	8,9,11	--	0.094(±0.023)	--	--	0.087(±0.001)	0.087(±0.003)	--	55.002(±0.051)	--	0.011(±0.001)	0.130(±0.004)	0.074	0.021(±0.00)	Zn,Y?,Yb(?)[4],Pb
Calcite (zoned)	1-5	--	0.188(±0.023)	--	--	0.087(±0.001)	0.068(±0.003)	--	55.255(±0.051)	--	0.010(±0.001)	0.137(±0.004)	0.082	0.019(±0.00)	Zn,Ba?,Yb(?)
Calcite (zoned)	A,B,C,E	--	0.211(±0.023)	--	--	0.086(±0.001)	0.054(±0.003)	--	55.010(±0.051)	--	0.013(±0.001)	0.135(±0.004)	0.083	0.021(±0.00)	Yb,Y,Cu(?)
Calcite (zoned)	F,G,I	0.007(±0.010)	0.256(±0.024)	--	--	0.086(±0.001)	0.097(±0.004)	--	54.873(±0.051)	--	0.011(±0.001)	0.117(±0.004)	0.063	0.033(±0.00)	Yb(?)
Calcite (zoned)	G,B	--	--	--	--	0.086(±0.001)	0.053(±0.003)	--	54.782(±0.051)	--	0.008(±0.001)	0.118(±0.004)	0.072	0.018(±0.00)	
Calcite (zoned)	G,K	--	0.186(±0.023)	--	--	0.085(±0.001)	0.061(±0.003)	--	54.896(±0.051)	--	0.007(±0.001)	0.164(±0.004)	0.133	0.021(±0.00)	
Calcite (late amber)	--	--	0.138(±0.023)	--	--	0.086(±0.001)	0.061(±0.003)	--	55.307(±0.051)	--	0.011(±0.001)	0.131(±0.004)	0.080	0.021(±0.00)	Y,Yb(?)
Calcite (late amber)	--	--	0.390(±0.024)	--	--	0.085(±0.001)	0.084(±0.003)	--	54.818(±0.051)	--	0.013(±0.001)	0.130(±0.004)	0.074	0.018(±0.00)	Yb,Ba
Host dolostone	5,9	0.078(±0.016)	16.936(±0.080)	--	39.996(±0.057)	0.048(±0.001)	0.357(±0.005)	0.297(±0.005)	14.025(±0.029)	0.145(±0.006)	0.080(±0.002)	0.361(±0.006)	0.181	0.025(±0.00)	Zn >> I & B,Ni,Ge(?),Cr(?),S
Host dolostone	I & B	0.010(±0.013)	19.469(±0.078)	0.612(±0.018)	5.775(±0.020)	0.047(±0.001)	0.115(±0.004)	0.332(±0.005)	29.786(±0.040)	0.177(±0.006)	0.052(±0.001)	0.185(±0.005)	0.106	0.029(±0.00)	Zn,Ni,Cr(?)
Sphalerite	8,9														Ge,Ga,Ca,Cu(?),Ba(?)
Sphalerite	2,5														Ge,Ga,Ca,Pb,Cu(?)
Galena	9														Sr,Ba,Cd(?)
Fluorite	9														Ba,Sr,S,Fe,Mn,Yb(?)
Barite	8														Sr,Ca

[1] See Figure 4 (page 17) for sample locations.

[2] Values represent Fe concentration considered to be in solid solution with calcite. The results presented for total iron (Fe_2O_3) may have been contaminated by the existence of trace amounts of pyrite. The assumption is made that all sulfur obtained in the above analyses are due to pyrite (FeS_2), i.e., there is no critical SO_4 present, with this assumption the appropriate amount of Fe has been subtracted from the Fe_2O_3 results in order to account for all sulfur. The residual Fe is considered to be Fe in solid solution with calcite.

[3] Wt %.

[4] Question marks (?) indicate that corresponding ($K_{\alpha\&\beta}$ and $L_{<\beta}$) peaks for these elements could not be evaluated properly due to peak overlap by higher intensity elements.

3. Analysis of amber calcite revealed significant Mg (up to 3,900 ppm), with no significant variation in the trace element concentrations of other elements when compared to earlier zoned calcite.

The results of qualitative analyses indicate that:

4. There are similarities between certain trace elements (including Y and Yb) in zoned calcite from the mine and outlying core samples.
5. Analyses of (zoned) calcite samples from the mine area indicate the presence of trance elements (including Zn, Ba and Pb) which were not detectable in outlying core samples and analyses of core (zoned calcite) revealed the presence of trace amounts of Cu which was not detectable in mine samples.

Host Dolostone

EDXRF was utilized to evaluate the host dolostone (mine and core) samples. The results of the quantitative and qualitative analyses (Table 4) indicate that:

1. Host dolostone in the area of the mine may be more siliceous than similar outlying core samples (approximately 40% SiO_2 in mine samples vs. 5% in core samples).

2. Ca, Mg and Al values are higher in core samples while sulfur and iron concentrations are significantly higher in the mine samples.

The results of the qualitative analyses indicate that:

3. There are similarities and differences in the trace element contents between mine and outlying core samples. Ni, Cr and Zn (the Zn concentration in the mine samples is significantly higher) were observed in both mine and core samples and Ge was detected only in the mine samples.

Sphalerite, Galena, Fluorite and Barite

The results of qualitative analyses on sphalerite, galena, fluorite and barite (Table 4, page 51) indicate that:

1. Sphalerite samples contain trace amounts of Ba, Ca, Ge, Ga, Cu and Pb.
2. Analyses of galena revealed the presence of trace amounts of Sr, Ba and Cd.
3. Analyses of fluorite indicated the presence of small amounts of Sr, Ba, Fe, Mn, S and Yb.
4. Barite contains trace-minor[1] amounts of Sr and Ca.

---

[1]The lower limit of detection for the elements under consideration in this study is 0.01%. The terms trace and minor as used here would encompass a range of concentrations (0.01-0.2%) and (0.2-2%), respectively.

Selected energy dispersive spectra of these samples are presented in Appendix D.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Cathodoluminescence and analytical chemistry can be used to determine the paragenetic relationships that exist at the Elmwood mine and in the surrounding area. For example, cathodoluminescence can be applied to distinguish sequences of calcite deposition at Elmwood. Three generations of calcite have been identified on the basis of cathodoluminescence, textural and physical properties: an early, zoned calcite (zones 1-3), that was introduced primarily before the sphalerite (there is some evidence that sphalerite was deposited with and is included in zone 2); a second generation of unzoned calcite that postdates the sphalerite; and a late, amber colored calcite that is also unzoned. The amber color is believed to be due to a combination of trace elements which include Fe, Mn and Yb. Based upon color and crystal form Kyle (1976) also identified three generations of calcite in the Elmwood area.

The absence of zoning in the second and third generations of calcite indicates that the characteristics of the chemical environment which affect zoning, i.e., the composition of the aqueous solution and or temperature or pressure conditions, did not fluctuate significantly from the beginning to end of these periods of (calcite) deposition.

The early, zoned calcite represents most of the gangue and preceded the major period of mineralization. Some of the sphalerite may have been deposited simultaneously with the zoned calcite. A record of the growth history of the early zoned calcite is represented as a sequence of light and dark orange cathodoluminescent bands that may reflect minor changes in the physiochemical environment during deposition.

There is petrographic evidence for a zone to zone relationship between the zoned calcite and some minor zoned dolomite. (This phenomena was observed frequently in the mine samples.) This suggests that the zoned calcite and dolomite were deposited simultaneously from the same solution under similar conditions. Cathodoluminescent petrography and analytical data by Oglesby (1976) suggest that calcite and dolomite grew simultaneously at various depths in the (Upper Jurassic) Upper Smackover Formation of Eastern Mississippi.

Folk (1975) states that the Mg/Ca ratios and salinity of natural solutions can influence the mineralogy, crystal size and the habit of the resulting carbonates. A Mg/Ca ratio approaching 1:1, reduced salinities, and slow crystallization (commonly under phreatic conditions) can produce both dolomite and calcite as limpid, euhedral rhombs.

Information obtained in this study suggests that zone 2 and possibly zoned dolomite developed (at least locally) in the presence of Zn-S bearing solution(s), e.g., the occurrence of sphalerite as inclusions in zone 2 and the apparent continued growth of zone 2 in the presence of sphalerite. The results of the qualitative analyses on the early, zoned calcite and host dolostone indicates that the mine samples contain elements that were not observed in corresponding ("unmineralized") (several km from the mine) core samples and that Yb, Y and Pb may be assisting Mn as activators to enhance cathodoluminescence in the zoned calcite.

The zonation pattern is widespread in the Elmwood area and reflects (among other things) variations in the trace element content and distribution between mine, mineralized and core, "unmineralized" samples. Note that a zonation pattern extends tens of miles in East Tennessee. Here the pattern in gangue dolomite can be correlated between the Mascot-Jefferson City district and the Copper Ridge district 30 miles (48 km) to the northeast (Ebers, 1976). Meyers (1974) was able to trace cathodoluminescent zonation in carbonate cements in the Lake Valley Formation (Mississippian) Sacramento Mountains, New Mexico, for 10 miles (16 km) in a north-south direction.

The preliminary results of the chemical analysis of the gangue calcite and host dolostone indicate that there may be a geochemical halo around the Elmwood mine. This is based primarily upon trace element data obtained by XRF analysis of mine and core samples. Further work utilizing a well-planned and controlling sampling approach may yield positive results.

Quartz, the first mineral to enter the late fracture system, frequently occurs as a thin veneer along fractures, on breccia fragments, as well as detrital grains in the host dolostone. The dolostone samples in the area of the mine appear to be more siliceous than similar outlying core samples. Petrographic observations indicate that silica deposition had decreased substantially during the deposition of early, zoned calcite and dolomite. Further study revealed that quartz occurs as inclusions in zone 2 and 3 of the zoned calcite and in the early sphalerite. The deposition of quartz during this period may signify the beginning of a change in the character of the mineralizing fluid(s).

The nature of the Elmwood mineral suite, i.e., well-developed, large, euhedral crystals of calcite, sphalerite, fluorite, galena and barite revealing sharp contacts, suggests that the physiochemical parameters that prevailed during the deposition of the early and post-sphalerite

gangue calcite were not significantly different from those of the environment of deposition of the ore minerals.

Evaluation of cathodoluminescent growth zones in the calcite indicate that there were relatively long periods of time during which the trace element (and other geochemical parameters) distribution was maintained during the deposition of each sequential zone. There is evidence of apparent micro-unconformities (depositional breaks or periods of nondeposition followed by slight dissolution of the outermost zones). It appears that the development of the Elmwood area gangue calcite (and less widespread dolomite and ore minerals) occurred on a relatively large scale. This may have been facilitated by extensive channel ways and fractures (interconnected system of open space) that could promote solution movements where conditions (temperature, CO_2 pressure, total pressure, trace element composition, salinity and pH) changed more or less synchronously with time. These channel ways did not appear to have closed at any time during the deposition of the ore and gangue mineralization sequence(s).

The relationships between the unzoned phases have not been established completely at this time. It is known that the unzoned calcite postdates the major sequence(s) of sphalerite deposition and the amber calcite represents the last of the gangue calcite to be deposited. A generalized paragenetic sequence is summarized in Figure 20.

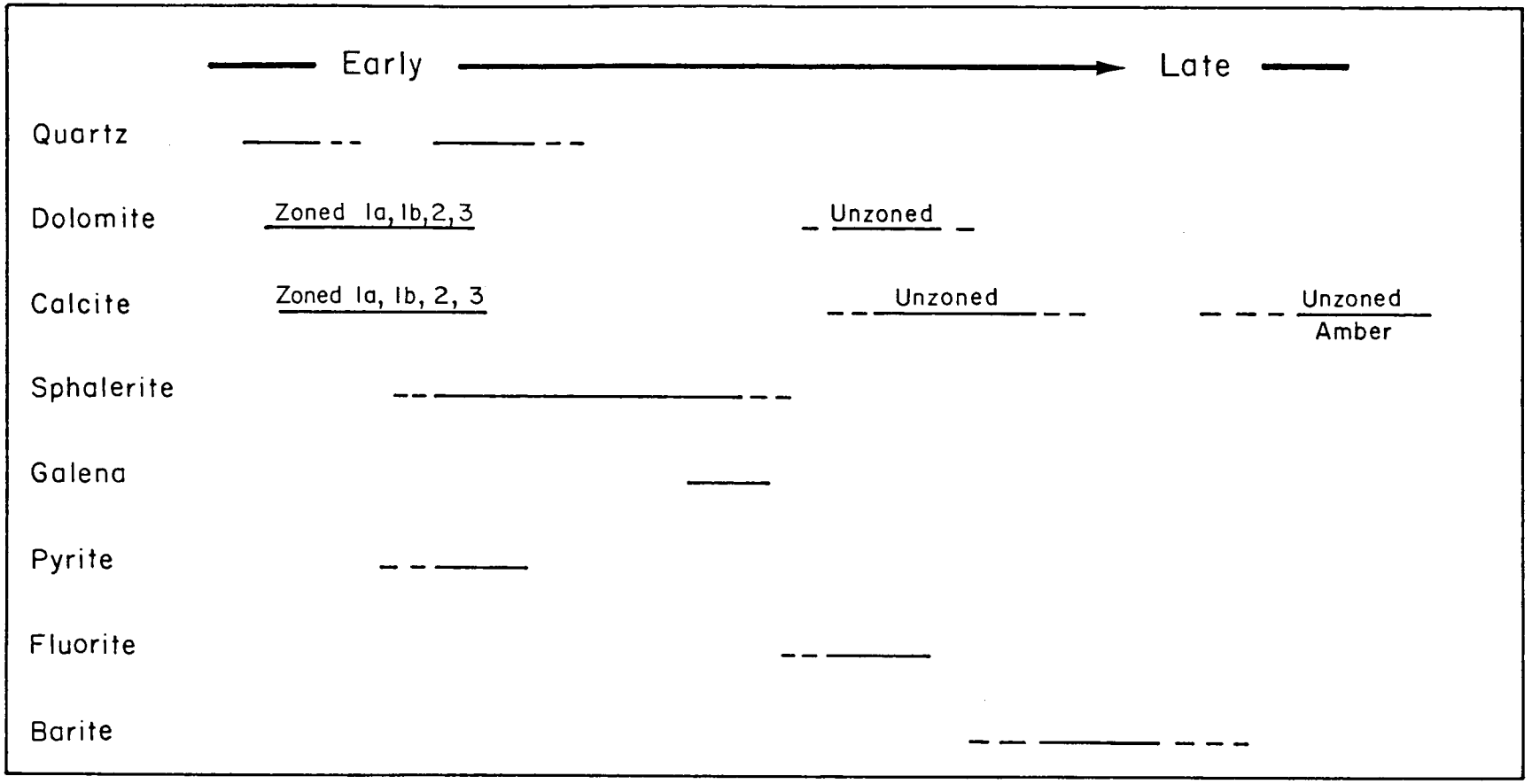


Figure 20. Generalized paragenetic sequence of mineral deposition at the Elmwood mine and surrounding area, Smith County, Tennessee.

Clearly more work is needed in order to acquire a better understanding of the details concerning the paragenetic relationships displayed at the Elmwood mine and surrounding area in Central Tennessee. Several subjects that warrant additional study include:

1. More effort should be concentrated on developing techniques to differentiate early diagenetic phases (unrelated to mineralization) from those directly related to the mineralization episode(s).
2. Additional samples should be taken at a greater distance from the Elmwood mine to determine the regional extent of the zonal pattern observed in this study. It may be that the zonal pattern will change further away from the Elmwood deposit.
3. Detailed samples should be taken within a selected area around the Elmwood mine (on host dolostone and calcite) at relatively small intervals through a vertical section to extend above and below a large ore zone to study possible changes in the zonal pattern and chemical characteristics on a small scale.
4. The extent and nature of silicification and its relation to mineralization should be considered further.

5. Coexisting zoned calcite and dolomite should be analyzed to determine if partitioning of trace elements (Fe, Mn and rare earths) occurred between these phases and the mineralizing fluids.

Finally, one might ask whether cathodoluminescence can provide useful information in the exploration for sphalerite in the Elmwood area. At this time the results are not conclusive because the total lateral and vertical extent of the zonation has not been determined. However, it has been established that early sphalerite deposition began during the deposition of zone 2 in calcite and dolomite. We might expect that any areas that were open at the time of deposition of the zoned calcite are at least potential sites for sphalerite deposition. Those areas which had not yet opened or which had already closed would probably be barren. Of course, other factors might have controlled the placement of sphalerite, but until more studies are completed this will remain uncertain.

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REFERENCES CITED

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APPENDIXES

APPENDIX A

OPERATING CONDITIONS AND STANDARDS USED IN EMP ANALYSES

The electron microscope was used to determine the Fe, Mn and Zn contents of individual CL zones in calcite and dolomite. Sphalerite was also analyzed. Operating conditions are presented in Table 5. Corrections for matrix effects were done according to the method described by Ziebold and Ogilvie (1964) for sphalerite analysis. Corrections for background, drift and deadtime were done by a Krisel Control Automation (D.E.C. PDP 11-15 computer). Background counts were obtained at each analysis point during carbonate analysis. Realizing that these EMP analyses are incomplete, no matrix corrections were applied. This, plus the low contents of the time elements, would place these analyses at a semiquantitative level, at best.

Traverses were made across the cathodoluminescent zones of the calcite and dolomite. Each analysis point (spacing 0.02 to 0.06 mm) was analyzed for Fe, Mn and Zn.

Standards used for the calcite and dolomite analysis included rhodonite (for Fe) and willemite (for Mn and Zn). Standards utilized in the sphalerite analyses include ZnS for Zn and S, MnF_2 for Mn, FeS_2 for Fe, CdS for Cd.

TABLE 5

OPERATING CONDITIONS FOR QUANTITATIVE ANALYSES WITH EMP

Gun Potential	15 kv
Gun Current	125 milliamps
Beam Current	.0400 microamps
Beam Diameter	Approx. 5 microns
Atmosphere	Vacuum (.01-.05 microns)
Counting Times	
Carbonates (Fe, Mn and Zn)	30 sec. or 20,000 counts
Sphalerite (Fe, Mn, Cd, Zn and S)	20 sec. or 10,000 counts

APPENDIX B

METHODS OF STUDY AND RESULTS OF PRELIMINARY XRF ANALYSES AT THE UNIVERSITY OF TENNESSEE

During the course of the analytical work it was suggested that XRF be used to facilitate a preliminary evaluation of the zoned calcite for Fe, Mn, Sr, Y, Cd, Hg, Pb and various rare earth elements to include La, Gd, Yb and Lu. Before any analysis of these elements was initiated, it was necessary to optimize the operating conditions of the instrument, i.e., to determine the proper settings for the best precision. PHA scans were done on several nearly pure samples (from ORNL and the Department of Geological Sciences). The results of this work and the standards used are presented in Table 6.

Initial analyses were done with several cleaved fragments (10-50 mm) of zoned calcite which were examined with cathodoluminescent petrography so as to obtain samples that displayed the extremities of luminescence, i.e., dark (zone 1) and light (zone 2). Counting times for peak and background evaluations were 100 seconds or 10,000 counts. Three sets of counts (peak and background counts on both sides of the peak) were done, then averaged. The background counts were then subtracted from the peak results. The final step was to determine the area of the irradiating beam

TABLE 6

RESULTS OF PHA PEAK SCAN

Material	Element	Peak	Source[1] (kv/ma)	Scin. Detector[2] (kv)	Baseline	Window	2θ
1. Hematite	Fe	K[3]	40/30	1.02	100	500	57.47
2. Gallium Oxide	Ga	K	30/25	.94	100	480	36.87
3. Germanium Oxide	Ge	K	35/20	.95	100	600	36.21
4. Celestite	Sr	K	30/25	.93	100	600	25.11
5. Yttrium Oxide	Y	K	30/25	.93	100	700	23.69
6. Cadmium Metal	Cd	K	30/25	.90	100	600	15.17
7. Lanthanum Oxide	La	L	35/20	1.10	150	650	83.89
8. Gadolinium Oxide	Gd	L	40/35	1.03	100	400	61.02
9. Ytterbium Oxide	Yb	L	40/35	1.00	100	500	49.03
10. Lutetium Oxide	Lu	L	40/35	1.00	100	500	47.42
11. Cinnabar	Hg	L	40/35	1.00	150	650	35.84
12. Galena	Pb	L	40/30	1.00	130	760	34.90

[1]W anode.

[2]Lif crystal.

[3]All peaks are alpha.

for each sample thereby obtaining the corrected counts per second according to the following procedure. The area of the irradiating beam is equal to 2 cm^2. If the area of the sample was 1.5 cm^2 and the initial counting rate was 300 counts per second, the corrected counts would be (2.0/1.5) × 300 = 400 cps.

The results of the preliminary XRF analyses are presented in Table 7 for Fe, Mn, Sr and Yb. Ga, Ge, Y, Cd, La, Gd, Lu, Hg and Pb were not detected. The Fe concentration in the zoned calcite samples did not vary significantly from light-zoned to dark-zoned samples. However, the light-zoned calcite samples from the mine gave higher counts for Mn than the dark-zoned calcite. There was an indication that Yb is present in small quantities in the mine calcite samples.

TABLE 7

RESULTS OF PRELIMINARY XRF ANALYSES

Sample and Location	Element and Peaks	Counts* (CPS)
Calcite from Mine Dark Zoned	Fe	48.0
	Mn	2.5
	Sr	14.2
	Yb**	8,2
Calcite from Outlying Core Dark Zoned	Fe	39.0
	Mn	ND
	Sr	22.0
Calcite from Mine Light Zoned	Fe	42.0
	Mn	9.5
	Sr	30.8
	Yb	6.6
Calcite from Outlying Core Light Zoned	Fe	43.5
	Mn	3.4
	Sr	12.8

*Counts corrected for background.

**Yb was not detected in core samples.

APPENDIX C

OPERATING CONDITIONS FOR EDXRF QUANTITATIVE ANALYSES

Quantitative analyses were done on TEFA model 6110 automated energy dispersive x-ray fluorescence analyzer (EDXRF) owned and operated by ORTEC Inc., of Oak Ridge, Tennessee. Operating conditions are presented in Table 8.

EDXRF utilizes a D.E.C. PDP 11-05 computer for quantitative calculations and interelement corrections. The XRF-FLINT program provides a linear least squares fit and exponential interelement corrections to x-ray intensities and provides a computer printout with concentrations (Wheeler, 1978).

TABLE 8

OPERATING CONDITIONS FOR QUANTITATIVE ANALYSES WITH EDXRF

Element	Na, Mg, Al, Si, P, S, Ca, Ti, Mn, Fe	Sr
Anode	Rh	Rh
Voltage (Kv)	10	30
Amperage (amps)	50	20
Filter	none	none
KeV	0-10	0-20
Atmosphere	vacuum	vacuum
Counting Time (seconds)	400	400

APPENDIX D

OPERATING CONDITIONS FOR EDXRF QUALITATIVE ANALYSES WITH SELECTED SPECTRA

Qualitative analyses were done on logarithmic plots of x-ray spectra of elements excited in each unknown with Rh and W anodes. Figures 21-27 illustrate examples of x-ray spectra along with the excitation conditions, filters, counting times and the identification of prominent peaks according to the proper emission energies (kev). Identifications of elements were done with corresponding K_{α} and β and L_{α} and β peaks. Frequently, the corresponding alpha and beta peaks could not be identified due to peak overlap by major elements. Ni, Y, Mo and Sn filters were used to depress the background for trace element evaluations.

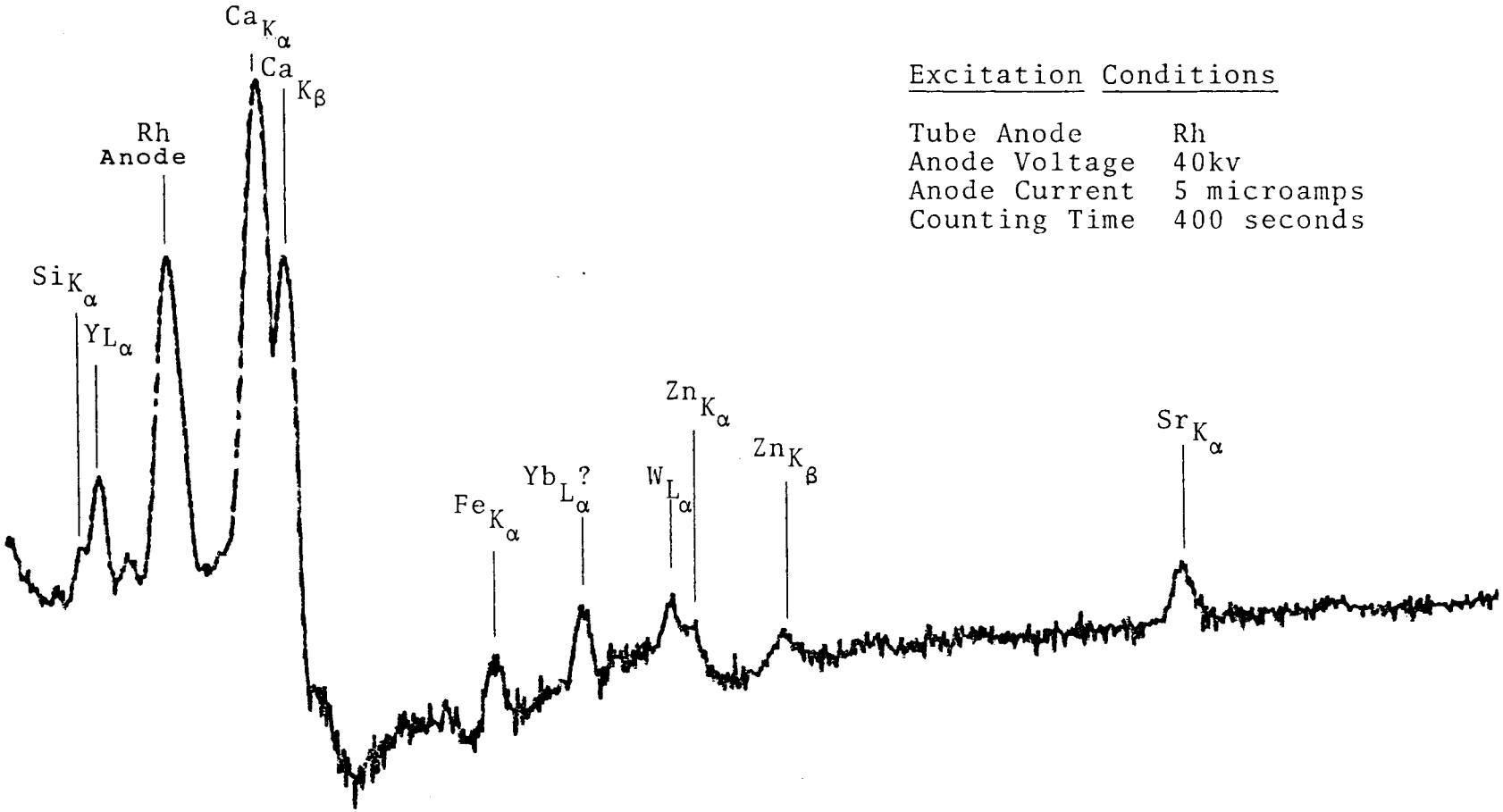


Figure 21. TEFA spectrum of zoned calcite (locations 8, 9 and 11) (logarithmic scale, 0-20 Kev).

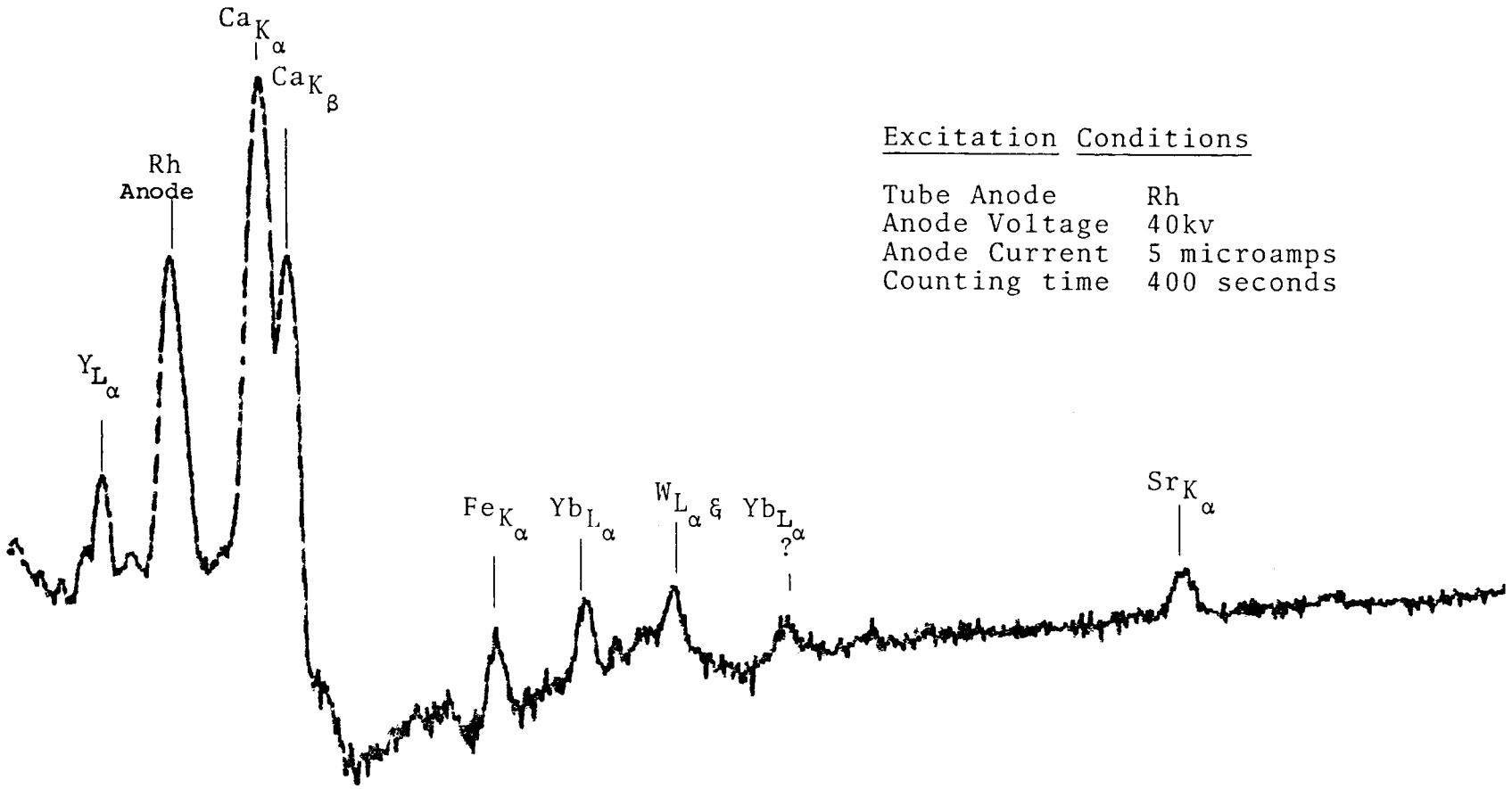


Figure 22. TEFA spectrum of amber calcite (Elmwood mine) (logarithmic scale, 0-20 Kev).

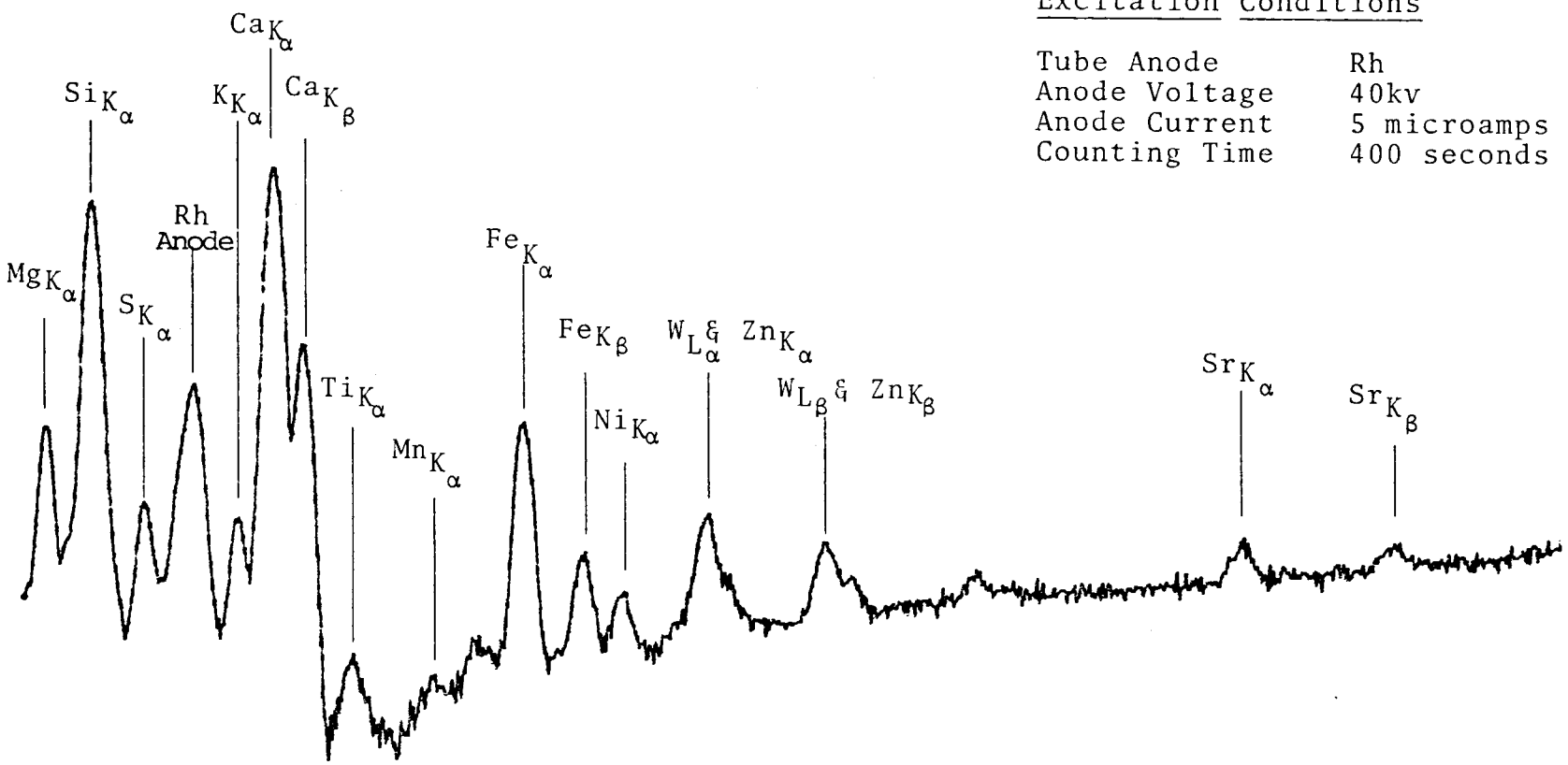


Figure 23. TEFA spectrum of host dolostone (locations 5 and 9) (logarithmic scale, 0-20 Kev).

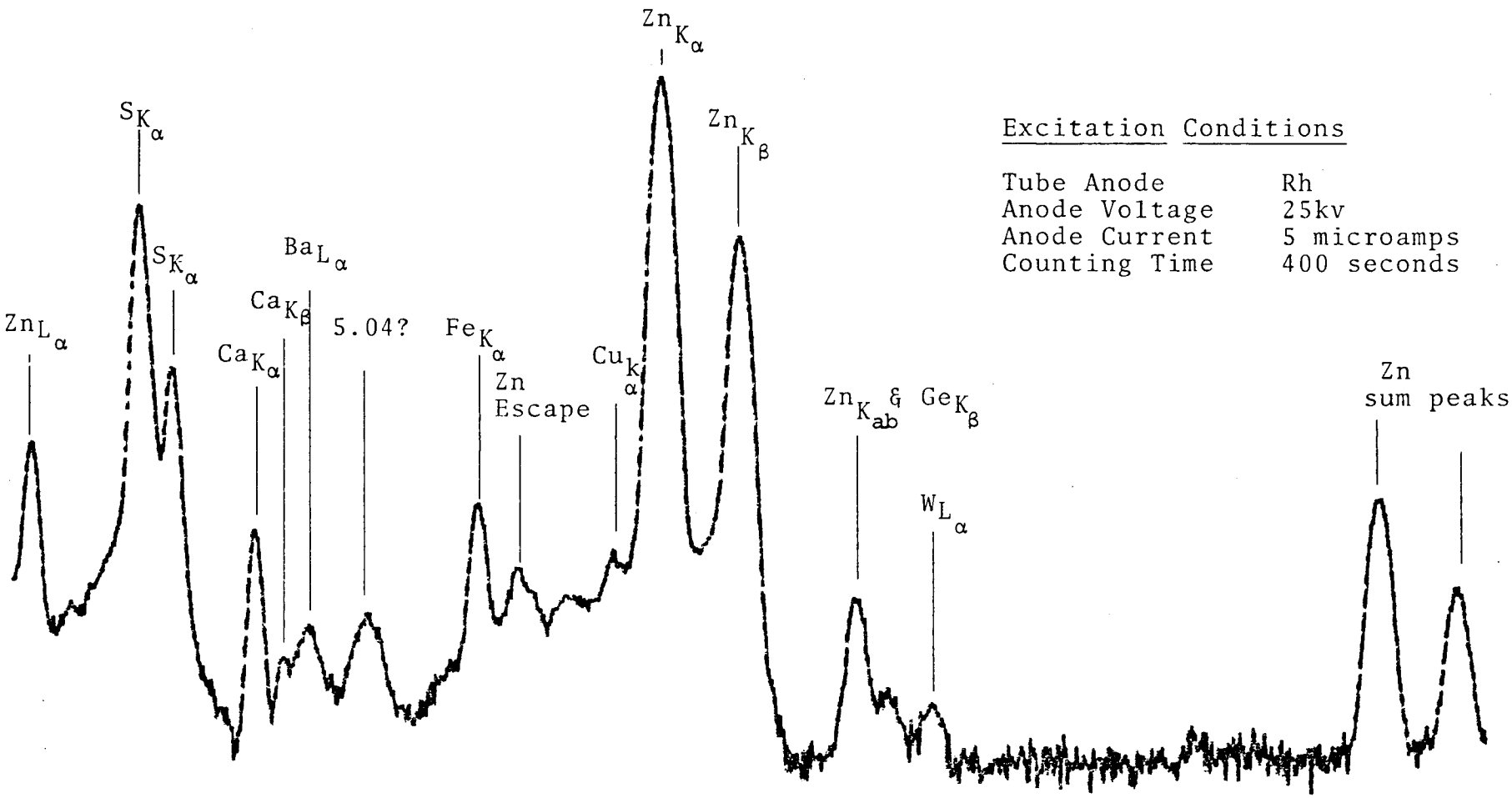
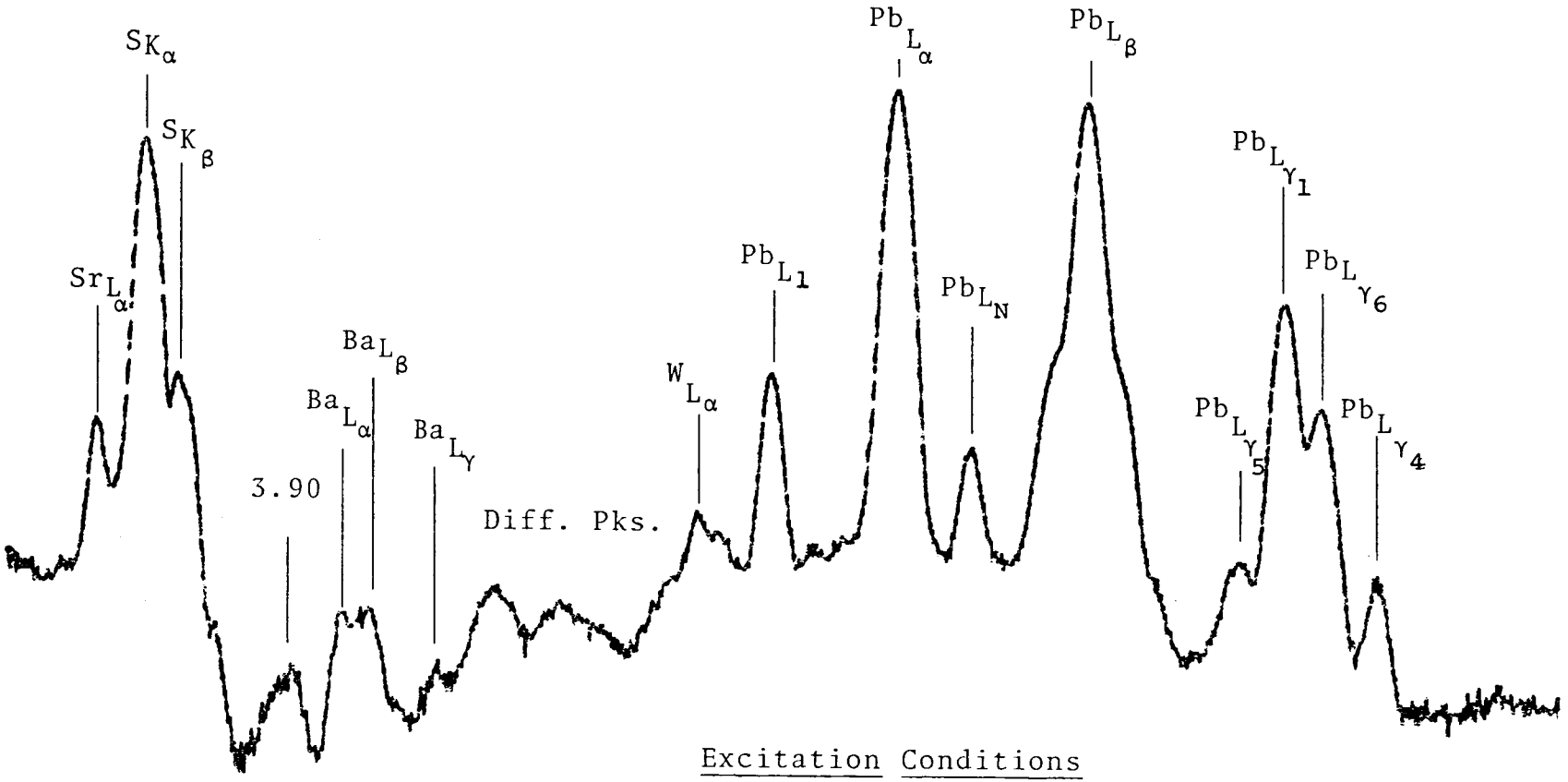


Figure 24. TEFA spectrum of sphalerite (location 1) (logarithmic scale, 0-20 Kev).



Excitation Conditions

Tube Anode Rh
Anode Voltage 40kv
Anode Current 5 microamps
Counting Time 400 seconds

Figure 25. TEFA spectrum of galena (location 9) (logarithmic scale, 0-20 Kev).

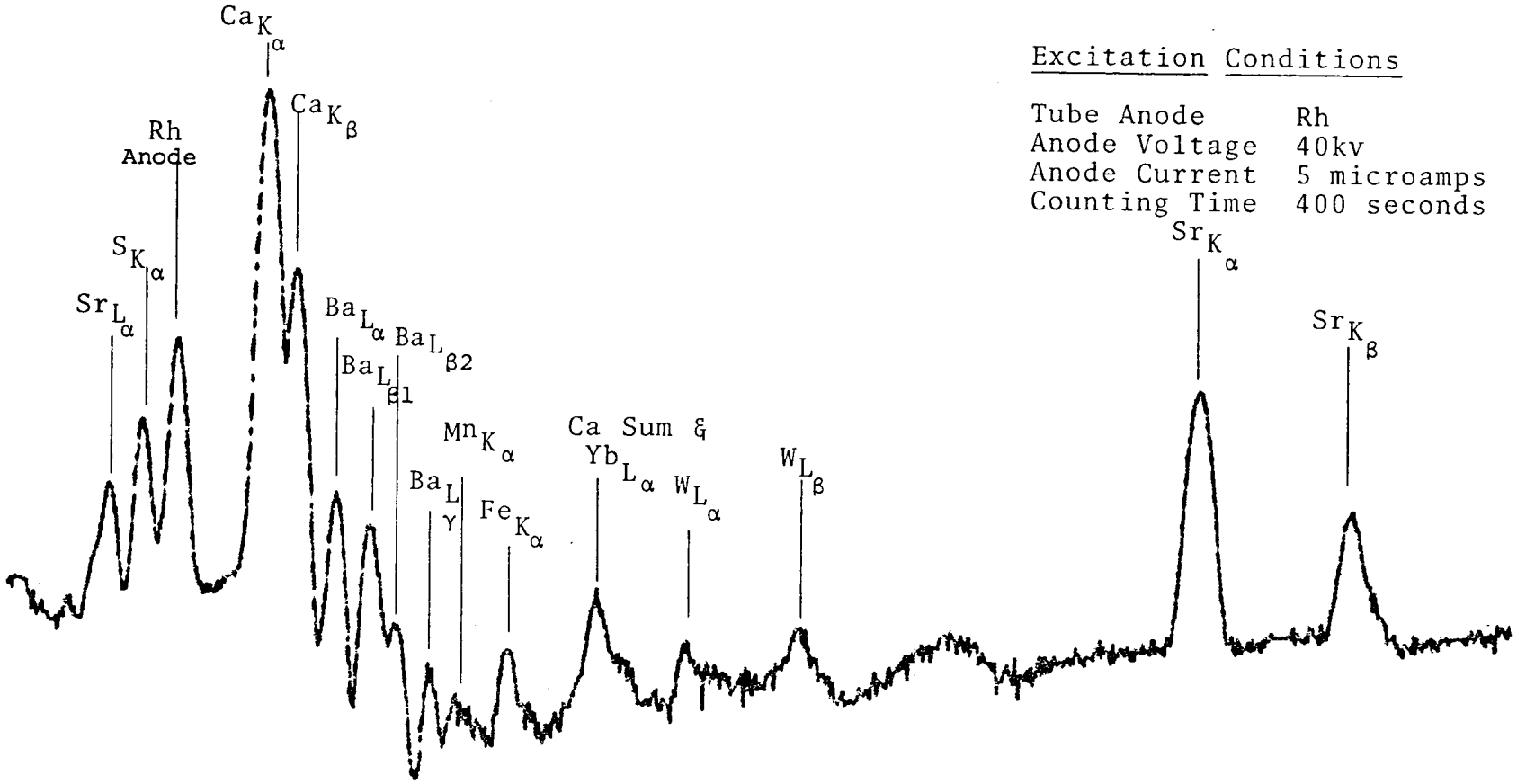
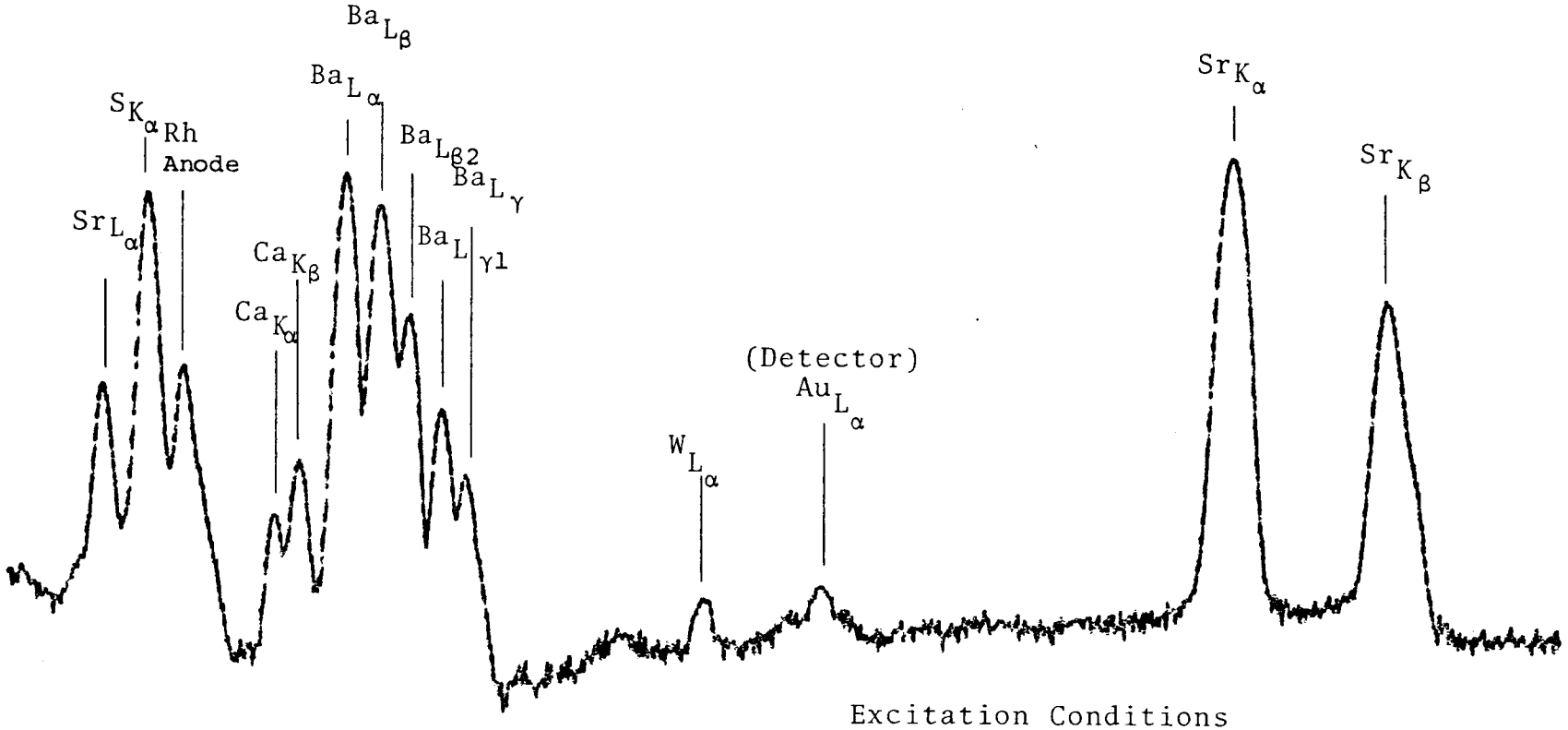


Figure 26. TEFA spectrum of fluorite (location 9) (logarithmic scale, 0-20 Kev).



Excitation Conditions

Tube Anode	Rh
Anode Voltage	40kv
Anode Current	5 microamps
Counting Time	400 seconds

Figure 27. TEFA spectrum of barite (location 8) (logarithmic scale, 0-20 Kev).

APPENDIX E

SAMPLE PREPARATION PROCEDURES AND PHOTOGRAPHY

Preparation of Samples

Ninety (2" × 3") thin sections were made in order to study the CL properties exhibited in the Elmwood mine and surrounding area. Three thin sections were made per sample locality on at least three different specimens to insure a representative sampling of each locality.

Hillquist epoxy was used as the mounting medium with very good results. A slight yellowing or discoloration was noted if the electron beam was finely focused on an area for 1-2 minutes; however, this discoloration did not affect the luminescent properties of the section. All thin sections were cut to .03-.06 mm thick and fine ground with a 400 mesh abrasive. As indicated by Ebers (1976) there does not appear to be any significant differences in CL clarity in thin sections ground with only 220 mesh powder or a polished thin section.

Twenty-two polished sections were made for use on the EMP. Specimens were selected for the purpose of analyzing individual CL zones in the calcite and dolomite in addition to obtaining quantitative determinations on sphalerite.

Twenty pressed pellets (including 10 calcite samples) were made from finely ground samples of calcite, dolomite,

host dolostone, sphalerite, galena, fluorite and barite for analysis with XRF. Preparation of pressed pellets was according to a TEFA analysis report, "Analysis of limestone and dolomite by EDXRF," November 11, 1977, from the Materials Analysis Division. The procedure included weighing 5 grams of a finely ground unknown which was placed into a tungsten carbide rotary swing mill and ground for 6 minutes. The resulting powder was pelletized into a wafer (1-1/4" O.D. × 1/2" thick) under 15 tons per square inch with boric acid as a backing material.

Photography

The best way to record cathodoluminescent phenomena accurately for comparative purposes is to use color photography. The reader is referred to Ebers (1976) for a detailed discussion of the advantages of photography including a description of the equipment, exposure and processing information and types of color slide film. All photographs were taken with either Kodak Ektachrome ASA 160 or ASA 200 color slide film[1] with normal developing. Exposure

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[1]In 1977 Kodak replaced the Ektachrome ASA 160 color slide film with the ED ASA 200. The ASA 200 film is supposed to furnish better results when photographing cathodoluminescence in carbonates because, unlike other high speed films, this one has a red base which is ideal for recording the reds and oranges of carbonate luminescence. There are significant differences in the color representation with the ASA 200 and the ASA 160 films; with the ASA 200 the reds have a significant orange component and the oranges are brighter than with the ASA 160 film (see page 31).

times for all cathodoluminescent photographs were between 1-3 minutes for photographs taken in cathodoluminescent light and 30-45 seconds for photographs in transmitted light.

VITA

Roland M. Larsen was born in Grand Falls, New Brunswick, on September 25, 1947. He attended elementary and high school in Limestone, Maine. In 1964 his parents relocated to Rochester, New York, where he worked in the highway and building construction industry until 1969. In 1970 he attended the Academy of Aeronautics and Hunter College in New York City. In 1972 he transferred to the State University of New York College at Brockport, New York, and received a B.S. degree in Geology in 1974. In the fall of 1974 he attended the University of Tennessee where he was a member of Sigma Gamma Epsilon. He received the M.S. degree in Geology in 1978.

He was honorably discharged from the USAR in 1973. Roland has had several years of experience as an exploration geologist in southeastern Canada and Alaska.

He is married to the former Theresa Hudela of Kingston, New York, and has three children.