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A GEOCHEMICAL STUDY OF THE RICKENBACH FORMATION AT THE FRIEDENSVILLE ZINC DEPOSIT, LEHIGH COUNTY, PENNSYLVANIA

by

Robert W. Keating

A Thesis

Presented to the Graduate Committee

of Lehigh University

in Candidacy for the Degree of

Master of Science

in

Geology

Lehigh University

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Left 13, 1983

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Professor in charge

Chairman of Department

ACKNOWLEDGMENTS

The writer is indebted to Dr. Dale R. Simpson, Professor of Geology at Lehigh University, for his suggestion of this topic and his support, discussions, and criticisms offered throughout the course of the investigation and writing of this manuscript. I am also grateful for the opportunity to have been a Research Assistant under his direction from 1981 to 1983. Also, I would like to thank Dr. Paul B. Myers, Jr. and Dr. James M. Parks for their helpful suggestions and critical reviews of this document.

The writer wishes to express his sincere thanks to all the people at the Friedensville zinc mine, especially Mr. Kenneth R. Cox and Mr. Walter E. Granlund, for allowing me to have access to the maps, core logs, and drill core at the mine. This study would not have been possible without their cooperation and invaluable assistance.

The writer appreciates the aid of his fellow geologists at Lehigh, most noteably Peter L. Sudano for his assistance in collecting samples, Geoffrey C. Seibel for his help in the chemical techniques used in this study, and lastly James F. P. Cotter for his photographic expertise evident in the prints presented in this document.

Also, I wish to express my gratitude to Laura J. Cambiotti for her patience and suggestions during the typing of this manuscript.

Foremost, I wish to express my sincere thanks to my parents and family for their unending moral and financial support throughout my undergraduate and graduate education at Lehigh. I would like to dedicate this thesis to them.

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> Bar graph of the mean values of zinc concentrations in the acid soluble fraction from the sampled horizons at the Friedensville zinc deposit.

deposit.

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ABSTRACT

The Friedensville zinc deposit is a stratabound deposit in the Rickenbach Formation, a dolomitic unit of Lower Ordovician age. The ore mineralization is in a solution-collapse breccia, formed during the Knox-Beekmantown unconformity. The deposit was studied by the examination of the textural characteristics and the minor element compositions of the carbonate fraction of the dolomite host using drill core from the deposit.

The dolomite in the ore zone is a medium-grey, massive dolomite which is structureless, brecciated, or siliceous and dolomitic mottled or laminated. Brecciation was the only lithologic feature related to the sites of zinc mineralization. Above the ore zone the rocks are structureless and faintly iron stained. Below the ore horizon is the Evan's Marker, a 30 to 40 meter thick unit consisting of argillaceous dolomite, argillaceous limestone, and a quartz and microcline veined dolomite. The Evan's Marker exhibits streaking and thinning of the clay layers and textures common to localized stress conditions.

Iron in the acid soluble fraction is relatively uniform in the ore zone, but it increases by 3-fold in the iron-stained samples overlying the ore, and by 5-fold in the Evan's Marker.

Manganese follows the same pattern as iron. Zinc and lead values are low and nearly constant for all the samples except the Evan's Marker dolomites which have a 5-fold enrichment in zinc and a 2-fold enrichment in lead.

There is no zonal distribution of the elements laterally or horizontally within the sampled area. It is concluded that the host rock in the ore horizon was not a source for the metals for the mineralization. However, the chemical data shows that the carbonates in the Evan's Marker are a proximal source of metallic ions for a mineralizing solution. The cannibalization of the limestone in the Evan's Marker from localized stress may have released these ions forming the mineralizing fluid.

INTRODUCTION

General Statement

The Friedensville zinc ore deposit is a rich, unusual stratabound deposit in the Rickenbach Formation, a dolomitic unit of Lower Ordovician age. Stratabound deposits have been the subject of study and controversy for more than a century. Many of the early studies of stratabound deposits centered on the Mississippi Valley deposits, and this leads to the name Mississippi Valley-type deposit. The Mississippi Valley-type deposits generally are in strata showing little deformation. In contrast, the Friedensville deposit is in deformed rocks. The major problems concerning the origin of stratabound deposits remain: 1) the source of the metallic ions; 2) the source of the mineralizing solution; and 3) the role of the host rock in the ore genesis.

The availability of drill core from the Friedensville deposit presented the unique opportunity to study the deposit. It is the purpose of this study to determine the mineralogical, textural, and geochemical trends about the Friedensville deposit using the drill cores. This integrated study should permit conclusions to be drawn on the mode of origin of the deposit and the source of the metallic ions and mineralizing solutions.

Statement of the Problem

Ohle (1980: p. 163) stated:

"Presently, geologists do not know the physiochemical reasons why Mississippi Valley-type deposits are where they are and why the ore is not present in other, seemingly just as likely places. The sites where they explore are in most cases chosen from empirical studies of stratigraphic, lithologic, and structural relationships."

Unfortunately, many of these studies are unsuccessful. It is hoped that the model of ore solution genesis and deposition presented in this thesis will aid prospecting for stratabound deposits.

Over the years two principal theories have been developed in regards to the source of the ore forming fluids in stratabound deposits. The first theory ascribes the mineralization to basinal brines in which the metal ions are an integral part of the basin sediment. During lithification the metal ions are extracted and expelled with connate water, transported to the sites of deposition, and deposited. The second theory ascribes deposition of the ore from hydrothermal fluids derived from a distant igneous source. Most present investigators support the brine theory.

In considering the genesis of the Friedensville deposit, the role of the host rock must be defined. This is the primary

objective of this study. Two hypotheses on the role of the host rock will be tested. The first hypothesis is to have a pregnant ore-forming solution pass through the host rock and deposit the metal sulfides. With this model the host rock lacks a role as a source of metallic ions, but could retain trace concentrations of the elements from the ore-bearing solutions. The second hypothesis is to have a barren solution come in contact with the host rock and abstract metallic ions or the sulfides through leaching or recrystallization, possibly from dolomitization.

Approaches to the Problem

The Rickenbach Dolomite exhibits a wide variety of textures throughout the formation; however, the zinc mineralization at Friedensville is generally restricted to a brecciated zone about 30 meters thick in the lower Rickenbach. This brecciated zone is thought to have formed from solution-collapse (Callahan, 1968) and will hereafter be termed a collapse breccia. This collapse breccia appears to be the major mode of ground preparation for mineralization.

In an effort to better understand the ore mineralization and its relation to the host rock, the textural, mineralogical, and geochemical trends near the mineralized portion of the Rickenbach Dolomite were examined using the drill core. The rocks were

grouped by lithologies and used to determine if a relationship exists between the textures and structures of the dolomite host and changes in geochemistry. The quantity and nature of the acid insoluble residue from these rocks was determined, and the acid soluble material was analyzed for the trace elements.

The study by Seibel (1982) on the geochemistry of the Epler Formation near Leesport, Pennsylvania is used as a reference for the concentration and partitioning of base metals between limestones and dolomites. Because Seibel showed that the carbonate fraction contains a higher concentration of metallic ions than the insoluble residue or the carbonaceous fraction, this study focused on the geochemistry of the carbonate fraction of the rocks. The carbonate fraction of the dolomite is defined for this study as that portion of the rock which is acetic acid soluble.

GEOLOGIC SETTING

Introduction

Paleozoic carbonate rocks in Saucon Valley are the host for the Friedensville ore deposit. These carbonate rocks are rimmed by Precambrian crystalline rocks and Cambrian quartzite (figure 1). The valley is approximately 58 square miles and has a karst topography.

Stratigraphy

Zinc mineralization occurs in the Beekmantown Group, a carbonate unit of Lower Ordovician age. Overlying the Beekmantown on an erosional unconformity is the Jacksonburg Formation of Middle Ordovician age. Conformably below the Beekmantown is the Cambrian formation designated locally as Allentown.

The Beekmantown Group in Saucon Valley is subdivided into two formations. The lower formation, designated the Rickenbach is a dark dolomite. It is massively bedded and has a stratigraphic thickness of 200-220 meters. The upper formation is the Epler Formation and it is characterized by 250-275 meters of light interbeds of limestone, dolomitic limestone, and limey dolomite (Drake, 1965). The principal ore horizon for the

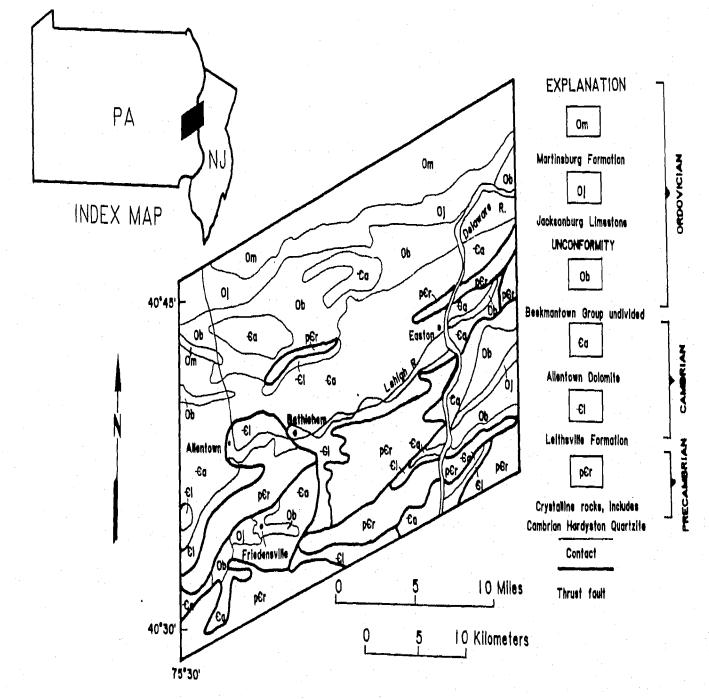


Figure 1. Index map showing the location of Friedensville and the general geology of the Lehigh Valley and adjacent areas, New Jersey - Pennsylvania (after Drake, 1969).

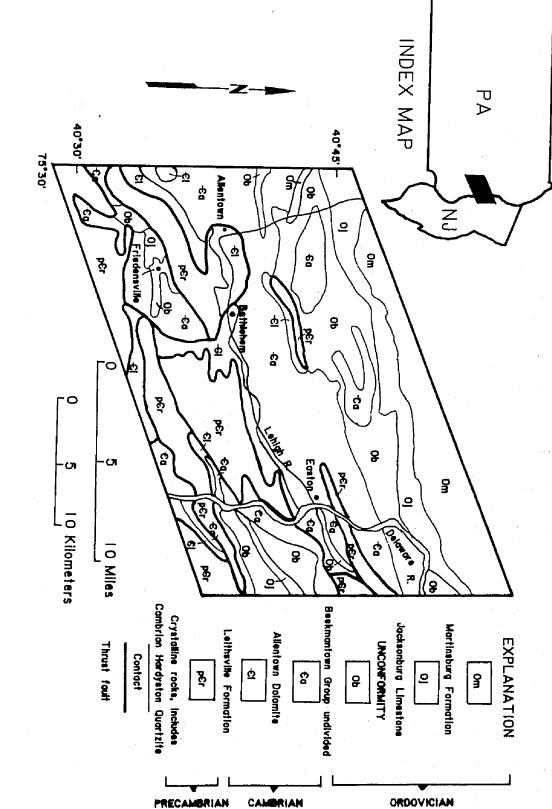


Figure 1. the Lehigh Valley and adjacent areas, New Jersey - Pennsylvania (after Drake, 1969). Index map showing the location of Friedensville and the general geology of

Friedensville deposit is a brecciated zone in the Rickenbach Formation. This zone is about 70 meters above a saccharoidal dolomite which is defined as the top of the Allentown Formation (Callahan, 1968).

The base of the Rickenbach Formation is placed at the bottom of the Evan's Marker, a medium to dark-grey unit which is 30-40 meters thick. The Evan's Marker is generally a thinly bedded dolomite that is locally a limestone, and is characterized by laminated shale partings. A rock unit with a texture similar to the Evan's Marker is absent from the lower part of the Beekmantown in the nearby Lehigh and Delaware Valley sections. Drake (1969) questions whether the Evan's Marker may correlate with the Stonehenge Limestone of Hobson's (1963) Berks County Beekmantown section or whether the entire Paleozoic section in Saucon Valley represents a different tectonic unit than the Lehigh and Delaware Valley sections.

Overlying the Evan's Marker, the Rickenbach contains a variety of beds, characterized as ribbony, thin, cherty, sandy, conglomeratic, and brecciated, that are interstratified with massive beds. Several light-colored beds containing scattered quartz sand grains and have been used as marker beds. These beds are the Callahan Marker and the Upper Sand Grain Marker. One dark colored sandy bed, the Trihartco Marker, is in the ore zone,

therefore is particularily useful even though thin, discontinuous, and difficult to identify in the mineralized environment (Callahan, 1968).

The upper boundary of the Rickenbach is placed at the first appearance of the light-colored interbeds of limestone, and dolomite of the Epler Formation. These beds contrast sharply in appearance with the overlying, dark-grey to black, shaley limestone of the Jacksonburg Formation (Callahan, 1968).

History of the Mine

Zinc mineralization was identified early in the nineteenth century on the Ueberroth farm north of Friedensville. After a process of producing zinc oxide was developed in 1853, production from the Ueberroth mine was started. During the period 1860 to 1893, operations were conducted intermittently from the Ueberroth, Old Hartman, New Hartman, Correll, and Triangle mines (figure 2), but in 1893 mining was abandoned due to the increasingly substantial inflow of water encountered as the mines were deepened.

The New Jersey Zinc Company acquired the properties in 1899 and proceeded to explore for an extension of the New Hartman ore body. In 1924 and again during the period of 1937 to 1942 a tonnage and grade that normally would be considered economic to

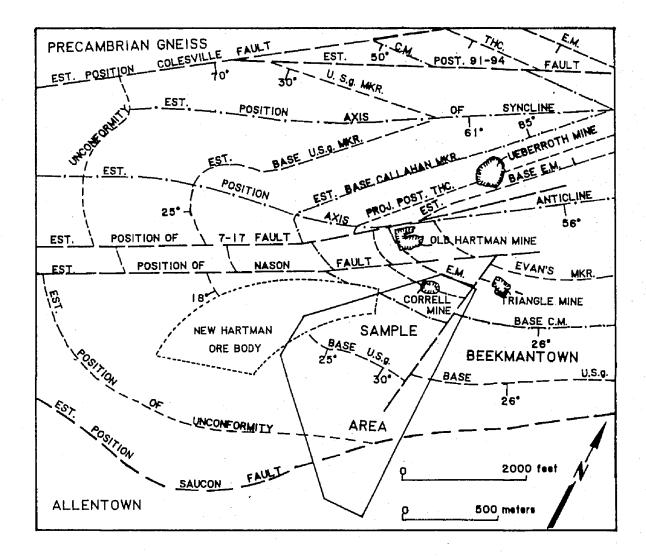


Figure 2. Geologic map of the region surrounding the Friedensville zinc deposit, Friedensville, Pennsylvania (after Callahan, 1968).

mine was outlined, however exploitation was defered because of the hydrologic uncertainties. Finally, in 1945 preparation for shaft sinking started and in 1952 the shaft was bottomed at 1261 feet. Installation of permanent pumping plants were completed in 1955, and development was started. After sufficient drawdown of the water table, mining was started in the New Hartman ore body in 1958 and has continued uninterrupted since that time (Callahan, 1968).

Structural Geology

The major structure in the vicinity of the ore deposit is a N60°E-trending doubly plunging anticline. This anticline is asymmetric with a vertical north limb at the Ueberroth pit and a south limb dipping about 25°. The south limb is exposed near the New Hartman mine. To the north of the Ueberroth pit is a syncline which is bounded on its north side by the Colesville fault and the Precambrian crystalline rocks of South Mountain (figure 2) (Callahan, 1968).

There are several sets of fractures and small scale faults in the ore body. The most prominent attitude of the fractures is north 40° to 60° east with dips ranging from 75° to 90° northwest. Some of the fractures are along ore boundaries. However, Callahan (1968) points out that the structure did not

control the localization of the ore inasmuch as ore deposits are present on all elements of the fold and are not related to faulting. Callahan (1968, p. 103) concluded that:

> "...tectonics merely deformed horizontally disposed ore bodies and determine their subsequent pattern and attitude of occurrance. Because the Taconic revolution is the earliest post-Beekmantown event in the area and the sulfide minerals themselves show evidence of deformation as well as indifference to structural setting, it is suggested that mineralization is pre-Taconic, that is Ordovician in age."

The structure of Saucon Valley is very complex. Saucon Valley is a small re-entrant of the Great Valley Province into the Precambrian rocks of the Reading Prong. Drake (1978) suggests that there may be as many as three tectonic units in the valley. There are two major thrust sheets, the Musconetcong nappe in the east edge of the valley, and the South Mountain nappe in the west side of the valley. These two thrust sheets are separated by the Black River Fault. A third thrust sheet of Precambrian rocks, the Applebutter thrust sheet, crops out in Saucon Valley, but the relative position in relation to the South Mountain nappe is unknown. Based on stream sediment data, Smith (1977) suggests that zinc mineralization may exist on both sides of the Black River Fault.

Ore Mineralization

Sphalerite is the major mineral of economic importance at Friedensville. The zinc mineralization, along with accessory pyrite, quartz, and dolomite, form the matrix of the brecciated zone in the lower Rickenbach. Fraser (1935) describes the primary ore as occurring; 1) as disseminated particles and as replacement masses in the brecciated dolomite, 2) as fissure and cavity fillings, and 3) as cementing matrix material of the brecciated areas.

The most important unit of mineralizations is a brecciated zone which conveniently brackets the Trihartco Marker. This breccia zone lies some 275 meters below the Knox-Beekmantown erosional unconformity which separates the Beekmantown Group from the overlying Jacksonburg Formation. Callahan (1968) emphasized that the breccia did not result from deformation but rather is composed of fragments derived from solution-collapse cemented by finer detritus resulting from the solution process.

Solution-collapse is a commonly used term for describing the breccia formation. However, the breccia formation may be the result of a two stage process which involves solution of the carbonate rocks and accompanying tension releasing fractures resulting from the removal of the confining material. Such tension release phenomena have been observed in the mine soon

after the excavation of new shafts (Walter Granland, personal communication, 1983).

Two distinct breccia types are present. The main mineralization is in what has been termed the "rubble breccia" and is found along the footwall. Rubble breccia has been described by Metsger and others (1973) as being completely disrupted, rotated, and transported angular fragments derived from cave collapse in a paleokarst system. All of the fragments within the rubble breccia have been derived from the Beekmantown Group. The angularity of the breccia fragments is probably the result of the tension releasing fractures.

The second breccia type is near the hanging wall and has been termed a "brickwork mortar" or "crackle breccia". Metsger and others (1973) concluded that this breccia forms from the slumping around the perimeter of the solution cavity. They are characterized by blocky fragments resembling crude brickwork. The fragments are slightly disoriented with a tendency to droop into the central zone of the underlying breccia. The "mortar" in the resulting brickwork pattern is generally honey-colored sphalerite, pyrite, and dolomite in diverse proportions.

There were two questions that arose after examination of the brecciated dolomite. The first question is why the clasts in the breccia appear floating and rarely have point-to-point contact.

The second question was whether fragments of breccia had been scavenged to form some of the cementing material or vein filling. To resolve these questions, angular fragments of crushed dolomite were bonded in epoxy. The composite was cut and sections showed that in two dimensions the clasts were rarely observed in point-to-point contact and most appeared floating. The pore filling of the model is about 40%, a value similar to the vein filling in the breccia. This similarity indicates that the clasts at Friedensville did not contribute significant material to the vein filling.

Sample Location

The drill hole sites selected for sampling in the study are located southeast of the main zone of mineralization. This sample pattern was chosen to evaluate lateral trends away from the main deposit. The location and identification number of the 14 drill holes sampled in this study are shown in figure 3.

The use of the drill core enabled sampling of stratigraphically equivalent horizons above and below the Trihartco Marker, the marker bed used to define the main ore horizon. Samples also were collected from the Evan's Marker which is approximately 50 meters below the ore horizon at the

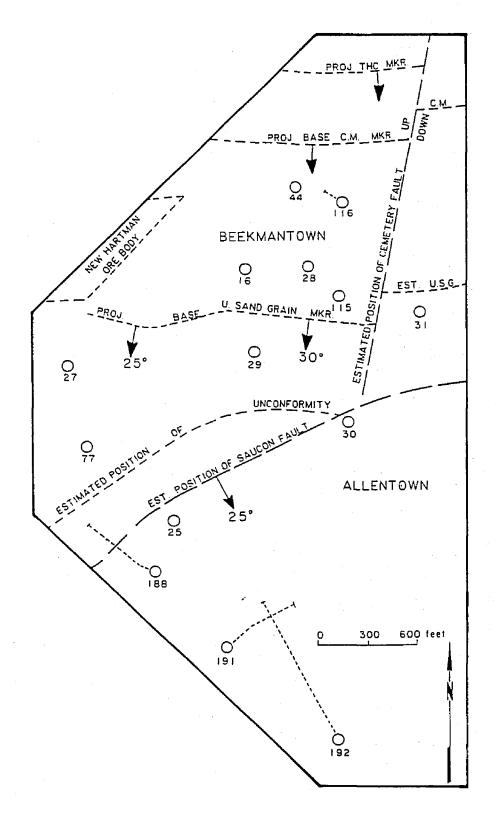


Figure 3. Location map of the 14 drill holes sampled in this study.

base of the Rickenbach Formation. Two drill holes were sampled from the surface to the ore horizon to characterize the Rickenbach host above the mineralized zone. All of the samples were labeled with the drill hole numbers and depth in feet.

NATURE OF THE CARBONATES

General Statement

The texture, fabric, and structure of the dolomite was determined and catalogued to define whether the ore mineralization was controlled or related to any feature of the rock. To simplify the study of the lithologies the samples were placed in three groups according to their stratigraphic position. These three groups are; 1) samples above the ore zone, 2) samples which bracket the Trihartco Marker in the ore zone, and 3) samples within the Evan's Marker. Each group was subdivided using textural characteristics. The classification and summary of the rock types is shown in table 1.

The characteristics of each sample were determined using broken, sawed, and etched surfaces. For etching, a ground surface was immersed in 10 percent hydrochloric acid for several minutes and then washed. If the study of the etched surfaces indicated that further examination was justified, a thin section was prepared for petrographic study.

Color, grain size, mineralogy, and depositional and post-depositional features were catalogued. Some features had forms suggestive of fossils, but identification was impossible. Color was determined using the Munsell rock color chart. The

TABLE 1

Stratigraphic Position	Subgroup No.	Sample Description
Above the	A-1	Dolomite, oxidized to tan, structureless
Ore Zone	A-2	Dolomite, grey, structureless
Ore Zone	B-1	Dolomite, grey, structureless
	B-2	Dolomite, grey, mottled or laminated
	B3	Dolomite, grey, siliceous laminated
	B-4	Dolomite, grey, siliceous mottled
	B-5	Dolomite, grey, microbrecciated
	В-6	Dolomite, grey, macrobrecciated
Evan's Marker	C-1	Dolomite, grey, siliceous or dolomitic structures
	C-2	Dolomite, dark grey, argillaceous
	C−3	Limestone, dark grey, argillaceous
	C-4	Dolomite, grey, veined with microcline and quartz

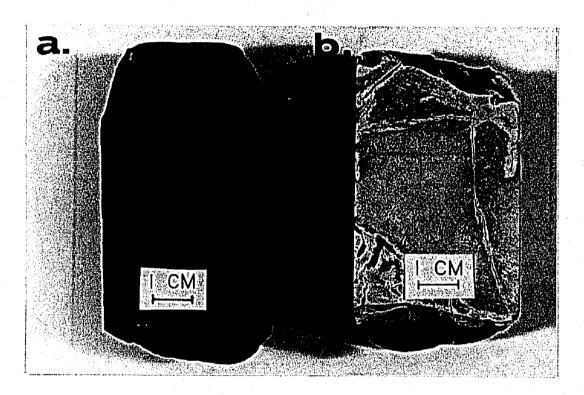
SUMMARY OF ROCK CLASSIFICATIONS OF THE CARBONATES OF THE RICKENBACH FORMATION AT FRIEDENSVILLE, PENNSYLVANIA.

size classification used in this study was based on the modified Wentworth grade scale for carbonate rocks by Leighton and Pendexter (1961). The mineralogy of the rocks was determined from etched samples, thin sections, and X-ray diffraction data. Staining of the etched samples was unnecessary as the calcite in the rocks was easily distinguished from the dolomite and quartz by its low relief. Features identified in the samples include dolomitic and siliceous mottling or layering. The two principal post-depositional features identified in all the samples are brecciation and veining.

Rock Descriptions

Rocks Above the Ore Zone

The first group of samples are located above the ore zone and were divided into two subgroups, A-1 and A-2. Subgroup A-1, termed the oxidized zone for lack of a better descriptive term, is composed of medium-light- to light-grey, very fine-grained dolomite. The rocks in this subgroup appear structureless with a few dolomitic and siliceous mottled samples. Veins of sparry dolomite and calcite are common. This subgroup is defined by the light color and the iron staining on old fracture surfaces. A few rocks were pinkish-grey due to the iron staining from pyrite oxidation (Plate la).



- Plate 1. a) Etched view of dolomite of subgroup A-2 with a structureless, massive texture, and medium-grey color.
 - b) Etched view of dolomite of subgroup A-1 showing oxidized light color, the characteristic feature of the rocks in the subgroup.

The rocks in subgroup A-2 are characterized by medium- to medium-light-grey, very fine-grained dolomite. As in subgroup A-1, most of the rocks are structureless (Plate 1b). A few rocks in this subgroup were dolomitic or siliceous mottled. Post-depositional sparry dolomite, calcite, and quartz veins cross-cut all the samples. Subgroup A-2 is contrasted with the rocks in subgroup A-1 by the absence of iron staining on old fracture surfaces and a darker color.

Rocks from the Ore Zone

In the ore zone the first group of samples, subgroup B-1, is characterized by a paucity of minerals other than dolomite. This subgroup consists of medium-grey, very fine-grained, massive dolomites. They are similar to the rocks in subgroup A-2. Subgroup B-2 is distinguished by thin laminae and mottling of light and dark colored dolomite (Plate 2a). Under the microscope the laminae and mottling appeared to be the result of a variation in crystal size. The laminae are crinkled, a feature which Hobson (1963) suggests implies that dolomitization occurred soon after the deposition of the carbonate sediments. Subgroup B-2 contains very few post-depositional microfractures and veins of sparry dolomite and calcite.

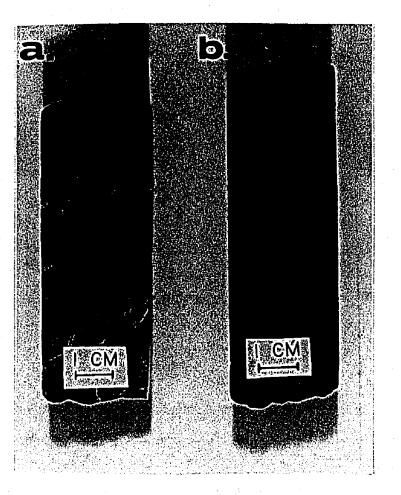


Plate 2. a

- a) Etched view of dolomite of subgroup B-2 showing light and dark dolomitic mottling.
- b) Etched view of dolomite of subgroup B-4 showing irregular black siliceous mottling.

Subgroup B-3, also from within the ore zone, is characterized by rocks that exhibit a siliceous laminated structure. These rocks are commonly medium-dark-grey to medium-grey, coarsely micrograined to very fine-grained siliceous dolomite. The regular, parallel bands are composed of tightly cemented quartz and rarely feldspar with carbonaceous material.

The rocks in subgroup B-4 have irregular, subparallel laminae and mottling of microcrystalline chert and chalcedonic quartz (Plate 2b). These features are commonly the result of post-depositional replacement of dolomite.

Microbreccia (B-5) and macrobreccia (B-6) are the brecciated samples from within the ore zone (Plate 3a and b). The distinguishing characteristic between the B-5 and B-6 subgroups is the relative size of the clasts. Clasts in the microbreccia subgroup (B-5) are generally between 1 and 10 mm. This is to be contrasted with the larger clasts in the macrobreccias (B-6). All of the brecciated samples contain some clasts which appear homogeneous in color and mineralogy and others which are heterogeneous and appear mottled or layered. The breccia clasts are commonly angular with irregular boundaries and appear suspended in cement. A few samples consist of rounded and subrounded clasts.

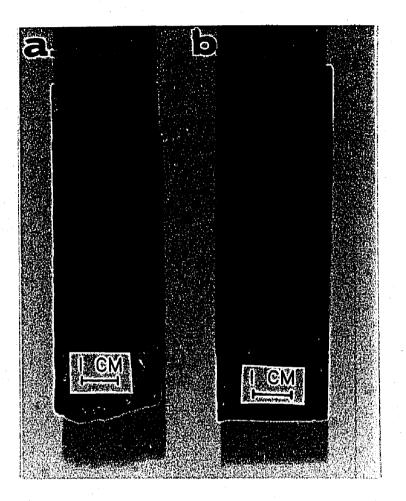


Plate 3.

- a) Etched view of microbrecciated dolomite of subgroup B-5. Clasts consist of the laminated dolomitic structures common to the rocks of subgroup B-2.
- b) Etched view of macrobrecciated dolomite of subgroup B-6.

The dolomite clast in subgroup B-5 and B-6 are medium- to medium-dark-grey, very fine-grained dolomite. Matrix material consist of sparry and detrital dolomite with different amounts of chalcedonic quartz, microcrystalline chert, calcite, pyrite, and sphalerite. Thin sections show that the sparry dolomite matrix contains crystals which are subhedral and euhedral and medium- to coarse-grained. The crystals are turbid with minute inclusions. Some sparry crystals of dolomite are attached to the surface of the clast and may have a complex intergrowth of microcrystalline quartz and sparry calcite. Calcite and quartz also occur as vug fillings in the matrix of the breccia.

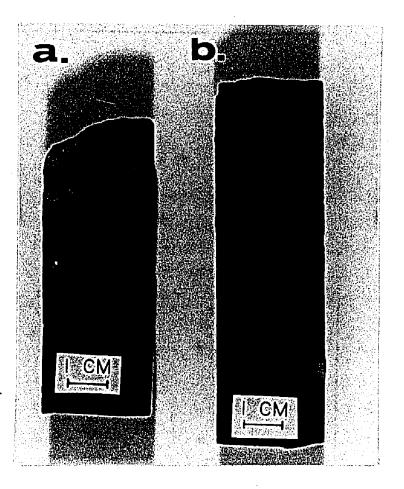
Rocks from the Evan's Marker

The lithologies of the Evan's Marker are varied, consisting of dolomite, argillaceous dolomite, argillaceous limestone, and a quartz and microcline veined dolomite. The dolomites in subgroup C-1 show siliceous mottling, laminae and layering, and brecciation. A typical rock in subgroup C-1 is a very fine-grained, medium to medium-light grey dolomite. Irregular tapering laminae are a feature unique to this subgroup. These laminae appear to consist of microcrystalline chert and carbonaceous matter. Grain boundaries between some of the dolomite crystals are sutured.

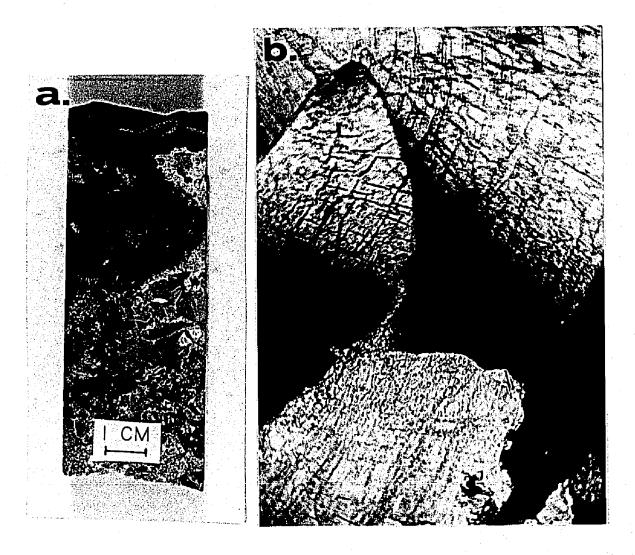
Rocks in subgroup C-2 are medium-grained, medium-dark grey argillaceous dolomite (Plate 4a). The rocks consist of dolomite and shale layers which are irregular and discontinuous, pinching and swelling along bedding planes.

Rocks in subgroup C-3 consist of medium-grained, medium-grey argillaceous limestone with very slight dolomitic mottling (Plate 4b). On etched surfaces, the argillaceous laminae have strong relief and are irregular and broken. Pyrite is common throughout the limestone samples. The black color of the calcite brought out by the etching may be due in part to a high concentration of carbonaceous matter.

The rocks of subgroup C-4 are medium-grey, micrograined dolomite with vugs of chalcedonic quartz, microcrystalline chert, microcline, sparry dolomite, and muscovite (Plate 5a). The microcline is dark-yellow-orange and very coarse-grained. The presence of this microcline is the most distinctive characteristic of the rock. Under the microscope the sparry dolomite crystals show curved cleavage traces (Plate 5b). These crystals have a radial extinction.



- Plate 4. a
- a) Etched view of argillaceous dolomite of subgroup C-2. Dolomite layers are light grey and siliceous layers are black.
 - b) Etched view of argillaceous limestone of subgroup C-3. Light grey patch at the base of the core is secondary dolomite. The shale layers are at the top of the core.





- Plate 5. a) Etched view of the coarse-grained chalcedonic quartz (colorless) and microcline (yellow) in the dolomite (grey) of subgroup C-4. Sparry dolomite (white) and microcrystalline chert (black) are also visible in the drill core.
 - b) Photomicrograph of sparry dolomite crystals from the core in Plate 5a showing curved cleavage traces (crossed nicols, 80X).

Summary and Discussion

A summary of the lithologies, textures, and structures in each drill hole is illustrated in the fence diagram in Plate 6. The diagram shows that no correlation was found between the lithologies within the ore horizon and the zinc mineralization. It is concluded that brecciation was the only lithologic feature related to the sites of zinc mineralization.

NATURE OF THE MINERALIZATION

Introduction

Butler (1935) described the primary sphalerite mineralization at Friedensville as occurring; 1) in large masses in the brecciated rock, 2) as open-space fillings in the crackle breccia, and 3) in small replacement veinlets. Pyrite is also widely distributed throughout the deposit. The characteristics of the sphalerite and pyrite in each of these three settings will be described.

Ore Textures

The massive ore is generally a fine- to medium-grained, grey sphalerite. This sphalerite has several textures as described by Butler (1935). Some of the sphalerite is not deformed, some is deformed and partly granulated, and some is fine-grained and appears mylonitic. Typical deformed sphalerite has curved twins with undeformed sphalerite along grain boundaries (Hoagland, 1976). Fractured and deformed pyrite also is found with the sphalerite in these massive ore settings. This massive ore is the most abundant and richest ore of the deposit.

The ore in open-space fillings is a fine- to medium-grained grey sphalerite. Rarely, the sphalerite has a colloform texture,

generally with light and dark grey interlayers. Layers in the colloform texture crudely parallel the surface of adjacent clasts. While layering is found throughout the massive ore zone, it is most prevalent in the open-space fillings. Most layers are poorly defined, but rarely they are distinct with yellow sphalerite layers and grey sphalerite layers (Plate 7). This yellow sphalerite was first reported in the northwestern corner of the New Hartman ore body; however, recent mining has uncovered yellow sphalerite at the 1590 foot level in the far southwestern part of the mine.

The exact cause of the color variation in the sphalerite is unknown. Differences in iron content of the sphalerite is a likely cause of the color variation. However, Roedder and Dwornick (1968) showed that although iron content does change with the banding at Pine Point, it can not be correlated with the band color. Fraser (1935) speculated that the lighter color may be due to the greater freedom from fractures and inclusions. Roedder (1968b) reports that the variation from light grey to dark grey banded sphalerite at Friedensville was due to minute opaque inclusions that outline former crystal terminations and give the banded appearance.

The third type of sphalerite is found in veinlets, as described by Butler (1935). These veinlets consist of small

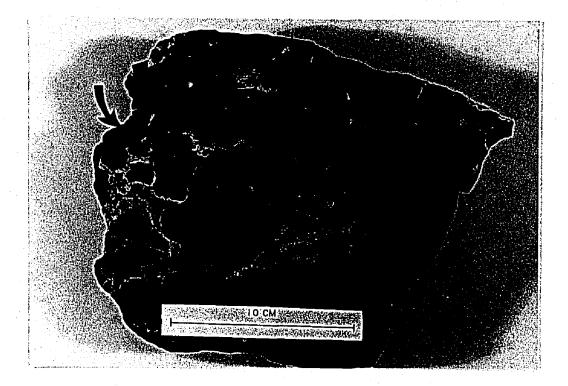


Plate 7. Etched sample of colloform, layered texture of yellow and grey sphalerite found in the openspace fillings of the crackle breccia (arrow). The light grey patches are fragments of the dolomite host showing the laminated structures common to subgroup B-2. masses of honey-colored sphalerite and pyrite. This type of mineralization is found throughout the ore horizon. In thin-section, the large grains of sphalerite commonly replace dolomite and rarely pyrite.

INSOLUBLE RESIDUE

Introduction

The insoluble residue of a carbonate rocks is the organic and inorganic material that is insoluble in acid. Differences in the nature and amount of the insoluble residue in the ore horizon may indicate reaction and products from the mineralizing solutions.

Seibel (1982) found that the insoluble residue of 13 dolomite beds from the Epler Formation in Berks County ranged from 7.1 to 24.1 weight percent with an average of 15.4 percent. Folk (1958) found an average of 12.6 weight percent insoluble residue in the 9 dolomite beds of the Axeman Formation of the Beekmantown Group in Centre County, Pennsylvania. These two studies serve as a reference for comparison of the insoluble residue in the vicinity of the Friedensville deposit.

Procedure

Separation of the insoluble residue and the carbonate fraction in the dolomite samples was performed using the procedure outlined by Barber (1974). Roughly 10 grams of the sample was ground to pass through a 53µm screen. One gram of the dry powdered sample was treated with 25% v/v acetic acid at 60°C

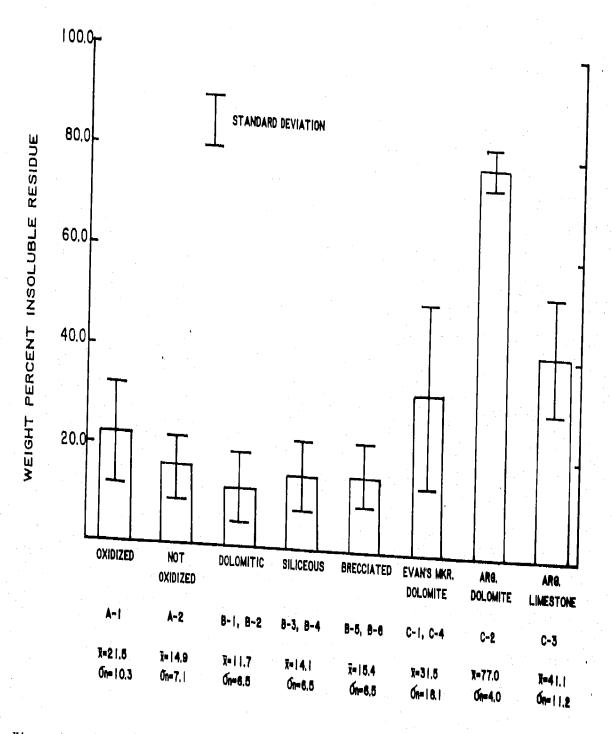
for 12 hours with occasional stirring. Barber (1974) reported that under these conditions generally less than 2% of the dolomite remained undissolved in the rocks and alteration of the non-carbonate fraction was minimal.

After the digestion, the solution was filtered through a 45µm millipore filter. The insoluble residue on the filter was washed with deionized water and dried in a dessicator at room temperature. A series of samples were reproduced in duplicate and triplicate and the largest difference was 5.0 relative percent. The solution was transferred to a 100-ml volumetric flask, made up to volume with deionized water, and stored for atomic absorption analysis. Blanks were prepared in a similar fashion.

Results

Bar graphs of the weight percent insoluble residue from the rock subgroups is shown in figure 4. The rock subgroups are those previously defined in the rock descriptions. Above the ore zone the oxidized subgroups have an average insoluble residue of 21.5%, which is greater than the remaining samples above the ore zone which are unoxidized and contain 14.9% insolubles.

The rocks from within the ore zone show a slight variation between the three subgroups. The brecciated and siliceous

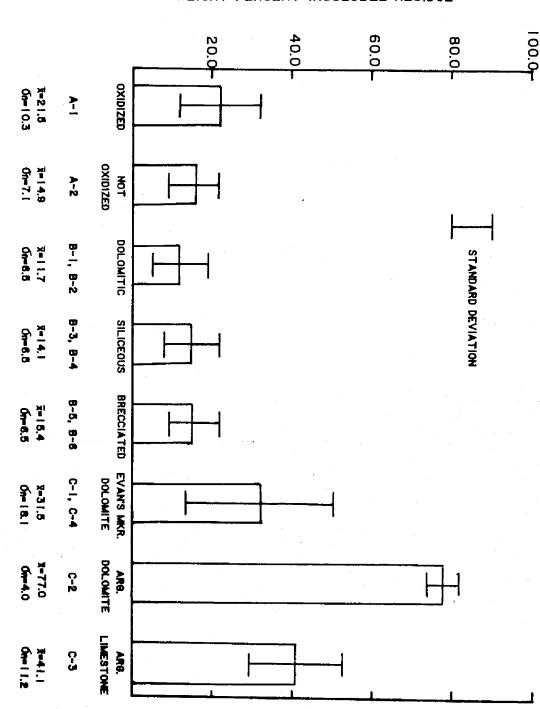




Bar graph of the mean values of the weight percent acid insoluble residue of the rock subgroups from the sampled horizons at the Friedensville zinc deposit.

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Figure 4. Bar graph of the mean values of the weight percent acid insoluble residue of deposit. the rock subgroups from the sampled horizons at the Friedensville zinc



WEIGHT PERCENT INSOLUBLE RESIDUE

samples have a slightly higher concentration of insoluble residue probably due to secondary silica which is absent in the dolomitic samples of the ore zone.

The values for the weight percent insoluble residue for the limestones and the dolomites of the Evan's Marker are much greater than the other subgroups. Except for samples from the Evan's Marker, the insoluble residue values are similar to those reported by Seibel (1982) and Folk (1958).

The insoluble residue for each subgroup was analyzed by X-ray powder diffraction for mineral identification. All diffraction scans were performed on a Philips APD-3600 automated diffraction unit using a scan rate of 2° 20/min., CuK α radiation, and a generator setting of 45 KV and 30 mA.

Quartz was the predominant mineral in the insoluble residue. Using the relative peak heights of the diffractograms, the remaining minerals in order of relative abundance are: microcline, pyrite, and illite. Diffraction peaks for rutile were not found in any diffractograms of the samples.

The same mineralogy was found for all insoluble residues; however, there were differences in the relative abundance of the minerals. The samples above the ore zone contained mostly quartz with very minor amounts of microcline, albite, and illite, and

only trace amounts of pyrite. The insoluble residue from within the ore zone consisted of quartz, microcline, and illite, but also contained large concentrations of pyrite and sphalerite. The Evan's Marker has three noteworthy differences. First, the veined dolomite of subgroup C-4 has large quantities of very coarsely crystallized microcline. Secondly, the argillaceous samples of subgroup C-2 and C-3 contain a 14Å clay, most probably chlorite. Lastly, the Evan's Marker contains significant amounts of pyrite.

In a recent study of the overlying Epler Formation (Seibel, 1982) the mineralogy of the insoluble residue in the order of abundance was; quartz, microcline, illite, pyrite, and rutile. These results are similar to the mineralogy found in this study with the exception of rutile which is absent.

STOICHIOMETRY OF THE DOLOMITE

Introduction

Dolomite stoichiometry was determined using the d-spacing of the (104) reflections from X-ray diffraction as described by Goldsmith and Graf (1958b). The data was collected on the Philips APD-3600 diffractometer using an internal silicon standard. Replication of several samples showed that the error in measurement is ± 0.40 mole percent CaCO₂.

Results

The mean and standard deviation of the mole percent $CaCO_3$ in the dolomites is given in table 2. The compositional range was 49.0 to 52.0 mole percent $CaCO_3$ in the dolomite with a mean of 50.7 percent and a standard deviation of 1.1 percent. There is a small compositional difference between the brecciated and the non-brecciated dolomites with the brecciated dolomites being more enriched in $CaCO_3$. The sparry dolomite is intermediate in composition, hence the enrichment of calcium in the brecciated dolomites is unrelated to the presence of the sparry dolomite. The cause for the relationship is unknown. It may indicate that calcium-rich ore solutions in the brecciated samples reacted with the brecciated dolomite.

TABLE 2

Rock Subgroups	No. of Samples Analyzed	Mole % CaCO ₃ ± Standard Deviation
Oxidized	8	51.0 ± 0.9
Unoxidized	7	50.1 ± 0.8
Dolomitic	9	50.8 ± 1.1
Siliceous	4	50.7 ± 0.5
Brecciated	18	51.1 ± 0.8
Non-brecciated ¹	20	50.5 ± 0.9
Sparry dolomite	2	49.9 ± 0.2
Evan's Marker ²	3 ·	50.8 ± 0.5
All samples	51	50.7 ± 1.1

MOLE PERCENT CaCO₃ IN THE DOLOMITE LATTICE FOR THE TEXTURAL SUBGROUPS.

¹Includes the dolomites in the unoxidized, dolomitic, and siliceous subgroups.

 2 Includes the dolomites in subgroups C-1, C-2, and C-4.

ELEMENTAL ANALYSIS OF THE CARBONATE FRACTION

Introduction

The chemical composition of the carbonate fraction of the dolomite mineral is controlled by the substitution of ions for calcium and magnesium. The objective in analyzing the trace element constituents of the carbonate fraction was to determine the contribution of the host rock to the zinc mineralization. The trace elements selected for the study were; iron, manganese, zinc, lead, strontium, and sodium. These elements were chosen because of their known abundance in carbonate minerals and basinal brines.

A major problem in chemical studies of carbonates is the uncertainty of contamination from the non-carbonate fraction of the samples (Robinson, 1980). Strong solvents may attack the non-carbonate phases, releasing metals which would be erroneously attributed to the carbonate fraction. A selective dissolution of the rock by a weak solvent will better reflect the amount of metal which is held in the carbonate fraction. Hirst and Nicholls (1958) and Barber (1974) have shown that acetic acid is the best weak acid for this type of study.

In the present study, sphalerite was found to be attacked by the acetic acid solvent resulting in abnormally high

concentrations of zinc in the mineralized samples. The possibility of some leaching of clays by the acetic acid will be discussed later.

Analytical Procedure

Sparry calcite and dolomite veins of 11 brecciated samples were manually separated from their enclosing rock. The extracted material was treated using the procedure previously discussed.

All of the trace elements were determined by Atomic Absorption Spectroscopy on a Perkin-Elmer Model 373 Spectrophotometer using a hundred-fold dilution. The instrument conditions are given in table 3. Several sets of standards were prepared using reagent grade materials of the following; Fe powder, MnCl₂, ZnCl₂, PbCl₂, SrCl₂'6H₂O, and NaCl dissolved in deionized water or acid. Fe standards were made in the range O-250 ppm; and Mn, Zn, Pb, Sr, and Na O-10 ppm. Standards were run before and after the samples to correct for any short term instrument drift. The concentrations of both the samples and the standards were recorded on a strip chart recorder. The blank concentrations were subtracted from each sample.

TABLE 3

Element	Current (mA)	Line (nm)	Slit (nm)	Flame	Flame Conditions		
Fe	5	248.3	0.2	Air-C ₂ H ₂	fuel lean		
Mn	5	279.5	0.2	Air-C ₂ H ₂	fuel rich		
Zn	10	213.9	0.7	$Air-C_2H_2$	fuel rich		
Pb	10	283.3	0.7	Air-C ₂ H ₂	fuel rich		
Sr	1.0	460.7	0.2	Air-C ₂ H ₂	fuel lean		
Na	7	589.0	0.7	Air-C ₂ H ₂	fuel rich		

INSTRUMENT SETTINGS FOR ATOMIC ABSORPTION SPECTROSCOPY.

Results

General Statement

The trace elements are reported as parts per million of the acid soluble carbonate fraction of each sample in Appendix I. The average reproducibility as determined from several samples was; Fe(15.0), Mn(8.0), Zn(20.0), Pb(20.0), Sr(15.0) and Na(20.0) relative percent, respectively.

The average value for each rock subgroup is given in table 4. For the subgroup averages, the range within the populations may be large. The degree of variation is illustrated by the standard deviation within the subgroups.

Iron

Iron in the carbonate fraction ranges from 850 to 17,000 ppm (figure 5). The oxidized samples of subgroup A-1 have over three times as much iron as the samples in subgroup A-2. Some of the pyrite in the oxidized samples may have oxidized and the iron oxide leached by the acetic acid; whereas in the unoxidized samples pyrite would undergo insignificant attack by acetic acid.

There are minor variations in the iron concentrations in the ore zone. The brecciated (mean 1265 ppm) and the siliceous (mean 1030 ppm) dolomites have greater concentrations than the dolomitic (mean 865 ppm) subgroup. There is a direct correlation

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Rock No. of Subgroup Samples Numbers in Subgroup				x̄±σn (ppm)									
		Fe		MnZn		n	Pb		Sr		Na	Na	
A-1	10	3,090	1095	220	85	15	5	40	5	145	30	120	35
A-2	15	945	510	85	20	10	5	40	5	85	10	215	40
B-1, B-2	56	865	410	80	20	30	20	40	10	100	20	205	55
B-3, B-4	23	1,030	395	80	10	25	20	40	10	110	30	215	45
B-5, B-6	62	1,265	515	90	15	25	25	40	10	110	25	215	60
Calcite Veins	6	1,730	1210	70	25	15	10	55	35	305	40	200	140
Dolomite Veins	5	3,965	2140	80	20	30	10	45	10	135	45	350	55
C-1, C-4	9	3,605	2115	130	45	20	10	45	15	120	25	250	130
C-2	2	17,260	810	450	20	160	15	75	60	200	50	300	75
C-3	3	5,975	2140	380	90	30	5	50	10	330	105	140	40

AVERAGE CHEMICAL COMPOSITIONS OF THE TEXTURAL SUBGROUPS FOR THE CARBONATES OF LOWER RICKENBACH FORMATION AT FRIEDENSVILLE, PENNSYLVANIA.

TABLE 4

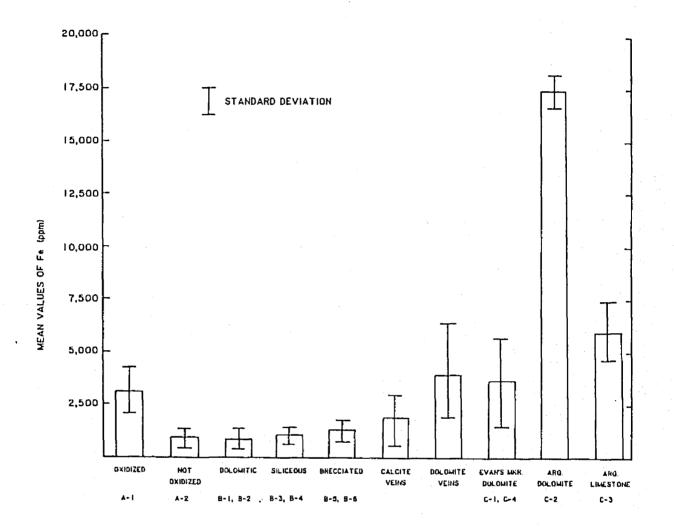


Figure 5. Bar graph of the mean values of iron concentrations in the acid soluble fraction from the sampled horizons at the Friedensville zinc deposit.

between iron content and weight percent insoluble residue suggesting that some iron has been leached from either pyrite or the clays of the insoluble residue during acid digestion (see figure 4). Another possible explanation is based on the high iron concentrations in the dolomite (mean 3965 ppm) and calcite (mean 1730 ppm) veins. These veins lack an insoluble residue; yet their iron concentration is high. Clearly, the brecciated samples would be most affected by the anomolous concentrations in the cement between the clasts.

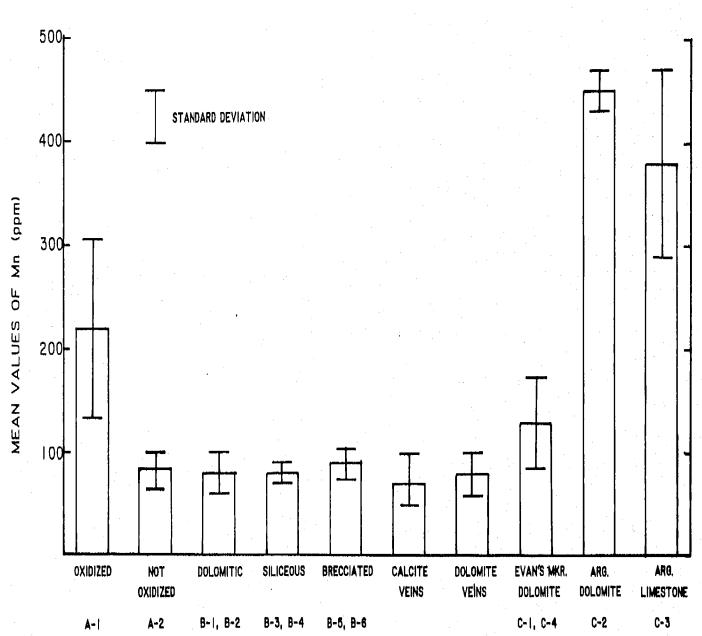
The iron concentrations in the samples from the Evan's Marker are much greater than the rocks from the overlying horizon, but the variation in the values show a direct parallelism with the weight percent insoluble residue. The iron in the argillaceous dolomites (mean 17,260 ppm) is similar to the value of 16,800 ppm reported by Weber (1964) for argillaceous dolomites from several different localities. The amount of iron in the argillaceous limestones (mean 5975 ppm) and the dolomite subgroups C-1 and C-4 (mean 3605 ppm) is high relative to the other subgroups. Some of the iron can be attributed to the degradation of the clay minerals and pyrite, but the magnitude of the increase precludes this being the sole explanation for the iron enrichment in the Evan's Marker.

Manganese

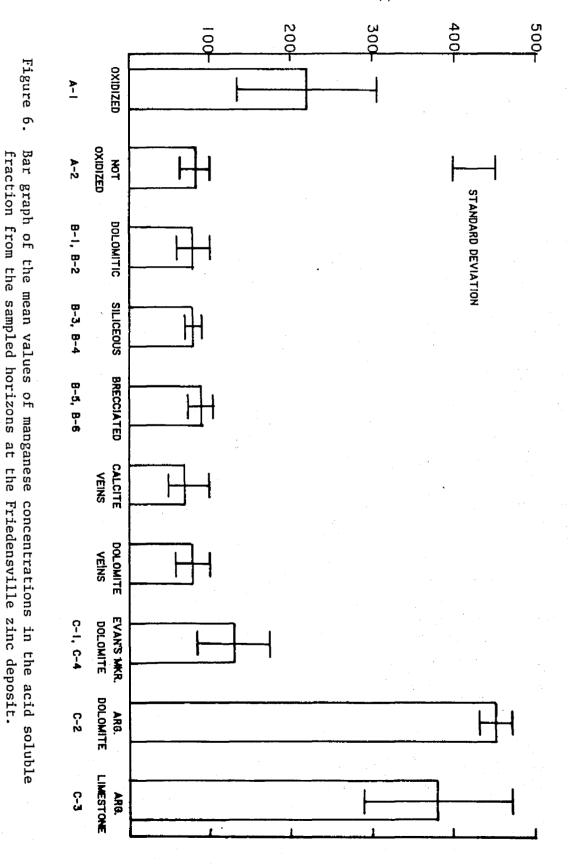
Manganese analysis for all the samples occurs over a much smaller range of means (70-450 ppm) compared to the iron (figure 6). Similarly to iron, the manganese concentrations in the A-1 samples (mean 220 ppm) is three times greater than the A-2 samples (mean 80 ppm). The oxidized samples must have been subjected to a process of secondary concentration of iron and manganese, perhaps through the weathering of pyrite or from the downward perculation of constituents in meteoric water.

The manganese concentrations within the ore zone and in the calcite and dolomite veins range from 70 to 90 ppm. These concentrations are slightly greater than the mean value of 46 ppm reported by Weber (1964) for the dolomites in the Nittany Formation in the Lower Ordovician Beekmantown Group near Bellefonte, Pennsylvania.

The dolomite subgroups C-1 and C-4 (mean 130 ppm), argillaceous dolomites (mean 450 ppm) and the argillaceous limestones (mean 380 ppm) in the Evan's Marker all show a significant increase in manganese compared to the overlying strata. This trend is similar to that found for iron. Weber (1964) reported a mean value of 640 ppm manganese in the argillaceous dolomites, almost three times as large as the value of 245 ppm for typical "primary" dolomites. However, Rao and



Bar graph of the mean values of manganese concentrations in the acid soluble Figure 6. fraction from the sampled horizons at the Friedensville zinc deposit.



MEAN VALUES OF Mn (ppm)

Naqvi (1977) and Brand and Veizer (1980) both concluded that manganese in limestones and dolomites is in the carbonate fraction and is not related to the insoluble residue.

<u>,Zinc</u>

Zinc was detected in all the samples in trace amounts with a few showing high concentrations from acid attack of the sphalerite. These anomalous high concentrations were omitted in the calculation of the means and standard deviations (figure 7). The oxidized samples (mean 15 ppm) have slightly higher concentrations than the unoxidized samples (mean 10 ppm), but not in the proportions of the iron and manganese values, hence the trend does not appear significant.

The zinc values are low and nearly constant for all samples except the Evan's Marker. In the Evan's Marker the chemical trends are similar to the patterns established by iron and manganese. The argillaceous dolomites (mean 160 ppm) contain significantly higher levels of zinc compared to the argillaceous limestones (mean 30 ppm) and the remaining dolomites in subgroups C-1 and C-4 (mean 20 ppm). Weber (1964) reported that although zinc is usually concentrated in the insoluble residue, it may be incorporated in the carbonate mineral and be present in very large concentrations.

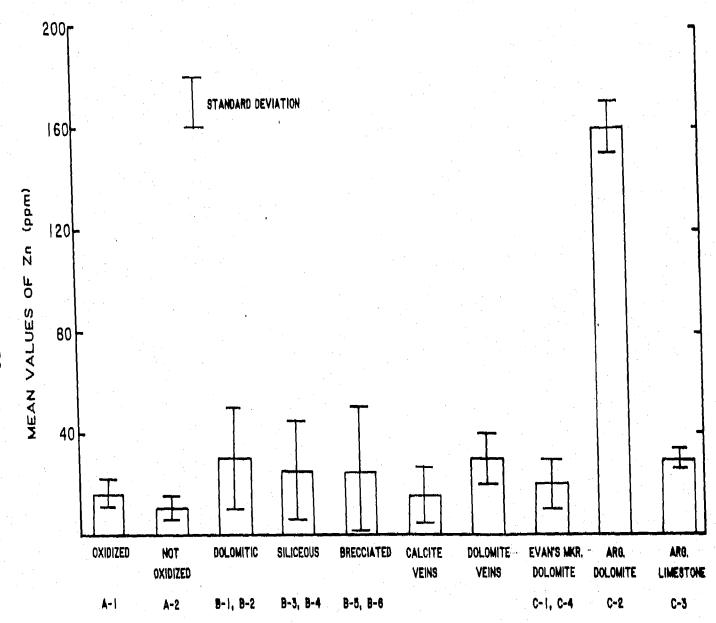


Figure 7. Bar graph of the mean values of zinc concentrations in the acid soluble fraction from the sampled horizons at the Friedensville zinc deposit.

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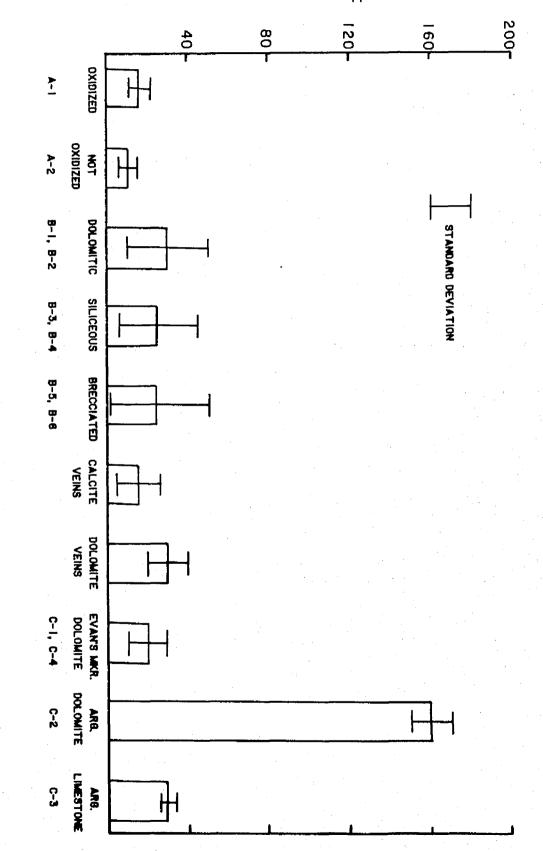


Figure 7. Bar graph of the mean values of zinc concentrations in the acid soluble fraction from the sampled horizons at the Friedensville zinc deposit. ٤3

MEAN VALUES OF Zn (ppm)

Lead

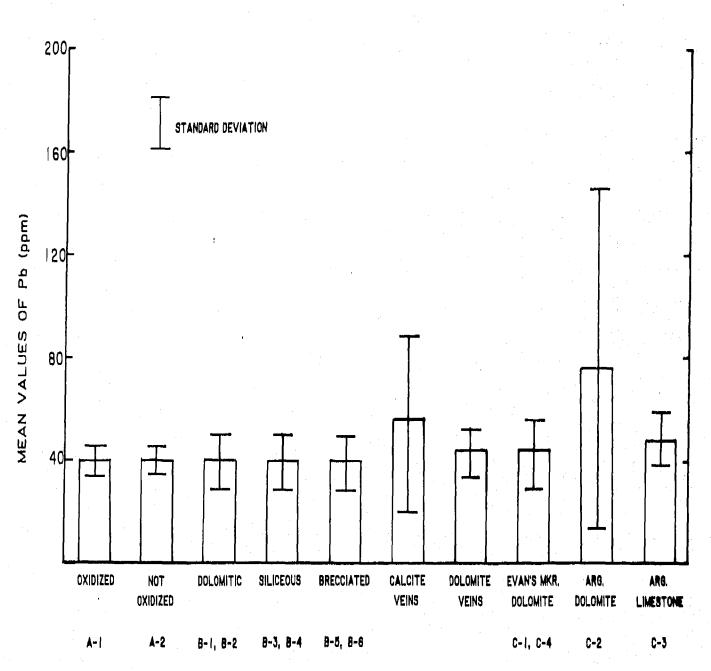
The distribution of lead in the samples is relatively uniform within each subgroup as well as between the subgroups (figure 8). Lead concentrations are slightly greater in the sparry calcite veins (mean 55 ppm) than the sparry dolomite veins (mean 45 ppm). This slight difference is probably due to a preference of lead to substitute for the larger calcium ion rather than the magnesium ion.

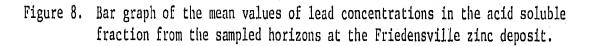
The lead concentrations in the Evan's Marker are more variable than in the overlying horizons. As was the case with iron, manganese, and zinc, the lead values are the highest in the argillaceous dolomites, but the magnitude of the increase is much less than for the other elements.

Strontium

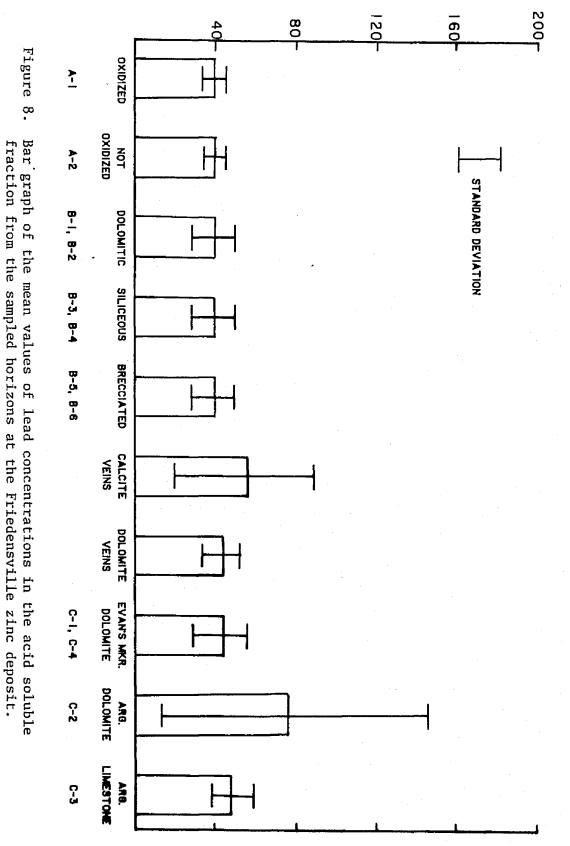
Strontium content resembles, but deviates in detail, from the iron and manganese trends (figure 9). Above the ore zone, the oxidized samples have approximately twice the concentration of strontium as the unoxidized samples. This suggests an enrichment of the trace elements in the oxidized zone.

Within the ore zone the strontium concentrations are uniform. The dolomitic samples (mean 100 ppm) are slightly less than the siliceous (mean 110 ppm) and brecciated samples (mean





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MEAN VALUES OF Pb (ppm)

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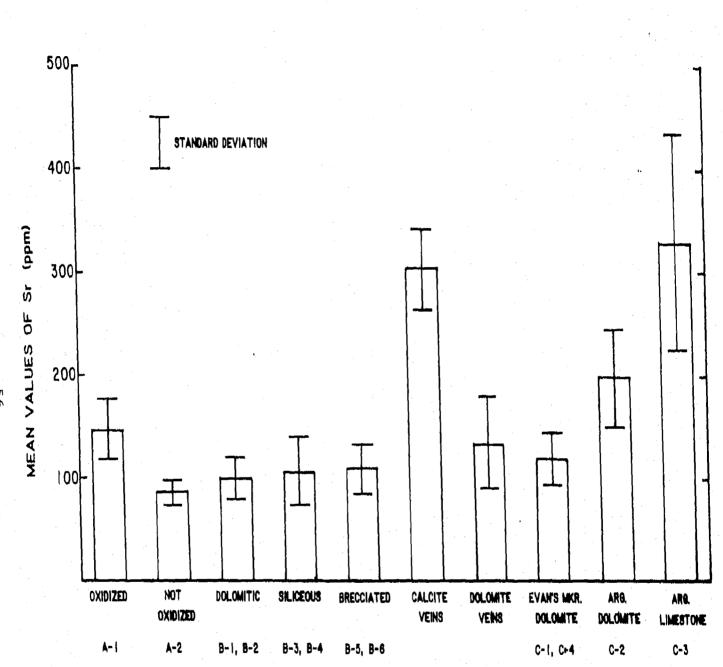
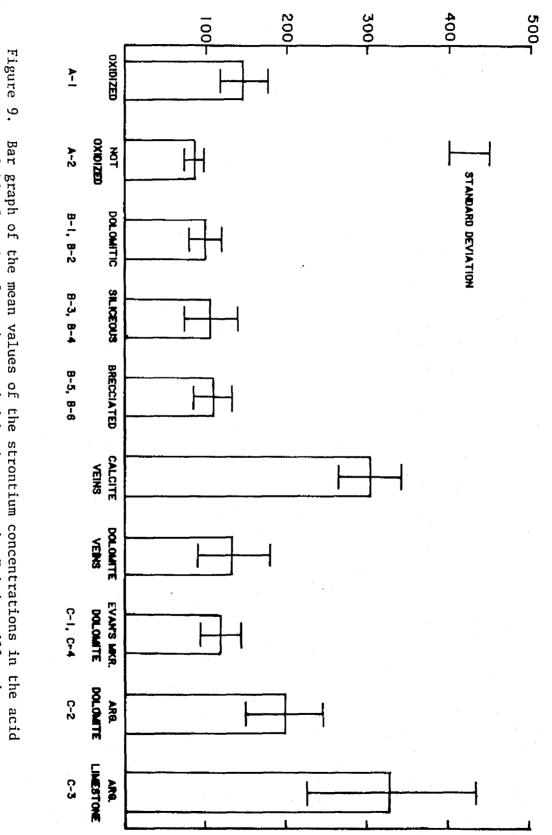


Figure 9. Bar graph of the mean values of the strontium concentrations in the acid soluble fraction from the sampled horizons at the Friedensville zinc deposit.



soluble fraction from the sampled horizons at the Friedensville zinc deposit.

95

MEAN VALUES OF Sr (ppm)

110 ppm). Strontium substitutes for calcium in carbonate minerals, therefore its bulk content in the carbonate rock is directly related to the calcite-dolomite ratio in the rock. Consequently, the minor increase in the ore zone from the values in the unoxidized samples is due to an increase in calcite in the matrix of the brecciated samples. This conclusion is supported by comparing the 3-fold difference between the sparry dolomite (mean 135 ppm) and the sparry calcite veins (mean 305 ppm).

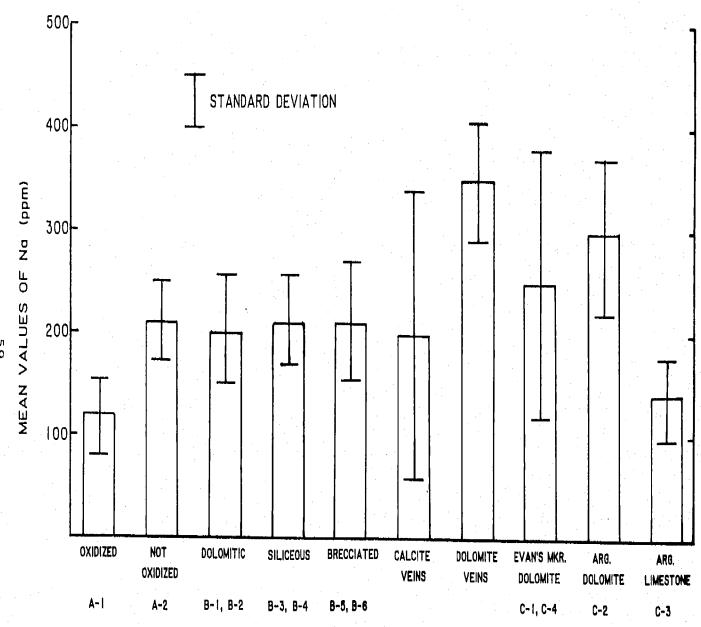
Veizer and Demovic (1974) reported a mean value of 110 ppm for 14 samples from dolomitic rocks with a solution breccia texture. They concluded that the strontium content of this group is more dependent on the nature of secondary alteration than on its original concentration and is very likely non-diagnostic. However, the similarity of their data to the values obtained in this study suggest that the genetic conditions that produce solution breccias may play a role in strontium contents of the secondary carbonate minerals.

In the Evan's Marker the argillaceous limestones (mean 330 ppm) have a greater strontium content that the argillaceous dolomites (mean 200 ppm). This is opposite from the trend for iron, manganese, and zinc. The concentration of strontium in the argillaceous dolomites is almost twice as large as all the other dolomitic samples.

Sodium

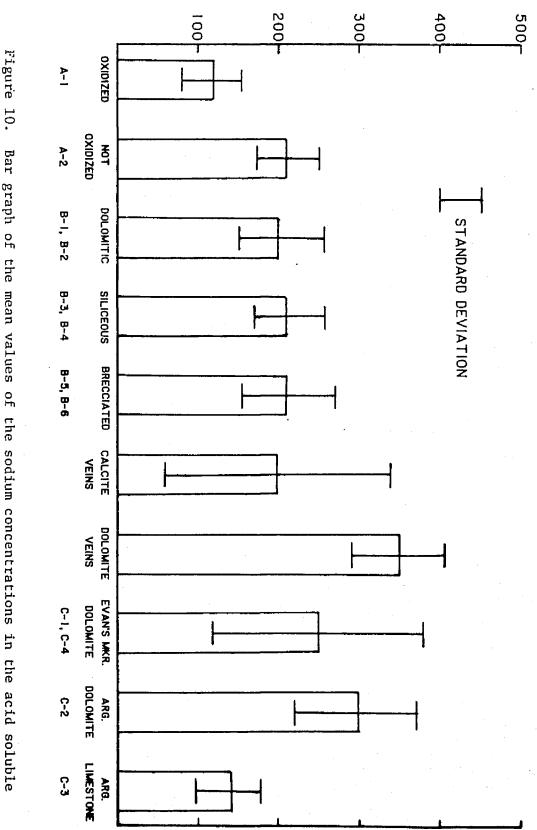
The trace element sodium presents difficulties in interpretation because sodium can occur in inclusions or substitute in the carbonate lattice, be leached from clay minerals, or be contamination. Because of these uncertainties, the sodium data is interpreted with reservation.

Above the ore zone, the sodium content of the oxidized samples (mean 120 ppm) is less than the unoxidized samples (mean 215 ppm), reversing the trend of the other trace elements (figure 10). Although the oxidized samples are enriched in iron, manganese, and strontium, it appears that sodium was leached from the carbonates in the meteoric-oxidizing environment. The samples from within the ore zone are characterized by a sodium content similar to the unoxidized samples. Sodium concentrations in the Evan's Marker are typical of the values in the other units with the exception of limestone (mean 140 ppm) which decreases slightly.





 Bar graph of the mean values of the sodium concentrations in the acid soluble fraction from the sampled horizons at the Friedensville zinc deposit.



Bar graph of the mean values of the sodium concentrations in the acid soluble fraction from the sampled horizons at the Friedensville zinc deposit.

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MEAN VALUES OF Na (ppm)

DISCUSSION

Nature of the Carbonates

The dolomitization of a limestone as a result of ore solution action is observed in several stratabound deposits, and some workers have proposed that the process of dolomitization has released metals for the ore mineralization. However, the process of dolomitization does not appear to be the source of metal ions for the formation of the Friedensville deposit. The clasts in the breccia at Friedensville consist of fine-grained laminated and mottled dolomite, characteristic of the surrounding host rock. This suggests that dolomitization occurred before brecciation preserving the original textural fabrics of the dolomite clasts. Furthermore, the dolomite in the Rickenbach Formation is laterally continuous throughout its mappable extent from the Lebanon Valley in Pennsylvania to the Delaware River (Hobson, 1963). It can be concluded that the ore formation of Friedensville is not related to any process of dolomitization of the country rock.

The contrast in the composition, textures, and structures between the rocks from the Evan's Marker and the remaining rock types indicates that these rocks were subjected to different conditions of formation. The irregularly tapering laminae and

sutured grain contacts in the samples in subgroup C-1 (Plate 8a and b) are typical of textures that Wanless (1979) and others have attributed to the process of pressure solution. Pressure solution is defined as the process whereby grains undergo dissolution about grain contacts due to strain in a crystal immersed in a solution. A film of residual noncarbonate material accumulates as a result of the dissolution of the carbonate grains. The irregularly tapering laminae visible in the sample in Plate 8 may be this film of residual noncarbonate material.

The thin clay seams in the argillaceous dolomites and limestones in subgroups C-2 and C-3 (see Plate 4) also are another indication that the Evan's Marker has been subjected to unusual conditions. The clay seams appear to be layers of insoluble material that has been concentrated by the large scale cannibalization of the carbonate rocks. These samples also exhibit streaking, shearing, and thinning of the clay layers, all textures common to rocks subjected to a localized stress. Wanless (1979) concluded that primary clay seams promote a lateral shear component during pressure solution. The shearing causes migration of stress-foci creating anastomosing secondary concentrations of insoluble residue like those present in the argillaceous samples.

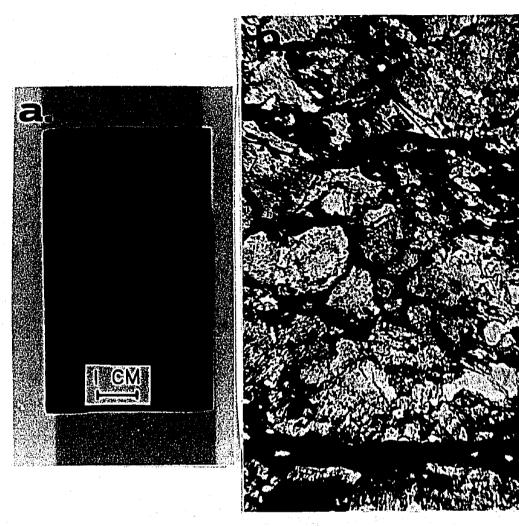


Plate 8. a)

- Etched dolomite from the Evan's Marker showing the irregular tapering laminae of insoluble residue. This texture has been attributed to the process of pressure solution.
- b) Photomicrograph of the irregular laminae of insoluble residue from the core in Plate 8a (plane polarized, 80X).

The experimental work of Chave and Schmaltz (1966) better defines the chemical processes that cause dissolution of calcite crystals as the result of increased stress conditions. They concluded that the energy added to a crystal during grinding increases its activity and solubility. Also, as the crystal becomes smaller, the surface energy of the solid increases, which increases the activity and solubility of that solid. Chave and Schmalz showed that a strained, fine-grained calcite crystal had an activity greater than 3 relative to a coarse, unstrained calcite crystal.

Dolomitization may even be a response to limestone dissolution. The coarse-grained secondary dolomite visible in the limestone shown in Plate 4b may be evidence for this mechanism of dolomitization. Taking this a step further, it is possible that the argillaceous dolomites may be a secondary dolomite formed from the dissolution process. The dolomite layers in these samples contain medium- to coarse-grained crystals and small pods of calcite, perhaps relics of a limestone precursor. It is possible that the increased values for the trace elements in the argillaceous dolomites are the result of the recrystallization from a limestone (see table 4).

The original lithology and texture of the Evan's Marker is unknown. It may be an isolated lens of clay-rich limestone or it

may represent the lateral thinning of the Stonehenge Formation. After compaction and cementation, a stress generated by lithostatic loading, tectonic movement, or even a decollement may have aided in the dissolution of the limestone. The result of the dissolution is a large scale thinning of the formation and a multitude of deformed textures in the rocks. The original thickness of the limestone is also unknown, but assuming the original insoluble residue was 10 weight percent, 5 to 7 volumes of limestone must be dissolved to reach the values of 77 weight percent insoluble present in the argillaceous dolomites.

The quartz and microcline veined dolomites in subgroup C-4 also exhibit unusual textures (see Plate 5). Although secondary quartz and microcline are common in stratabound deposits, the large crystal size of these minerals is unique to Friedensville. The genesis of these veins is unknown. They may be related to the ore mineralization or formed during another period. Perhaps these veins represent mineralized channelways that carried the ore solutions into the solution breccia chimney.

Nature of the Mineralization

Some investigators proposed that colloform textures, such as those displayed in Plate 7 resulted from deposition as a gel. However, Roedder (1968b) concluded that the colloform sphalerite assemblages indicate that the crystals grew directly as minute druses of continuously euhedral crystals projecting into an ore fluid. Based on Roedder's observations and the ore textures, it can be concluded that the sphalerite at Friedensville grew from nucleation in a supersaturated solution in the open voids of a breccia.

Elemental Analysis

The primary objective of this study was to define the role of the host rock in the genesis of the ore deposit. The first hypothesis involves a pregnant ore solution depositing metal sulfides with no contribution of metals from the host rock. In this model, the adjacent country rock may be enriched in metals. In support of this theory, Kennedy (1953) concluded that the abnormally high iron and zinc levels in the carbonates near the ore deposits in the Wisconsin lead-zinc district were due to the impregnation of the country rock from the ore solutions.

The second hypothesis is to have the host rock supply the metal ions through leaching or recrystallization of the dolomite rocks. As a barren solution moves toward the deposit, the metals in the host rock are leached by the solutions, creating a potential ore-forming fluid.

Chemical data in table 4 shows no pattern of depletion of trace elements in the carbonate minerals within the ore zone. This suggests that the host rock did not provide the metals for the ore deposit. Trace element levels are uniform between the brecciated and massive dolomites. There is also no zonal distribution of the elements laterally or horizontally within the sampled area. Furthermore, the dolomite in the ore zone does not appear to contain enough metals to form an ore deposit by surface leaching and there is no textural evidence to support leaching through recrystallization. It can be concluded that the lateral and overlying host rock did not contribute the metal ions for the ore deposition.

There is an increase in iron content in the brecciated samples, but as previously mentioned, this way be due to the iron-rich sparry matrix. The other trace elements show no enrichment in the ore zone. Although there is no detectable enrichment in trace elements around the ore zone, the colloform ore textures are strong evidence that pregnant solutions invaded the breccia zone and deposited sulfides. Ore deposition may have been relatively rapid in the realm of geologic time, not allowing

the wall rock to reach chemical equilibrium with the ore solution. If this is true, an enrichment such as Kennedy observed may be subtle and undetectable with the methods used in this study.

The chemical data in table 4 does show that the insoluble-rich carbonates in the Evan's Marker provide a proximal source of metallic ions for a mineralizing fluid. Iron is enriched 10-fold in the carbonate minerals of the argillaceous dolomites and 2- to 3-fold in subgroups C-1, C-2, and C-4 relative to the other samples. Manganese and zinc in the Evan's Marker argillaceous samples shows a 5-fold increase, and strontium a 2-fold increase. Lead is slightly enriched in the Evan's Marker.

With the increase in iron, manganese, and zinc concentrations in the argillaceous dolomites, there is a concomitant increase in the insoluble residue. If the limestone dissolved from stress, it is possible that the trace elements in the limestone precursor were concentrated in a recrystallized dolomite lattice. However, the trace element content in the original limestone is unknown, consequently the significance of this trend is difficult to establish. It will be assumed for this study that most of the metals were released from the calcite lattice during dissolution.

Model for the Genesis of the Friedensville Deposit

The initial event in the formation of the Friedensville deposit was the development of the solution-collapse breccia. This process began with the regional uplift and erosion of the pre-Jacksonburg formations along the Knox-Beekmantown unconformity (Callahan, 1968). Karstification and the development of a subsurface drainage system in the upper portion of the Beekmantown Group followed. The formation of the solution-collapse breccia completed the ground preparation for the ore deposition.

Next, an undefined stress event increased the solubility of the limestone and caused widespread dissolution in the Evan's Marker. This dissolution is evidenced by the thin layers of deformed insoluble residue. The dissolved limestone contributed ions for secondary dolomite formation within the Evan's Marker and released ions into the surrounding solutions. These zinc-rich fluids migrated up into the overlying porous regions, perhaps utilizing open channelways that are now marked by the coarse-grained quartz and microcline veins.

It is beyond the scope of this study to propose a definitive mechanism for ore deposition; however, the model lends itself to certain possibilities. As the zinc-rich fluids moved into the

porous bed, the decrease in pressure may have caused boiling and then cooling of the ore solutions, resulting in the deposition of the sulfide minerals. Another possible mechanism of deposition applicable to this model would be the mixing of a metal-rich solution from the Evan's Marker and a sulfide-rich solution in the breccia. Degassing of CO₂ from the ore solution as it enters the porous breccia may play a role in ore deposition.

The process of rapid boiling due to the drop in pressure is an especially attractive mechanism because the boiling would concentrate residual cations in the fluid phase. This process would account for the high salinities of 12 to 26 weight percent that Roedder (1967b) reports from the freezing of 7 fluid inclusions in the late stage calcite at Friedensville. Salinities in this range are common to many stratabound deposits.

In critically evaluating this model, the question arises as to whether dolomite, the principal accessory mineral in the breccia matrix, can form from fluids derived from the dissolution of limestone. An influx of magnesium ions of which there are several possible sources, is required for dolomite precipitation. The original limestone could have contained an average of 10 mole percent MgCO₃, typical of most limestones, which would be released during dissolution under stress. Magnesium also could have been supplied by local intersticial waters, organic

material, or from other limestone areas. Consequently, there appears to be an adequate supply of magnesium to form dolomite in the breccia cement without invoking special outside sources.

The work of Lovering (1969) shows that exotic, magnesium-rich fluids are not needed to precipitate dolomite in the temperature range of 100° to 150°C. This range of temperatures of formation has been well established through fluid inclusion investigations on stratabound ore deposits. Lovering gathered data from several sources and constructed a chart showing the stability relationships of calcite and dolomite in hydrothermal solutions as a function of temperature and Ca/Mg molar rations (figure 11). This chart illustrates that at Ca/Mg molar ratios in the range of 1 to 3, and temperatures in the range of 100 to 150°C, dolomite will crystallize from solution. As dolomite crystallization proceeds, the ratio will increase, and in the late stages of mineralization, the fluid will enter the calcite field causing calcite to precipitate. The projected path of crystallization for the solutions in the ore deposit is outlined in figure 11. Johannes (1966) reported that pressure differences had little to no effect on the position of the phase boundaries.

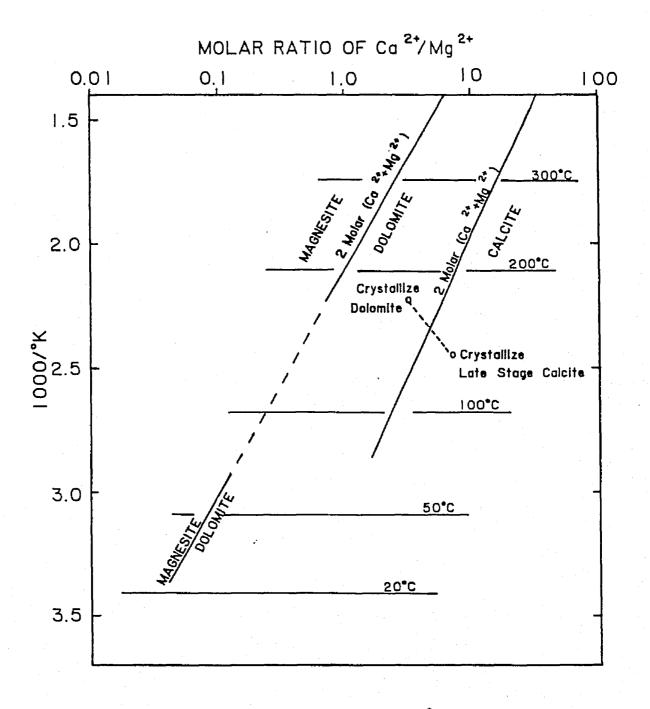


Figure 11.

The molar ratios of Ca²⁺/Mg²⁺ chloride solutions precipitating, replacing, or in equilibrium with calcite, dolomite, and magnesite, 10° to 450°C. Projected path of Friedensville gangue crystallization is shown by the dashed line (after Lovering, 1969). Another question that should be addressed is whether there is sufficient zinc available from the dissolution of the limestone in the Evan's Marker to produce this deposit. A simplified and conservative materials balance was performed and the details of the calculations are present in Appendix II. This materials balance showed that the 30 ppm zinc released from the dissolution of 20 meters of limestone in an area one square kilometer was enough to produce 1,800,000 metric tons of zinc. Considering the following; 1) the calculation was based on only one square kilometer, 2) zinc from approximately one volume of limestone was used in the calculation, and 3) the total production from the Old Hartman-New Hartman-Corral ore body from 1958 to 1975 was 430,000 metric tons of zinc (Smith, 1977), this model accounts for a total zinc tonnage much greater than the total production to date at the Friedensville deposit.

Application as a Prospecting Technique

The textural and geochemical trends outlined in this study provide information that can be utilized in future exploration of stratabound ore deposits. Searching for a halo of trace elements to locate an ore deposit appears to be an impracticable method for geochemical exploration. Alternatively, review of previously mapped subsurface regions may uncover thinly interbedded shale

and carbonate sequences, similar to the Evan's Marker. If these rocks show large scale dissolution textures, there may be associated sulfide mineralization in a proximal porous zone. Rich metal concentrations in these carbonates would provide further evidence for nearby mineralization.

The Woodbury Prospect, an isolated mineralized region in Bedford County, Pennsylvania may have a genesis similar to the model suggested here. Van Ness (1974) reported sphalerite and galena mineralization was found in a dolomite breccia in what is thought to be part of the Beekmantown Group. Drill hole data (figure 12) shows the presence of shale beds and shale partings in the dolomite beds approximately 75 meters below the main horizon of mineralization. Tectonic deformation and subsequent pressure solution may have contributed to the localization of the sulfides in this deposit.

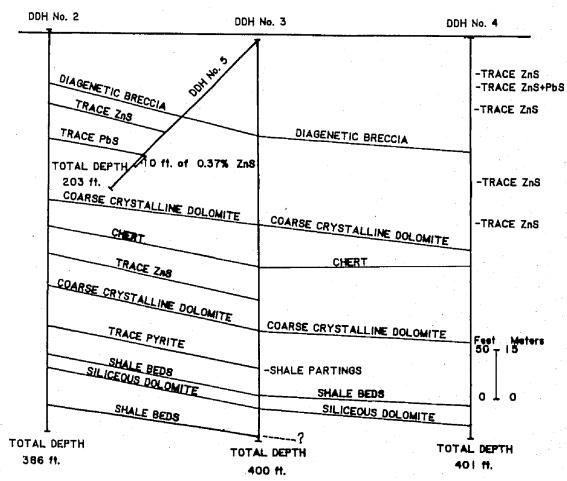


Figure 12. Data from diamond drill holes 2, 3, 4, and 5 from the Woodbury Prospect, Bedford County, Pennsylvania, showing shale beds and shale partings at the base of the drill holes (after van Ness, 1974).

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CONCLUSIONS

The primary objective of this study was to define the role of the host rock in the genesis of the Friedensville ore deposit. It can be concluded that the lateral and overlying host rock did not contribute the metal ions for mineralization through diffusion, leaching, or recrystallization of the carbonate host rock. Chemical data shows no pattern of depletion of trace elements in the carbonate minerals within the ore zone and the trace element levels are uniform between the brecciated and massive dolomites. There is no zonal distribution of elements laterally or horizontally within the sampled area. Furthermore, the dolomite in the ore zone does not contain enough metals to form an ore deposit by surface leaching. Textural evidence eliminates the possibility of the host contributing metal ions through recrystallization or dolomitization.

The colloform ore textures are strong evidence that pregnant solutions invaded the breccia zone and deposited sulfides. However, there is no detectable enrichment in trace elements around the ore zone. Ore deposition may have been relatively rapid in the realm of geologic time, not allowing the wall rock to reach chemical equilibrium with the ore solution. If there is an enrichment in the wall rock, it may be subtle and undetectable with the methods used in this study.

The chemical data does show that the insoluble-rich carbonates in the Evan's Marker provides a proximal source of metallic ions for a mineralizing fluid. Iron is enriched 10-fold in the carbonate minerals of the argillaceous dolomites and 2- to 3-fold in the remaining samples in the Evan's Marker relative to the overlying horizons. Manganese and zinc in the Evan's Marker argillaceous samples shows a 5-fold increase, and strontium a 2-fold increase. Lead is slightly enriched in the Evan's Marker.

The original lithology and textures of the Evan's Marker is unknown. It may be an isolated lens of clay-rich limestone or it may represent the lateral thinning of the Stonehenge Formation. Whatever the case may be, the clay seams and the irregular tapering laminae in the limestones and dolomites in the Evan's Marker are an indication that these rocks have been subjected to unusual conditions. These textures appear to be the result of a stress generated by lithostatic loading, tectonic movement, or even a decollement. This undefined stress event increased the solubility of the limestone causing widespread dissolution in the Evan's Marker. The dissolved limestone contributed ions for the secondary dolomite formation within the Evan's Marker and released ions into the surrounding solutions. These zinc-rich fluids migrated up into the overlying porous region and deposited the metal sulfides.

The textural and geochemical trends outlined in this study provide information that can be utilized in future exploration of stratabound ore deposits. Searching for a halo of trace elements to locate an ore deposit appears to be an impracticable method for geochemical exploration. Alternatively, review of previously mapped subsurface regions may uncover thinly interbedded shale and carbonate sequences, similar to the Evan's Marker. If these rocks show large scale dissolution textures, there may be associated sulfide mineralization in a proximal porous zone. Rich metal concentrations in these carbonates would provide further evidence for nearby mineralization.

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APPENDIX I

Sample Number	Weight % Insoluble Residue ^{*1}	Fe*2	Trac Mn ^{*3}	e Elemen Zn ^{*4}	nts in p Pb ^{*5}	ppm Sr ^{*6}	*7 Na
<u>Drill Hole Nu</u>	mber 16						
708	10.4	770	75	155	30	120	260
733	12.9	700	65	190	55	115	170
738	11.7	465	70	180	35	150	195
744	11.6	990	70	360	45	90	170
755	14.5	680	80	510	35	140	171
758 Thc.M. ^{*8}	18.0	1040	100	510	30	230	225
762	14.1	1270	90	25	40	90	165
774	21.1	1510	90	95	45	145	140
779	31.6	2410	150	1585	170	195.	140
.784	6.4	2060	85	240	35	170	200
817	24.4	1560	100	195	30	125	160
860 E.M. ^{*8}	24.5	2145	125	125	25	165	185
900 E.M.	77.0	16,690	435	1.60	1.5	225	245

INSOLUBLE AND TRACE ELEMENT VALUES FOR EACH SAMPLE

*1 Average reproducibility was 5.0 percent for each value.
*2 Average reproducibility was 15.0 percent for each value.
*3 Average reproducibility was 8.0 percent for each value.
*4 Average reproducibility was 20.0 percent for each value.
*5 Average reproducibility was 20.0 percent for each value.
*6 Average reproducibility was 15.0 percent for each value.
*7 Average reproducibility was 20.0 percent for each value.
*8 Thc.M. is Trihartco Marker. E.M. is Evan's Marker.

Sample	Weight % Insoluble		Trace	Elements	in	ppm	
Number	Residue	Fe	Mn	Zn	Рb	Sr	Na
Drill Hole Nu	umber 25						
1343	4.5	770	70	65	40	80	275
1368	11.1	710	70	750	30	110	330
1373	3.9	335	65	85	30	120	330
1378	4.7	660	65	50	30	110	375
1390	19.2	670	75	1160	20	115	200
1393 Thc.M.	10.2	770	95	75	30	135	145
1397	8.7	690	75	10	25	120	210
1408	8.2	565	55	10	25	125	220
1413	6.5	525	60	15	25	115	235
1418	9.3 、	1170	80	10	20	110	160
1443	7.8	770	60	810	30	120	255
1598 E.M.	34.4	5275	370	30	40	110	105
Drill Hole Nu	umber 27						
1018	8.5	450	60	90	25	125	235
1042	3.0	570	65	125	30	90	155
1047	11.7	675	60	50	25	105	190
1052	20.0	825	70	70	25	110	190
1064	18.3	845	70	10	25	120	175
1068 Thc.M.	16.3	1170	95	70	25	150	185
1071	16.1	1395	80	10	25	115	195
1083	19.2	1450	95	15	35	85	230
1088	15.5	1705	100	25	20	115	280
1093	4.6	860	70	70	25	90	190
1118	28.4	1925	102	42	20	100	215
1190 E.M.	6.1	1755	115	10	20	120	165

Sample	Weight % Insoluble		Trace	Elements	in	ppm	
Number	Residue	Fe	Mn	Zn	РЬ	Sr	Na
Drill Hole Nur	nber 28						
725	4.6	505	65	1.0	50	1.05	195
745	13.1	760	80	380	45	130	245
754	3.2	580	70	20	50	125	285
759	7.2	755	95	400	50	1.30	265
771	13.9	825	110	45	35	115	250
774 Thc.M.	11.6	1130	105	325	45	155	260
778	13.5	1940	100	655	50	125	200
790	6.6	920	75	115	50	145	240
795	17.4	2060	95	15	50	160	215
800	8.9	1405	90	1.5	50	155	160
825	4.5	965	95	10	50	95	275
900 E.M.	29.5	4965	145	10	45	115	265
Drill Hole Nur	nber 29						
937	8.6	630	55	25	25	90	190
961	17.2	620	105	10	40	85	205
966	11.1	900	80	350	35	90	200
971	9.1	825	70	415	40	100	195
983	14.1	1235	95	690	40	120	200
987 Thc.M.	11.7	700	80	20	45	125	140
990	9.8	875	100	30	40	120	180
1002	12.8	895	110	905	45	150	190
1009	11.5	1435	100	265	40	160	155
1012	14.1	1480	100	260	40	160	190
1037	11.1	1270	100	40	35	130	130

Sample	Weight % Insoluble		Trace	Elements	in	ppm	
Number	Residue	Fe	Mn	Zn	Рb	Sr	Na
Drill Hole Nu	umber 30						
1172	5.8	605	65	405	35	85	240
1197	9.0	1625	70	15	45	70	220
1202	14.8	1105	70	475	40	80	250
1219	9.5	630	60	15	50	100	210
1222 Thc.M.	5.8	975	80	15	50	75	190
1226	10.6	975	80	10	35	100	135
1238	10.6	895	75	15	30	85	225
1243	18.6	1425	100	35	35	110	160
1248	13.3	1305	95	90	35	90	175
1272	9.1	990	85	20	35	60	240
1370	54.0	7585	475	35	65	350	130
Drill Hole Nu	umber 31						
886	2.8	290	55	10	35	75	155
911	5.7	445	75	80	35	100	295
915	21.7	665	80	10	40	185	115
933	20.3	1315	90	10	45	115	180
936 Thc.M.	14.4	1215	85	30	40	105	180
940	24.2	1505	85	1.5	40	150	100
952	17.9	730	110	15	35	110	190
957	5.2	680	70	5	25	80	200
962	3.3	890	70	5	35	120	155
987	18.9	1925	90	60	55	135	195
1140 E.M.	39.3	3710	1.90	15	45	145	215

Sample	Weight % Insoluble		Trace	Elements	in	ppm	
Number	Residue	Fe	Mn	Zn	Рb	Sr	Na
Drill Hole Num	nber 44	,					
431	12.2	570	80	380	40	115	290
456	10.0	610	75	45	40	105	21.5
463	17.3	985	85	140	40	100	130
467	23.1	1175	85	640	45	95	195
478	7.5	630	85	515	40	110	155
481 Thc.M.	17.7	630	95	45	45	105	95
484	21.3	780	85	870	45	.90	120
496	23.8	1630	110	60	45	110	1.05
501	17.7	830	75	965	25	80	210
508	39.6	21.05	115	1335	25	85	205
531	30.7	2575	125	750	50	1.30	205
631	25.1	3265	210	50	55	110	140
Drill Hole Num	iber 77				•		
190	15.0	5505	185	25	40	135	150
330	17.3	2320	210	25	40	100	120
362	12.7	1810	100	20	40	135	130
455	15.3	2950	190	10	40	135	115
500	22.0	3270	350	10	40	150	130
600	9.6	2985	175	5	35	180	165
650	39.6	3475	295	15	45	125	170
700	30.0	2785	1.05	10	45	215	140
750	14.1	1535	100	10	40	150	115
802	18.4	590	85	10	40	85	240
852	18.7	765	75	20	40	180	240

Sample Number	Weight % Insoluble Residue	Fe	Trace Mn	Eleme Zn	nts in Pb	ppm Sr	Na
Drill Hole Nu			· · · ·				
<u> </u>				10		0.5	015
959	7.8	780	90	10	35	85	21.5
1000	8.3	1095	105	10	30	80	145
1025	33.4	10,270	325	60	35	70	240
1100	16.0	2475	130	10	35	110	265
1176	13.5	880	75	100	140	110	255
1199	14.1	1200	90	710	50	100	235
1204	6.4	705	1.00	115	45	95	235
1210	16.8	1515	85	40	60	100	235
1221	11.2	880	60	10	50	80	240
1224 Thc.M.	13.5	1355	75	10	45	105	155
1.228	22.3	1710	80	10	50	100	195
1245	12.1	2140	105	5	45	100	165
1250	33.6	3300	95	15	50	100	245
1275	12.7	1500	80	10	45	105	200
1305 E.M.	13.1	1450	95	5	45	100	375
Drill Hole N	umber 115		· · · ·				
730	24.6	1470	100	45	45	100	185
756	11.0	1145	100	390	35	120	225
795	30.0	1585	85	850	40	115	320
800	17.8	950	70	590	35	130	215
805	3.8	435	60	40	35	105	235
81.8	13.8	740	65	15	35	115	245
820	8.3	740	55	10	. 30	100	220
823	9.9	845	65	60	30	120	185

Sample Number	Weight % Insoluble Residue	Fe	Trace Mn	Elemen Zn	ts in Pb	ppm Sr	Na
Drill Hole N	umber 115 (co	<u>nt.)</u>					
840	33.9	1785	95	40	50	125	135
845	11.7	625	75	600	50	155	200
871	22.5	2075	95	65	45	145	175
1000 E.M.	80.6	17,835	465	155	140	230	350
<u>Drill Hole N</u>	umber 116						
100	17.2	4105	165	25	45	125	85
150	36.1	2675	325	15	115	150	65
200	19.2	735	65	10	40	165	105
240	9.7	865	70	10	50	140	210
275	17.8	880	75	10	45	95	110
300	9.6	665	70	5	40	100	60
350	20.4	910	80	10	45	80	215
400	11.0	890	65	30	42	80	165
425	13.6	540	75	10	45	80	220
475	4.9	500	60	10	40	80	135
508	13.6	640	80	35	45	90	190
536	14.4	680	75	10	45	80	215
541	24.4	1270	90	55	40	80	145
544	13.7	595	75	20	35	70	250
558	22.3	2045	80	175	40	100	190
561 Thc.M.	15.1	1470	90	585	55	75	250
568	7.9	535	70	15	50	60	280
577	19.5	1330	95	65	30	95	170
582	4.7	1375	1.05	20	30	70	190

APPENDIX	Ι	(cont.)	
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Sample	Weight % Insoluble		Trace	Elements	in	ppm	
Number	Residue	Fe	Mn	Zn	Pb	Sr	Na
Drill Hole Nu	ımber 116 (con	<u>t.)</u>		· · · · · ·		<u></u>	<u>, a theory</u>
587	19.6	2200	110	155	35	95	250
608	69.7	4686	210	1205	85	135	240
713 E.M.	40.7	3025	60	1.5	55	· 85	315
Drill Hole Nu	umber 188			1 ·			
1460	17.0	600	80	405	50	90	195
1465	10.6	1265	100	1045	40	85	295
1495	4.3	510	75	35	30	75	245
1510	11.9	895	75	110	40	90	215
1525	13.0	875	70	15	35	. 90	275
1535	12.8	885	85	70	50	85	295
1560	2.4	1155	90	5	55	1.05	280
1660 E.M.	68.9	8425	140	40	135	145	495
Drill Hole Nu	umber 191						
1700	3.6	600	80	20	40	90	295
1725	3.5	475	70	30	40	85	285
1735	16.7	880	110	565	45	95	245
1750	5.1	1385	115	130	40	95	380
1753	8.3	1315	115	425	40	95	190
1765	20.5	1590	135	70	40	95	320
1775	8.8	890	85	20	45	80	250
1800	16.8	1020	85	5	50	100	225
1910 E.M.	34.9	5070	290	30	50	220	180

Sample Number	Weight % Insoluble Residue	Fe	Trace Mn	Element Zn	s in Pb	ppm Sr	Na
Drill Hole N	umber 192	<u> </u>	<u> </u>				
2113	17.4	615	105	585	55	90	1.45
2135	8.0	500	60	50	35	80	125
2145	17.2	535	70	485	55	100	125
2161	9.8	430	75	445	35	90	315
2167	11.7	780	70	415	45	80	280
2175	13.1	575	75	75	45	100	280
2186	20.6	1180	80	30	45	105	140
2210	29.0	860	95	1410	50	100	135
2300 E.M.	26.4	3695	115	240	55	110	80
<u>Sparry calci</u>	te vein fill	ing	• • •				
25-1373		1350	45	385	125	360	90
25-1393		1105	40	15	50	290	90
30-1238	·	6280	105	10	35	325	380
116-577	· · ·	895	70	30	35	405	120
188-1525		1445	70	10	30	260	665
130177 ^{*9}		3855	75	235	70	305	315
<u>Sparry dolom</u>	ite vein fil	ling			•		
28-759		5430	210	360	55	120	375
188-1485		1505	105	15	35	205	270
191-1735		11,500	250	35	50	150	325
191-1753		21,300	465	2510	30	95	385
NJ-8 ^{*9}		4960	120	135	45	105	395

*9 Hand specimens from Friedensville mine. Exact location is unknown.

APPENDIX II

CALCULATION OF THE MATERIALS BALANCE OF ZINC IN THE EVAN'S MARKER AVAILABLE FOR MINERALIZATION

The total amount of zinc in a volume of rock equivalent to a square kilometer times 20 meters (approximate thickness of 1 volume of the limestone in the Evan's Marker) is calculated as follows:

100,000 cm x 100,000 cm x 2000 cm = 2.0×10^{13} (cc) cm³

 2.0×10^{13} cc = 1 volume of limestone.

Assume a density of 3.0 gm/cc for limestone rock and a value of 30 mg/kg for the zinc concentration.

$$3.0 \text{ gm/cc} \ge 2.0 \ge 10^{13} \text{ cc} = 6.0 \ge 10^{13} \text{ gm}$$

$$\frac{6.0 \times 10^{13} \text{ gm}}{100 \text{ gm/kg}} = 6.0 \times 10^{10} \text{ kg}$$

6.0 x 10¹⁰ kg x .030 gm/kg Zn = 1.8 x 10⁹ gm zinc or
1.8 x 10⁶ metric tons zinc.

Robert William Keating was born on December 30, 1959 in Darby, Pennsylvania. He received his primary education in the Delaware County area of Pennsylvania. He graduated from Cardinal O'Hara High School in 1977. In September of 1977 he entered Lehigh University as an accounting major, but after his sophomore year he changed to geological sciences. In January of 1982 he received his B.S. in Geological Sciences with honors. He was a research assistant to Professor D. R. Simpson from 1981-1983. He received his M.S. in Geological Sciences in October of 1983. And the rest is history.

VITA

