THE DISTRIBUTION AND COMPOSITION OF SULFIDE MINERALS AT BALMAT, NEW YORK

A manuscript submitted for publication

by

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In Partial Fulfillment of the Requirements

For the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1960

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ABSTRACT

In the Balmat area, northern New York, tabular deposits of sulfide minerals are found parallel to the layering in folded, siliceous magnesian marbles of a metamorphic complex commonly referred to as the Pre-Cambrian Grenville series. Sphalerite, pyrite, and locally, pyrrhotite and galena have replaced the carbonate minerals in parts of the marble units. The contacts between ore and marble are, in general, diffused over distances of inches to feet. Access to the ore is provided through the Balmat No. 2 and No. 3 mines.

The isotopic composition of lead from primary galena is homogeneous within an individual mine. The model age of this lead is in agreement with the age of the mineralization determined by other means -- about a billion years. The isotopic composition of lead and the concentrations of lead and uranium in two samples of marble were investigated. The isotopic composition of the leads in the marble is not homogeneous. Calculations indicate that the isotopic composition of lead in the marble was probably not homogeneous a billion years ago. Unless the isotopic composition of lead in the ores is a homogeneous mixture of lead from an isotopically inhomogeneous source, it is doubtful that the lead in the ores was derived from the surrounding marbles.

Cobalt and nickel concentrations in pyrite from grains disseminated in the metasedimentary rocks away from the ore bodies are greater than 200 ppm. Most samples of pyrite from the ore bodies of the No. 2 and No. 3 mines contain less than 50 ppm each of cobalt and nickel. From these differences in concentrations, the author believes that it is unlikely that the pyrite of the ores is genetically related to the pyrite in

the metasedimentary rocks.

Studies of textural relations suggest that pyrrhotite formed after most of the sphalerite, which in turn formed after most of the pyrite in the ore bodies. By use of the experimentally determined systems, FeS-ZnS-S and FeS-FeS_2, it is inferred from the amounts of iron in sphalerite and sulfur in pyrrhotite that the bulk of the sulfide minerals in the No. 2 mine formed above 320°C. This estimation assumes a total pressure of 3 kilobars. The absolute temperature of formation of pyrrhotite indicated by the FeS-ZnS-S system is about 150° higher than that indicated by the FeS-FeS_2 system.

The concentrations of individual minor elements in sphalerite and pyrite range considerably among specimens of the same sulfide mineral from the same level and ore body. An exception is cadmium in sphalerite which has a narrow concentration range around 1400 ppm in both the No. 2 and No. 3 mines. The ratio of the concentrations of minor elements between sphalerite-pyrite pairs varies considerably also. This variation probably indicates that the minor elements did not achieve a well-developed equilibrium distribution between pyrite and sphalerite during the formation of the ores.

INTRODUCTION

The Balmat-Edwards mining district, in the northern part of the state of New York, is well known for its output of sphalerite ore (Brown and Engel, 1956). It also has yielded large amounts of commercial talc, and is sometimes referred to as the Gouverneur talc district (Engel, 1949) after Gouverneur, the largest village nearby. The major rocks of the district represent a complex of folded siliceous magnesian marbles and gneisses injected by synkinematic granites. The rocks of the metamorphic complex are Precambrian in age, and seem to be lateral extensions of the so-called Grenville series of southeastern Ontario and western Quebec (Engel and Engel, 1953a). They are overlain with angular unconformity by the unmetamorphosed Potsdam sandstone (Brown and Engel, 1956). On the basis of fossils found in the upper parts of the formation, the age of the Potsdam sandstone is felt to be Upper Cambrian by Cushing (1905) and Walcott (1923).

In the Balmat area, at the southwest end of the district, sphalerite, pyrite, and locally pyrrhotite and galena replaced the carbonate minerals in the marble units. There is little or no replacement of the associated quartz and calc-silicate minerals. Sphalerite and pyrite are the major sulfide minerals in the ore bodies, which also contain primary pyrrhotite, galena, marcasite, anhydrite, barite, and secondary (supergene ?) minerals--magnetite, hematite, white sphalerite, chalcopyrite, and chlorite (Brown, 1936a, 1936b). The secondary minerals are chiefly restricted to brecciated parts of the primary sulfide ore bodies. Pyrrhotite is accompanied by trace amounts of chalcopyrite, and these minerals are rarely found with either barite and anhydrite or the secondary minerals.

The present study is concerned with the concentrations of minor elements in the sulfide minerals and with the isotopic composition of lead in galena of the ore bodies in the No. 2 and No. 3 mines at Balmat. Pyrite, disseminated in marble and pyritic schist surrounding the ore bodies, was analyzed for minor elements, and its composition compared with that of pyrite in the ore bodies. Analyses were also made of the isotopic composition of lead in two samples of marble enveloping the ore, and the results were compared with the values found for the isotopes of lead in galena of the ore bodies. These studies, which were correlated with the spatial distribution of the minerals, were undertaken in an effort to provide information concerning: 1) the source of the metals found in the sulfide minerals, 2) the temperatures of formation of the sulfide minerals, and 3) the distribution of minor elements in ore minerals.

Acknowledgments. The writer is indebted to Dr. A. E. J. Engel of the California Institute of Technology under whose guidance this investigation was carried out, to Dr. J. S. Brown of the St. Joseph Lead Company who gave much advice on the geology of the area studied, and to Dr. C. C. Patterson of the California Institute of Technology who aided and encouraged the study of the isotopes of lead.

Financial support for the work was obtained chiefly through a Kennecott Copper Company Fellowship during the years 1957-58 and

1958-59. The Pan American Petroleum Company provided a fellowship for the year 1956-57.

The writer is greatly indebted to the St. Joseph Lead Company for making available geologic maps of the No. 2 and No. 3 mines at Balmat, and more specifically to Dr. John S. Brown, Mr. N. H. Donald, Mr. Severn P. Brown, Mr. David B. Dill, and Mr. Edward R. Lea who mapped the geology in the mines for the St. Joseph Lead Company. Thanks also are due to Dr. Arthur Rose, Dr. James Noble, and Dr. Barclay Kamb for their stimulating discussions during the progress of the research and to Dr. R. H. Jahns, Dr. L. T. Silver, Dr. G. J. Wasserburg, and Dr. Samuel Epstein for their critical reading and constructive criticism of the manuscript. The polished sections and thin sections for this study were prepared by Mr. Rudolph von Huene.

GEOLOGIC SETTING

Balmat-Edwards District

The areal geology of the Balmat-Edwards district has been described in detail by Brown and Engel (1956), whose identifications and designations of rock units were used throughout this study. A geologic map of the Balmat area, simplified from Brown and Engel (1956), is shown herein as Figure 1.

The sulfide deposits of the Balmat-Edwards district are emplaced in layers of marble which lie stratigraphically above a thick paragneiss (Engel and Engel, 1953b, 1958). Both marble and gneiss are complexly folded, metamorphosed, and injected by synkinematic granites and pegmatites. The major structural feature in the Balmat area is the southwestern nose of a refolded, isoclinal syncline, overturned to the southeast.

The primary sulfide minerals in the ore bodies occur mainly as replacements of dolomite and calcite. Metamorphic silicates -- quartz, diopside, tremolite, and anthophyllite -- persist in the ore as grains and masses. In brecciated parts of the ore, hematite, magnetite, white sphalerite, galena, and chalcopyrite occur as secondary (supergene ?) minerals accompanied by much chlorite (Brown, 1936b).

The sulfides are in tabular ore bodies which have their long dimensions parallel to the layering of the enclosing metasedimentary rocks. The contacts between the sphalerite ore bodies and the country rock are diffused over distances of inches to feet except where the country rock is a rusty marble unit designated rm 15 (Fig. 1) or a talc-tremolite schist unit designated ts 13. Scattered grains of sulfides are present in both marble and schist units as far as 30 miles northeast of Balmat (Engel and Engel, 1958, p. 1385). In addition, these investigators report local small veins and disseminated grains of pyrite and pyrrhotite with traces of sphalerite and galena in the major unit of paragneiss (qbg of Brown and Engel, 1956).

Uraninite, zircon, and biotite from pegmatites and granite gneisses intrusive into the Grenville-like rocks in a large semi-circular area to the west of Balmat have been age-dated by several isotopic analytical techniques (Aldrich, et al., 1957, p. 104; Davis, et al., 1958, p. 178; also see Cumming, et al., 1955 for a compilation of ages). Most of the dates indicate that a significant event or events occurred in the range 950-1200 million years ago, with much of the data suggesting a value near 1050 million years. Recent potassium-argon measurements by Dr. G. J. Wasserburg (personal communication) on phlogopite from marble in the Balducci quarry, about nine miles north of Balmat, indicates that this mineral crystallized 1000 to 1200 million years ago.

This writer believes that the date, 1050 ± 150 million years ago, represents the most recent episode of severe metamorphism in a large area that includes Balmat.

No. 2 mine

The sulfide minerals in the No. 2 mine are principally a replacement of carbonate minerals contained entirely within the calc-silicate marble unit cdm 14 (Fig. 2). The mineralized rock was divided into six ore bodies on the basis of geography, abundances of macroscopic minerals, and type of wall rock, for use in the study of minor elements. The samples for analysis were taken from three levels in the central, lower, and lower-west ore bodies and from one level in the upper-Streeter and lower-Streeter ore bodies (Fig. 2).

The central ore body is associated with the flattened nose of a large drag fold on the south flank of the major syncline of the area. This ore body is characterized by abundant quartz and calcium-magnesium silicates in the ore. Pyrrhotite is irregularly distributed. Pyrite is more abundant than sphalerite. The wall rocks are subunits of the cdm 14 marble unit. The main mass of pyrrhotite in the mine occurs with discrete grains of chalcopyrite slightly offset to the east of but overlapping with the main mass of the sphalerite and pyrite of the central ore body. This tabular ore body trends north, dips vertically, and plunges northward at angles of 30-35° (Fig. 2). Sphalerite constitutes about 15 percent of the ore.

The lower-west ore body is on the southern limb of the same drag fold as the central ore body. The lower-west ore body is characterized by massive sphalerite. Small amounts of barite are present. The talc-tremolite ts 13 unit is the footwall and hanging wall of the ore in many places (Fig. 2).

The lower ore body is northeast of the lower-west ore body. The lower ore body contains more galena than any other ore body. Galena forms about one percent of the ore. Barite and anhydrite are irregularly distributed. Pyrrhotite is restricted to areas "A" and "B" as shown in Fig. 2. Sphalerite, pyrite, and silicates are about equally distributed. The wallrocks are subunits of the cdm 14 unit near the base of the unit. This ore body dips at about 30-35° with a northerly component to the dip.

The upper-Streeter ore body contains sphalerite and pyrite in about equal amounts. Pyrrhotite is absent. The rusty marble rm 15 unit is the hanging wall. The lower-Streeter ore body contains some pyrrhotite along with pyrite and sphalerite disseminated in silicates. The talc-tremolite ts 13 unit is the footwall. The Streeter ore bodies trend about N40°E and dip about 30-35°NW.

No obvious wall-rock alteration products are associated with the ore of the No. 2 mine. Secondary mineralization is localized in the lower and lower-west ore bodies.

No. 3 mine

The sulfide minerals in the No. 3 mine are principally replacements of carbonate minerals in the fetid, graphitic marble unit fd 7 and the calc-silicate marble units sm 6 and sm 8. The samples from the No. 3 mine were taken from the upper- and lower-Gleason and the Loomis ore bodies. The Gleason ore bodies follow a set of drag folds that plunge about 25° NNE (E. R. Lea, personal communication) and are contained in the sm 6 unit. The Loomis ore body is associated with a structural terrace at the contact of unit fd 7 with unit sm 8.

The ore bodies of the No. 3 mine are characterized by sphalerite with a low content of iron, about one percent pyrite in the ore, general absence of galena, and absence of pyrrhotite and marcasite. The ore bodies are distinguished from one another by stratigraphic position rather than by mineralogy. Secondary mineralization is found in the upper-Gleason ore body. No obvious wall-rock alteration minerals are associated with the Gleason ore bodies. Around the Loomis ore body, the medium-gray, graphitic fd 7 marble is bleached white in a zone as much as eight inches thick; this may be a wall-rock alteration effect (E. R. Lea, personal communication).

AGE AND PARAGENETIC SEQUENCE

In order to deduce geologic implications from the data obtained through the compositional studies, it is necessary to know the order of formation of the sulfide minerals. This section is concerned with the absolute time of emplacement of the ores into the marbles and the paragenesis of the minerals in the ore bodies. For this purpose, the author has examined the textural relations of minerals in about 250 polished sections and 30 thin sections. A summary of the conclusions on the paragenesis of the ores as derived from the work of the author, of Engel and Engel (1958), and of Brown (1936a, 1936b, 1947) is given in Fig. 3. Only those textural relationships of minerals that are pertinent to this study will be discussed below.

The minerals that were examined in this study are the silicates--diopside, tremolite, serpentine, talc, and chlorite; the sulfides--pyrite, sphalerite, galena, pyrrhotite, chalcopyrite, and marcasite; the sulfates--anhydrite and barite; the oxides--magnetite and hematite; and the carbonates--dolomite and calcite.

It is clear that the sulfide minerals were formed in the calc-silicate dolomitic marbles subsequent to the development of diopside and tremolite. Sphalerite in particular grew around and filled cracks in grains of diopside (see Brown, 1947, Plate 8, p. 544). Almost all the pyrite in the ore bodies was formed earlier than sphalerite. In perhaps 10 percent of the pyrite grains, sphalerite filled cracks in and replaced the pyrite. The cracks in pyrite filled with sphalerite suggest that the pyrite was microbrecciated before the sphalerite was introduced into the area. The writer's observations on the relations of pyrite and sphalerite are in accord with those of Brown (1936a, p. 249).

Pyrrhotite also fills cracks in pyrite, and hence evidently was formed later than the pyrite. It is thought that most of the pyrrhotite formed after sphalerite was emplaced in the No. 2 mine, but the evidence is only fair. In rare occurrences, pyrrhotite forms "veinlets" in sphalerite. Pyrrhotite nowhere forms an "emulsion" texture suggestive of unmixing of FeS from sphalerite, but the "emulsion" texture is a common feature of chalcopyrite in sphalerite at Balmat. Also, there is no suggestion that sphalerite fills fractures or veins in pyrrhotite. The most common occurrence of pyrrhotite in the No. 2 mine is with chalcopyrite in masses offset to the east of but overlapping with the central ore body. This chalcopyrite fills fractures in pyrrhotite that continue through grains of sphalerite, which indicates that this chalcopyrite is later than the adjacent sphalerite.

The close association of pyrrhotite with chalcopyrite may indicate that the pyrrhotite and the chalcopyrite are younger than much of the sphalerite. Sphalerite is known to dissolve iron. It may be that the pyrrhotite that filled cracks in sphalerite was dissolved by the sphalerite. Brown did not indicate a relationship between sphalerite and pyrrhotite, but the relationship of pyrrhotite and chalcopyrite reported here is in accord with his view (Brown, 1936a, p. 252).

Euhedral pyrite is not commonly observed at Balmat except for pyrite enclosed in pyrrhotite. This feature might be interpreted in several ways and will be discussed further in a discussion below on the composition of pyrrhotite. Some of the pyrrhotite found in the No. 2 mine has been partially or completely altered to marcasite. In some cases marcasite is found at the intergranular boundaries of grains of sphalerite. Thus marcasite also is thought to have formed later than sphalerite in the No. 2 mine. The position of marcasite in the paragenetic sequence is tentatively placed with barite and anhydrite on the basis of relative chemical stabilities. Marcasite is previously undescribed at Balmat.

During the course of the examination of the polished sections, a common microscopic relation observed between galena and sphalerite was that of sphalerite aligned along the cubic cleavage of galena. The feature suggests that some of the galena in the No. 2 mine formed before the adjacent sphalerite. Much galena, however, follows the intergranular boundaries of sphalerite. There is fair evidence, then, that the period of formation of galena overlapped that of sphalerite. Galena was observed in only two of the polished sections examined of the ores from the No. 3 mine. In each case the galena was either along the intergranular boundaries of or in veins through sphalerite.

A very striking textural relationship is that between galena and talc. Talc is found to markedly penetrate galena along cleavages. It is clear that talc in the mining areas formed later than galena.

The inferred sequence of formation of diopside and tremolite, then the sulfides, followed by talc and serpentine permits a good estimate of the absolute time of formation of the ores. Engel and Engel (1958,

p. 1385) report that the paragenesis of the minerals in the marbles of the Balmat-Edwards district during the late stages of the most recent episode of severe metamorphism was:

diopside → tremolite → anthophyllite → serpentine → talc

It appears that the sulfide minerals were formed during the retrograde metamorphism of the rocks around Balmat, as stated by Engel and Engel (1958, p. 1385).

The lengths of time involved in the retrograde metamorphism are not known. Also, the effects of retrograde metamorphism on the minerals containing the radio-active elements and their decay products are not known. However, the concordancy of much of the data on the time of metamorphism suggests that the effects of retrograde metamorphism, if significant, were relatively short lived. Thus, the author believes that the age of 1050 ± 150 million years also is the age of the formation of the primary ore at Balmat, as well as the time of the most recent severe metamorphism of the rocks in the area.

SAMPLING PROCEDURE AND SAMPLE PREPARATION

A representative example of the distribution of sulfide samples is given in Fig. 2 for the No. 2 mine. The locations of surface samples are given in Fig. 1. Samples of sphalerite were chosen primarily to delineate the distribution of iron in sphalerite both horizontally and down the plunge of the ore bodies. In order to find whether several distinct populations of ore were formed in any one mine, the ore zone was divided into ore bodies on the bases of macroscopic mineralogy and on the lithology of the wall rocks. Sphalerite and pyrite from these ore bodies were analyzed for the concentrations of minor elements to determine whether the ore bodies could be distinguished on the basis of minor and trace elements in the minerals. An attempt was made to analyze at least four samples from each level of each ore body studied. Samples of galena were chosen for isotopic analysis of lead to test the homogeneity of lead isotopes in and between ore bodies. Samples of marble taken from a marble unit associated with a sphalerite ore body without galena were used for an isotopic study of the constituent lead.

The first 25 samples of sphalerite were obtained by crushing the specimens in a large agate mortar and handpicking twice under 3X magnification those grains retained on a 40 mesh brass-screen. These samples were used solely for the study of the concentrations of iron. Subsequently 13 of the 25 specimens were resampled by the method outlined below and reanalyzed for iron because the initial values appeared to be too high. In comparison with the original data, 9 of the 13 reruns were in good agreement, while the other four were indicated to contain about two percent less FeS in the sphalerite than the original samples.

Polished sections were made of nearly all other specimens of ore. Sphalerite, pyrite, and pyrrhotite samples were collected from the polished sections by drilling 5 to 20 milligrams of mineral powder with a portable dental drill using an S. S. White No. 2 carbide burr. Drilling of the polished section was observed under 80 power magnification on the stage of a metallographic microscope with both vertical and strong-oblique illumination. The color of the sphalerite powder is very sensitive to contamination from pyrite, galena, and magnetite (which turn the brownish powder black) or from the carbonates and silicates (which turn the brownish powder white). The pyrite samples collected by the drilling method are thought to be at least 95 percent pure. The sphalerite samples are thought to be about 98 percent pure or better, with most of the contamination coming from silicates.

Calcite samples from marble were obtained by prying individual grains of translucent calcite from the freshly broken surface of a hand specimen of rock. Pyrite samples from dolomitic marble were obtained in the same manner as calcite, but, following the collection of the grains, the pyrite was crushed in an agate mortar to a size of about one-half millimeter or less. Then individual fragments were hand picked twice under 10X magnification. Pyrite samples from the pyritic schist were obtained by crushing the rock in a diamond mortar and hand picking the grains. The pyritic schist samples were selected from the freshest appearing rock and were ground in an agate mortar to an impalpable powder.

Galena samples for mass spectrometric work were small cleavage flakes broken from a grain of galena with a steel needle. Carbonate samples for lead isotope work were hand specimens of marble from which the outside rind was cleaved with an acid cleaned steel chisel. The hand specimen was then broken into pieces weighing about 30 grams, one of which was selected for analysis. Galena in samples 20N and 25N occurred as microscopic blebs along the grain boundaries of sphalerite. These samples of galena were collected by hand picking grains of sphalerite and analyzing the total lead.

METHODS AND RESULTS OF ANALYSIS

Introduction

The analytical data were obtained by x-ray fluorescence, emission spectroscopy, x-ray diffraction, and mass spectrometry. The analytical techniques are described in the following sections.

Iron In Sphalerite

General. The content of iron was determined for 19 samples of sphalerite associated with pyrite and pyrrhotite, and for 176 samples of sphalerite associated with pyrite away from pyrrhotite. These analyses delineate: 1) the homogeneity of the concentration of iron in sphalerite, 2) the kinds of changes in concentration within individual ore bodies, and 3) the kinds of differences in the amounts of iron in sphalerite among ore bodies.

Analytical Techniques. The concentrations of iron in sphalerite were determined on a modified Phillips Norelco x-ray fluorescence spectrometer using a high purity tungsten Phillips FA-60 tube. The ratio of the intensities of the 2nd order Kα zinc radiation to the 1st order Kα iron radiation was measured by a flow proportional counter. The intensity ratio was plotted against the independently determined ZnS/FeS weight ratio, for a set of standards, on a log-log graph. The standards used were natural specimens of sphalerite studied analytically by Doe (1956), Fryklund and Fletcher (1956), and Rose (1958). The standards were reanalyzed by E. Godijn of the California Institute of Technology. In the reanalyses, iron was determined by a ceric ammonium sulfate titration; zinc was precipitated as zinc ammonium phosphate, ignited at 900°C, and weighed as zinc pyrophosphate (Rose, 1958, p. 87). A standard curve was constructed each day from five standards which were intermixed with the unknowns.

The amount of FeS in a specimen was determined from the weight ratio of ZnS to FeS, with the assumption that sphalerite consists entirely of FeS and ZnS. The amounts of MnS, CdS, and copper, found by emission spectrography in 90 percent of the samples, were found to introduce an error of less than 0.1 percent FeS by weight in the concentration of FeS. The amounts of manganese and copper present in the samples were found to be too small to introduce significant absorption effects on the intensities of zinc and iron radiation.

The standard deviation of the curve for intensity ratio versus concentration ratio, constructed from the standards, was 2.3 percent of the ZnS/FeS weight ratio at the 90 percent confidence level. The results of the analyses of iron in sphalerite are given in Table 1. The differences found between sphalerite samples from an individual hand specimen were independent of the average content of iron, and the standard deviation of the difference was found to be 0.18 percent FeS by weight (Table 2).

Table la: FeS in sphalerite from the No. 2 mine, Balmat, New York (B. R. Doe, analyst)

Sample Number	FeS (Wt. %)	Po or Mr	Possible Contaminants
500 L, Central Ore Body			
A1	11.9	-	F-cp, py
A2	10.6	Mr	F-mr
A3	12.3	-	Clean
A4	12.1	Not Recorded	
A5a	11.4	-	Clean
A5b	12.5	Po	Clean
A6	10.9	-	Clean
A7	12.0	Mr	F-cp
A8	12.3	Po	Clean
A9	9.8	Mr	Clean
A10	10.4	-	F-cp
B1	11.0	Not Recorded	
B2	9.1	Not Recorded	
B3	8.9	Mr	Clean
B4	9.2	-	Clean
B5	11.7	Po	A-cp
500L, Lower Ore Body			
C1	13.2	Po	S-cp
C2	9.6	-	Clean
C3	8.6	-	A-cp;mg
C4	7.4	-	F-cp
C5	6.5	-	S-cp
C6	9.6	-	Clean
C7	7.5	-	F-cp
C8	7.1	Not Recorded	
C9	7.2	Not Recorded	
500L, Lower-West Ore Body			
D1	8.7	-	Clean
D2	10.9	Po	Clean
D3	10.0	Not Recorded	
D4	6.8	Not Recorded	
D5	8.2	-	Clean
D7	5.8	-	Clean
D8	7.7	-	Clean
D9	7.6	Not Recorded	
D10	7.9	-	F-cp
1100GS, Central Ore Body			
F1	7.5	-	F-cp, py
F2	9.0	-	S-cp
F3	10.4	-	F-cp
F4	8.3	-	Clean
F5	7.6	-	F-cp
F6	11.8	-	C-cp
F8	12.4	-	A-cp
F9	9.7	-	Clean
F10	9.2	-	Clean
F11	8.8	-	S-cp
F12	11.4	Po	A-cp
F13	14.3	Po, Mr	A-cp
F15	11.9	-	F-cp
F16	11.8	-	Clean
F17	11.1	-	F-cp
F18	12.7	Po	S-po
G1	10.0	-	Clean
G2	9.8	-	Clean
G3	10.8	-	Clean
G5	10.3	-	Clean
G6	11.2	-	Clean
G7	10.8	-	F-cp
G8	10.6	-	F-cp
G9	9.1	-	S-cp, py
G11	10.8	-	-
G12	8.3	-	Clean
G13	10.6	-	-
G14	9.0	-	F-cp
G15	10.0	-	F-cp
G16	10.6	-	F-cp
1100GS, Lower Ore Body			
H1	10.0	-	F-cp
H2	11.4	-	F-cp
H3	10.4	-	Clean
H5	8.8	-	F-cp
H6	6.9	-	Clean
H7	8.7	-	F-cp
H8	8.8	-	S-cp
H9	7.9	-	S-cp
H10	8.6	-	S-cp
H12	7.2	-	A-cp
H13b	10.9	-	F-cp
H14	9.2	-	A-cp
H15	9.8	-	S-cp, py
H16	9.6	-	C-cp
1100GS, Lower-West Ore Body			
I1	6.8	-	Clean
I2	7.4	-	Clean
I4	8.3	-	F-cp
I5	6.8	-	F-cp
I6	5.7	-	F-cp
I7	6.8	-	F-cp
I8	6.0	-	Clean
I9	10.7?	Mr	Gn, hm
I10	7.9	-	Clean
I11	10.9	-	F-cp, py
I12	8.8	-	Clean
I13	8.1	Mr	Clean
I14	7.9	-	S-cp
I15	11.0?	Mr	A-cp;mg
1100GS, Upper-Streeter Ore Body			
J1	8.5	-	F-cp
J3a	8.0	-	Clean
J3b	8.4	-	Clean
J4	8.0	-	F-cp
J5	6.8	-	Clean
J6	6.2	-	Clean
J7	7.6	-	Clean
J8	11.1	-	A-cp
1100GS, Lower-Streeter Ore Body			
K1	11.9	Po	C-cp
K2	10.6	-	S-cp
K3	11.4	-	Clean
K4	12.2	Po	C-cp
K5	12.3	-	F-cp
K6	11.4	-	C-cp
K7	10.5	-	S-cp
K8	10.9	-	S-cp
1500GS, Central Ore Body			
P1	8.0	-	Clean
P2	8.7	-	Clean
P3	8.0	-	S-cp, py
P4	7.8	-	Clean
P5	7.8	-	A-cp
P6	8.3	-	S-cp
P7	9.3	-	F-cp, py
P8	12.8	Po	S-cp
P9	10.6	Not Recorded	
P11	12.7	-	S-cp
P12	13.5	Po	Clean
P14	10.4	Po	C-cp
P15	9.4	-	Clean
P16	9.9	-	F-cp
P17	11.6	Po	F-cp
P18	11.4	-	A-cp
P19	9.6	-	F-cp
P20	12.2	-	F-cp
Q1	13.9	Po, Mr	F-cp
Q2	10.4	-	Clean
Q3	15.8?	Po	A-cp, po
Q4	10.4	-	Clean
Q5	12.5	-	F-cp
Q6	12.2	-	F-cp
Q7	13.6	Po	A-cp
Q8	14.1	Po	A-cp
Q9	11.4	Po	C-cp
Q10	10.3	-	F-cp
Q11	9.2	Not Recorded	
Q12	8.6	-	F-cp
Q13	8.8	-	F-cp
Q14	12.4	-	A-cp;mg
Q15	9.8	-	F-py
Q16	12.0	-	A-cp
Q17	8.8	Not Recorded	
1500GS, Lower Ore Body			
R1	6.4	-	Clean
R2	7.6	Not Recorded	
R3	9.1	-	Clean
R4	6.6	-	F-cp
R5	10.9	Not Recorded	
R6	14.0	Po, Mr	S-cp
R7	11.1	-	Clean
R8	7.9	-	F-cp
R9	6.2	-	Clean
R10	11.6	-	F-cp
R11	9.4	-	F-cp
R12	7.4	Not Recorded	
R13	10.1	-	S-cp
R14	10.4	-	A-cp;mg
R15	7.7	-	Clean
1500GS, Lower-West Ore Body			
T1	8.3	-	A-cp
T2	6.8	-	Clean
T3	9.0	-	A-cp;mg
T5	10.7	-	S-cp
T6	8.3	-	Clean
T7	7.4	-	F-cp
T8	7.4	-	F-cp;hm
T9	8.6	-	S-cp
T10	7.3	-	Mg
T11	8.0	Not Recorded	
T12	7.9	-	F-cp
T13	6.7	-	F-cp;mg
T14	8.7	-	F-cp;mg

Table lb: FeS in sphalerite from the No. 3 mine, Balmat, New York
(B. R. Doe, analyst)

Sample Number	FeS (Wt. %)	Po or Mr	Possible Contaminants
300L, Upper-Gleason Ore Body			
1N	1.8	-	S-py
2N	3.1	-	Clean
3N	2.6	-	Clean
4N	2.4	-	Clean
5N	2.8	-	Clean
700BMS, Upper-Gleason Ore Body			
6N	2.2	-	Clean
7N	2.3	-	Clean
8N	1.8	-	Clean
9N	3.2	-	Clean
10N	2.4	-	Mg
11N	3.0	-	S-cp;mg
12N	3.0	-	S-py
13N	7.1	-	Clean

Sample Number	FeS (Wt. %)	Po or Mr	Possible Contaminants
700BMS, Middle-Gleason Ore Body			
14N	2.1	-	Clean
15N	3.0	-	Mg
16N	3.1	-	S-mg
17N	3.0	-	Clean
18N	2.9	-	Clean
19N	3.2	-	S-py
20N	4.4	-	Clean
21N	3.4	-	Clean
900GS, Loomis Ore Body			
22N	3.6	-	F-cp, py
23N	3.4	-	Clean
24N	2.9	-	F-py
25N	4.2	-	S-cp

Gn - galena
Hm - hematite
Mg - magnetite
Mr - marcasite
Po - pyrrhotite
Py - pyrite
Sl - sphalerite

A-abundant (>0.1 percent by volume)
C-common (>1000 blebs/polished section)
S-some (100-1000 blebs/polished section)
F-few (10-100 blebs/polished section)
Clean (no danger from contamination)

L - level
GS - grizzly sublevel
BMS - bottom mining sublevel

Table 2: A test of the homogeneity of the iron content of sphalerite

a. Hand Specimens

Sample Number	FeS (Wt. %)	Possible Contaminants	Sample Number	FeS (Wt. %)	Possible Contaminants
D1a	9.22	F-py	10Na	2.48	Clean
b	8.73	S-py	b	2.36	Clean
D2a	11.10	A-cp	13Na	7.00	Clean
b	10.93	S-py	b	7.20	Clean
D3a	10.40		R3a	9.08	Clean
b	10.00		b	9.08	Clean
D5a	8.13		R6a	14.08	S-cp
b	8.20		b	13.80	F-cp
F13a	14.90	A-cp	R10a	11.97	S-cp
b	13.80	S-po	b	11.63	F-cp
J8a	8.00	A-cp	R12a	7.78	
b	7.90	C-py, cp	b	7.04	
1Na	1.91	Clean	A4a	12.25	
b	1.68	Clean	b	12.25	

b. Several feet of separation

Sample Number	FeS (Wt. %)	Sample Separation
R7a	11.1	5 feet
b	12.4	
T7a	7.4	3 feet
b	7.4	
H5	8.8	10 feet
H6	6.9	
Q8	11.4	8 feet
Q9	14.1	

A - abundant blebs
C - common blebs
S - some blebs
F - few blebs
Clean - no danger

py - pyrite
cp - chalcopyrite
po - pyrrhotite

Discussion. To determine the homogeneity of iron in a specimen of sphalerite, two different polished sections were prepared from each of 15 different hand specimens. The results of the study (Table 2) indicate that the concentration of iron in sphalerite does not change appreciably over distances of several inches. Table 2 also includes five samples of sphalerite separated by three to 15 feet. From these data and the larger list of data from Table 1, it appears that specimens must be taken from intervals of at least three feet in order to find significant differences in the amounts of iron in primary sphalerite.

As further evidence of the homogeneity of iron in a sphalerite sample, the color of sphalerite in thin sections and drill cores were studied. Differences of about one percent by weight or more in the amounts of FeS in sphalerite yield changes in the brownish color of sphalerite that are perceptible to the eye. Only rarely were differences in the color of sphalerite noted near grains of pyrite or pyrrhotite. Thus the differences in the iron content of sphalerite, over the distance of a thin section, appear to be less than one percent. An exception to this is sphalerite in the zone of secondary mineralization. In this zone, colorless rims, approximately 0.1 mm thick or less, of sphalerite grains are adjacent to chlorite, magnetite, and hematite. In the No. 3 mine, some sphalerite was coated by narrow rims of a black opaque substance, presumably magnetite. The colors of the cores of the larger grains of sphalerite do not appear to be affected by the secondary mineralization. Thus if precaution is taken, representative samples of the amount of iron in primary sphalerite may be obtained from these samples.

The highest concentrations of iron in sphalerite were found in samples where sphalerite is associated with both pyrrhotite and pyrite. Pyrrhotite is present in parts of the central, lower-Streeter, and lower ore bodies of the No. 2 mine. Pyrite is present throughout all the ore bodies. In between the parts of an ore body with the highest concentrations of iron in sphalerite and those parts with lower concentrations, there is the suggestion of a transition in the iron content of the sphalerite. The zone extends about 50 feet beyond the occurrence of pyrrhotite with the sphalerite. An example of such a transitional zone is shown in Fig. 4 of the northern part of the central ore body.

No significant variations were found in the average values of the iron content in sphalerite with increasing depth in an ore body (Table 3).

Individual ore bodies were found to contain sphalerite with characteristic contents of iron. The average values of the concentrations of iron are presented in Table 3 along with the standard deviations of the averages.

Table 3 shows that the sphalerite in the ore bodies of the No. 3 mine contain about 2.9 percent FeS by weight. On the other hand, the sphalerite in all the ore bodies in the No. 2 mine average 8.2 percent or more FeS by weight. Only sample 13N from the No. 3 mine (7.1 percent FeS by weight) is similar in iron content to any of the specimens of sphalerite analyzed from the No. 2 mine. The sphalerite of the lower-west ore body in the No. 2 mine averages about two percent FeS by weight less than the central ore body. The iron content of sphalerite in

Table 3: The average content of iron in sphalerite and the standard deviation of the range of concentrations

Level	Central Ore Body	Lower Ore Body	Lower-west Ore Body	Sphalerite associated with pyrrhotite
	FeS (Weight percent)			
No. 2 mine				
500 Level	10.9	8.5	8.3	12.4
1100 GS	10.3	9.2	8.3	12.8
1500 GS	10.8	9.1	8.1	12.8
Average	10.7	9.1	8.2	12.7
Std. Dev.	1.6		1.2	1.5

No. 2 mine	Upper-Streeter	Lower-Streeter
	FeS (Weight percent)	
1100 GS	7.9	11.4
Std. Dev.	0.8	0.7

No. 3 mine	All ore bodies
	FeS (Weight percent)
Average	2.9
Std. Dev.	0.6

the lower ore body is intermediate between the values for sphalerite in the central and lower-west ore bodies. The upper-Streeter ore body contains sphalerite with amounts of iron comparable with those in the lower-west ore body, and the concentration of iron in sphalerite of the lower-Streeter ore body is similar to that in sphalerite of the central ore body.

The significance of the concentrations of iron in sphalerite will be described in the section on Temperature Of Formation Of the Ores.

Minor Elements

General. Analyses of the concentrations of minor elements were made of 74 samples of sphalerite from the mining areas, 32 samples of pyrite from the mining areas, and 9 specimens of pyrite from the surrounding metasedimentary rock. In addition, the amounts of minor elements were determined for 9 samples of calcite, seven samples of dolomite, and three samples of pyritic schist from four metasedimentary units. These analyses provide information concerning: (1) the types of ranges in the concentrations of minor elements that are to be expected within minerals of an individual ore body; (2) the types of differences in the average concentrations of minor elements between ore bodies; (3) the types of differences in the concentrations of minor elements between pyrite of the ore bodies and pyrite disseminated in metasedimentary rocks of the same area; and (4) the distribution of the concentrations of minor elements between sphalerite and pyrite of the ores.

Analytical Technique. The concentrations of minor elements in minerals and rocks were determined by arc-excitation emission spectrography. Weighed samples were burned to completion, and a set of standards was included on each spectrographic plate with the unknowns.

The spectrograph, electrodes, wave-length range, plates, processing of plates, calibration of plates, and conditions of excitation used in these analyses were the same as described by A. A. Chodos in Engel and Engel (1956, p. 1379). The conditions of excitation were modified for sulfide samples which were excited at 13-amperes short-circuit rather than 19-amperes. The densitometer used was a Jarrell-Ash model number JA-2100.

Standards for sphalerite were made by mixing "Spec-Pure" oxides of the elements with a ZnS phosphor that contained 102 ppm silver as an excitor. Barium was used as a flux in the manufacture of the ZnS, but blanks of the phosphor revealed only perceptible quantities of silver as a minor element. Standards for pyrite and galena were made by mixing "Spec-Pure" oxides with natural specimens of pyrite and galena that did not contain spectrographically perceptible quantities of the trace elements of interest except for bismuth in the galena. Bismuth in galena was determined by use of rock standards. Pyrrhotite was analyzed as if it were pyrite. Samples of marble, pyritic schist, and calcite were analyzed by the rock analysis method described by A. A. Chodos in Engel and Engel (1958, p. 1379).

The electrode charge consisted of 4 mg of powdered mineral or standard, 4 mg of "Spec-Pure" graphite, and 12 mg of a 9:1 mixture of Na_2CO_3 and quartz. The charge was homogenized in a Wig-L-Bug for 15 seconds. More than 90 percent of the samples were analyzed in duplicate.

The analytical procedure for sphalerite was tested for internal consistency, and the results were compared with those obtained on shared samples of other investigators. At the end of a six-month period, the indicated values of cadmium in sphalerite ran 30 percent higher than those analyzed at the beginning of the period. Nearly all the samples of sphalerite were analyzed during the first six weeks of the period. These early results are about 10 percent greater than the values obtained by Fryklund and Fletcher (1956), Burnham (1959) and E. S. Lenher at the Pennsylvania State University. No obvious explanation was found for the change in the indicated amounts of cadmium. Concentrations of indium and germanium probably are known only to an order of magnitude owing to difficulties encountered in correcting for interfering elements. The reproducibility of the results for barium and chromium were so variable that the concentrations of these elements probably are also known only to an order of magnitude.

Discussion. Most of the barium and lead found in sphalerite undoubtedly is from included barite and galena. Much of the silver in sphalerite probably is a by-product of the inclusion of some galena in the sample; however, it is doubtful that the 28 ppm of silver found in specimen B4 was contributed by galena, as the amount of lead found in the sample is only 1400 ppm. Perhaps most of the copper found in sphalerite can be accounted for by included blebs of chalcopyrite. However, no blebs were observed in specimens B3 and B4, for example; yet, the former analyzed 300 ppm and the latter 700 ppm of copper. The copper may be in submicroscopic blebs or perhaps in the sphalerite structure. Most of the zinc, lead and barium in pyrite probably is from included sphaler-

Table 4a: Minor elements in sphalerite (in ppm) at Balmat, New York (B. R. Doe, analyst)

Sample Number	Ag	Ba	Cd	Cu	Ga	Ge	In	Mn	Ni	Pb
500L, Central Ore Body, No. 2 Mine										
A2	9	X00	1300	70	10	-	X0	4800	-	200
A6	8	X0	1400	200	9	-	X0	4000	-	65
A10	13	X0000	1400	150	6	-	X00	7800	-	1600
B1	6	X000	1400	350	7	X	X0	5000	-	300
B3	4	X0000	~1000	300	10	-	X00	1600	-	85
B4	28	X000	1600	700	1	-	X00	7600	-	1400
1100GS, Central Ore Body, No. 2 Mine										
F1,F2	4	X0	1300	150	2	-	X0	3700	-	80
F4	2	X	1200	~650	3	-	X0	1900	-	25
F15	5	X0	~1100	60	20	-	X0	4600	-	90
F16	3	X0	1600	150	2	-	X0	3700	-	2
G1	3	X00	1400	100	4	-	X0	2300	-	300
G5	4	X000	1400	100	15	-	X0	2600	-	6
G14[1]	8	X00	1200	90	8	-	X0	3300	-	6000
G15	32	X0	1400	150	10	-	X0	4600	-	19000
1500GS, Central Ore Body, No. 2 Mine										
P2	2	X	1600	200	3	-	X0	2200	-	2
P4	2	X0	1400	55	2	-	X0	2400	-	30
P5	4	X0	1100	900	3	-	X00	5800	-	15
P6	8	X0	1400	800	4	-	X0	4600	-	150
P7	4	X0	1400	200	4	-	X0	2400	-	30
P11	4	X0	600	150	4	-	X00	16000	-	100
P12	2	X0	1800	250	6	-	X00	5800	-	20
P15	4	X00	1200	80	4	-	X0	5300	-	8
P20	6	X000	940	100	9	-	X00	14000	-	450
Q2	0.9	X00	1200	50	9	-	X0	3600	-	30
Q4	2	X00	1400	100	16	-	X0	4000	-	10
Q5	0.6	X000	920	400	10	-	X0	4400	-	2
Q7,Q8,Q9	2	X000	980	1400	4	-	X0	5000	-	3
Q12,Q13	1	X0000	940	300	15	-	X00	6300	-	6
Q14	6	X0	1600	40	2	-	X00	12000	-	1000
500L, Lower and Lower-West Ore Bodies, Undivided										
C2	12	X00	1300	80	8	-	X0	1800	-	1600
D1	2	X	1100	150	2	-	X00	14000	-	70
D5	13	X000	~1200	300	4	-	X	1800	-	5200
D7a[1]	6	X00	2400	150	40	-	X	410	7	750
D10	11	X	1500	250	10	-	X	470	6-	170
1100GS, Lower and Lower-West Ore Bodies, Undivided										
H2	40	X00	1500	90	3-	-	X00	11000	-	4300
H5,H6	3	X00	1600	150	6	-	X0	860	-	420
H13b	2	X000	2500	30	4	X-	X	2200	-	1-
I7	4	X00	1400	300	2	-	X	680	-	60
I13	2	X00	1500	~400	2-	-	X	830	-	8
1500GS, Lower and Lower-West Ore Bodies, Undivided										
R3	2	X00	1400	80	9	X-	X0	1700	6-	3200
R6	4	X0	1400	75	2	-	X00	1600	-	240
R10b	4	X0	1300	55	2	-	X00	12000	-	150
R11	8	X000	1400	150	3	-	X0	3000	4-	180
T6	5	X00	1400	400	2	X	X0	1600	-	160
T7a	4	X0	2200	90	4	-	-	580	-	70
T12	12	X00	1600	350	3	-	X	650	-	360

Table 4a: (continued)

Sample Number	Ag	Ba	Cd	Cu	Ga	Ge	In	Mn	Ni	Pb
100GS, Upper-Streeter Ore Body, No. 2 Mine										
J1	18	X000	1500	300	65	X0	X00	11000	100	3600
J3b	0.5	X0	1300	55	4	X-	X00	6800	-	2-
J5	2	X000	1500	200	8	-	X0	4600	-	75
J6	0.6	X0	1400	150	8	X-	X	1100	-	1-
J7	0.6	X000	1500	100	4	-	X	1600	-	4
J8	2	X00	1200	850	15	-	X00	16000	-	2
1100GS, Lower-Streeter Ore Body, No. 2 Mine										
K2	7	X0	1400	40	4	X	X0	4200	5	1400
K3	6	X00	1400	100	10	X	X0	4600	10	2200
K5	4	X0	1300	70	8	X	X00	9900	10	20
K7	1	X000	1500	20	1	-	X0	5600	-	4
300L, Upper-Gleason Ore Body, No. 3 Mine										
1N	2	X00	1600	350	200	X0	X0	650	100	15
2N	2	X	1100	400	150	X-	X	1400	5-	4
4N	2	X	1200	400	150	X-	X0	2600	2-	20
5N	1	X-	2000	250	55	X	X	1000	5-	3
700BMS, Upper-Gleason Ore Body, No. 3 Mine										
6N	2	X	1100	550	70	X0	X	540	10-	6-
8N	2	X	1200	1500	500	X-	X	700	10	4
10N	4	X0	1600	350	7	-	-	480	-	-
12N	1	X	1500	850	25	X0	X	1000	2-	4
700BMS, Middle-Gleason Ore Body, No. 3 Mine										
15N	1	X	1600	200	90	-	X	850	25	4
16N	2	X-	1300	400	45	-	X	910	1	3
17N	2	X	1600	400	40	X	X	1400	1	3
19N	2	X	1600	550	45	-	X0	5800	9	3
21N	2	X	2000	550	200	X-	X	1200	-	10
900BMS, Loomis Ore Body, No. 3 Mine										
22N	2	X	1400	550	15	X0-	X	1300	-	4
23N	5	X	1000	300	150	-	X0	3800	7	70
24N	1	X000	1300	300	50	X-	X0	2400	-	10
25N	5	X0	1600	1400	45	X-	X0	2600	-	2500
*	0.5	3	30	1	3	3	3	3	3	3
#	17	25a 45b	8.5	15	37	?	27	10	?	28

1- Samples not analyzed in duplicate

*- Average minimum concentration resolved

#- Standard deviation in percent multiplied by $(1/2)^{1/2}$ to yield the deviation for pairs.

a- Standard deviation for pairs for concentrations greater than 100 ppm.

b- Standard deviation for pairs for concentration less than 100 ppm.

Looked for but not found: Au, Be, La, Nb, Pt, Sc, Ta, As, Sb, Ti

Lines observed: Bi- 1N,D7a, J1,K3,K5; Cr- A10,B4,G4,H2,Q2,Q5 Co: P2,J1,K2,K3,K5; Mo- F15,F16,J1,J6,K3; Sn- 1N (10ppm), 24N (10ppm), J1 (50ppm)

Table 4b: Minor elements in pyrite and pyrrhotite (in ppm) at Balmat, New York (B. R. Doe, analyst)

Sample Number	Ag	Co	Cr	Cu	Mn	Ni	Pb	Ti	V	Zn	Possible Contam.
Pyrite, No. 3 Mine, All Ore Bodies											
2N	1	35	XO	45	48	50	80	-	-	12000	Sl
5N	1-	50	XO	160	40	30	-	-	-	10000	Sl
8N	2	50	XO	130	58	20	-	-	-	28000	Sl
10N	1-	100	XOO	76	57	20	35-	-	-	26000	Sl
Pyrite, 500L, Central Ore Body, No. 2 mine											
A3	3	~15	XO	~15	340	-	-	-	50	7300	Sl
A7	2	70	XO	46	140	-	-	-	65-	31000	Sl
A10	11	13-	XOO	15	120	-	2800	-	50	2800	Clean
B3	4	30	XO	26	100	15-	280	-	65	4200	Gangue
Pyrite, 1100GS, Central Ore Body, No. 2 Mine											
F6	13	15	X	240	460	-	50	-	65	38000	Sl
G1	8	20	XO-	54	140	-	150	-	50-	20000	Sl
G5b	7	15	XO-	16	130	-	50	-	-	3400	Dolomite
G12	12	40	XO	31	160	8	2800	-	65	160	Clean
Pyrite, 1500GS, Central Ore Body, No. 2 Mine											
P4	10	25	XO	25	260	12-	-	-	60	30000	Sl, frac.
P19	12	10-	X	~12	160	-	250	-	-	2100	Clean
Q7	16	1000	XO	12000	280	40	400	-	65	18000	Sl, frac.
Q14	51	15	XO	90	460	15-	-	-	75	190	Clean
Pyrite from Metasedimentary Rocks, Surface											
sm 4-1	8	300	XO	85	10	350	-	-	-	~400	
sm 4-2	6	250	X	110	10	250	-	250	-	3000	
sm 4-3	6	1000	XO	26	25	1000	-	-	-	200	
sm 4-4	10	900	XO	30	25	600	1000	-	-	100	
ps 2-1	5	250	XO	20	21	800	-	250	130	100	
ps 2-2	10	300	XO	120	240	500	200	1500	270	100-	
ps 2-3	8	300	XO	8	3-	1000	-	300	80	200-	
rm 15-ff	10	~25	X	82	75	150	500	700	-	200-	
hpg 1-ff	6	~2500	XO-	~80	15	10000+	-	-	-	300	

Sample Number	Ag	Co	Cr	Cu	Mn	Ni	Pb	Ti	V	Zn	Possible Contam.
Pyrite, 1100GS, Streeter Ore Bodies, Undivided, No. 2 mine											
J1	8	8-	XO	3-	38	-	1400	-	-	1800	Clean
J7	2	30	XO	6	110	15	70	-	-	1400	Clean
K1	4	3-	XO	35-	47	15	75	-	-	300	Clean
K7	2	30	XO	3-	56	30	41	-	-	5500	Sl
Pyrite, 500L, Lower and Lower-West Ore Bodies, No. 2 Mine											
C1	2	15	XO	25	700	-	35	-	60	14000	Sl, frac.
D1	8	4-	XO-	47	390	-	160	-	85	14000	Sl, frac.
D6	13	15	XOO	5	160	-	1800	-	50	18000	Sl, frac.
D7b	9	~10	XO	10	110	-	10000+	-	40-	15000	Sl, frac.
Pyrite, 1100GS, Lower and Lower-West Ore Bodies, No. 2 Mine											
H4	4	20	XO	3-	320	10	600	-	-	9600	Sl
H11	6	3-	XOO	36	77	8	350	-	-	3400	Clean
I3	8	12-	XOO	40	240	10	140	-	-	28000	Sl, frac.
I11	~16	~7	XOO	3-	~80	-	660	-	-	9600	Sl, frac.
Pyrite, 1500GS, Lower and Lower-West Ore Bodies, No. 2 Mine											
R3	6	8	XO	3-	48	-	2200	-	-	9800	Sl
R10	12	3-	XO	46	740	-	150	-	-	5500	Sl, frac.
R13	14	3-	XO	6	380	9	4000	-	-	17000	Sl
T7	16	~16	XOO	18	210	-	450	-	-	20000	Sl, frac.
Pyrrhotite, No. 2 Mine											
A5b	10	3-	XO	80	35	100	-	-	-	300	Clean
1100BMS	~75	-	-	440	85	125	-	-	-	900	Clean
1300L	~150	-	X-	2900	250	150	-	-	-	12000	Sl, cp
P13	300	-	X-	2000	150	150	2000	-	-	13000	Sl, cp
Q3	~40	-	XO	46	70	100	-	-	-	600	Clean
Q8a	8	-	XO	~700	30	150	-	-	-	200	Clean
Q8b	14	-	XO	2500	200	150	300	-	-	~600	Clean
Q9	4	-	XO	12	15	150	-	-	-	1200	Sl
*	3	3	10	3	10	10	30	100	30	100	
	18	21	40	13	8	25	14	?	35	19	

Looked for but did not observe: Au, Be, Cd, Ge, Sc
Barium (unstandardized) present in most samples

Present below sensitivity: As (3000ppm), Bi (100ppm), In (10 ppm), Sb (1000ppm), Sn (100ppm)
*Minimum concentration resolved (avg.); Standard deviation for pairs in percent

Table 4c: Concentrations of minor elements in galena (in ppm) (E. Godijn, analyst)

Sample Number	Mine	Ag	Bi	Cu	Mn	Sb	Sn	Zn
26N	No. 3	650	10-	50	X	X	-	1%+
R9	No. 2	1700	20	10-	-	X	-	0.02%-
F19	No. 2	1200	10	10-	X	X	-	1%+

X- unstandardized line is present

Table 4d: Concentrations of minor elements in carbonate minerals and pyritic schist (in ppm) (B. R. Doe, analyst)

Sample Number	Mineral	Carbonate Minerals							
		Ba	Cr	Cu	Mg	Mn	Pb	Sr	Location
cdm 14-j	calcite	5000	3	-	7500^3	1200	45	1600^3	500L, C
cdm 14-l	calcite	1000	4	-	6000	660	35	1200	500L, L
cdm 14-p	calcite	100	3	-	6500	930	20	2000	500L, C
cdm 14-e	calcite	6000	4	-	3500^2	920	35	2000^2	1100GS,C
cdm 14-f	calcite	1500	3	6-	6000	2700	150	1400	1100GS,LW
cdm 14-h	calcite	2500	3	-	2500	490	80	2300	1100GS,C
cdm 14-a	calcite	400	40	-	5000^1	660	50	2200^1	1500GS,L
cdm 14-c	calcite	650	6	-	5000	2300	65	1800	1500GS,L
cdm 14-d	calcite	750	4	-	5500	1500	60	1500	1500GS,L
sm 4-1	dolomite	20	-	-		810	-	180	Surface
sm 4-2	dolomite	4	-	10-		370	-	100	Surface
sm 4-3	dolomite	15	-	-		450	-	60	Surface
sm 4-4	dolomite	25	-	-		780	-	190	Surface
fd 7-1b	dolomite	700	-	7		240	-	240	900BMS,Lo
fd 7-1n	dolomite	300	4	40		230	100	140	900BMS,Lo
fd 7-2	dolomite	9	-	10		500	-	140	900L, Lo
fd 7-3	dolomite	10	-	-		710	-	100	Surface
Maximum sensitivity		2	2	2	60	4	10	2	
Standard deviation		22	14	?	4	25	23	25	percent

1. Mg-5000, Sr-2400; 2. Mg-3500, Sr-2000; 3. Mg-7200, Sr-1600; all by Cu spark analysis, E. Godijn, analyst.

C- central, L- lower, LW- lower-west, Lo- Loomis ore bodies

Sample Number	Total sample										
	Ag	Ba	Co	Cr	Cu	Mg	Mn	Ni	Pb	Sc	Sr
ps 2-1	0.6	900	20	40	30	4500	35	210	55	13	40
ps 2-2	1	2000	15	130	150	8000	700	100	250	12	250
ps 2-3	1	300	10	35	250	3500	10	170	15	8	9

Sample Number	Ti	V	Y	Zn	Location
ps 2-1	2500	350	50	80	Surface
ps 2-2	4500	700	85	250	Surface
ps 2-3	1500	200	20	90	Surface

ite, galena, and barite, respectively.

One of the purposes of the present investigation was to determine the distributions in the concentrations of minor elements within and between the ore bodies at Balmat. The data are presented in Table 4. For information about minor elements in sulfide minerals from other mining districts, the reader is referred to the review by Fleischer (1955) and to the recent investigations by Burnham (1959) and Rose (1958).

Cadmium in sphalerite is the minor element with the smallest range in concentrations. The content of cadmium in sphalerite ranges between 1000 and 2000 ppm with a geometric mean of 1400 ppm for each of the No. 2 and No. 3 mines.

Aside from cadmium in sphalerite, a notable feature is the large range in the concentrations of minor elements between specimens from the same level and ore body. For example, the content of manganese in sphalerite from the central ore body ranges between 1600 and 7800 ppm on the 500 level, 1900 and 4600 ppm on the 1100 grizzly sublevel, and 2200 and 16000 ppm on the 1500 grizzly sublevel (Table 4a). The minor element with the greatest range of concentrations is indium, in sphalerite. The ratio of maximum to minimum concentrations for indium in specimens of sphalerite from the same level and ore body was found to be about 100. None of the minor elements in pyrite ranges as greatly in concentration as indium in sphalerite and none has as small a range as cadmium in sphalerite. At Balmat, the order of increasing range of concentrations in sphalerite is Cd, Mn, Ga and Ge, Cu, and In. The order of increasing range of concentrations in pyrite is Mn, Co, Ag, Ni, and Cr. These large irregular ranges in the amounts of minor elements within individual ore bodies hamper investigations of the changes in average contents of minor elements with increasing depth in an ore body. Also, studies of the differences in the average concentrations of minor elements between minerals of different ore bodies are hindered.

No uniform gradients in the amounts of minor elements in sphalerite down the plunge of individual ore bodies were found. The type of change found is expressed by the concentration of manganese in sphalerite from the central ore body. The geometric mean of the concentration of manganese is 4600 ppm on the 500 level, 3300 ppm on the 1100 grizzly sublevel, and 5000 ppm on the 1500 grizzly sublevel. There are, however, suggestions of a uniform increase in the amounts of manganese and silver in pyrite of the central ore body. The geometric mean of the content of manganese in pyrite on the 500 level is about 130 ppm (range: 70-310 ppm), 170 ppm on the 1100 grizzly sublevel (range: 110-440 ppm), and 220 ppm on the 1500 grizzly sublevel (range: 120-420 ppm). These mean values of concentration have been corrected for manganese contributed to pyrite by contamination of the sample with sphalerite, assuming that all the zinc found in pyrite is contributed by included sphalerite. Silver has a geometric mean of 4 ppm on the 500 level (range: 2-11 ppm), 10 ppm on the 1100 grizzly sublevel (range: 7-13 ppm), and 14 ppm on the 1500 grizzly sublevel (range: $<$10-51 ppm). The amounts of lead found in the pyrite are small. Only a few tenths of a part per million of the average concentrations of silver in pyrite can be accounted for by inclusion of galena with the pyrite samples. A "t" test for lognormal statistics at the 90 percent confidence level indicates that the geometric mean of the concentrations of silver on the 500 level and 1500 grizzly sublevel are probably not the same. A similar test on manganese yields similar results. Among the elements analyzed, uniform gradients in the mean contents of minor elements down the plunge of the ore bodies are difficult to determine because of the large ranges in concentration between specimens from the same level and ore body and the relatively small size of the gradients.

The differences between the average concentrations of minor elements in minerals of different ore bodies also are small compared to the large differences between specimens from the same ore body. Ore bodies could not be distinguished on the basis of the amounts of cadmium in sphalerite. However, the sphalerite of the No. 3 mine was found to contain more Ga, Cu, and Ge and less Mn than the sphalerite of the No. 2 mine. Pyrite from the No. 3 mine contains somewhat more Co and Ni and less Mn and Ag than pyrite from the No. 2 mine (Table 4).

Within the No. 2 mine, the amounts of cobalt in pyrite and manganese in sphalerite are higher for the central ore body than in the combined lower and lower-west ore bodies. In general, the amount of iron found in sphalerite of a particular ore body distinguishes that ore body as well or better than do minor elements. For example, ore bodies in which sphalerite contains the most iron also contain sphalerite with the most manganese. An exception is the upper-Streeter ore body in which sphalerite contains similar amounts of iron but more manganese than sphalerite of the lower-west ore body. A possible explanation to the low-content of manganese in sphalerite of the lower-west ore body involves the secondary mineralization of chlorite, magnetite, and hematite. All but one specimen of sphalerite in the No. 2 mine that contain less than 1000 ppm of manganese are associated with secondary minerals. It may be that manganese was more extensively leached from sphalerite by the secondary mineralization than was iron.

With regard to pyrite, the geometric mean of the content of cobalt in pyrite of the central ore body is about 30 ppm (range: < 10-1000 ppm), whereas the equivalent value for pyrite of the combined lower and lower-west ore bodies is about 8 ppm (range: < 3-20 ppm). Other elements were not found useful in distinguishing the ore bodies of the No. 2 mine.

The data of Table 4 show that the differences between the cobalt and nickel contents of pyrite from the No. 2 and No. 3 mines are small. On the other hand, there is an impressive difference between the concentrations of cobalt and nickel in pyrite from the metasedimentary rocks and the pyrite of the ore bodies. Pyrite from the metasedimentary rocks was found to contain amounts of cobalt and nickel each greater than 200 ppm, whereas most samples of pyrite from the ore bodies contained cobalt and nickel each in quantities less than 50 ppm. In addition, titanium appears to be in greater amounts in pyrite of the metasedimentary rocks. Many specimens of pyrite from the ore bodies contain higher amounts of manganese and chromium than does pyrite from the rocks surrounding the mines. The concentrations of vanadium are less than 30 ppm in most specimens of pyrite from the ore bodies. Pyrite from the pyritic schist was found to contain 30-250 ppm of vanadium, whereas the concentration of vanadium in pyrite from the marble is less than 30 ppm. Therefore, the amount of vanadium distinguishes pyrite from the pyritic schist from both pyrite in the ore bodies and pyrite in the marble. The concentrations of copper and silver are uniformly distributed in the various kinds of pyrite.

Samples of pyrite from metasedimentary units were not obtainable to any significant depth beneath the surface. Variations in the concentrations of minor elements in metasedimentary rocks down the dip of the units were investigated by analyzing nine samples of calcite from a calcitic sub-unit of the cdm 14 unit in the No. 2 mine. No large gradients in the concentration of minor elements in calcite were found over a vertical distance of about 1000 feet (see Table 3). From these data, it seems reasonable to assume that surface samples are representative of the same rocks to depths of a few thousand feet.

The differences between the concentrations of cobalt and nickel in the different kinds of pyrite are probably not due to local fractionation effects between phases or to contamination of the samples by accompanying nickel- and cobalt-rich minerals. No cobalt- and nickel-rich minerals were observed in polished sections of the pyrite from the metasedimentary rock. In addition to the analyses of minor elements in pyrite from both marble and pyritic schist, samples of marble, purified of pyrite, and samples of pyritic schist, not purified of pyrite, were analyzed for the contents of minor elements. Essentially all the cobalt but possibly only half of the nickel in the pyritic schist is in the component pyrite. Essentially all the cobalt and nickel in marble are in the constituent pyrite. Also, the concentrations of cobalt and nickel in the pyrite from the country rocks are greater than the concentrations of these elements in sphalerite or pyrrhotite of the ores. Some possible geologic implications of these differences in concentration are given in the section on Source Of The Metals For The Ores.

Table 5: Comparison of the concentrations of cobalt and nickel in pyrite of the ore bodies with pyrite from metasedimentary rocks away from the ore (in ppm)

Location	No. of samples	Cobalt		Nickel		Ti	Mn[2]
		GM[1]	Range	GM	Range	GM	GM
2 mine, C	12	< 30	1000	< 15	40	-	170
2 mine, L and LW	12	8	15	< 6	10	-	180
2 mine, LS and US	4	< 10	30	< 20	30	-	50
3 mine, all	4	50	60	30	50	-	30
sm 4 (marble)	4	500	750	500	750	250-	15
ps 2 (py. schist)	4	300	10	750	600	500	< 70
'vein' pyrite rm 15	1	25	-	150	-	700	75
hpg	1	2500	-	10000+	-	-	15

[1] GM, the geometric mean = $(X_1 \cdot X_2 \cdot X_3 \cdot \cdots \cdot X_n)^{1/n}$

[2] Corrected for manganese contributed by contamination of pyrite with sphalerite. All zinc in pyrite is assumed to come from included sphalerite.

C is the central ore body, L and LW are the lower and lower-west ore bodies, US and LS are the upper-Streeter and lower-Streeter ore bodies.

10000+ means greater than 10000 parts per million
10- means less than 10 parts per million

The distribution of minor elements between sphalerite and pyrite of the ores was also analyzed. To this end, samples of sphalerite and pyrite were taken from each of 12 different polished sections of ore from the No. 2 mine and 4 polished sections from the ore of the No. 3 mine. The results of these analyses are given in Table 6. The ratio of the concentration of a minor element in sphalerite to that in pyrite was found to range considerably within the No. 2 and No. 3 mines. This ratio for manganese in the No. 2 mine ranges between 3 and 1100. The ratio for copper ranges between 0.5 to greater than 78. Because chalcopyrite was observed as blebs in sphalerite, the meaning of the ratio for copper is not clear. However, it probably is worthwhile noting that those samples with the highest ratios for manganese between sphalerite and pyrite also have, in general, the highest ratio for copper.

Although the ratios of concentrations of minor elements were determined for 16 specimens, samples T7a, 6N, 8N, and 10N contain secondary minerals and these samples do not seem to be representative of samples away from secondary mineralization. Among the remaining 11 specimens from the No. 2 mine, 7 have concentration ratios for manganese between 10 and 30. The standard deviations in the ratios due to the analytical uncertainties are about 13 percent. Although ratios for manganese were found as high as 1100, there is a suggestion of a frequent occurrence of a ratio of about 15 between the pairs of sphalerite and pyrite samples. This value is close to the ratio for the average concentration of manganese in sphalerite to the average concentration of manganese in pyrite determined from all the data in Table 4 for the No. 2 mine. This ratio of the average concentrations is 24.

Table 6: Fractionation factors of copper and manganese between sphalerite and pyrite

Sample Numbers	(1) FeS(Mole%) in Sl	(2) Mn(Mol.%) ratio Sl/Py	[(2)/(1)] x 100	Cu(Mol.%) ratio Sl/Py
No. 2 mine				
A10	11.3	71	630	8
B3	9.8	14	140	10
D1	9.7	11	110	3
G1	11.0	25	230	1.5
J1	9.3	1100	12000	> 78
J7	8.4	12	140	13
K7	11.5	220	1900	> 5
P4	8.6	12	140	2
Q14	13.6	21	150	0.5
R3	10.0	100	1000	> 21
R10b	12.6	13	100	1
T7a	8.1	3	37	4
No. 3 mine				
2N	3.4	48	1400	8
6N	2.4	13	540	3
8N	2.0	19	950	18
10N	2.6	9	350	4

Sl- sphalerite Py- pyrite

Three of the four specimens from which pyrite and sphalerite were sampled, to represent the No. 3 mine, contain secondary magnetite. Of these four samples, only 2N may be used to represent the primary mineralization. This specimen has a ratio of 48 for manganese between sphalerite and pyrite. The data on the ratios of concentrations of minor elements between sphalerite and pyrite for the No. 2 mine demonstrate that it is dangerous to base a representative concentration ratio for a mine on one specimen. In the No. 2 mine, the ratio of the average concentrations of manganese in sphalerite and pyrite approximate the most abundant value of the ratio found from mineral pairs. This ratio of the average concentrations between the two minerals in the No. 3 mine is 56. A possible geologic interpretation of these concentration ratios is presented in the section on Temperature Of Formation Of The Ores.

Summary. The concentrations of most minor elements are irregularly distributed in sphalerite and pyrite of a particular ore body. However, there is some suggestion of a small, uniform increase in the average contents of silver and manganese in pyrite as its occurrence is traced down the plunge of the central ore body.

The geometric mean of the amount of cadmium in sphalerite is close to 1400 ppm for all ore bodies. Amounts of iron, gallium, and manganese in sphalerite and cobalt and manganese in pyrite were found of some use in distinguishing ore bodies from one another.

Pyrite from marble and pyritic schist away from the ore bodies contains greater than 200 ppm each of cobalt and nickel. On the other hand, most specimens of pyrite from the ore bodies contain less than 50 ppm each of cobalt and nickel.

The ratios of the concentrations of manganese and copper in sphalerite to the concentrations in accompanying pyrite were found to range greatly. The most common ratio for manganese between sphalerite and pyrite in the No. 2 mine is about 15. The equivalent ratio for the No. 3 mine is about 50.

Lead Isotopes

General. The isotopic compositions of lead in galena were obtained from specimens from three ore bodies in the No. 2 mine and from two ore bodies of the No. 3 mine. In addition, the isotopic compositions of lead were determined for two samples of dolomitic marble (fd 7 unit). Sample fd 7-2 was taken from the 900 level near the shaft of the No. 3 mine. Sample fd 7-3 was collected from a half mile to the west of the shaft near Sylvia Lake.

Analytical Techniques. The ratios of lead isotopes in galena and marble and the concentrations of uranium and lead in marble were measured on a solid-source mass spectrometer, described by Chow and McKinney (1958). The results of the measurements are given in Table 7.

The chemical procedures used to isolate the lead are those used by C. C. Patterson (personal communication). In all chemical procedures either pyrex glassware or Teflon-ware were used, and all evaporation stages were performed in a nitrogen tank. All chemicals used were either redistilled or reprecipitated. Galena was dissolved in HCl. The lead ions were complexed with ammonium citrate and KCN. The pH was adjusted to 8.5-9, and the lead was removed by a double dithiozone extraction. Iron was removed by a double ether extraction preceding the complexing of the lead, for galena from blebs in sphalerite and for lead from marble.

The marble samples were dissolved in 6.5 N HCl. The residues were treated with HF and perchloric acid to decompose any silicate present. Any residual graphite remaining (sample fd 7-2) was leached with HCl until the acid remained clear and colorless. In the isotope dilution procedures to determine the concentrations of lead and uranium in marble, the sample was diluted with quadruple distilled water to one liter and aliquots of 100 ml were removed and "spiked" with known amounts of lead and uranium. Iron was removed from the aliquot used for the analysis of uranium by an ammonium carbonate extraction. Uranium was extracted from the aliquot by a double hexone extraction.

Reproducibility of the ratios of lead isotopes has been studied by Chow and McKinney (1958) and Chow and Patterson(1959), on the same mass spectrometer used in the present study. Inasmuch as the same mass spectrometric procedures were followed, the corrections to raw data, precisions, and reproducibility used in this study were those indicated by these investigators. Chow and Patterson (1959) estimated that, at the 90-percent confidence level, the uncertainty in the isotopic ratios of lead was 0.3 percent of the Pb^{206}/Pb^{204} ratio, 0.1 percent of the Pb^{206}/Pb^{207} ratio, and 0.2 percent of the Pb^{206}/Pb^{208} ratio.

Discussion. No differences were found in the isotopic compositions of lead among four samples of primary galena from the No. 2 mine. Similarly, no significant differences were found in the isotopic compositions of lead between three samples of galena from the No. 3 mine. The

Table 7: Isotopic composition of lead in galena and in marble at Balmat, New York (B. R. Doe, analyst).

Sample Number	Rock or Mineral	Location	Date	Atom Ratios 206/204	s	206/207	s	206/208	s
26N	gal	500L, No.3 mine	11-24-58	16.9_2	0.06	1.0808	0.003	0.456_2	0.004
20N	gal+sph	700BMS-G1, No.3 mine	3-12-59	16.97	0.05	1.083_0	0.002	0.4579	0.003
25N	gal+sph	900GS-Lo,No.3 mine	2-25-59	16.88	0.05	1.0837	0.002	0.457_4	0.001
D5	gal	500L-LFW,No.2 mine	2- 3-59	17.1_1	0.07	1.087_1	0.003	0.460_4	0.001
F19	gal	1100GS-C,No.2 mine	12- 3-58	17.07	0.03	1.087_5	0.002	0.461_3	0.001
J1	gal	1100GS-LEU,No.2 mine	2-16-59	17.07	0.04	1.088_2	0.002	0.460_6	0.002
R9	gal	1500GS-LW,No.2 mine	1-16-59	17.07	0.06	1.0868	0.002	0.460_0	0.002
fd 7-2	marble	900L-shaft,No.3 mine	5- 6-59	18.1_0	0.08	1.159_1	0.002	0.4917	0.001
fd 7-3	marble	Surface,Sylvia L.	6-11-59	19.3_5	0.06	1.228_0	0.003	0.521_0	0.003

Marble	U ppm	Pb ppm	Pb/U (wt)	U^{238}/Pb^{204} atomic
fd 7-2	0.64	3.2	5.0	12.2
fd 7-3	0.083	0.48	5.8	11

s - is the standard deviation of ratios of isotopes found on a sample on the day of analysis and constitutes only a part of the error involved in the variation of the observed ratios in comparison to their true value. The values of s are not multiplied by $1/\sqrt{N}$ which varies between 0.16 and 0.26.

data of Table 7 indicate that the Pb^{206}/Pb^{207} ratio of the lead from the No. 2 mine is about 0.3 to 0.7 percent greater than the equivalent ratio for lead from the No. 3 mine. The values of the isotopic ratios of lead found for the No. 2 mine in the present study are similar to those reported by Brown and Kulp (1959) for lead from galena concentrate and jordanite of the No. 2 mine.

The isotopic ratios of lead from the sample of marble, fd 7-2, are different from the corresponding ratios of marble sample fd 7-3. There are also mineralogic differences between the two samples. Sample fd 7-2 was composed of equigranular, coarse-grained dolomite with traces of diopside and talc and contained 0.26 percent graphite by weight. Sample fd 7-3 was composed of coarse-grained, equigranular dolomite (65 percent by volume) and diopside (35 percent by volume) with traces of talc and tremolite. The isotopic compositions of lead in marble bear the following relation to lead from galena of the ore bodies:

Marble Sample	$\frac{Pb^{206}}{Pb^{204}}$	$\frac{Pb^{207}}{Pb^{204}}$	$\frac{Pb^{208}}{Pb^{204}}$	Mine (Average)	$\frac{Pb^{206}}{Pb^{204}}$	$\frac{Pb^{207}}{Pb^{204}}$	$\frac{Pb^{208}}{Pb^{204}}$
fd 7-2	18.10	15.62	36.81	No. 2	17.08	15.71	37.08
fd 7-3	19.35	15.76	37.14	No. 3	16.92	15.63	37.02

The Pb^{206}/Pb^{204} ratios for lead from marble are much greater than those for lead from galena. The difference between the Pb^{208}/Pb^{204} ratios of marble and galena is surprisingly small. Some geologic interpretations of this isotope study are given in the section on <u>Source Of The Metals For The Ores</u>.

X-Ray Diffraction

Analytical Technique. Measurements were made of the (220) lattice spacing of sphalerite, the (102) spacing of hexagonal pyrrhotite, and the (202) and ($\overline{2}02$) spacings of monoclinic pyrrhotite on an x-ray diffractometer using manganese filtered K_{α} radiation (wavelength - 1.93597 Å). Smear mounts of the samples were prepared on lucite disks which were rotated in the beam of x-rays. Spectrographically pure NaCl was used as an internal standard. The edge of the unit cell of NaCl was taken to be 5.6402 Å at 26°C as given by the U. S. Bureau of Standards. The spacings of sphalerite and pyrrhotite were compared with the (220) spacing of NaCl.

In the diffractometer study, the location of a peak was determined by measuring the intensity of the diffracted radiation in increments of $0.01^{\circ}\ 2\theta$. The analyses were performed at $25^{\circ} \pm 1^{\circ}$C. The uncertainty in the (220) spacing of sphalerite and in the spacings of pyrrhotite is ± 0.0003 Å. The results of the diffractometer studies are given in Tables 8 and 9. Table 8 gives the length of the lattice edge of sphalerite uncorrected and corrected for the contributions to the lengths of the edge of the lattice from manganese and cadmium (after Kullerud, 1953). Table 9 gives the data for the (102) spacing of hexagonal pyrrhotite and for the (202) and ($\overline{2}02$) spacings of monoclinic pyrrhotite.

Sphalerite. As can be seen from the data of Table 8, there is a relationship between the length of the lattice parameter of sphalerite and the concentration of iron in sphalerite determined by x-ray fluorescence. The relationship of the length of the lattice parameter to the concentration

Table 8: Lattice parameters of sphalerite (in Å)

Sample Number	a_o ($\pm$ 0.0008)	a_o[1] ($\pm$ 0.0008)	FeS(Wt.%) fluorescent
P12(a,b)	5.419_5	5.418_4	13.5
Q5	5.417_2	5.416_{50}	12.5
R3(a,b)	5.417_0	5.416_{47}	9.1
T6	5.416_4	5.416_0	8.3
T12	5.414_7	5.414_4	7.9
1N(a,b)	5.411_6	5.411_3	1.8

[1] Corrected for the contribution of manganese and cadmium to the lattice edge by the relations given by Kullerud (1953). Manganese and cadmium were determined by emission spectrography.

Table 9: Lattice spacings of pyrrhotite (in Å)

Sample Number	Monoclinic ($\bar{2}02$)	(202)	Center of peak
A5b	2.058_8	2.052_2	2.056_4
1100BMS	2.062_9	2.052_6	2.057_8
1300L	2.062_3	2.052_6	2.057_3
P13	2.062_4	2.052_3	2.057_1
Q3	2.060_8	2.053_4	2.056_4
Q9	2.059_6	2.052_9	2.056_4
			Hexagonal (102)
Q8a			2.065_2
Q8b			2.065_6

of iron in sphalerite was previously determined by Skinner, et al.(1959). The uncertainty in the lattice measurements in the present study is equivalent to about 2 percent FeS by weight. The relation between lattice spacings and iron content (Table 8) indicates that most, if not all, the iron in sphalerite at Balmat is in the lattice and not in submicroscopic defects.

Pyrrhotite. When the concentrations of minor elements in pyrrhotite are low, the bulk composition of hexagonal pyrrhotite can be accurately determined by x-ray diffraction (Arnold, 1956). The concentrations of cobalt, nickel, and other minor elements are found to be very low in the pyrrhotite from Balmat (Table 4b). Measurements of the (102) spacing of hexagonal pyrrhotite and the (202) and ($\bar{2}$02) spacings of monoclinic pyrrhotite are given in Table 9. The relation between lattice spacing and composition is given by Arnold (personal communication) as:

$$(102)\text{Å} = 2.0918 - 0.0077\,(50 - \text{Fe}) - 0.00069\,(50 - \text{Fe})^2 .$$

Using this expression, the sample of pyrrhotite Q8 contains 47.3 atomic percent Fe.

INTERPRETATIONS

Source Of The Metals For the Ores

In the discussion of the geology of the Balmat area (see above) it was stated that scattered grains of sulfide minerals are present in both marble and schist units as far as 30 miles northeast of Balmat. In addition, the contacts between the ore bodies with the marble wall rocks are not sharp. Disseminated grains of pyrite and sphalerite may be present for several feet away from the massive parts of the ore bodies. Evidence from the textural relations between the ore minerals and the silicate minerals of the marble units suggest that the ore bodies were formed during the retrograde stage of the last severe metamorphism. These factors suggest that the ore bodies may have formed by accretion of the metals from the surrounding metasedimentary rocks. The study of minor elements and the study of lead isotopes should place certain limitations on the source of the elements that form the ores of the No. 2 and No. 3 mines.

Studies of textural relations suggest that pyrite was formed before the other sulfides in the ore bodies. The differences are small between the amounts of minor elements in pyrite of the No. 2 mine and the No. 3 mine (Table 5). The differences in the concentrations of minor elements between pyrite disseminated in layers in pyritic schist and pyrite disseminated in marble are also fairly small. However, there is an impressive difference between the amounts of cobalt and nickel in pyrite from the metasedimentary rocks and pyrite from the ore bodies. Pyrite disseminated in the metasedimentary rocks contains more than 200 ppm each of cobalt and nickel. The amounts of cobalt and nickel are each less than 50 ppm in most samples of pyrite from the ores. It is clear from the data on minor elements that the pyrite of the ore bodies is not a representative sample of the pyrite from the metasedimentary rocks away from the mines. Unless there was some large, unexpected fractionation process operating, it is unlikely that the pyrite in the mining areas is genetically related to the pyrite in the metasedimentary rocks away from the sulfide ore bodies.

In addition to the study of minor elements, a study was made of the isotopic composition of the lead in samples of marble and of the lead from galena of the ore bodies. In order to compare the isotopic ratios of lead in the ores with the lead in the marble, it is necessary to correct the lead in the marble for the radiogenic decay of uranium and thorium since the time of formation of the ore bodies. It must be assumed that the marble has remained a closed system with respect to lead and uranium since the time of formation of the ores. The assumption is probably valid. Geologic studies of the Balmat-Edwards area have failed to reveal any evidence of a major change in the Precambrian rocks or minerals subsequent to the billion year metamorphism. As noted in the section on Age and Paragenetic Sequence, it is inferred that the time of the primary mineralization at Balmat was about 1050 ± 150 million years ago. The concentrations of uranium and lead in the marble samples are given in Table 7. The corrected isotopic compositions of lead in the marbles bear the following relation to lead from galena of the ore bodies:

Marble Sample	$\frac{Pb^{206}}{Pb^{204}}$	$\frac{Pb^{207}}{Pb^{204}}$	Mine (Average)	$\frac{Pb^{206}}{Pb^{204}}$	$\frac{Pb^{207}}{Pb^{204}}$
fd 7-2	16.05	15.46	No. 2	17.08	15.71
fd 7-3	17.53	15.63	No. 3	16.92	15.63

It appears that the two specimens of marble had different isotopic compositions of lead a billion years ago. From this it is felt that the isotopic composition of lead in the metasedimentary units was not homogenized during the last, severe metamorphism of the rocks in the area. The number of specimens examined from the metasedimentary rocks is small. These two samples of marble may not contain the extreme range in the isotopic compositions of lead in the metasedimentary rocks. However, unless the isotopic composition of lead in the ores is a homogeneous mixture of lead from an isotopically inhomogeneous source, it is doubtful that the lead in the ores was derived from the surrounding marbles.

The concentrations of thorium were not determined. It was not found advisable to assume a value for the ratio of uranium to thorium in the marbles. Thus, the Pb^{208}/Pb^{204} ratio could not be corrected for the decay of thorium over the last billion years. It was stated above that the differences between the ratios of Pb^{208}/Pb^{204} for lead of the ores and lead from the marble are small. If marble specimens fd 7-2 and fd 7-3 contain more than 0.2 and 0.03 ppm of thorium respectively, then the ratio of Pb^{208}/Pb^{204} in the marble a billion years ago would have been insufficient for the marble to have contributed significant amounts of lead to the ores. However, 0.2 and 0.03 ppm for the concentrations of thorium in carbonate rocks are not unreasonably low.

In addition to the consideration of the metasedimentary rocks that envelop the sulfides as a source of that ore, the isotopic composition of the lead in galena can be used to estimate more general characteristics of the source of the ores. A model age for galena from Balmat was calculated from the Pb^{206}/Pb^{204} and Pb^{207}/Pb^{204} ratios by the Houterman-Holmes equation. The isotopic composition of lead at the time of the origin of the earth was chosen to be the values obtained by Patterson (1956) for the lead from troilite in meteorites. The age of the earth was chosen to be 4.55×10^9 years (Patterson, 1956). The model age for the galena from Balmat was calculated to be 1100 million years which is in excellent agreement with the inferred age of 1050 ± 150 million years. The uncertainty to which the isotopic ratios of lead in galena and in troilite can be measured and the uncertainty in the decay constants of uranium probably introduce a doubt into the model age of about 100 million years. Using the model age as the age of the galena, a present day ratio of the U^{238}/Pb^{204} ratio may be calculated for the model source. The calculation uses the Pb^{206}/Pb^{204} ratio of galena and the Pb^{206}/Pb^{204} ratio for lead from troilite. The present day ratio of U^{238}/Pb^{204} in the model source is calculated to be about 9.1 with an analytical uncertainty of about 0.2. This ratio is similar to those calculated for lead from ores of several other districts (see Catanzaro and Gast, 1960; Stanton and Russel, 1959).

The lead-model age of the ores is compatible with the age of the ores determined by other means. This suggests that the only change in the uranium to lead ratio in the source of the lead throughout geologic time was due to the radiogenic decay of uranium with the corresponding accumulation of the decay products. Whether the source was an isotopically homogeneous "substratum" or a representative sample from an isotopically heterogeneous assemblage of crustal rocks is not known. The contents of minor elements in pyrite from the ore bodies are different from the contents of minor elements in pyrite disseminated in marble and pyritic schist away from the ore bodies. This suggests that the sulfides in the ore bodies were not derived by accretion of the metals from the metasedimentary rocks enveloping the ores.

Temperature Of Formation Of The Ores

Several different methods have been employed in an effort to determine the temperatures of formation of the sulfide minerals at Balmat. Certain limitations may be placed upon the temperatures involved by the minerals present in the ore and the associations of these minerals. The concentrations of iron in sphalerite and of sulfur in pyrrhotite may indicate temperatures of formation when the associations between sphalerite, pyrrhotite, and pyrite are understood. Under equilibrium conditions, the partitioning of minor elements between sulfide phases may indicate the relative or absolute temperatures at which the equilibrium was established. The means of estimating the temperatures involved in formation of the ores at Balmat will be discussed in the order they are introduced above.

Minerals and Mineral Associations.

The first sulfide mineral formed in the mining areas was pyrite (Figure 3). Kullerud and Yoder (1959, p. 562) report that pyrite cannot exist above 800°C at several kilobars total pressure. Marcasite was one of the last sulfide minerals to form in the No. 2 mine. Although the effect of total pressure on the inversion of marcasite is not known, Kullerud and Yoder (1959, p. 539) indicate that marcasite cannot exist for long periods of time at 400°C without inverting to pyrite. Thus, in the late stages of sulfide mineralization, the temperature of formation of the marcasite was probably less than 400°C.

No obvious wall rock alteration products are associated with the ore except for the bleaching of the graphitic dolomite around the Loomis ore body in the No. 3 mine. Reasons were given in the section on Age And Paragenetic Sequence to believe that the ores were introduced to the mining areas during a retrograde stage of metamorphism of the marbles. The lack of any wall rock alteration around the ores may indicate that the sulfide minerals throughout the period of their formation were formed at close to the temperatures of formation of anthophyllite, serpentine, and talc in the surrounding rocks. The retrograde metamorphism presumably implies a decrease in temperature and/or pressure from the peak temperature and pressure during the metamorphism. Engel and Engel (1958, p. 1374) indicate that the probable maximum temperature of the metamorphism in question in the area near Balmat was 550°C. The sulfide ores, then, could have formed near or below 550°C.

Iron in Sphalerite. The amount of iron in sphalerite is controlled by temperature, total pressure, and the bulk chemistry of the system. Iron enters sphalerite approximately as FeS, since the metals and sulfur in sphalerite balance stochiometrically. If pyrrhotite coexists in equilibrium with sphalerite, the amount of iron found in the sphalerite will be principally a function of temperature and total pressure. On the other hand, if pyrite is the coexisting iron mineral, the iron that enters sphalerite must lose half of its sulfur. In the latter case, the iron content of sphalerite will be a function of the fugacity of the sulfur species as well as of temperature and total pressure. If the iron is initially present as an oxide, the iron must gain sulfur and lose oxygen in order to be dissolved in quantity in sphalerite. As pyrrhotite has very crudely the formula FeS, the solubility of pyrrhotite in sphalerite will be only slightly affected by the fugacities of the accompanying volatile constituents. However, if pyrite and iron oxide minerals constitute the iron phase rather than pyrrhotite, the amount of iron that can be accommodated in sphalerite will be controlled by the fugacities of the volatile constituents, such as sulfur, oxygen, and hydrogen, as well as by temperature and total pressure.

The relationship between temperature, total pressure, and the amount of iron that sphalerite will dissolve, when associated with FeS, was determined by Kullerud (1953; also, 1959). A note on the relationship between the content of iron in sphalerite associated with pyrite at a given temperature was given by Barton and Kullerud (1958). These investigators found that, if FeS_2 is the accompanying iron phase, sphalerite will dissolve a smaller quantity of iron at a given temperature than if FeS is the iron phase. This is in accord with the discussion given above. The implication is that the amount of iron in sphalerite associated with pyrite will give a minimum temperature of formation if the temperature is determined from the solvus for the FeS-ZnS system.

The conversions from weight percent to mole percent for FeS, MnS, and CdS in sphalerite given in Kullerud (1953) are incorrect. Kullerud (personal communication) has given the following recalculated values for the maximum solubility of iron in sphalerite at several temperatures:

T(°C)	FeS Wt. %	FeS Mol. %	T(°C)	FeS Wt. %	FeS Mol. %
894	36.5	38.9	600	19.0	20.6
850	33.0	35.3	500	14.7	16.0
800	29.8	32.0	400	11.0	12.0
750	26.7	28.7	300	7.45	8.2
700	24.0	25.9	200	4.80	5.3
			138	3.6	4.0

With reference to the list of values given above, Skinner, Barton and Kullerud (1959, p. 1046) state:

> "Temperature determinations using the sphalerite geothermometer based on the original solvus curve should be viewed with caution pending further studies."

The effect of total pressure on the solubility of FeS in ZnS has been calculated by Kullerud (1953), assuming that FeS enters sphalerite in ideal solution. The volume of FeS with the sphalerite structure was determined by extrapolating, to 100 percent FeS, the curve for the change in volume of ZnS with increasing concentrations of iron. One test of the calculation, employing a bomb experiment at 1000 atmospheres, was in agreement with the calculation. It was found that the temperature needed to maintain a given concentration of FeS in sphalerite, associated with hexagonal FeS, must be 20-25°C higher for each kilobar increase in the total pressure on the system.

A major problem to be considered is the relationship between the concentration of iron found in sphalerite and the temperature at which the sphalerite approached saturation with iron. The phase diagram of the FeS-ZnS system was determined by both the process of dissolution of FeS into and the exsolution of FeS out of sphalerite. The reaction rates of FeS and ZnS are appreciable above 400°C. The time required for the quantity of FeS in sphalerite to come into equilibrium, at temperatures above 400°C, was less than a year. Below 400°C, Kullerud could not obtain equilibrium, and the points on the phase diagram were located by extrapolating data from higher temperatures. The equilibrium concentration of FeS in sphalerite was frozen into the structure by quenching the samples. In many processes in nature, the cooling of a sample is much more slow than in laboratory procedures; yet, sphalerite samples in nature are known to contain FeS in a supersaturated state for presumably a billion years. Sphalerite at Balmat is such an example. It is a matter of interpretation as to when the iron content of sphalerite, found upon analysis, became frozen into the lattice.

Kullerud (1959) has demonstrated that the processes of exsolution on natural samples of sphalerite may be extremely slow. He found that FeS did not exsolve from a natural specimen of sphalerite heated to 500°C for a year. This sphalerite contained enough iron to indicate a temperature of 620°C. At Balmat, textures that possibly suggest exsolution of FeS from sphalerite are rare and, when present, would not contribute more than about one-half percent FeS to the sphalerite analysis.

At Balmat, sphalerite was deposited into a system containing pyrite without pyrrhotite. This sphalerite contains greater than 6 weight percent FeS in the No. 2 mine and greater than 2 percent FeS in the No. 3 mine. Since the rates of reaction in the system FeS-ZnS are known to be appreciable, the lack of differences in the content of iron in sphalerite over short distances suggests that, at some temperature and fugacities of gaseous species, the concentration of iron in sphalerite approached an equilibrium quantity with pyrite. It is assumed that the concentration of iron in sphalerite has not significantly altered since the time of formation of the sphalerite. Therefore, the sphalerite probably formed at greater than 320°C, assuming a total pressure of 3 kilobars. It is inferred from textural relations discussed above that pyrrhotite formed in a system containing both sphalerite and pyrite. Sphalerite associated with the pyrrhotite contains iron (12.8 ± 1 percent FeS by weight) indicative of a temperature of 510° ± 50°C (with a total pressure of 3 ± 1 kilobars). This temperature is assumed to be close to the temperature at which pyrrhotite is formed.

Certain gradients in the concentration of iron in sphalerite are indicated to exist between the areas where sphalerite is associated with both pyrrhotite and pyrite and those areas where pyrite is the only iron phase (for example, see Figure 4). It is these gradients that the author previously interpreted to represent gradients in temperature (Doe, 1956; also see Kullerud, 1959, p. 328). What now seems to be a better interpretation is given below.

At Balmat, pyrrhotite was formed after pyrite and most of the sphalerite, during the most recent episode of metamorphism in the Balmat area. The high content of iron in sphalerite associated with pyrrhotite probably represents an approach of equilibrium between sphalerite and pyrrhotite at the conditions of formation of the pyrrhotite. The transition zones, then, would represent a transition from the conditions under which pyrrhotite was formed to those under which pyrrhotite was not stable. These transition zones in the concentration of iron in sphalerite could be explained by a drop in temperature and/or change in the fugacity of volatile species away from pyrrhotite. The lack of wall rock alteration around pyrrhotite and the disseminated nature of the pyrrhotite grains suggest that pyrrhotite formed at near the temperature of formation of the minerals in the country rock. This temperature would be similar to or somewhat less than the temperature at which sphalerite formed, because pyrrhotite formed later than sphalerite in the retrograde metamorphism. Therefore, it appears that the transition zones are probably a manifestation of change in the fugacity of volatile species rather than a drop in temperature away from pyrrhotite.

The FeS-FeS_2 System. A phase diagram for the system FeS-FeS_2 has been determined by Arnold (1956, 1957, 1958). According to Arnold (1957), the effect of total pressure on the solubility of pyrite in pyrrhotite is negligible, in the range of compositions represented at Balmat. The composition of the pyrrhotite at Balmat indicates a temperature of about 340°C. Sphalerite associated with pyrrhotite was interpreted to indicate a temperature of formation of the pyrrhotite of about 510° ± 50°C. Although there is uncertainty in the phase diagram of the FeS-ZnS system, the proposed corrections to the system indicate that the temperatures given by the uncorrected diagram are too low (Skinner, et al., 1959). There is a distinct discordance between the temperatures indicated by the FeS-ZnS system and the Fe-FeS_2 system as applied at Balmat. This kind of discordance is also noted by Skinner (1958, p. 559) in the Nairne pyritic formation in Australia and to a lesser extent by Stone

(1959, p. 1019) in the Naica District, Chihuahua, Mexico. On the other hand, Arnold (1958) found good agreement between the temperatures indicated by the two systems. At Balmat, small euhedral grains of pyrite are commonly found within and on the fringes of pyrrhotite. These may represent pyrite exsolved from pyrrhotite upon cooling. If this is correct, the composition of the pyrrhotite at Balmat indicates a minimum value of the temperature at which the pyrrhotite formed.

Fractionation of Minor Elements Between Sphalerite and Pyrite. The ratio of the mole fractions of an element present in each of two minerals will be called the fractionation factor. In the case of two minerals such as sphalerite and pyrite, it is likely that minor elements are present in pyrite in the form AS_2 and in sphalerite as AS. If this is the case, a transfer of a minor element between the two phases will involve a reaction such as:

$$(AS_2)^{py} = (AS)^{sl} + \tfrac{1}{2}S_2$$

$$K_A = ({}^{a}AS)^{sl}({}^{p*}S_2)^{\frac{1}{2}} / ({}^{a}AS_2)^{py} = \exp(-\Delta F^{o}_{A} / RT) \qquad (1)$$

where K_A is the equilibrium constant for the reaction given; $({}^{a}AS)^{sl}$ is the activity of the minor element specie "A" in sphalerite; $({}^{a}AS_2)^{py}$ is the activity of the minor element specie "A" in pyrite; $({}^{p*}S_2)$ is the fugacity of sulfur in the system; $-\Delta F^{o}$ is the standard free energy of the reaction; and T is the temperature in degrees Kelvin. The fractionation factor will then be a function of the fugacity of sulfur as well as of temperature, of the degree of approach of equilibrium, and total pressure.

The reaction involved in the transfer of a minor element between sphalerite and pyrite is probably more complicated than has been assumed in Equation 1. For example, the reaction might involve H_2S and H_2 rather than S_2. These complications can be eliminated if they occur in similar fashion for two different minor elements. If the equilibrium for the two minor elements between the phases was approached at the same time, dividing the equilibrium constant for one minor element by the other yields:

$$K_A/K_B = ({}^{a}AS)^{sl}({}^{a}BS_2)^{py} / ({}^{a}AS_2)^{py}({}^{a}BS)^{sl} = \exp\left[-(\Delta F_A^o - \Delta F_B^o)/RT\right] \tag{2}$$

Thus, Equation 2 shows that the fugacities of the volatile constituents cancel upon the division of the equilibrium constants if the reactions are of the same form. The ratio of the fractionation factors for two minor elements then becomes a function of temperature and how close equilibrium is approached. By studying the ratios of the fractionation factors, it should be possible to obtain some information on how closely the sulfide minerals approached an equilibrium assemblage at some particular temperature and total pressure.

It was concluded above that pyrite and sphalerite approached equilibrium with respect to iron at some temperature above 320°C. The ratio of the fractionation factors for iron and manganese distributed between sphalerite and pyrite should be independent of the fugacities of the sulfur species (Equation 2). The data of Table 6 indicate that the ratios of these fractionation factors range between 37 and 12,000 (column 3) for the No. 2 mine. In addition, there is no well developed correlation between the iron content of sphalerite and the fractionation factor for manganese. It is difficult to account for these relations by a change in temperature with equilibrium being maintained. For example, see the rates of change with temperature of the fractionation factors for cadmium, selenium, and manganese distributed between sulfide minerals (Bethke and Barton, 1959, p. 1570). The range of the ratios (Table 6) probably indicates that an equilibrium distribution of manganese between sphalerite and pyrite was not well developed. Apparently equilibrium was achieved more readily by some constituents than by others. Geothermometers based upon the exchange of minor elements between sulfide minerals may be difficult to apply to ore deposits.

CONCLUSIONS

At Balmat, it is unlikely that the pyrite in the ore bodies is genetically related to the disseminated grains of pyrite found in the metasedimentary rocks away from the ore bodies.

A common lead age, determined from the isotopic composition of lead from galena of the ores, is in good agreement with the age of the mineralization determined by other means -- about a billion years.

The concentrations of iron in sphalerite and sulfur in pyrrhotite at Balmat indicate that the bulk of the ores in the No. 2 mine formed above 320°C. It seems likely that the amounts of iron in sphalerite associated with pyrrhotite are representative of the temperatures and total pressure of formation of the pyrrhotite. However, this temperature is indicated by the FeS-ZnS system to be about 500°C, whereas that indicated by the $FeS-FeS_2$ system is about 340°C. This discordance may be accounted for, at least in part, by the exsolution of some pyrite from pyrrhotite.

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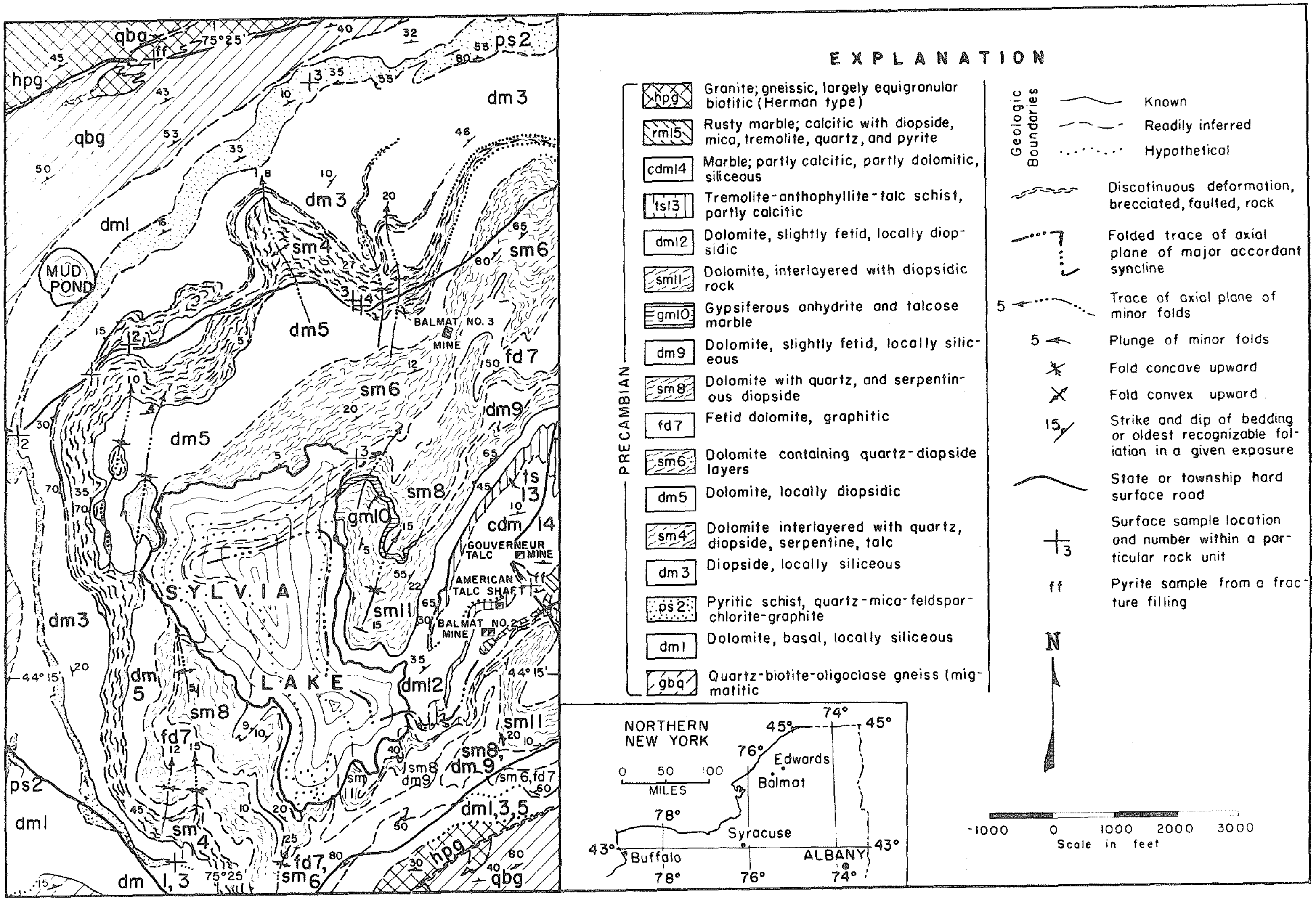

Figure 1: Geology of the Balmat Area (A partial copy of Plate 2 in Brown and Engel, 1956)

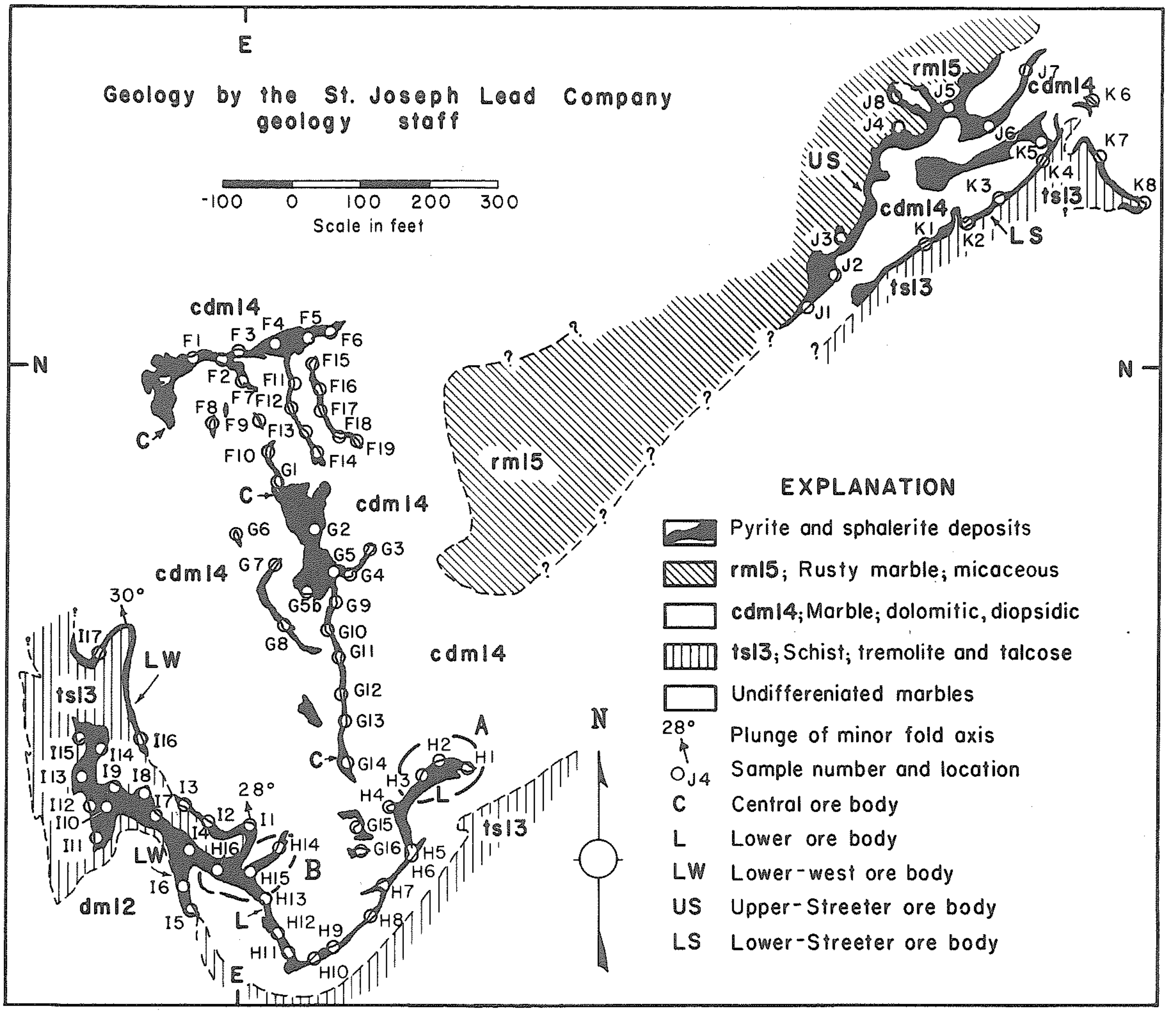

Figure 2: Geology and distribution of samples on the 1100 foot grizzly sublevel of the Balmat No. 2 mine.

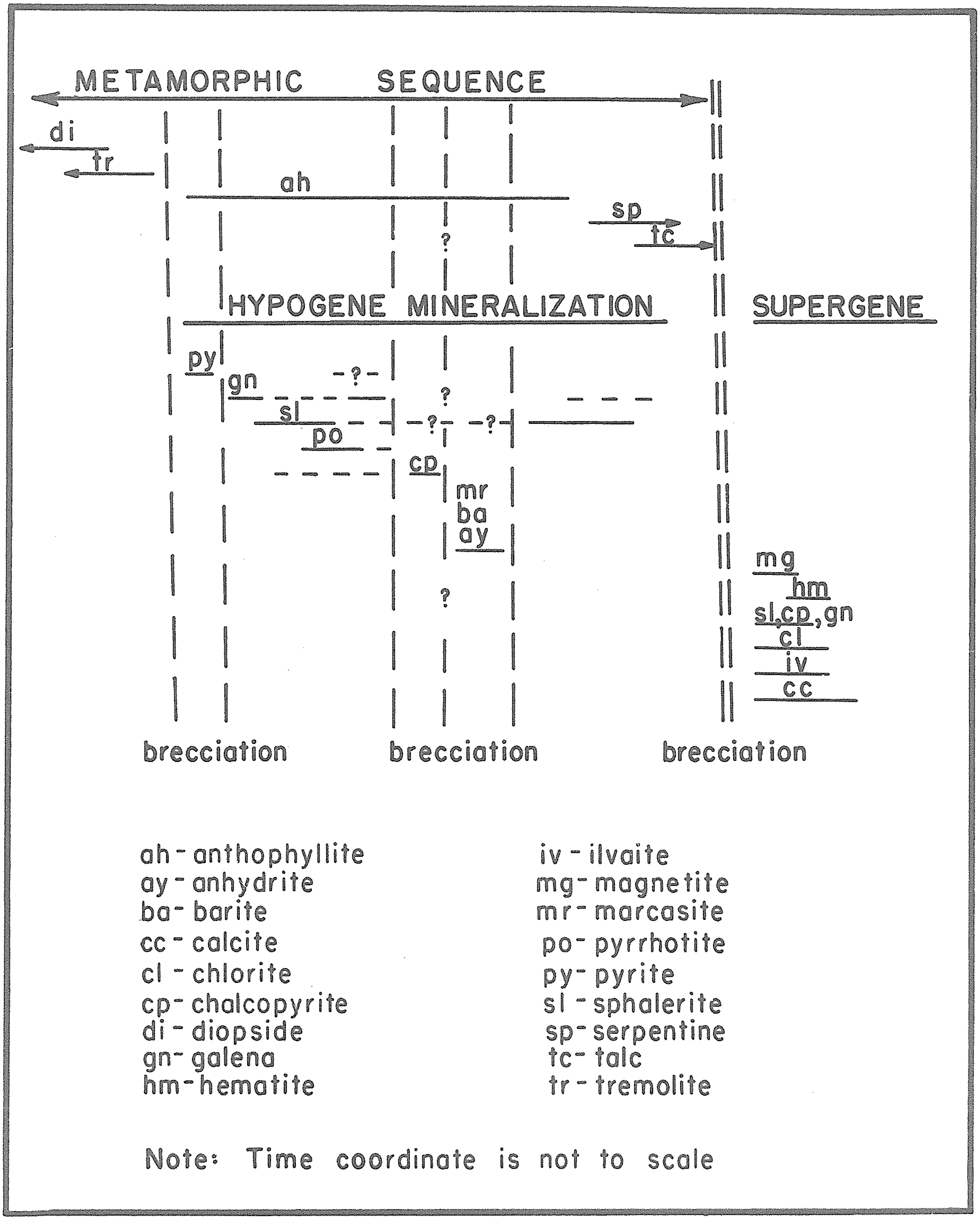

Figure 3: Paragenesis of the sulfide minerals in the descending temperature phase of the most recent episode of severe metamorphism in the Balmat area.

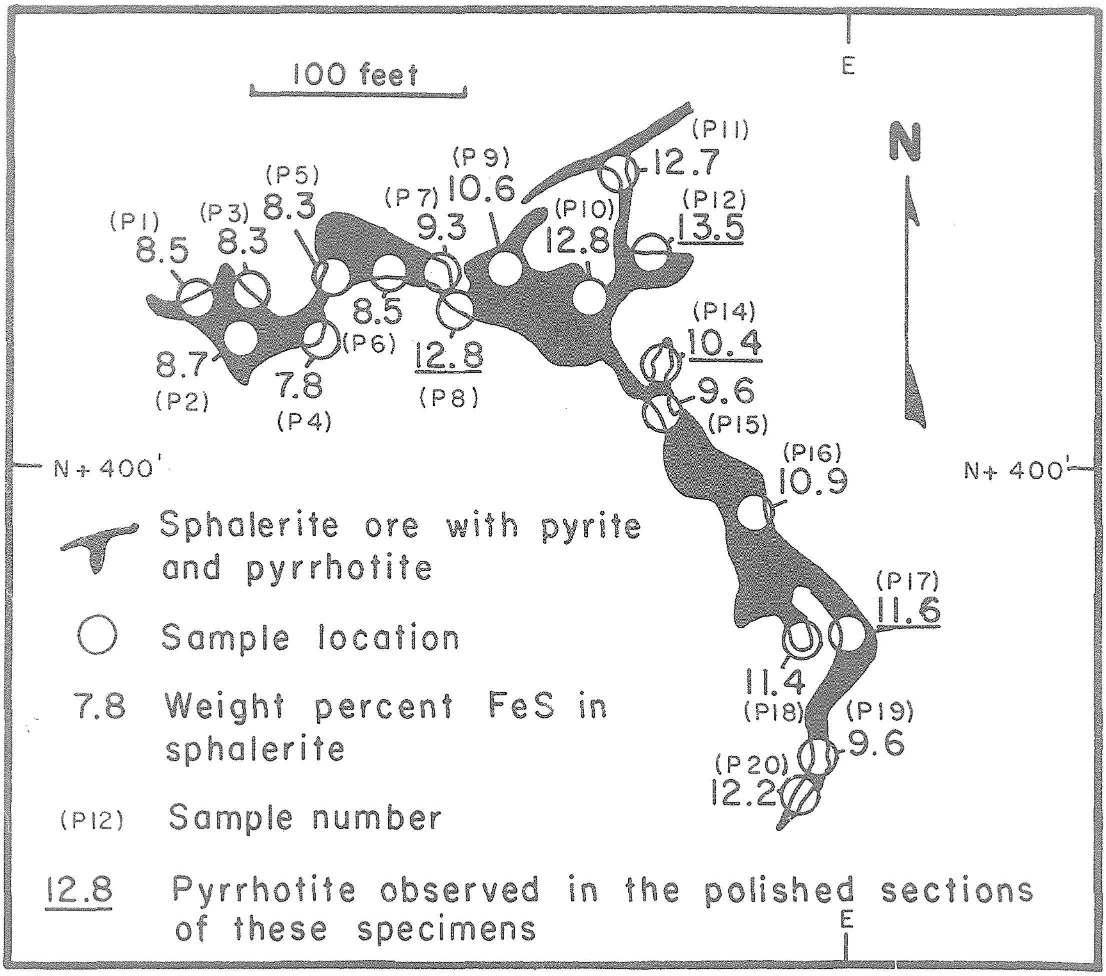

Figure 4: Variations in the content of iron in sphalerite of the central ore body, 1500 foot grizzly sub-level, Balmat No. 2 mine.

THE DISTRIBUTION AND COMPOSITION OF SULFIDE MINERALS AT BALMAT, NEW YORK

Thesis by

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In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1960

ACKNOWLEDGEMENTS

The author is greatly indebted to Dr. A.E.J. Engel who served as doctoral dissertation advisor on this research at the California Institute of Technology; to Dr. J. S. Brown who originally suggested Balmat as an area fitting many of the requirements the author stated to him, and who gave much geological advice on the area under study; and to Dr. C. C. Patterson who aided and encouraged the reconnaissance study of lead isotopes.

Financial support was obtained basically through a Kennecott Copper Company Fellowship with research funds during the years 1957-58 and 1958-59. The Pan American Petroleum Company provided a fellowship for the year 1956-57. The St. Joseph Lead Company hired the author during the summer of 1957 to enable gaining first hand knowledge of the ore bodies and collection of samples.

Further, I am greatly indebted to the St. Joseph Lead Company for providing the geologic maps required of the No. 2 and No. 3 Balmat mines, and more particularly to Dr. J. S. Brown, Mr. N. H. Donald, Mr. S. P. Brown, Mr. David B. Dill, and Mr. Edward R. Lea who have done the actual geologic mapping presented in this study. Mr. Severn P. Brown collected the samples for the preliminary study, and Dr. Philip Bethke served as advisor on the preliminary study at the Missouri School of Mines.

Also, I would like to acknowledge the stimulating discussions held with Dr. Arthur Rose, Dr. James Noble, Dr. G. J. Wasserburg, and Dr. Barclay Kamb. Mr. Arthur Chodos and Miss Elizabeth Godijn advised on the emission spectrographic work and x-ray fluorescent and diffraction

work. Mrs. Judith Kawafuchi aided the author on the isotopic composition and isotope dilution studies of lead and uranium. The author, of course, assumes the responsibility for the accuracy of all material contained in this investigation.

Many thanks are due to Mr. Rudolph von Huene for preparation of the three hundred polished and thin sections, and especially for developing the polished-thin section for study of opaque and translucent minerals on one slide.

ABSTRACT

The sphalerite and pyrite from the No. 2 and No. 3 mines at Balmat, New York, and pyrite from the surrounding country rock are analyzed for minor and trace elements. The iron content was determined in 18 samples of sphalerite associated with pyrite and pyrrhotite, and in 177 samples of sphalerite associated with pyrite without pyrrhotite. Analyses for minor and trace elements were made of 74 samples of sphalerite from the mining areas, 32 samples of pyrite from the mining areas, and nine specimens of pyrite from the surrounding metasedimentary rock. In addition, trace and minor elements were determined in nine samples of calcite, seven samples of dolomite, and three samples of pyritic schist from four metasedimentary units. The isotopic composition of lead was determined in seven specimens of galena and in two samples of marble. The compositional studies of minerals are related to geologic features of the ore bodies and the surrounding metasediments in order to clarify the (1) relative and absolute age of the deposition of the sulfides, (2) temperature and pressure at which the sulfides were emplaced, (3) source and composition of the ore forming fluid, and (4) causes of the zonal pattern of the minerals in the ore bodies.

The primary mineralization occurred during a period of hydration of the surrounding metasediments, after the growth of tremolite and before the formation of talc. Tremolite and talc formed during the metamorphism and retrograde metamorphism of the Grenville series near Balmat. The metamorphism is thought to have occurred about 1050 million years ago. The ore fluid successively deposited pyrite, then galena and iron-rich sphalerite followed by pyrrhotite and chalcopyrite. Subsequently much of the pyrrhotite was altered to marcasite. The marcasite is thought to have formed during the deposition or remobilization of anhydrite and barite. The mineralization concluded with the deposition of iron-poor sphalerite. Recurrent microbrecciation of the metasediments and ores can be correlated with the time sequence of formation of the various ore minerals in various parts of the mines. The ore fluid followed the separate zones of microbrecciation and deposited the sulfides at nearly the temperature of the country rock. On the basis of the space and time relationship between the zones of microbrecciation and different ore minerals, it is inferred that the composition of the ore fluid reaching the site of deposition of the sulfides changed with time.

The isotopic composition of lead from galena indicates that the source of the galena is compatible with the following model - a homogenized substratum in which radiogenic lead from the decay of uranium and thorium has been added to lead of meteoritic composition without disruption from the time of origin of the earth until the time of extraction of the ore fluid.

A part of the pyrrhotite found in the No. 2 mine was formed in an area containing sphalerite and pyrite. The iron content of sphalerite

(12.5 ≠ 1 percent FeS by weight) associated with pyrrhotite and pyrite is found to be significantly higher than in areas where sphalerite occurs without pyrrhotite. It is inferred that in the region containing pyrrhotite the sphalerite became saturated with FeS at the temperature of formation of pyrrhotite. From the estimates of others on similar areas, the total pressure during the deposition of the ores at Balmat is assumed to be 3 ± 1 kilobars. By use of the phase diagram for the FeS-ZnS system, the temperature of deposition of pyrrhotite is found to be 510°.

The composition of pyrrhotite was investigated by the measurement of lattice spacings. Only one specimen of pyrrhotite was found to contain the necessary hexagonal structure for use with published plots of lattice spacing versus composition. By use of the phase diagram for the FeS-FeS_2 system, a temperature of formation of pyrrhotite based on one specimen is indicated to be 340°C. The discordance in the temperature estimate using two different geothermometers is thought to be due at least in part to exsolution of pyrite from pyrrhotite at a temperature lower than that of the formation of pyrrhotite.

The variation in the iron content of sphalerite associated with pyrite is thought to be mainly due to variations in the fugacity of sulfur species rather than changes in temperature. By use of the phase diagram of the ZnS-FeS_2-S system, the temperature of formation of sphalerite (6-9 percent FeS by weight) associated with pyrite in the No. 2 mine is indicated to be greater than 320°C. Sphalerite associated with pyrite in the No. 3 mine contains 2-3 percent FeS by weight.

Calculations based on the partitioning of trace and minor elements between sphalerite and pyrite give a first approximation of the temperature at which equilibrium was approached in the No. 3 mine of 300-350°C.

Once sphalerite acquires a particular concentration of iron, it is quite resistant to change due to following geologic events. At the temperatures of formation of the sulfides at Balmat, however, reaction between sphalerite and pyrrhotite must have been comparitively rapid. Alternation of pyrrhotite to marcasite did not seem to affect the concentration of iron in sphalerite. Supergene mineralization of magnetite, hematite, and chlorite leached iron from sphalerite grains, but the leached zone is usually 0.1 millimeter thick or less and only rarely attains a thickness of one millimeter. On the other hand, the content of manganese in sphalerite from the zones of supergene mineralization is much lower than sphalerite away from the zones. The concentration of cadmium in sphalerite from both mines falls in the range 1000 to 2000 parts per million with an average value of 1400 parts per million. The content of cadmium in sphalerite does not seem to be sensitive to temperature or accompanying mineral phases or the supergene mineralization.

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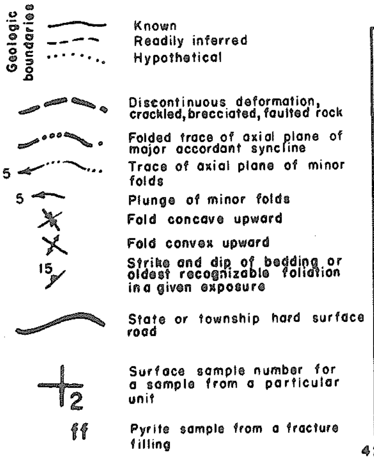
I. INTRODUCTION

General Some of the most fundamental questions involved in geology are those of historical geology - i.e., relative and absolute chronology of events, and whether or not and in what way two events are related. The importance of time is implied in the definition of event as "something which occurs in a certain place during a particular interval of time" (American College Dictionary, 1956). Other questions frequently of interest are the temperature(s) and pressure(s) at which reaction of earth materials takes place and the source from which movement of the earth materials started. In most reactions in the crust of the earth, a material balance prevails in which a phase or phases of a particular composition are introduced and others are extracted.

A base metal deposit is formed in a particular place over a particular interval of time with a specific relation to events occurring around it. There is a source of material for the deposit and a material balance during deposition. A compositional study has been made on the major sulfide minerals of the ore deposits and surrounding metasedimentary rock at Balmat, St. Lawrence County, New York, in the Grenville subprovince (Fig. 1) in order to obtain answers to the fundamental questions outlined above about the formation of a base metal deposit. A particular effort has been made to determine the temperature of deposition of some of the sulfides of the Balmat ores by use of the FeS-ZnS system (Kullerud, 1953) and the FeS-FeS_2 system (Arnold, 1958). The paragenesis of the ore deposits is reanalyzed, and conclusions on the relation of the age of ore mineralization to the metamorphism of the surrounding

EXPLANATION

Precambrian		hpg	Granite, gneissic, largely equigranular, biotitic (Hermon type)
		uym	Marble, undifferentiated, largely dolomitic, partly silicated, locally calcitic
	GRENVILLE SERIES	mgl6	Median gneiss, quartz-two mica-two feldspar migmatite and amphibolite
		rml5	Rusty marble, calcitic with diopside, mica, feldspars, tremolite, quartz and pyrite
		cdml4	Dolomite partly calcitic marble, silicated
		tsl3	Tremolite-anthophyllite-talc schist, in part calcitic
		dml2	Dolomite, slightly fetid, locally diopside
		sml1	Dolomite, interlayered with diopsidic
		gml0	Gypsiferous anhydrite and talcose marble
		dm9	Dolomite, slightly fetid, locally silicated
		sm8	Silicated dolomite, dolomite interlayered quartz, and serpentinous diopside
		fd7	Fetid dolomite, graphitic
		sm6	Silicated dolomite, dolomite containing quartz-diopside layers
		dm5	Dolomite, locally diopsidic
		sm4	Silicated dolomite, dolomite interlayered with quartz, diopside, serpentine, talc
		dm3	Dolomite, locally silicated
		ps2	Pyritic schist, quartz-mica-feldspar-chlorite-graphite
		dm1	Basal dolomite, locally silicated
		qbg	Quartz-biotite-oligoclase gneiss (migmatitic)



A Partial Copy of the Geology of The Balmat Area by J.S. Brown and A.E.J. Engel (1956, Pl. 2)

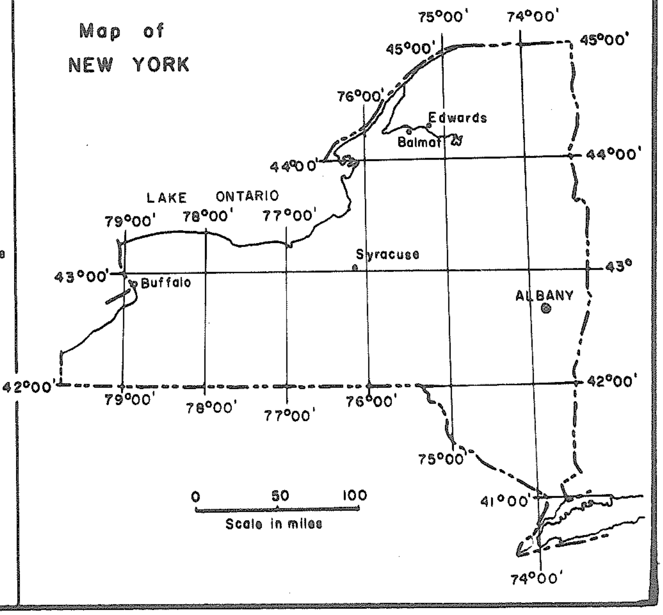


Fig. 1: Geology of the Balmat Area (A partial copy of

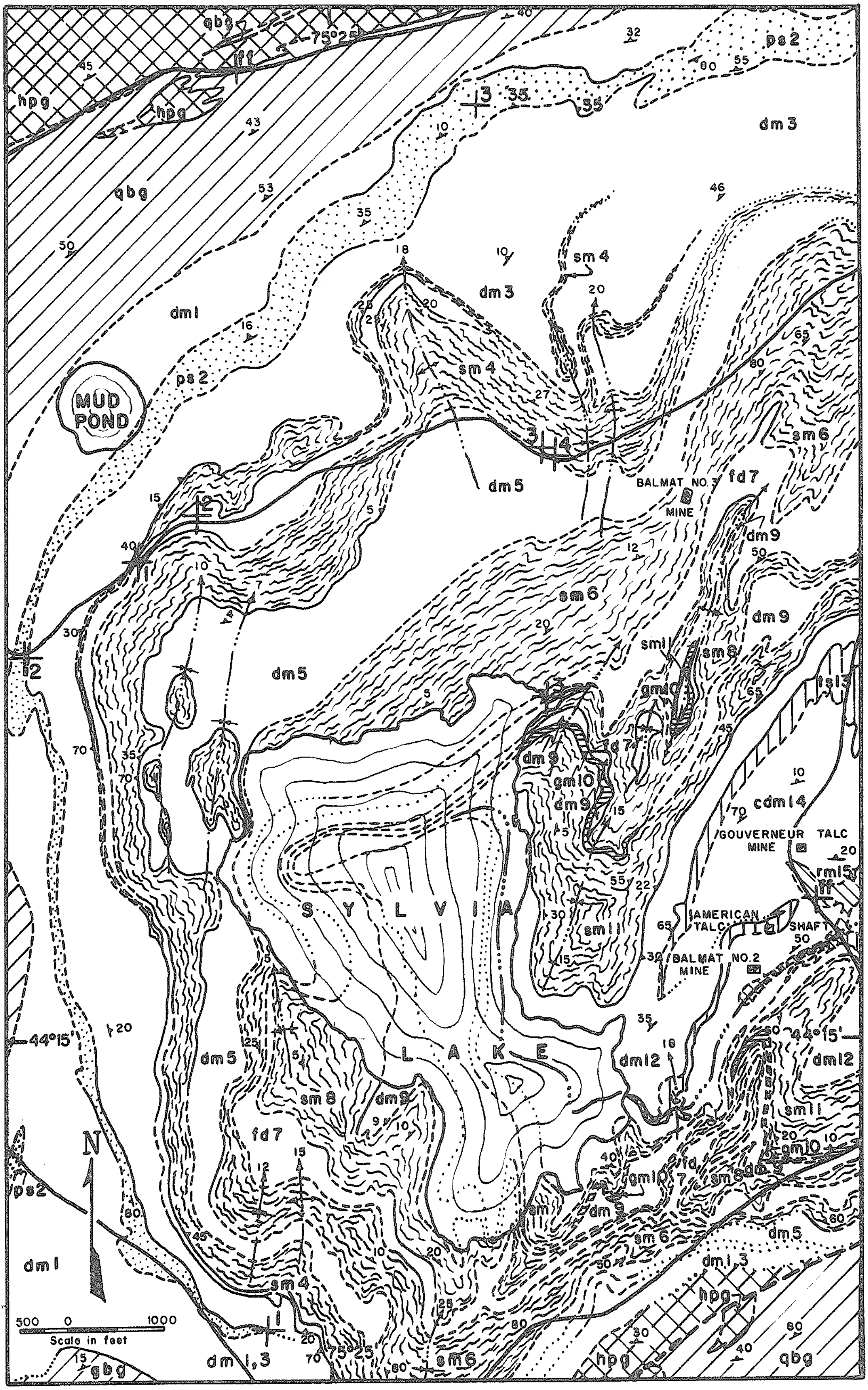


Plate 2 in J.S. Brown and A.E.J. Engel, 1956) metasedimentary rock are reconsidered and compared with the conclusions of Brown (1936a), Engel and Engel (1959), and Brown and Kulp (1959). A possible origin of the ore fluid is presented and compared with the suggestions of Engel (in press) and Brown (1936a, 1948). Engel suggests that the ore may have been derived from the enclosing metasedimentary rock. Brown (1936a) first suggested that the ore was derived from an igneous intrusion, probably not uncovered at present. Later Brown (1948) suggested that the ore fluid was derived directly from a substratum (mantle ?).

In the Balmat-Edwards area there are four mines (three in operation at the present time) in which sphalerite is the principal mineral produced. The ores also contain from 1 to 50 percent pyrite, minor amounts of galena, and localized occurrences of pyrrhotite. The Balmat No. 2 mine, Hyatt mine, and Edwards mine are described in more or less detail in Brown (1936a and b, 1947). The Balmat No. 3 mine was started in 1949 and is presently undescribed in the literature although it is shown on the geologic map of Brown and Engel (1956), and the occurrence of the ore is mentioned in the text. The labels of the No. 2 and No. 3 mines are reversed on the geologic map of Brown and Engel (1956).

Talc mining is also abundantly carried on in the Balmat-Edwards district except that in the literature on talc the district is usually referred to as the Gouverneur talc district (Engel, 1949).

Previous Work The Balmat-Edwards mining district has been the subject of many geologic studies including those of Newland (1916), Smyth (1918), Spurr (1924), Brown (1936a, 1936b, 1947), Brown and Engel (1956), Brown and Kulp (1959), Engel (1948), and Engel and Engel (1958).

The deposits of sphalerite and pyrite in the Balmat-Edwards district have been listed as Precambrian since the earliest reports (Newland, 1916; Smyth, 1918). Brown and Kulp (1959) state that:

> "These ores have been assumed to be of Precambrian age but geologic data for this conclusion are not compelling."

From common lead isotope data of galena and jordanite, Brown and Kulp (1959) conclude the age of the ore galena is 1050 ± 100 million years using the Houtermanns-Holmes model of lead evolution. Brown and Kulp (1959) comment that the age of the mineralization is concordant with the age of the Grenville metamorphism. Brown (1936a) feels that the sulfides of the ore body are later than the formation of diopside and tremolite in the Grenville metamorphism, and, in spite of the widespread occurrence of serpentine and talc throughout the district, Brown concludes that (1936a, p. 253):

> "Talc is the most abundant of the deep-seated alteration products. It has commonly been regarded as derived mainly from tremolite, and in the talc mines that may well be true. In both Balmat and Edwards ore, however, talc was derived mainly from diopside. In the early stages it formed along cleavages and cracks, finally completely replacing the diopside, and beyond that it has been widely distributed as a replacement of carbonate and barite and a filling of cracks in sulphides."

Brown (1936a) concludes that the talc and serpentine associated with the sulfides are post-ore hydrothermal alteration products. Brown (1936a) gives a generalized paragenesis of the primary ore as:

(meta)diopside and (meta)tremolite ⟶ brecciation ⟶ pyrite ⟶ sphalerite ⟶ galena-? ⟶ pyrrhotite ⟶ chalcopyrite ⟶ barite and anhydrite ⟶ (hydrothermal) serpentine and talc.

Engel and Engel (1959, p. 1385), give a metamorphic sequence for the Grenville marble as diopside → tremolite → anthophyllite → serpentine → talc. Also Engel and Engel (1958, p. 1385) state that:

> "The more iron-rich sphalerites, along with some of the pyrite and pyrrhotite, were introduced during the anthophyllite stage of retrograde metamorphism in the marble. The formation of less iron-rich sphalerites and of iron sulfides continued, however, throughout the period in which serpentine and early talc formed (Brown, 1936; A.E.J. Engel in press). Much talc postdates all the sulfides."

The suggestion of Engel and Engel is that the Balmat-Edwards sulfide ores were introduced during the retrograde metamorphism of the metasedimentary rocks around Balmat and Edwards, and would thus have the same general age as the Grenville metamorphism.

Recent age dating work by Aldrich et. al. (1957, p. 105) in the Grenville subprovince north, west, and south of the Balmat-Edwards area indicates the period of the most recent, severe metamorphism in the area of interest occurred 1050 ± 100 million years ago. Age dating by potassium-argon methods on phlogopite from marble near Balmat by Dr. G. J. Wasserburg (unpublished) suggests crystallization of the phlogopite between 1080 and 1170 million years ago.

Brown (1936b) also describes a period of post-metamorphic, preglacial supergene mineralization of white sphalerite, willemite, galena, and chalcopyrite with magnetite and hematite. The supergene processes are related by Brown to solution cavities containing gneiss and granite boulders. The cavities may extend to greater than 365 feet below the surface. The zone of supergene mineralization is associated also with macrobrecciated marble at least down to the 1500 foot level in the No. 2 mine, the deepest level developed at this date.

In most of the early studies in the Balmat-Edwards district (Smyth, 1918; Newland, 1916; Brown, 1936a), the conclusion was that the ores were derived from igneous masses at depth and deposited by ascending solutions that in part replaced marble. Later Brown (1948, p. 140) presented a hypothesis based in part on his studies at Balmat that the ore fluid comes from some homogeneous zone at a depth of about 37 miles (60 kilometers) or "on top of the peridotite basement". Brown's later conclusion was partly based on his study of the porosity and impervious nature of the marbles of the Balmat-Edwards area (Brown, 1947) and partly upon the universal lack of certain types of intrusives accompanying specific types of sulfide ores. Engel (in press) suggests that the ore fluid may have been derived during metamorphism of the surrounding marbles and/or gneisses. Engel's suggestion came as a result of finding traces of pyrite, sphalerite, and pyrrhotite in most metasedimentary units between Balmat and Pyrites, New York, a distance of up to 30 miles from Balmat. Others (S. P. Brown, D. B. Dill, personal communication) have commented on the ubiquity of traces of sulfides in all the marble units of the Balmat-Edwards area.

For several reasons, temperature and total pressure are frequently considered together and will be done so here. Brown (1948, p. 153) classifies the Balmat ores as mesothermal which implies from his figure (p. 130) a depth of burial at the time of formation of the sulfides of three to five miles (and conventionally a temperature range of 200° to 300°C, Bateman, 1950, p. 358). Kullerud (1953) in connection with his study of the FeS-ZnS system analyzed three sphalerites from the Balmat-Edwards district and found between 8.3 and 8.9 weight percent FeS in the sphalerite. Kullerud did not determine whether or not pyrrhotite rather than pyrite was the coexisting iron mineral with his samples of sphalerite so that the temperature implied by the iron content of sphalerite should be considered a minimum value. The temperature of the formation of sphalerite given by Kullerud is 325° to 340°C at a total pressure of formation of one atmosphere or 375° to 390°C, if the total pressure of formation was 2000 atmospheres. Doe (1956) made a study of 25 spatially located samples from the Balmat No. 2 mine and found variable iron content in the sphalerite. Two of the 25 samples (A4 and C1 of this study) contained pyrrhotite with sphalerite and the rest pyrite with sphalerite. The inferred temperature of formation of sphalerite from coexisting pyrrhotite and sphalerite is 430° to 460°C with no correction for total pressure or 480° to 510°C assuming 2 kilobars total pressure. Doe explained the variable iron content of sphalerite as evidence of thermal gradients of 225°C in range; however, further studies of the FeS-ZnS system make the gradient evidence questionable.

Many studies involving geothermometers significantly sensitive to the total pressure of formation arbitrarily choose a pressure of two kilobars (or five miles of burial). In many solid solution geothermometers, an error in the total pressure estimate of one kilobar will introduce an error in the temperature estimate of about 25°C. The total pressure at the time of the formation of the ores may have been somewhat larger than the previously assumed value. Buddington (1959, p. 676) says, "The depth of the base of the mesozone or top of the catazone where the amphibolite facies starts must likewise have a substantial range, perhaps from as shallow as 5 miles to as deep as 10 miles." On the other hand, the maximum depth of burial at the time of metamorphism of the Grenville series was probably less than 9-12 miles (Buddington, 1959, p. 676; Rosenqvist, 1952, p. 102; Tuttle and Bowen in Adams, 1952, p. 38). With the thoughts of Buddington and others in mind, the total pressure is estimated to fall into a range of burial of 5-9 miles or 3 ± 1 kilobars pressure at the time of the introduction of the ores at Balmat.

Some aspects of the nature of the ore-forming fluid have been discussed previously. Brown (1947, p. 539) after a porosity study of the Balmat-Edwards marbles and ores concluded that the porosity of the rocks was too low to permit passage of copious quantities of water so that the fluid must have been a vapor in which water played a minor role. Brown also felt that the passage ways for the ore fluid were microbrecciated zones in marble. Engel (in press), however, points out that the sulfides were introduced between the formation of tremolite (2.2 weight percent H_2O) and serpentine (up to 14 weight percent H_2O) which he feels are indicative of significant quantities of H_2O in the Balmat-Edwards area at the time of ore introduction. Doe (1956) thought that correlation of zones of high-iron sphalerite between the 1500 grizzly sublevel and the 500 level indicated that at one stage of the mineralization the ore fluid rose from north to south inclined with the horizontal by about 35°. Doe (1956) indicated that if the ore fluid was rich in H_2O then the temperatures determined for the formation of the ores imply that the H_2O was in a supercritical state if the salinity was less than 10 percent.

Brown (personal communication) indicated that the location of the ore passage ways inferred by Doe (1956) did not agree in two of the three cases with known geological information, and suggested a more detailed study coupled with better geological information. Subsequently, the author spent 3-1/2 months of 1957 at Balmat as an employee of the St. Joseph Lead Company learning the stratigraphy, mapping the geology, and drawing cross-sections of the geology of the No. 2 mine. A collection of samples was made at that time with a few days spent at each of the Balmat No. 3, Edwards, and Hyatt mines. An additional nine days in 1958 were spent taking additonal samples from the surface and underground at Balmat, New York, on a Kennecott Copper Company Fellowship grant.

II. GEOLOGIC AND STRUCTURAL SETTING

General The general areal geology of the Balmat-Edwards area has been described in a complete fashion in Brown and Engel (1956) who have divided the Grenville marble into 16 distinct units. The marble units are thought to overlie the major paragneiss described at length by Engel and Engel (1953b, 1958). Other major rock units represented are amphibolite and the phacolithic California granite and Hermon granite gneiss (Brown and Engel, 1956). Throughout this study the designation of units will be that of Brown and Engel (1956). Frequent reference may be found necessary to the geologic map of the Balmat area (Fig. 1). Fig. 1 is a copy of a part of the Geology of the Balmat Area (Brown and Engel, 1956, Pl. 2) from which drill holes and the areas where the Potsdam sandstone crops out have been omitted.

The Balmat area is the southwestern end of a refolded, isoclinal, doubly-plunging syncline overturned to the southeast and situated on the southern limb of an anticlinorium trending NE-SW (Brown and Engel, 1956). Most minor structural features of the area plunge 5-35°, NO-15°W. The trace of the axial plane of the Balmat-Edwards syncline is NE-SW.

The primary sulfides occur mainly as replacements of carbonate minerals with little evidence of any replacement of silicates- quartz, diopside, tremolite, or anthophyllite. Secondary sulfides (Brown, 1936b) occur primarily in fractured pyrite and sphalerite where much or all of the pyrite has been converted into magnetite and hematite. The secondary minerals are in general accompanied by much chlorite and a trace of ilvaite. Minute quantities of specularite, magnetite, white sphalerite and chlorite have been observed in vugs, polished sections, and thin sections of the No. 3 mine in this study.

No. 2 Mine The sulfides of the No. 2 mine are replacement products entirely contained within the partly calcitic, mostly dolomitic, silicated marble unit (cdm 14 of Brown and Engel, 1956).

The ore bodies studied in this investigation are the central ore body, lower-west ore body, lower-far-west ore body, the upper-Streeter ore body, and the lower-Streeter ore body. One ore body, the Sylvia Lake ore body, which is somewhat to the northwest of the other ore bodies has not been visited by the author and will not be discussed further. The central ore body is located on a flattened nose of a large drag fold. The attitude of the central ore body is about N0°E, vertical and plunges about 30-35°, N0°E. The other ore bodies are on the southern limb of the large drag fold and have attitudes of about N 90°E, 30-35°N. The shapes of the ore bodies are controlled by crenulations of the large drag fold.

One crenulation occurs in the central ore body below the 900 level due to development of a drag fold at and below that level (northern part of Fig. 3a and 4). The result is a protuberance of ore to the west of the main part of the central ore body with a hanging wall of calcitic marble and a footwall of diopsidic-dolomitic marble. Both the hanging wall and footwall rocks are subunits of cdm 14. The main part of the central ore body is contained within a serpentinous-diosidic-dolomitic marble subunit of cdm 14. Another crenulation to the south of the central ore body (southwestern parts of Fig. 2, 3a, and 4) caused by a drag fold correlated on all levels of interest forms a protuberance to the west of the central

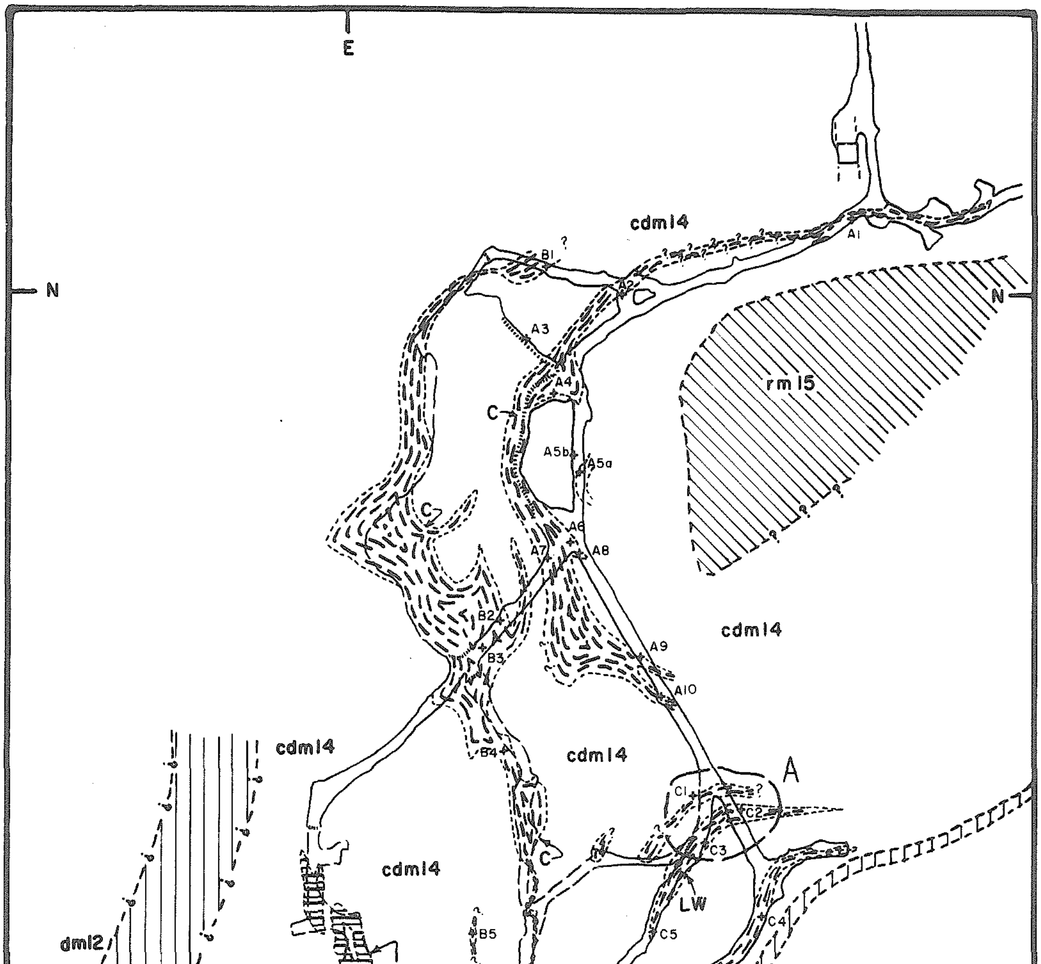


Fig. 2: Geology and distribution of samples on the 500 foot level of the Balmat No. 2 mine, west of shaft.

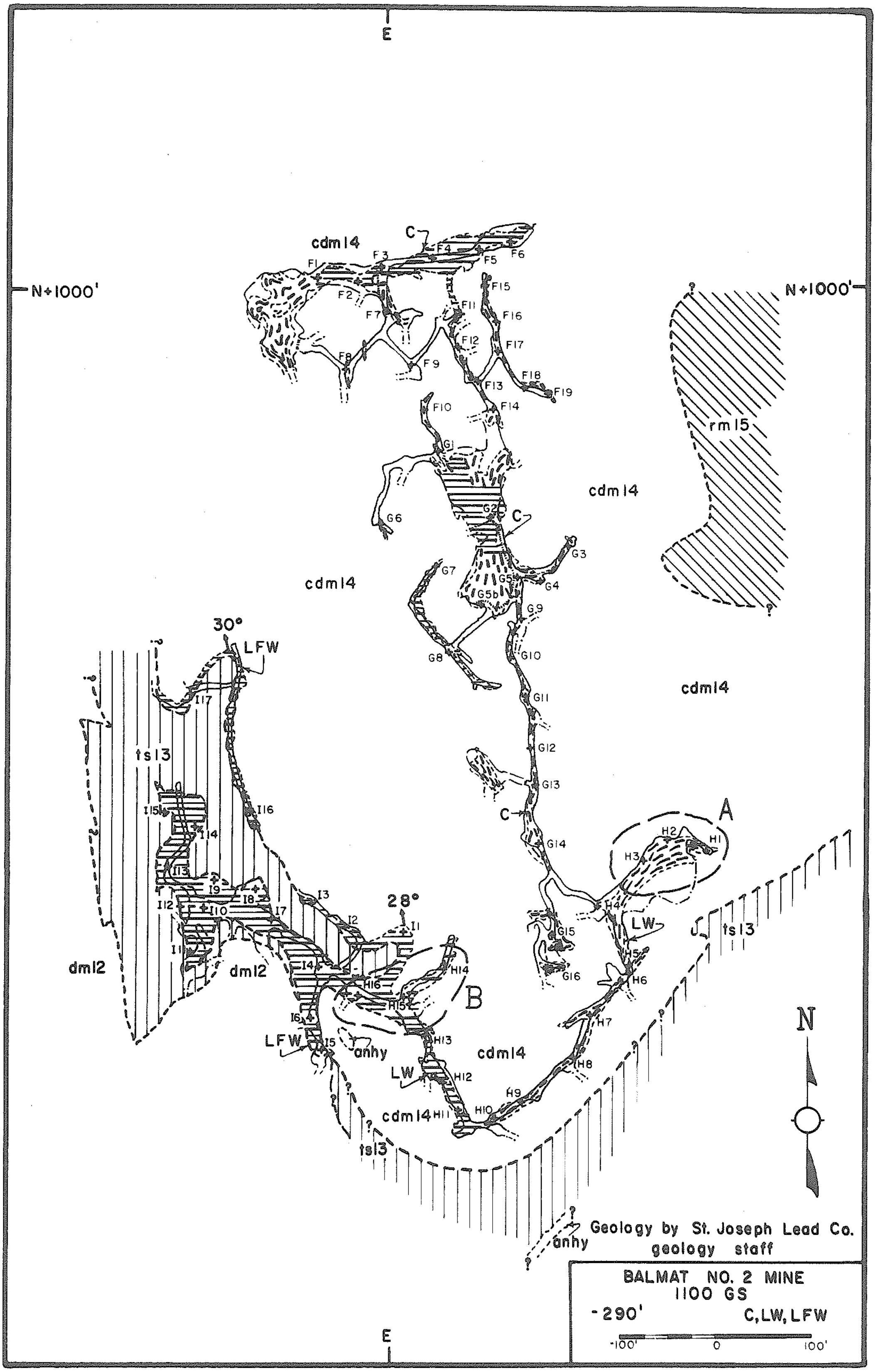
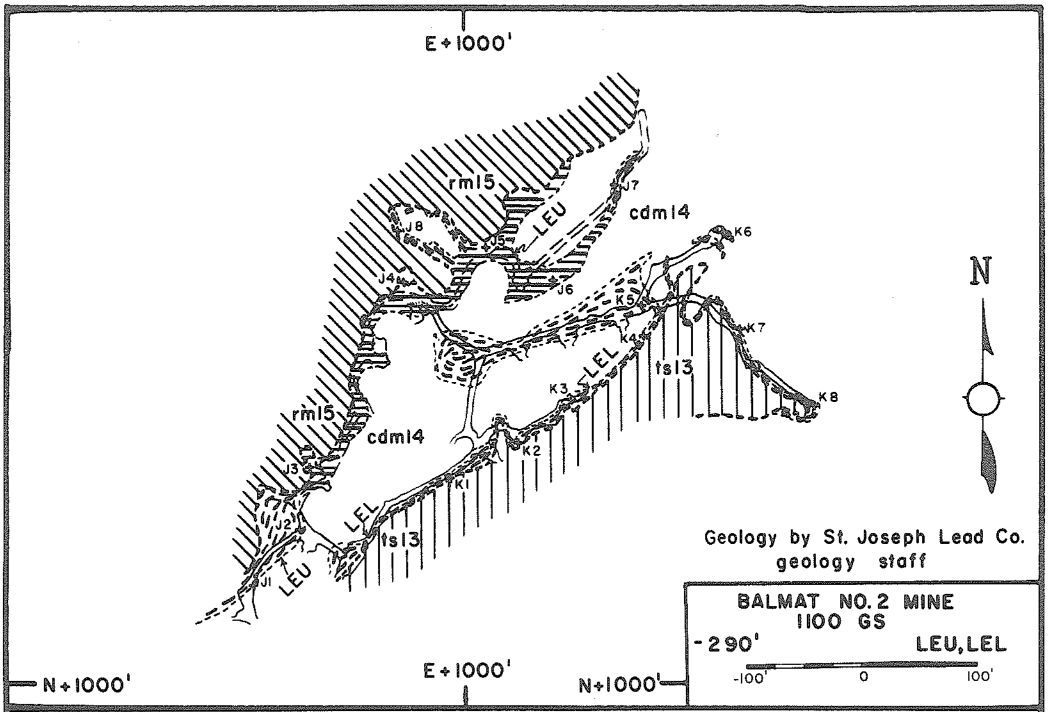


Fig. 3a: Geology and distribution of samples on the 1100 foot grizzly sublevel of the Balmat No. 2 mine, west of the shaft.



Geology by St. Joseph Lead Co. geology staff

EXPLANATION

Precambrian

Grenville Series

▤ Massive sulfides } mainly pyrite and sphalerite
▨ Disseminated sulfides } mainly pyrite and sphalerite

rm15 Rusty marble

cdm14 Dolomite, partly calcitic, silicated; undifferentiated

ts13 Tremolite, anthophyllite, talc schist

dm12 Dolomite marble

☐ Undifferentiated Grenville series

28° Direction and amount of plunge of minor fold axis

+J4 Sample number and location

Drift outline

Wall of stope or former drift outline

Ledge between drift and stope

Raise or stope inclined upward

Unit contact and contact between sulfides and unreplaced unit

Contact between replaced unit and sulfides

? ? Questionable position of contact

N Arbitrary north coordinate

E Arbitrary east coordinate

C	Central ore body
LW	Lower west ore body
LFW	Lower far west ore body
LEU	Upper-Streeter ore body
LEL	Lower-Streeter ore body
500L	Level in feet below surface
-290'	Elevation in feet, sea level datum

Scales of all maps are in feet

Fig. 3b: Geology and distribution of samples on the 1100 foot grizzly sublevel, east of the shaft, in the No. 2 mine.

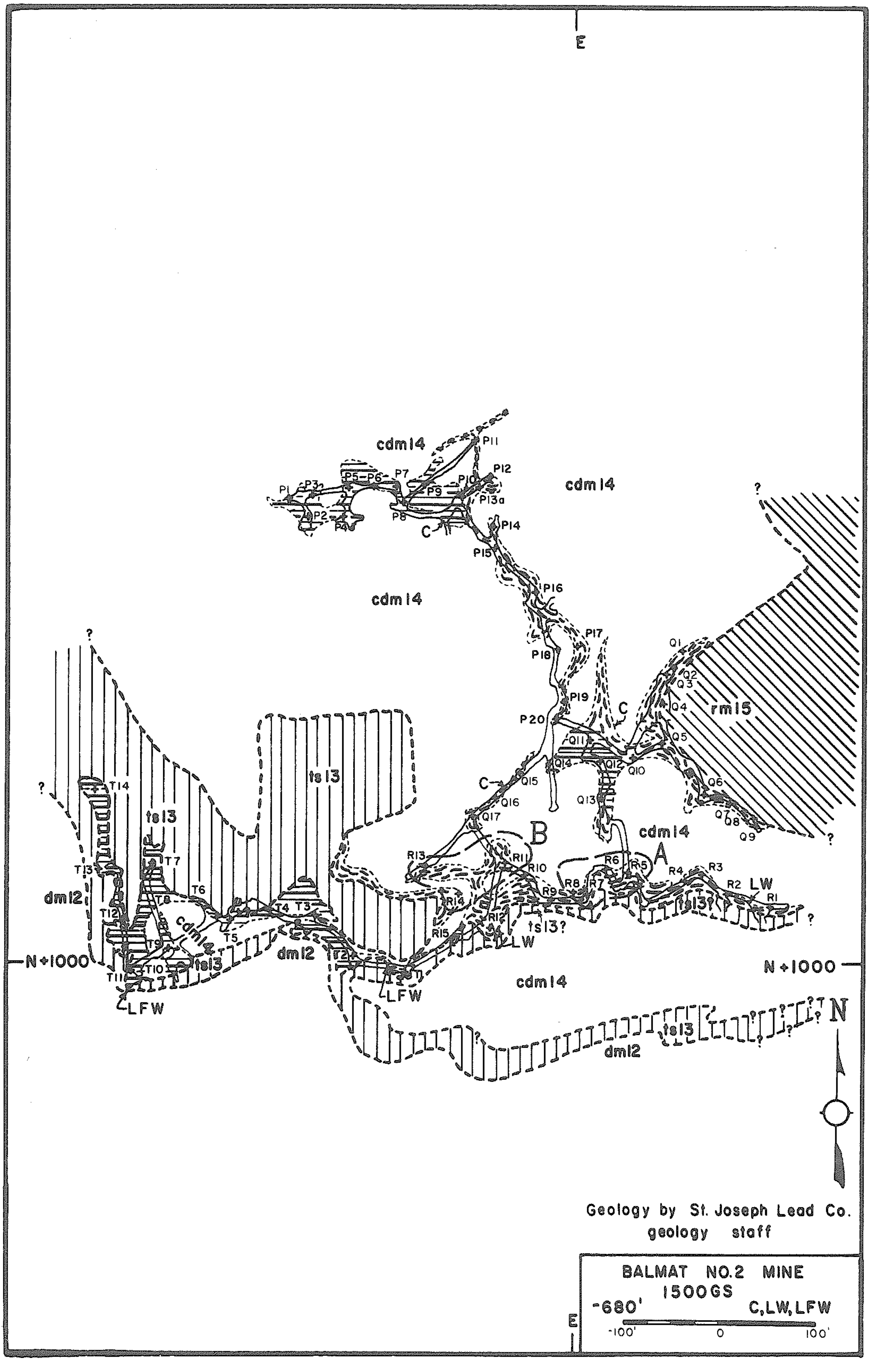


Fig. 4: Geology and distribution of samples on the 1500 foot grizzly sublevel of the No. 2 mine, west of the shaft.

ore body with a hanging wall basically composed of a quartz-diopside marble subunit of cdm 14 and a footwall in part of a tremolite-anthophyllite-talc schist unit (ts 13 of Brown and Engel, 1956) and in part a white dolomitic marble unit (dm 12 of Brown and Engel, 1956).

East of the central ore body are two ore bodies called the Streeter ore bodies. The upper Streeter ore body has a rusty marble unit for a hanging wall (rm 15 of Brown and Engel, 1956) and a footwall of cdm 14 undifferentiated (northern part of Fig. 3b). The lower Streeter ore body has cdm 14 undifferentiated as a hanging wall and ts 13 as a footwall (southern part of Fig. 3b).

The white quartz-augen calcitic marble mentioned above roughly splits the cdm 14 unit in half and is the only subunit or unit in the mine area with abundant calcite rather than dolomite. It has been pointed out to the author by S. P. Brown and J. S. Brown (personal communication) that the dolomite of dm 12 triboluminesces red, the tremolite of ts 13 triboluminesces yellow, and the calcitic marble does not triboluminesce, properties which aid greatly in underground mapping. At the present time detailed studies of the structure and subdivisions of the cdm 14 unit are being performed by Severn P. Brown (thesis in preparation). The cdm 14 unit will not be subdivided on the maps of this study.

The structures within the No. 2 mine are highly complex. Attenuation of units and subunits, contraction and expansion of drag folds with depth, and refolding of drag folds makes it possible locally for any of the units and subunits discussed above to act either as the footwall or hanging wall or both of any of the bodies of ore (see Fig. 2, 3a, 3b, and 4).

The ore of the No. 2 mine has been split into ore bodies on the basis of macroscopic mineralogic content and position with reference to the central ore body. The area of rock for some distance to the east of the central ore body is included in the shaft pillar of the mine so that little geologic information is available. The central ore body is noted for the siliceous nature of the ore (Brown, 1936a, p. 250), abundance of pyrite, and irregular presence of pyrrhotite. The western protuberance of the central ore body develops with depth at the expense of the rest of the central ore body. The western protuberance to the south of the central ore body may be divided into two ore bodies - the lower-far-west ore body characterized by the massiveness of sphalerite, paucity of pyrite, and absence of pyrrhotite (Brown, 1936, p. 250); and the lower-west ore body characterized by the presence of a small percentage of macroscopic galena, barite, and anhydrite (Brown, 1936a, p. 252).

The upper-Streeter ore body may possibly be related to the central ore body, but the upper-Streeter does not have macroscopic pyrrhotite, and in general has the rusty marble as a hanging wall instead of subunits of cdm 14.

The lower-Streeter ore body has ts 13 as a footwall as do the lower-west ore bodies; however, the lower-Streeter differs from the lower-west ore bodies in that the former contains pyrrhotite and the ore is characterized by the diffuseness of sulfides in marble whereas the lower-west ore bodies only locally contain pyrrhotite and the ore is more massive.

In general all contacts between ore and country are diffuse. Solid sulfides grade to solid country rock over a range of a few inches to a few feet. The principal exceptions to the latter are the contact between ore and rusty marble and ore and ts 13 (Brown, 1947) where the contact between ore and country rock is razor sharp. Locally small clots of sulfides occur in the wall rock away from the main mass of sulfides and may be 1-6 feet long or longer and 1-24 inches wide or wider. The clots are in many areas within a few feet of the larger, main mass of sulfides, but similar features may occur within various subunits of cdm 14 some hundreds of feet away from the main mass of ore. In some places in the mine, the contact between ore and country rock is drawn upon the abundance of clots and not at the edge of the seemingly larger main mass of ore. In the upper-west, lower-far-west, and lower-west ore bodies, there seems to be some tendency of the richer ore accumulations occurring in structural terraces at subunit contacts (S. P. Brown, personal communication). Also, the tendency of ore to accumulate at the contacts of unlike lithologic units along zones of microbrecciation and to replace into the more calcareous unit was remarked upon by Brown (1947, p. 531). Supergene mineralization (Brown, 1936b) is in general localized in the lower-west and lower-far-west ore bodies.

Minor faults of less than one foot displacement, striking at high angles to the beds and associated with extreme attenuation of the limbs are the only form of faulting noted in the No. 2 mine.

No. 3 Mine The structures involved in the ores of the No. 3 mine are much simpler than those encountered in the No. 2 mine (see Fig. 5). One major set of ore bodies, the Gleason, is contained as a replacement

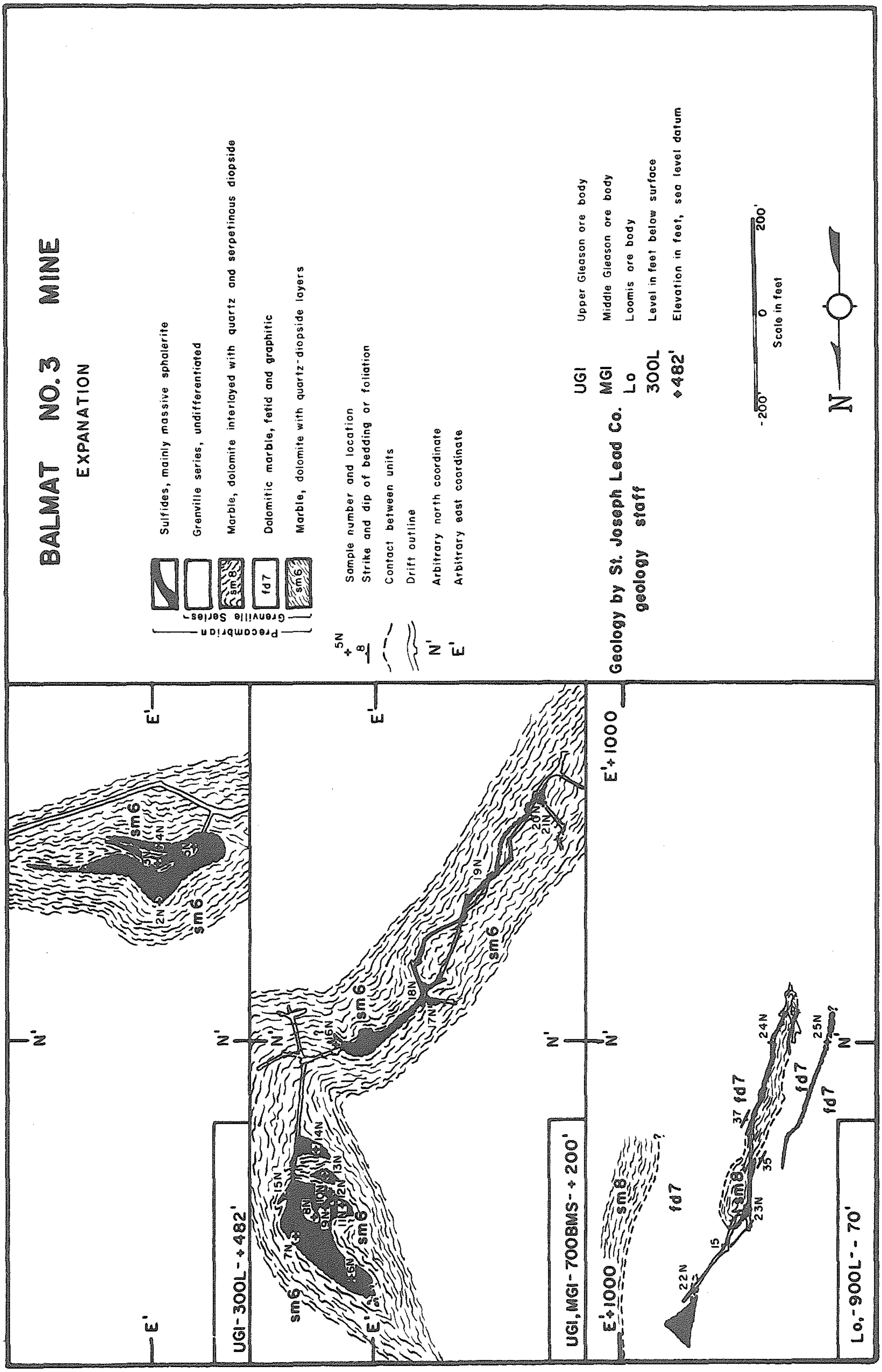


Fig. 5: Geology and distribution of samples from several horizons in the Balmat No. 3 mine.

product of a dolomitic marble containing quartz-diopside layers (sm 6 of Brown and Engel, 1956). The Gleason ore bodies are termed - upper, middle, and lower. The Gleason ore bodies studied in this report are the upper and middle. The lower-Gleason, not shown in Fig. 6, is found immediately above the contact of sm 6 and fd 7 of Brown and Engel, 1956. Some post ore faulting with movement of 50 feet or more is observed in the No. 3 mine. The Gleason ore bodies follow a system of drag folds which are known to be continuous down through the sm 6 and fd 7 beds (E. R. Lea, personal communication). The plunge on the drag folds is about 25°NNE. The fd 7 unit is a fetid-graphitic-H_2S bearing dolomitic marble.

The Loomis ore body is at the contact of fd 7 with sm 8. Some of the sulfides replaced the fd 7 unit, but it is not clear whether or not the bulk of the ore replaced the fd 7 or the sm 8 unit. The Loomis ore body is about 700 feet east of the Gleason ore body and is associated with a nearly horizontal structural terrace.

The Gleason and Loomis ore bodies are characterized by low-iron sphalerite, about one percent pyrite, general lack of galena, and no known occurrences of pyrrhotite or marcasite. The ore bodies are distinguished by their stratigraphic positions and not upon mineralogy.

III. CHRONOLOGY

Relative Age (Paragenesis) Brown (1936a) presented a paragenetic sequence for the Balmat No. 2 and Edwards mines which he revised somewhat in 1947 and 1948. Engel and Engel (1958, and in press) discuss briefly the time relation of sulfide emplacement to retrograde metamorphism of the Balmat-Edwards rocks. In the process of collecting samples for the analytical work of this study, about 250 polished sections and three dozen thin sections were analyzed. A composite paragenetic sequence derived from the reports of others and by the author from his own work is summarized in diagrammatic form below. The sequence below is only intended to show the relative positions in time at which the separate phases were formed and in no way does a long bar indicate necessarily a longer period of deposition or formation in years than a short bar. The abbreviations used in Fig. 6 are:

Silicates - diop (diopside), trem (tremolite), anth (anthophyllite), serp (serpentine), talc (talc)

Sulfides - py (pyrite), sl (sphalerite), gn (galena), po (pyrrhotite), cp (chalcopyrite), mr (marcasite)

Sulfates - bar (barite) and anhy (anhydrite)

Oxides - mg (magnetite) and hm (hematite)

Diopside Brown (1936a) did not distinguish between the times of formation of diopside and tremolite. Engel and Engel (1959 and in press) state that some tremolite was contemporaneous in time of formation with diopside but that much tremolite is definitely younger than most of the

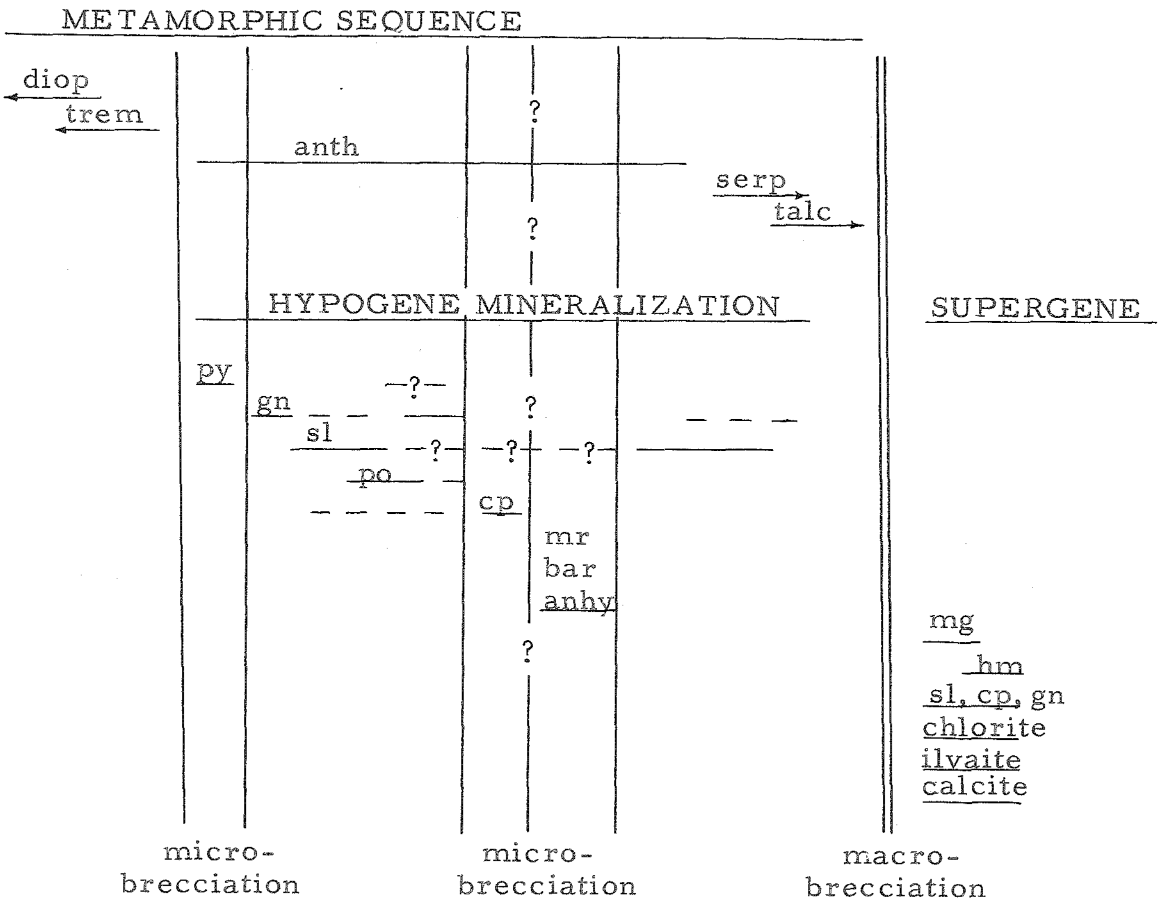


Fig. 6: Paragenetic sequence of emplacement of Balmat sulfides in the descending temperature phase of Grenville metamorphism.

diopside. The diopside throughout the No. 2 mine area has been altered more or less to serpentine and in some places to talc. In pods containing both minerals, tremolite may have a more euhedral character than diopside.

Tremolite Tremolite is widely distributed throughout the mine area, but occurs predominately near and in the ts 13 unit.

Microbrecciation The pre-pyrite microbrecciation is easily recognized in polished sections from crack fillings of pyrite and other sulfides in the silicates (Brown, 1936a).

Anthophyllite In the few thin sections studied, no mineral other than talc possessed parallel extinction. Therefore the range of anthophyllite is accepted from the work of Engel and Engel (1958).

Pyrite The stage of microbrecciation of diopside and tremolite, which occurred before the introduction of pyrite, was mentioned by Brown (1947, p. 539). Brown also reported (1936a, p. 249) that the predominant crystal form of pyrite was the pyritohedron and, "the cube is seldom or never seen". A small amount of pyrite fills cracks in pre-ore silicates but over 50 percent of the pyrite is as anhedral grains that apparently replaced carbonate minerals with little or no effect on the silicates of the country rock. Most subhedral to euhedral pyrite that was observed was cubic which is somewhat at variance with Brown's study. Pyritohedrons of pyrite were observed mainly in the meta-sediments surrounding the ore bodies and with pyrrhotite in the ore bodies. The grain size varies from less than 0.1 millimeter in diameter to greater than a centimeter with 1-2 millimeters being the most representative size. The regions of coarsest pyrite have little or no accompanying sphalerite, and pyrite-rich regions generally extend beyond sphalerite-rich regions. Pyrite constitutes possibly about 50 percent of the ore sulfides, but may drop to 10-20 percent or less of the ore in the lower west ore bodies of the No. 2 mine. In the No. 3 mine, pyrite constitutes only about one percent of the ore.

Microbrecciation Possibly 10 percent of the pyrite grains have cracks filled by sphalerite. The larger the grain of pyrite, the more likely sphalerite exists as a fracture filling. In describing the microbrecciation between the deposition of pyrite and sphalerite, Brown (1936a, p. 249) states, "In rare cases, primary sphalerite fills cracks in pyrite."

Galena The relationship between galena and sphalerite was stated by Brown (1936a, p. 250) as, "With sphalerite the contacts in some cases suggest molding of galena on sphalerite and in other cases are ragged or indefinite." The bulk of the galena in the Balmat mines displays neutral grain boundaries with sphalerite and pyrite. Possibly 20 percent of the galena grains show at least some evidence of replacement by talc or serpentine along cleavage (Pl. 2b). The relationship between talc and galena is very striking and was described by Brown (1936a, p. 251). A feature in the No. 2 mine not reported by Brown (1936a) but found in this study is penetration and replacement of galena along cubic cleavages by sphalerite (Pl. 3a). On the other hand, microscopic galena of the No. 3 mine is usually found as intergranular fillings and in cracks in sphalerite. Discontinuous "veinlets" of galena in sphalerite (Pl. 3b) may also indicate some deposition of galena later than sphalerite.

Only one occurrence of macroscopic galena has been observed in the No. 3 mine. Microscopic occurrences of galena were only observed in 3 of 28 polished sections from the No. 3 mine (Table 1). In the No. 2 mine, macroscopic galena occurs mainly in the lower-west and central orebodies (D. B. Dill, personal communication). From the study of polished sections, it would appear that galena becomes more widespread with depth throughout the lower-far-west orebody.

Supergene galena is associated with white sphalerite, magnetite, and hematite, and found in highly fractured pyrite (Brown, 1936b).

Primary galena is found as microscopic blebs accompanying chalcopyrite in sphalerite, between grains of sphalerite and pyrite, in fractures of silicates, between grains of sphalerite, and as macroscopic pods of galena up to three inches or more across.

The period of deposition of primary galena is thought to have started before and to have extended past the deposition of sphalerite in the No. 2 mine. Examination of many pyrrhotite bearing samples under high magnification revealed small amounts of chalcopyrite and a silvery mineral that may be galena. The euhedral pyrite in contact with pyrrhotite may be contemporaneous with pyrrhotite. If the relation between pyrite and pyrrhotite is correct, the deposition of galena probably extended throughout the period of deposition of pyrrhotite at the contact of pyrite euhedra and anhedral pyrrhotite. Galena and chalcopyrite often occur together with neutral contacts as fracture fillings in pyrite, but only chalcopyrite was observed to fill cracks in pyrrhotite. For the latter reason, it is thought that deposition of galena stopped before the main mass of chalcopyrite was formed. Only a very small amount of galena is thought to have formed during or after the formation of chalcopyrite in the No. 2 mine. In the No. 3 mine, galena occurs as intergranular fillings and veins in sphalerite, but quantitatively the galena in the No. 3 mine is so small that many sources could be postulated for the galena observed.

Sphalerite Sphalerite possibly was formed in several generations, but all sphalerite will be discussed here. Both the texture and composition of sphalerite were studied extensively for this investigation. The conclusion of this study is that there are three main types of sphalerite in the region. The bulk of the sphalerite in the No. 2 mine is reddish brown in thin section and polished section (oblique light) and possibly forms 80-100 percent of the sphalerite in the No. 2 mine. The reddish-brown sphalerite is the earliest in the paragenetic sequence. The second most widespread type, but never totaling more than a few percent of the sphalerite of the No. 2 mine, was first noticed as a resinous vein material accompanying serpentine and talc but with magnetite absent. Thin sections revealed that the resinous sphalerite exhibited a colloform like intergrowth with serpentine and talc (see Pl. 1). Along most talc and serpentine fracture fillings in sphalerite there appears a thin bleach zone (much less than 1/10 mm) in the sphalerite which probably represents leaching of iron from the sphalerite. However, there is a class of sphalerite grains of much greater size than the thickness of the leach zone that possess the amber color of the colloform sphalerite over the entire grain. The resinous colored sphalerite is similar in color to the bulk of the sphalerite in the No. 3 mine. It may be that the mass of the sphalerite in the No. 3 mine represents the main area of deposition of resinous colored sphalerite with only minor quantities deposited in the No. 2 mine, but correlation is speculative.

The third type of sphalerite is almost pure white (or colorless) and is associated with the supergene mineralization described by Brown (1936b). The white sphalerite may occur as microcrystalline aggregates or as leached rims (Pl. 6a) of large grains of reddish brown sphalerite. The leached rim in the case of white sphalerite may approach 1 mm in thickness. The latter leaching seems to be closely associated with late chlorite forming solutions. The white sphalerite occurs almost entirely in the macrobrecciated portion of the lower-west ore bodies. Supergene sphalerite, specular hematite, magnetite, and chlorite have been observed on the 700 bottom mining sublevel in the upper Gleason ore body of the No. 3 mine. Supergene sphalerite in the No. 3 mine also occurs in geodes where the sphalerite has grown as tetrahedrons on top of specular hematite. The association of hematite and sphalerite in vugs is thought to support the idea that these minerals were formed at a much later period than the metamorphism of the Grenville series.

Neither serpentine nor talc are common in the thin sections studied of the No. 3 mine ore, but both where present seem to form fracture fillings in the sphalerite.

The grain size of sphalerite seems to be largest in the No. 3 mine and the lower-far-west orebody of the No. 2 mine. The average grain size is about 1-2 mm but may range between 0.01 mm - 1 cm or more (Brown, 1936a, p. 249).

Plate 2a shows features interpreted as indicating deposition of sphalerite around silicate grains. It is thought that sphalerite replaced carbonate grains but formed mainly intergranular fillings with silicate grains. Carbonate grains occur very rarely in the ore in the No. 2 mine. The author agrees with Brown (1936a, p. 250) that ".. most sphalerite replaced carbonate, and the common inclusions of sulfides in silicates are generally explainable as replacements of carbonate inclusions." The latter statement, however, is not true in the No. 3 mine where much carbonate occurs with the ore and replacement is not complete.

Pyrrhotite Unfortunately Brown (1936a, p. 251) did not state a relationship between pyrrhotite and sphalerite or galena, but he did say, "Its (chalcopyrite) primary occurrence is entirely as minute inclusions in primary sphalerite, the type that is ascribed by some to ex-solution and by others as replacement." About pyrrhotite, Brown states (1936a, p. 252), "Chalcopyrite may partially or completely encircle the pyrrhotite grains, as if it were later." However, the age relation between sphalerite and pyrrhotite might be of great importance to this study. Plate 4a shows a case in which a pyrrhotite vein cuts sphalerite. A more common occurrence (Pl. 4b) is of a discontinuous veinlet of pyrrhotite between two blebs of pyrrhotite. The latter features might be interpreted as exsolution of pyrrhotite from sphalerite, but there are three reasons why the author does not feel that many of the discontinuous veinlets of pyrrhotite are due to exsolution:

1. In most examples observed, the discontinuous veins lead to larger grains of pyrrhotite.
2. There are only a small number of pyrrhotite veins to each sphalerite grain (within the resolving power of the microscope). The discontinuous veinlets are associated with and composed in part of chalcopyrite veins of the same form, but pyrrhotite never displays an "emulsion texture" common to the most widespread habit of chalcopyrite.
3. In examination of polished sections with strong oblique light, there is no suggestion of the sphalerite around the pyrrhotite having a lighter or darker color than the sphalerite farther away. Thus there is no fine coloration effect to suggest that the source of the pyrrhotite was from the sphalerite. A sole exception was found in sample P14 (Fig. 5a) which suggests pyrrhotite earlier than sphalerite and also possibly suggests some

exsolution of pyrrhotite from sphalerite.

Dr. J.A. Noble was kind enough to examine several of the polished sections containing pyrrhotite and came to the conclusion that the pyrrhotite in these specimens was later than the sphalerite (private communication). Thus the author concludes with confirmation that most of the pyrrhotite in the No. 2 mine was deposited later than the adjacent sphalerite.

The association of chalcopyrite with pyrrhotite is very striking, particularly where chalcopyrite forms discrete grains. Since the occurrence of chalcopyrite as blebs in sphalerite is much more widespread than that of grains of chalcopyrite with pyrrhotite, it is concluded that there are two generations of chalcopyrite - one before pyrrhotite and probably as an exsolution phenomenon from sphalerite, and a second slightly later than pyrrhotite. The most common area of abundant pyrrhotite and chalcopyrite is in silicated rocks slightly displaced from the main area of pyrite and sphalerite mineralization but there is some overlapping. Several other small areas of pyrrhotite and chalcopyrite grains exist - two in the south-west orebody (see A and B, Fig. 2, 3a, 4) and also the lower-Streeter ore body. A more complete investigation of the upper-Streeter ore body probably would reveal some pyrrhotite near sample J8. The association of pyrrhotite with chalcopyrite that is later than sphalerite also suggests that pyrrhotite is later than sphalerite.

In rare cases pyrrhotite is found filling cracks in pyrite; however, a common relationship is that of euhedral pyrite cubes and pyritohedrons in pyrrhotite (Fig. 5b). This relationship may be explained in several ways, but the two most attractive explanations are that (1) pyrite formed contemporaneously with or after the formation of pyrrhotite, and (2) the euhedral pyrite is a product of exsolution in part or totally from pyrrhotite. Case (1) above might well be applicable if the system were closed since Kullerud and Yoder (1959) found that in closed systems the field of the formation of pyrrhotite without pyrite is all but univariant with the total sulfur content of the system. A much more likely model would seem to be that a system depositing sulfides is open with respect to the gaseous components of the ore fluid and that the fugacity of the gaseous components is externally controlled. If the euhedral pyrite is later than pyrrhotite, it is not clear why the euhedral pyrite is so closely associated with pyrrhotite unless the pyrite cannot form euhedral crystals against the other minerals present. Kullerud and Yoder (1959, p. 546) found rapid exsolution of pyrite from pyrrhotite at very high temperatures with the pyrite forming reaction rims around the pyrrhotite. No exsolution lamellae were observed in the pyrrhotite at Balmat. It may be that the iron sulfide exsolved from pyrrhotite recrystallized as pyrite in eudral forms. The author favors case (2) above of exsolution of the euhedral pyrite from the pyrrhotite. The latter conclusion is one of some importance with reference to a later section on thermometry.

Microbrecciation   Chalcopyrite as a fracture filling in pyrrhotite is the evidence for this stage of microbrecciation.

Chalcopyrite   The most common occurrence of chalcopyrite in the Balmat mines is as random blebs in individual sphalerite grains. In an individual polished section, some sphalerite grains will be dotted with random and oriented blebs of chalcopyrite as small as the resolving power of the microscope whereas other grains may have few blebs and most grains none. This erratic type of occurrence of chalcopyrite has been previously noted by Rose (1958, p. 22) in the Central Mining District of New Mexico. As the polished sections were studied, the number of chalcopyrite blebs resolvable at medium power were noted in a semi-quantitative manner - (1) abundant (thought to be more than 0.1 area percent from point counting techniques); (2) common, greater than 1000 blebs per polished section; (3) some, between 100-1000 blebs per polished section; (4) few, between 10-100 blebs per polished section; and (5) clean, no danger from chalcopyrite contamination in sphalerite samples drilled from that particular polished section. High power was needed to resolve chalcopyrite blebs in the sphalerite of the No. 3 mine. Even if marcasite and pyrrhotite are counted as one mineral, chalcopyrite is still more extensively distributed than pyrrhotite.

Comparison of Table 5 with Table 7 indicates that correlation between the copper content of sphalerite and the relative number of chalcopyrite blebs is not good. Moreover, emission spectrographic analysis of 74 sphalerite samples revealed the highest copper content in sphalerite at Balmat is 0.14 percent by weight. There are several ways for accounting for the discrepancy. (1) Irregular amounts of copper may be dissolved in sphalerite and only a part of the copper found is due to the presence of chalcopyrite blebs; (2) irregular distribution of chalcopyrite blebs with depth similar to what is observed on the surface makes it impossible to estimate the volume content of chalcopyrite in sphalerite from an areal estimate.

Supergene chalcopyrite was observed in relations as described by Brown (1936b).

Microbrecciation Brown (1936a, p. 252) noted that some barite and anhydrite filled cracks in earlier sulfides. There is little chance of telling whether or not there is a stage of microbrecciation between the sulfides and sulfates because chalcopyrite rarely forms large masses in the Balmat mines; however, a stage of microbrecciation is postulated as preceding the introduction of barite and anhydrite. The latter is to account for the spatial separation of the zones where pyrrhotite and chalcopyrite were deposited from those where barite and anhydrite were introduced.

Marcasite Marcasite has not been described previously from the Balmat-Edwards area. It occurs with pyrrhotite within the sphalerite zone of mineralization and constitutes a partial to total alteration product of pyrrhotite. The relationship between marcasite and barite or anhydrite is not known. Marcasite is later than the sphalerite associated with pyrrhotite. Little is known about the conditions of formation of marcasite, but it is synthesized in acid sulfate solutions. On the basis of relative stabilities, marcasite is correlated with the introduction of barite and anhydrite. The relations of marcasite to pyrrhotite are very similar to those shown by Edwards (1954, Fig. 129).

Barite Brown (1936a) described barite as having formed later than sphalerite; however, in 1948 Brown decided mainly on theoretical grounds that barite preceded the sulfides. If Brown's 1948 conclusion is true, barite was reworked at a later date because barite clearly fills fractures in sulfides. Smyth (1918, Pl. 5) shows pictures of barite being replaced by serpentine at Edwards, New York. This mine is similar in many respects to the Balmat mines and is only 12 miles to the northeast. In Pl. 12 (Smyth, 1918), Smyth shows light colored sphalerite of the type classified late by Engel and Engel (1948) replacing barite at Edwards. It appears that barite was introduced to the ore zone at Balmat after pyrite and after the bulk of the dark sphalerite but before the formation of light colored sphalerite and serpentine. Macroscopic barite is localized in the lower-west ore body, but studies of the minor elements in sulfides indicate barium is more widespread throughout the No. 2 mine than previously thought. Some possible implications of the latter are discussed later.

Anhydrite Anhydrite generally occurs in macroscopic quantities in the same general area of the No. 2 mine as barite. The age of barite and anhydrite is not distinguished, but, with relation to the sulfides, Brown (1936a, p. 252) states, "It (anhydrite) is interstitial to sulphides, fills cracks in sphalerite and is replaced by talc, or altered into gypsum along contacts with talc." In 1956, Brown and Engel described from the Balmat area a discontinuous anhydrite gypsum unit (gm 10) that may well represent an original sedimentary chemical precipitate. The problem of anhydrite in the mine is much like barite, and, although the author did not observe any anhydrite in the thin sections examined, it is thought that anhydrite was at least reworked in some fashion in the late stages of formation of the sulfides to form fracture fillings. It is felt by D.B. Dill (personal communication) that anhydrite is uncommon above the 1300L and seems to be becoming more abundant at depth although J.S. Brown feels this relation may be due to leaching in the higher levels.

Serpentine The post-ore silicates are extremely fine grained (less than 10 microns), and much serpentine seems to be mixed in with a light greenish mineral thought to be chlorite. Macroscopic chlorite is strongly localized in the lower-west orebody. Its color in thin section is generally light brown. The author was not able to determine the age relations between serpentine and talc, but, in veins that contained both, talc had more continuity than serpentine which might indicate that talc was somewhat later than serpentine. The author has accepted the observations of Engel and Engel (1959).

Talc Veinlets of talc are widely distributed throughout the mine. Talc and serpentine occur with resinous sphalerite in the central and upper west orebodies. Talc extensively penetrates galena along the cubic cleavage and the latter two minerals may be surrounded by greenish serpentine. The bulk of the chlorite is found in the lower-far-west ore body where chlorite replaces talc, diopside, and pyrite (Pl. 6a).

Macrobrecciation The macrobrecciation is easily observed in the lower-far-west and lower-west orebodies. The zone of macrobrecciation allows a minor flow of water into the mine. In general, the macrobrecciation can be correlated with solution cavities formed at a time much past the end of the Grenville metamorphism (for details see Brown, 1936b).

Supergene Mineralization The author tends to agree with Brown (1936b) that white sphalerite, hematite, and magnetite in the macrobrecciated zones and in vugs are of supergene origin. In the No. 3 mine, the author has observed two cases in which free faces of specular hematite and light-amber colored tetrahedrons of sphalerite have grown in vugs. The close association of much chalcopyrite and galena with magnetite and hematite in the lower-west and lower-far-west ore bodies probably indicates a supergene origin for the associated chalcopyrite and galena, also. Silicates in the zone of supergene alteration were apparently altered to chlorite and a small amount of ilvaite (Brown, 1936b). Small veinlets of calcite are abundant in this zone also (Pl. 6b).

In conclusion, the author agrees with most of the observations of preceeding workers on the paragenesis of the Balmat ores. They have described the microbrecciations mentioned in this study, but, except for the pre-pyrite brecciation, have not emphasized them to the extent of this investigation. The emphasis is made in an effort to clarify the reasons for mineral segregations observed in the Balmat mines. Interpretations divergent from previous studies are (1) placing the time of deposition of some galena before that of sphalerite; (2) outlining the period of deposition of pyrrhotite; and (3) defining the distribution of marcasite, a mineral previously undescribed from Balmat.

Absolute Age Estimates of the absolute age are discussed in the introduction. Engel and Engel (1959) have stated that they feel the Balmat mineralization is mostly contained between the formation of tremolite and retrograde stages of metamorphism in which talc formed in the Balmat area. The author concurs with the study of Engel and Engel. Brown and Kulp (1959) on the other hand, state that geologic data do not compel a Precambrian age for the ores. Brown (1936a) feels that there was a post sulfide hydrothermal alteration of diopside to talc, but at the same time grants the presence of large talc-tremolite deposits in the area. The retrograde alteration of diopside and tremolite to serpentine and/or talc is not an unusual sequence. The post-sulfide alteration of diopside and tremolite to talc and serpentine seems best explained in the manner of Engel and Engel.

The identification of the sulfide mineralization at Balmat with the Grenville retrograde metamorphism indirectly indicates the approximate age of the Balmat mineralization. Recent age studies by Aldrich, et al. (1957, p. 104) yield the following distribution of metamorphic ages of the Grenville metamorphism and the areal relation to Balmat.

Table 1: Estimates of the absolute age of the metamorphism of the Grenville series

Location	Relation to Balmat	Age (millions of years) K-A	Rb-Sr	238/206	235/207
Wilberforce, Ont.	N	975	1000	1040	1050
Cardiff Twp, Ont.	N	1010	1030	1020	1020
Bancroft, Ont.	NW	890	990		
Wavy Lake, Ont.	N	1025	1075		
Natural Bridge, N.Y.	W			1025	1065
Canada Hill gneiss, N.Y.	S	930	1030	1020	1060
Storm King granite, N.Y.	S	900			

Recent data of Dr. G. J. Wasserburg (unpublished) on phologpite from the Balducci Quarry, Gouverneur, New York, indicate the age of formation of the phlogopite by potassium-argon dating is 1170-1080 million years, the difference arising in different size fractions of the mineral. Thus an age of 1050 ± 100 million years should be a satisfactory age both for the metamorphism near Balmat and introduction of sulfide ores.

IV. SOURCE OF THE ORE FLUID

Previous suggestions for the source of the fluid that deposited the sulfide ores at Balmat (see Introduction) are discussed below with reference to new data.

If the pyrite in the metasediments was exposed to a large quantity of the ore fluid that deposited the sulfide ores or if the pyrite of the metasediments was deposited from that ore fluid, then it might be expected that pyrite in the metasedimentary units should have amounts of trace and minor elements similar to the pyrite in the sulfide ores. In fact, it was first suspected that the pyrite in the ores of the No. 3 mine (in an abundance of only about one percent) might be normal metasedimentary pyrite. Therefore, pyrite from the sulfide deposits and surrounding metasedimentary units at Balmat were examined for minor element content by emission spectrographic analysis (Appendix 3B gives details of the analytical procedure). The complete list of pyrite analyses is given in Table 7. The essentials are summarized in Table 2.

The data in Table 2 show a striking difference between the contents of cobalt and nickel in pyrite of the metasedimentary units compared to the values observed in pyrite of the ore. The "vein" pyrite is pyrite taken from fracture fillings in the rm 15 unit (rusty marble) northeast of the No. 2 mine and in the hpg unit (Herman granite type gneiss) about 1.2 miles northwest of the No. 3 mine. The fractures are probably post-metamorphic so that the pyrite of the fracture fillings probably has a post-metamorphic origin. Titanium appears to be concentrated in the country rock. The data for manganese are not conclusive, but pyrite from the main sphalerite bodies of ore seems to have higher contents of

Table 2: Comparison of the concentrations of cobalt and nickel between pyrite from the ore bodies and pyrite from the rocks of the metamorphosed Grenville series.

Location	No. of Samples	Cobalt Avg	Cobalt Range	Nickel Avg	Nickel Range	Ti Avg	Mn* Avg
2 mine, C	13	20	1000	10-	40	-	120
2 mine, L-W	11	15	15	10-	10?	-	160
2 mine, U-S	2	8-	8?	15-	15	-	35
2 mine, L-S	2	30	0	22	15	-	
3 mine, all	4	60	65	30	50	-	50
sm 4(marble)	4	600	750	550	750	250-	20
ps 2(py. sch.)	3	300	10	500	600	700	85
'vein' pyrite							
rm 15	1	25	-	150	-	700	75
hpg	1	2500	-	10000/	-	-	15

10000 / means greater than 10000 parts per million,
10- means less than 10 parts per million
C means the central ore body, L-W is the lower-west ore bodies, U-S is the upper-Streeter ore body, L-S is the lower-Streeter ore body.

* Corrected for manganese contributed by contamination of pyrite with sphalerite. All zinc in pyrite is assumed to come from included sphalerite. Where the manganese content of sphalerite is unknown, it is assumed to be one percent.

manganese than pyrite from the country rock. Microscopic analysis of polished sections made from the samples of pyrite obtained by hand picking did not reveal any foreign materials that might contribute significant quantities of the trace elements of interest. Silver, chromium, and copper concentrations are similar in the various kinds of pyrite. The pyrite in marble may not be distinguishable from pyrite of the pyritic schist by the concentration of cobalt and nickel; yet, pyrite from the pyritic schist contains 30-250 parts per million vanadium, whereas vanadium was undetected in pyrite from the marble unit. Pyrite in the central and upper-Streeter ore bodies of the No. 2 mine was found to contain about 50 parts per million vanadium; whereas, in the pyrite from other ore bodies in the No. 2 and No. 3 mines the amounts of vanadium are below the limit of detection (less than 30 parts per million).

In the Balmat area today, the surface of the earth forms roughly a horizontal section through a complexly folded and refolded metamorphic sequence of rocks. Nine samples of calcite from a calcitic subunit of cdm 14 were analyzed for trace and minor elements on three levels comprising a vertical distance of 1000 feet. No significant gradients of trace elements in calcite were noticed over the vertical distance that was sampled (see Table 8). From these data, it seems reasonable to assume that by sampling the surface the rocks of the same units at depth are also represented at least to a few thousand feet below the surface. For a more complete study, information is also needed on sulfides from the major paragneiss and the amphibolites of the area. The latter has not been done; yet, the similarity of the concentrations of cobalt and nickel in pyrite from such unlike rock types as the pyritic schist, the silicated marble unit, and the pyrite from fracture fillings suggests high cobalt and nickel concentrations relative to the pyrite found in the ore bodies will be characteristic of the pyrite in the metasedimentary rocks in the Balmat region. The concentration of cobalt in the total rock of the ps 2 unit is about the same as Engel and Engel (1958, p. 1397, 1401) report for the major paragneiss (10-20 ppm) although the nickel content is much greater in the pyritic schist.

In order to obtain some idea of the fractionation of cobalt and nickel between pyrite and other minerals of the country rock, samples of total rock were analyzed for minor and trace elements. Data for total rock are given in Table 8. It would appear that all of the cobalt but possibly only half of the nickel are in pyrite in the pyritic schist. In the marble, it appears that nearly all of the cobalt and nickel is in the pyrite. It might be that some of the sphalerite in the ore bodies contains appreciable amounts of cobalt and nickel. Both pyrite and sphalerite samples were collected from each of 11 different polished sections. Only one of the 11 polished sections had more cobalt and nickel in sphalerite than in pyrite. The concentration of cobalt and nickel in the sulfides of the ores is low. Thus it is thought that the values given for the contents of cobalt and nickel in pyrite are not significantly affected by fractionation or contamination.

Due to unlike contents of minor elements in pyrite of the country rock compared to pyrite of the sulfide ore bodies, it is inferred that pyrite of the country rock and pyrite of the ore bodies were not both in equilibrium with the same ore fluid. Therefore, it will be concluded that pyrite of the metasedimentary rocks and ore did not have the same origin, and that pyrite of the country rock was not exposed to copious quantities of the ore fluid that formed the sulfide ore bodies. It is suggested that more than one source is needed to account for the sulfides that are found at least in trace quantities throughout every unit of the Grenville series between the Balmat-Edwards area and Pyrites, New York (for distribution of sulfides see Engel and Engel, 1959, p. 1385). No statement is made about the ore fluid passing through the marbles and schists at depth since this would not necessarily be reflected in surface sampling.

Because the ore bodies of the No. 2 and No. 3 mines are in many respects quite different in mineralogy and composition, a study of the isotopic composition of lead in galena and in marble was undertaken in the hopes of demonstrating whether or not the sulfides from the two mines came from the same source. The results of the lead isotope study are summarized in Table 3. Reproducibility of ratios of lead isotopes have been extensively studied by Chow and Patterson (1959) who found that two leads may be significantly different if the Pb(206)/Pb(207) ratios of the two samples differ by more than 0.2 percent of the ratio. On the latter basis, leads from respectively the No. 2 and No. 3 mines at Balmat are significantly different from each other (see Table 3).

Emission spectrographic analysis indicates that the concentration of lead in the ores of the No. 3 mine is less than 10 parts per million. It is possible that much of the lead in the sulfides of the No. 3 mine was lead incorporated from the rock during replacement of the marble. In order to get some idea whether or not the latter is true, two lead extractions were performed on total marble samples from the fd 7 (fetid marble) unit. The lead and uranium analytical procedures are outlined in Appendix 3C. Since marble contains appreciable contents of uranium and thorium, it is necessary to make corrections to determine the composition of lead in marble at the time of the formation of the sulfide ores. If the lead in the marble is corrected for lead added by the radiogenic decay of uranium during the last billion years, the comparison of lead in the marble with lead in galena is as follows:

Table 3: Isotopic composition of lead in galena and in marble at Balmat, New York (B. R. Doe, analyst).

Sample Number	Rock or Mineral	Location	Date	Atom Ratios 206/204	s	206/207	s	206/208	s
26N	gal	500L, No. 3 mine	11-24-58	$16.9\underline{2}$	0.06	$1.080\underline{8}$	0.003	$0.456\underline{2}$	0.004
20N	gal+sph	700BMS-Gl, No. 3 mine	3-12-59	$16.9\underline{7}$	0.05	$1.083\underline{0}$	0.002	$0.457\underline{9}$	0.003
25N	gal+sph	900GS-Lo, No. 3 mine	2-25-59	$16.8\underline{8}$	0.05	$1.083\underline{7}$	0.002	$0.457\underline{4}$	0.001
D5	gal	500L-LFW, No. 2 mine	2- 3-59	$17.1\underline{1}$	0.07	$1.087\underline{1}$	0.003	$0.460\underline{4}$	0.001
F19	gal	1100GS-C, No. 2 mine	12- 3-58	$17.0\underline{7}$	0.03	$1.087\underline{5}$	0.002	$0.461\underline{3}$	0.001
J1	gal	1100GS-LEU, No. 2 mine	2-16-59	$17.0\underline{7}$	0.04	$1.088\underline{2}$	0.002	$0.460\underline{6}$	0.002
R9	gal	1500GS-LW, No. 2 mine	1-16-59	$17.0\underline{7}$	0.06	$1.086\underline{8}$	0.002	$0.460\underline{0}$	0.002
fd 7-2	marble	900L-shaft, No. 3 mine	5- 6-59	$18.\underline{10}$	0.08	$1.159\underline{1}$	0.002	$0.49\underline{17}$	0.001
fd 7-3	marble	Surface, Sylvia L.	6-11-59	$19.3\underline{5}$	0.06	$1.228\underline{0}$	0.003	$0.521\underline{0}$	0.003

Marble	U ppm	Pb ppm	Pb/U
fd 7-2	0.64	3.20	5.0
fd 7-3	0.083	0.48	5.8

s - is the standard deviation of ratios of isotopes found on a sample on the day of analysis and constitutes only a part of the error involved in the variation of the observed ratios in comparison to their true value. The values of s are not multiplied by $1/\sqrt{N}$ which varies between 0.16 and 0.26.

Marble Sample	$\frac{206}{204}$	$\frac{207}{204}$	Mine Average	$\frac{206}{204}$	$\frac{207}{204}$
fd 7-2	16.05	15.46	No. 3	16.92	15.63
fd 7-3	17.53	15.63	No. 2	17.08	15.71

If the lead in the marbles are corrected to 1200 million years ago, the ratios are decreased by about 0.4 from the value given above of 206/204 and about 0.04 for the 207/204 ratio.

The abundance of Pb(208) is abnormally low in the lead in the marble. Any correction for the radiogenic decay of thorium will make the ratios still lower. No thorium analyses were performed, and it is not found advisable to assume any thorium/uranium ratio for marbles. Evans and Goodman (1941) gave the thorium concentrations of four different limestones from four different localities as being between 0.16 and 2.0 parts per million. Subsequently Breger (1955) gave the thorium contents of two chalks as being 2.8 and 2.0 parts per million. Adams, et. al. (1958, p. 272) found between 0.6 and 5.1 parts per million thorium for six limestones and chalks from four different formations. The aforementioned investigators also analyzed for the concentrations of uranium, and the thorium to uranium ratios given by the above investigators lie between 0.15 and 2.1.

If it is assumed that no appreciable amount of thorium is present in the fs 7 unit, the value for the 208/204 ratio given in Table 3 becomes a maximum. If fd 7-2 and fd 7-3 contain more than 0.2 and 0.03 parts per million of thorium respectively, it is most unlikely that they could have contributed significant amounts of lead to the ores.

The lead in the two marble samples are different today and remain different after correcting for the radiogenic addition of lead. The discordance may be accounted for in either of two ways - (1) the composition of lead throughout the section was heterogeneous and was never homogenized during the Grenville metamorphism and/or (2) a geologic event subsequent to the Grenville metamorphism added or removed uranium or lead from the marbles. If (1) above is considered the case, it is of some importance to note that the range of uranium lead values for the lead of the marble overlap the uranium lead values for lead from the ores. Consequently the ore lead may be the homogeneous product of a mixture of inhomogeneous leads of the Grenville rocks such as encountered in the fs 7 unit. Since the concentration of thorium in the marble is unknown, the possiblity must be considered that the lead in the ore was derived from the country rock.

In consideration of (2) above, geologic studies of the Balmat-Edwards area have failed to reveal any evidence of a post-Grenville metamorphic event; however, about 15 miles northwest of Balmat at Rossie, New York, Brown and Kulp (1959) have described and analyzed the composition of lead from a calcite vein. Some of the calcite veins pass through the Potsdam sandstone which indicates an age younger than Cambrian. Brown and Kulp give the lead composition of the one galena as:

206/204	207/204	208/204
19.28	15.63	39.61

The uranium leads are within the range found for the lead of the fs 7 marble uncorrected for radiogenic addition since the Grenville metamorphism, but the vein thorium lead is much more radiogenic than the fs 7 thorium lead. There is some question as to the derivation of the

Rossie veins, but the abundance of calcite in the veins might suggest derivation from the Grenville marbles. Difficulties are encountered in reconciling the low thorium lead contents of the fs 7 marble with the high thorium lead concentrations of the galena in the calcite veins. Again the suggestion is that the isotopic composition of the lead in individual units was not homogenized during the Grenville metamorphism.

It is found from concentrations of lead isotopes in the fs 7 unit that more work would be needed to state conclusively whether or not the ores of the No. 2 and No. 3 mines could have been derived from adjacent marble units as a homogeneous "sweat product" from an isotopically inhomogeneous source. On the other hand, trace element studies of pyrite from the ore bodies and from the surrounding metasedimentary rocks suggest that the ore fluid that formed the sulfide ore bodies could not account for the pyrite from the adjacent rock units. If the ore fluid traversed horizontally through the adjacent marbles, no evidence was preserved in the content of minor elements of the pyrite in the country rock.

It has been suggested that the composition of lead within individual lithologic units was inhomogeneous at the time of Grenville metamorphism. The inhomogeneities between or across units other than the one that was studied may be as great or greater than what was observed. If so, this variation would be greater than 9 percent of the 206/204 ratio, 3 percent of the 207/204 ratio, and one percent of the 208/204 ratio. The composition of lead in galena has been determined from deposits in several different parts of the Grenville subprovince (Table 4). While interlaboratory correlations of data are not as good as intralaboratory correlations, variations of lead isotope ratios are less for galenas from different ore deposits (206/204 about 4 percent, 207/204 about 2 percent, and 208/204 about 2 percent) than the variations found in the study of one marble unit.

Lithologic sections compiled by Engel (1956, p. 80) indicate that the abundance of marble grades from about half the exposed section near the western portion of the Grenville subprovince to about one percent in the central portion and that corresponding increases occur in the thickness of paragneiss. If the galena in the various ore bodies are postulated to have a source in some metamorphic unit(s) at depth, it must also be postulated that the individual source units that occur several hundred miles apart yield galena ores that are all relatively uniform in isotopic composition. Whereas the deposits at Balmat could not be evaluated by lead isotope ratios as to whether or not the adjacent metasediments could have supplied the galena, consideration of what is known of the isotopic composition of galena in the Grenville subprovince places severe restrictions upon the source being the surrounding metasediments.

Over the past several years the hypothesis of deriving ores and some other rock types (i.e., pegmatites) from a homogeneous substratum, existing essentially unaltered since the formation of the earth, has become attractive to an increasing number of geologists and geochemists. The principal proponent of the hypothesis that sulfide ores are derived from such a homogeneous substratum has been John Brown (1948) who included such a source in his metallurgical hypothesis of ore genesis. Brown credits to Gregory (1928) the proposal of a deep

Table 4: Galena lead isotope data from the Grenville Subprovince

Location		Atom Ratios			Reference or Analyst
		206/204	207/204	208/204	
Balmat, N.Y.,	2- 500	17.11	15.74	37.17	Doe, B.R.
	2-1100	17.07	15.70	37.00	Doe, B.R.
	2-1100	17.07	15.69	37.07	Doe, B.R.
	2-1500	17.07	15.70	37.10	Doe, B.R.
gn	3- 500	16.92	15.65	37.08	Doe, B.R.
gn+sl	3- 700	16.97	15.67	37.05	Doe, B.R.
gn+sl	3- 900	16.88	15.58	36.90	Doe, B.R.
Balmat, N.Y., (Conc.)		16.96	15.54	36.77	Brown and Kulp (1959)
Jordanite	2-1300	17.06	15.62	36.99	
Edwards, N.Y., (2100)		16.80	15.60	36.92	
Rossie, N.Y., (Surface) Post-Potsdam Ss. calcite vein		19.28	15.63	39.61	
Anacon, P.Q.	(423)stope	16.55	15.64	36.46	Cummings, et. al. (1955)
	(615-60)	16.53	15.64	36.44	
	(826-50)	16.49	15.58	36.33	
Tetrault, Que.		16.82	15.70	36.62	
		16.27	15.16	35.6	Nier, et. al. (1941)
L. Baskatong, Que. (Ciglen Claims)		16.59	15.64	36.71	Cummings, et. al. (1955)
Frontenac Twp., Ont.		16.79	15.40	36.49	
New Calumet, Ont.		17.22	15.75	37.20	

2-500:	No. 2 mine, 500 level
2-1100:	No. 2 mine, 1100 grizzly sublevel
2-1500:	No. 2 mine, 1500 grizzly sublevel

sl - sphalerite; gn - galena

seated origin of ores not necessarily associated with igneous activity. Two methods of dating absolute age have arisen based upon an origin of galena from a homogeneous substratum accumulating radiogenic lead undisturbed since the origin of the earth: (1) it is assumed that radiogenic Pb(206) and Pb(207) are added to primordial lead up to the time of removal of lead from the substratum, and (2) involves an estimate of the U(238)/Pb(204) ratio existing now in the substratum coupled with measurement of radiogenic Pb(206) added to primordial lead until the time of removal of lead from the substratum. Method (2) above will be better than method (1) if the U(238)/Pb(204) ratio can be estimated more accurately than the Pb(207)/Pb(204) ratio can be measured. Catanzaro and Gast (1959) determine the best value of the U(238)/Pb(204) ratio to be 9.0 with a range from 8.5-9.5.

For the galenas at Balmat to fit the substratum hypothesis, the common lead ages should be concordant with the absolute ages. The age of the Grenville metamorphism seems to lie between 900 and 1200 million years in the Balmat area, and it appears that the age of the ore bodies fit into the same range (see section on Absolute Age).

For the purposes of calculation, the age of the ore bodies is chosen as 1000 million years, the age of the earth as 4550 million years (Patterson, 1956), the decay constant of U(235) as 9.71×10^{-10} and of U(238) as 1.54×10^{-10} yr.$^{-1}$ (Fleming, Ghiorso, and Cunningham, 1952), the average values for the Pb(206/204) ratio for the No. 2 and No. 3 mines are respectively, 17.08 and 16.92, and respectively, 15.71 and 15.63 for the Pb(207/204) ratio. Primordial lead is accepted to have the composition of lead in troilite as found by Patterson, et al. (1955).

Using method (1) above the age for the No. 3 mine is given as 1010 million years and method (2) gives 1340, 1100, and 850 million years if the U(238)/Pb(204) ratio is chosen respectively, as 9.5, 9.0, and 8.5. Method (1) for the No. 2 mine gives 1000 million years with method (2) giving 1260, 1020, and 740 million years respectively, for U(238)/Pb(204) ratios as above. Recalculation of data of Brown and Kulp (1959) for the Edwards mine (15 miles to the northeast of Balmat) indicates 1060 million years by method (1) and 1400, 1190, and 925 million years by method (2) respectively for U(238)/Pb(204) ratios as before.

The data determined by common lead are compatible with the age determined by the metamorphism of the Grenville area. The compatibility could be due to:

1. Derivation of the ores at Balmat from a homogeneous substratum accumulating radiogenic lead from the decay of uranium and thorium. The radiogenic lead is added to primordial lead from the time of origin of the earth to the time of extraction of the ore fluid. The effect of contamination of the ore fluid by lead added between the source and the site of deposition is assumed to be negligible. Alteration of the lead between the time of deposition and the time of analysis is assumed to be negligible.

2. Derivation of the ores at Balmat from the adjoining country rock or other rock units in which various isotopic compositions of lead were coincidentally mixed in the proper proportions to give a lead of the correct isotopic composition.

It has been mentioned above that a slight discordance is noted between the leads of the No. 2 and No. 3 mines. Certain differences are also noted between the mineralogic contents of the two mines - relative abundances of pyrite, galena, pyrrhotite, and marcasite are markedly lower or absent in the No. 3 mine as compared to the No. 2 mine (Table 5). The content of iron in sphalerite is much lower in the No. 3 mine than in the No. 2 mine (about 2-3 percent FeS against 6-14 percent). Also some differences exist in the concentration of minor and trace elements of sphalerite in the two mines - indium is less, manganese is less, copper and gallium are more abundant in the No. 3 mine.

The concentration of cadmium in sphalerite may prove to be an important source indicator. Whereas most minor elements when detectable have large ranges of variation (from a factor of two to several orders of magnitude), the content of cadmium in sphalerite is remarkably constant within individual ore bodies as shown by the data of Rose, 1958; Burnham, 1955; and Fryklund and Fletcher, 1956. Within the error of measurement of cadmium by emission spectrographic procedures, no systematic differences are noted in the content of cadmium in sphalerite between the No. 2 and No. 3 mines. The lack of differences in the cadmium content of sphalerite between the two mines may well be indicative of similar sources. Reasons will be presented in the section on geothermometry for believing the No. 3 mine was deposited at a lower temperature than the ore of the No. 2 mine. It would be expected that the partition of cadmium between sphalerite and ore fluid would be influenced to some degree by temperature as well as by the concentration of a particular cadmium species in the ore fluid. The impression is, however, that sphalerite is an excellent carrier of cadmium and is less influenced by temperature than by the Zn/Cd ratio in the ore fluid.

It is inferred that the isotopic composition of the lead and the concentration of cadmium in the ore fluids that deposited the sulfides in the No. 2 and No. 3 mines were similar. The composition of the small amount of lead found in the No. 3 mine would be more subject to alteration during the replacement of the country rock than the lead of the galena in the No. 2 mine. The mineralogic and compositional differences observed between the ores of the two mines are thought to be best explained by ore fluids from a common source being introduced into the various mining areas at slightly different times. Also, the source of the ore fluid is thought to be either primarily or secondarily derived from a homogenized substratum at depth. Comparison then of concentrations of trace elements in pyrite and information on the isotopic composition of lead between the sulfide ores and the surrounding units of the Grenville series suggests but does not conclusively prove that the sulfide deposits at Balmat were not derived from the surrounding rocks.

V. TEMPERATURE AND PRESSURE OF DEPOSITION

Using the approximations of other workers as given in the Introduction, the total pressure during ore deposition is estimated at a somewhat higher value than given in previous studies of the Balmat-Edwards district. Because of the identification of the deposition of the ore with Grenville retrograde metamorphism, the value for total pressure that will be assumed in this study is 3.0 ± 1 kilobars as given in the Introduction.

The major aim of this study is an attempt to determine the temperature and temperature range involved in primary sulfide formation at Balmat, New York. One possible sulfide geothermometer is the pyrrhotite-sphalerite system as reported in Kullerud (1953), Skinner, et. al. (1959), and Barton and Skinner (in press, American Minerologist). In general the theory assumes that sphalerite is deposited into a system containing pyrrhotite with the sphalerite becoming saturated with FeS from pyrrhotite at the time of deposition. However, at Balmat, paragenetic information indicates that the reverse process occurred, that is, that most of the pyrrhotite was deposited into a system containing sphalerite and that sphalerite came into equilibrium with pyrrhotite at the time of deposition of pyrrhotite.

Another solid solution series possibly suitable for geothermometry is the pyrite-pyrrhotite system as developed by Arnold (1958). A reconnaissance study of the $FeS-FeS_2$ system was performed at Balmat, but in general was found to be not applicable or in disagreement with temperatures indicated by coexistent sphalerite. Most of the pyrrhotite samples encountered at Balmat were apparently not hexagonal, and further it is suspected that extensive exsolution of pyrite from pyrrhotite subsequent to deposition has taken place accounting for the euhedral pyrite nearly always associated with pyrrhotite.

There is still considerable doubt about the results of experiments used to determine the solubility of FeS in ZnS, and there are several corrections that have been made to the original phase diagram as worked out by Kullerud. Kullerud (1953, p. 76) mistakenly quoted and used an a_o for pure ZnS in angstrom units that was given in kX units in the source of the data (Skinner, et. al., p. 1044). Kullerud also incorrectly converted the weight percent data to mole percent for FeS, MnS, and CdS (Doe, 1956, p. 8). A third correction involves the suspicion that the FeS used by Kullerud (1953) was partially oxidized. Skinner and Barton (1958) pointed out that the effect of substituting oxygen for sulfur in sphalerite is to decrease the lattice parameter. Kullerud standardized his data for the relation between the lattice parameter of ZnS and concentration of FeS in sphalerite by sealing a mixture of known amounts of FeS and ZnS in a bomb and heating to a high temperature until all the FeS was dissolved in the ZnS. Then he determined the lattice parameter of the specimen that contained both FeS and presumably oxidized FeS. The result was a lattice parameter smaller than would have been found if pure FeS was used with the ZnS (Skinner, et. al., 1959, p. 1041).

When Kullerud determined the location of the points on the solvus of the FeS-ZnS system, he added an excess of a mixture of FeS (and oxidized FeS) to ZnS but assumed that the iron was all as FeS. Then he heated the bomb to a specified temperature for a period of time long enough for the sphalerite to become saturated with FeS and determined the FeS content from the standard curve mentioned above. There were undoubtedly two effects that occurred because the FeS was partially oxidized - (1) a value for the iron concentration in sphalerite that was too high because with an excess of the FeS-oxidized FeS mixture the reaction was principally one involving unoxidized FeS and ZnS with no resulting shrinking of the structure due to oxygen, and (2) the presence of oxygen may have affected the solubility of FeS in ZnS (Skinner, et. al., 1959, p. 1046). The result of (1) above is that the solvus of the solubility of FeS in ZnS should be at a higher temperature for a given concentration of FeS than quoted by Kullerud (1953). The effect of (2) is presently being evaluated by Kullerud.

A further complication in the use of the FeS-ZnS system to determine the temperature of formation of the assemblage is due to the fact that sphalerite dissolves appreciable quantities of manganese and cadmium. Kullerud (1953, p. 119) examined the possibility that inclusion of MnS and CdS in sphalerite might increase or decrease the solubility of FeS in sphalerite. Kullerud found that about two percent MnS by weight and one percent CdS by weight in sphalerite did not affect the solubility of iron in sphalerite. On the other hand, Skinner (1959) found that one mole percent of MnS in sphalerite rather than zero percent lowered the concentration of FeS in sphalerite from 32.0 to 30.9 mole percent at 800°C and from 25.8 to 24.8 mole percent at 700°C. Barton and Skinner (in press) found that the increase in the lattice parameter is not linear with increasing concentrations of MnS as well as FeS in sphalerite. Although the concentration of CdS in sphalerite is generally less than the concentration of MnS, it was reported by Kullerud (1953) that the effect of CdS on the lattice parameter of sphalerite is about 10 times that of an equivalent mole percentage of ZnS.

Kullerud (1953) experienced great difficulty in saturating ZnS with FeS at temperatures below 500°C and was unable to saturate ZnS with FeS within a period of a year at temperatures at and below 400°C. Kullerud was forced to calculate the points on the solvus below 400°C. It is not understood what the exact implications are of geological examples that fall in the range of temperatures where the reactions are very sluggish. Copper is often found as blebs of chalcopyrite in sphalerite in a form which possibly indicates an origin as an exsolution product from sphalerite. The effect of chalcopyrite on the concentration of iron in sphalerite has not been investigated.

Some of the difficulties mentioned above in the application of the FeS-ZnS system in geothermometry may be eliminated. Very small variations in the length of the edge of the unit cell indicate large variations in the concentration of FeS. The lattice parameter of ZnS containing 14.4 mole percent FeS is only about 0.0067 Å larger than that of pure ZnS. To evade the difficulties inherent in measuring the lattice parameter of ZnS plus the difficulties involved in correcting the lattice parameter for quantities of dissolved MnS and CdS in this study, the concentration of FeS in ZnS is measured by x-ray fluorescent methods which have been standardized with natural sphalerites. In the standards the quantities of iron, manganese, and cadmium have been determined by several different methods in several different laboratories (see Appendix 3A). The uncertainty of the effect of chalcopyrite on the solubility of iron in sphalerite is thought to be eliminated because of the low concentration of copper found in sphalerite samples at Balmat (less than 0.1 percent by weight of copper). The error in the conversion from weight percent to mole percent has been corrected (Kullerud, personal communication).

The concentration of CdS in sphalerite at Balmat (about 0.12 mole percent) is probably sufficiently low so that the solution of FeS in ZnS will be unaffected. If the latter is not the case, the concentration of iron in sphalerite for a system of FeS and ZnS with CdS probably would not have the concentration of FeS in mole percent lowered by more than the amount of the CdS found in the natural system or about 0.12 mole percent. Sphalerite found with coexisting pyrrhotite contains an average of about 1.2 mole percent MnS. Skinner (1959) has not determined the effect of MnS on the solubility of FeS in sphalerite at the temperatures involved at Balmat, but his data at 700 and 800°C indicate that sphalerite from a system free of manganese would contain about 1.2 mole percent more FeS than sphalerite that contains 1.2 mole percent MnS at the same temperature. Since the phase diagram for the FeS-ZnS system does not include cadmium or manganese, 1.3 mole percent FeS should probably be added to the average values at Balmat to determine a temperature from the phase diagram.

Skinner, et. al. (1959) show that the standardization curve used by Kullerud would indicate that a sample of sphalerite such as found at Balmat should have 2.9 mole percent FeS added to the amount found to compare with the phase diagram as quoted by Kullerud (1953). It is not known what effect the presence of oxygen had on the solubility of FeS in sphalerite, but, if it is significant, the correction is probably opposite to the other corrections discussed above.

The combined effect of an addition of 1.3 mole percent FeS because of the presence of MnS and CdS in sphalerite and addition of 2.9 mole percent FeS from the revised phase diagram of Kullerud would indicate a temperature of formation about 100° higher than if the two corrections are not made. Since the revision of the phase diagram of the FeS-ZnS system is not complete, these corrections are not used in this study but add to the uncertainty of conclusions based on temperatures derived from the FeS-ZnS system.

Because pyrrhotite is rare in most base metal deposits, many have been interested in using the FeS-ZnS geothermometer with pyrite-sphalerite. Preliminary work has been done on the pyrite-sphalerite geothermometer by Barton and Kullerud (1959, p. 288) who state:

> "It is seen that the curves Sp/FeS/V and Sp/Py/Po/V diverge above 600°C and for purposes of practical measurement coincide at some temperature between 500°-600°C. Kullerud's curve is thus applicable to any pyrrhotite-pyrite-sphalerite assemblage below this temperature."

If pyrrhotite is absent, Barton and Kullerud (1958, p. 228) feel that the use of the FeS-ZnS system for the pyrite-sphalerite system would designate a minimum temperature of formation since FeS is the most soluble iron phase known in sphalerite. Barton and Kullerud (1958) further feel that the absence of elemental sulfur from the natural system defines a maximum temperature because of the presence of a liquid with a high sulfur content in the FeS-ZnS-S system at high temperatures. The latter of course assumes that the sulfur was not influenced by other components found in natural systems such as H_2O and H_2S which might either destroy the liquid phase or transport it away from the depositional site of interest.

In the analytical procedure used, the assumption must be that any iron rich components other than sphalerite included in the analysis are either insignificant in quantity or are exsolution products from sphalerite and should be included in the analysis. In x-ray diffraction analysis it must be assumed that no exsolution of FeS has occurred. It is estimated that the average sample of sphalerite may contain 0.3 percent FeS due to pyrite contamination and has been subtracted from the averages (Appendix 3A). There is some danger of submicroscopic replacement of sphalerite by pyrrhotite, but samples containing microscopic veinlets of pyrrhotite were not used in the analysis.

The last and probably most fundamental problem to be discussed might be termed the <u>great dilemma</u> of solid solution geothermometry. In bomb runs, it is possible to chill the bomb to keep the two components of the solid solution series from exsolving and many cases in nature may be similar. Kullerud (1953, p. 110) estimates - from the rate of exsolution of synthetic FeS-ZnS solid solutions at several high temperatures - that sphalerite at 200°C should come into equilibrium at that temperature with pyrrhotite by exsolution in about 46 years; yet, natural occurrences of ZnS are known which are suspected to have retained FeS in a greatly supersaturated state for up to 10^6 years or even 10^9 years. Is then the composition of a solid solution series observed today the composition at the time of crystal formation or some other value? The association of high iron sphalerite with later pyrrhotite shows that later events at possibly lower temperatures can significantly change the system particularly in high temperature regions.

Kullerud (1959, p. 319) reports that synthetic sphalerite-pyrrhotite mix crystals formed at 700°C and maintained at 500°C for about a year had come into equilibrium with the 500°C temperature within that time. On the other hand, samples from Broken Hill, which contain FeS indicative of 700°C were heated to 500°C for about a year and did not exsolve any pyrrhotite. The mechanism that arrests exsolution is not known.

It is difficult to determine whether or not equilibrium between FeS and ZnS was established. One good indicator is the uniform coloring of sphalerite grains. No color change has been observed at the interface of pyrite and sphalerite or pyrrhotite and sphalerite. On the other hand, in the supergene alteration zone, sphalerite at the interface of chlorite and sphalerite showed bleaching of the sphalerite over short distances. In the No. 3 mine, some grain edges and fracture interfaces were nearly black and opaque which may be the influence of magnetite although the sphalerite of the areas containing magnetite and sphalerite in the No. 2 mine are snow white. It would seem then that at some temperature and pressure equilibrium between pyrite and sphalerite and pyrrhotite and sphalerite was closely approached. It is thought that sphalerite only came into equilibrium with pyrrhotite in the immediate zone of pyrrhotite deposition and that the farther a sphalerite sample is from the area of deposition of pyrrhotite the closer the FeS content approaches that of the pre-pyrrhotite equilibrium of sphalerite with pyrite. Since the iron content of the sphalerite near marcasite does not seem to be affected by the formation of marcasite presumably at lower temperatures, the indication is that marcasite did not disturb the equilibrium that was established at some temperature higher than that of marcasite formation.

It is felt by some (Rose, 1958) that reaction between pyrite and sphalerite indicates that equilibrium was not established. However, it must be postulated that pyrite and sphalerite came into equilibrium in the solid state and not with an ore fluid presumably under-saturated with respect to iron. The pyrite-sphalerite reaction could just as well be a manifestation of the result of the establishment of equilibrium as the reverse; hence it is felt that reaction of pyrite with sphalerite is at best a neutral criteria.

Many of the problems in using the $FeS-FeS_2$ system as a geothermometer are similar to those of the FeS-ZnS system. Both systems involve an expansion of the lattice with increase of the solute phase and are thus pressure dependent to a small degree. Preliminary work by Arnold (1957) indicates that the effect of pressure on the pyrite-pyrrhotite system is insignificant at temperatures of about 300°C but becomes about 30°C/kilobar at a temperature of about 500°C. Kullerud (1953) indicates from calculations involving extrapolated data that the pressure effect on the FeS-ZnS system is about 20°C/kilobar. The presence of cobalt and nickel in the system will probably influence the amount of pyrite dissolved in pyrrhotite; however, the cobalt and nickel contents of pyrrhotite at Balmat are very small whereas the manganese and cobalt contents of sphalerite are relatively large. The effect of composition on lattice spacings in pyrrhotite is much greater than in sphalerite. This fact allows the composition of pyrrhotite to be determined by lattice parameters much more easily than sphalerite with pyrrhotite having an analytical error in the temperature of about ± 3° relative to about 50°C in sphalerite with the same error in the lattice spacing. One difficulty exists in work with pyrrhotite that is not encountered in sphalerite; namely, pyrrhotite converts from hexagonal to monoclinic symmetry below 325°C (Arnold, personal communication). The relationship of the monoclinic parameters to the hexagonal parameters and iron content is not known. All but one of the pyrrhotite samples analyzed from Balmat are of the monoclinic structure. For pyrrhotites of the proper hexagonal structure, analysis by studies of lattice parameters is probably of sufficient accuracy for a determination of the composition.

It is more difficult to tell whether equilibrium has been approached in the system pyrite-pyrrhotite than in the system sphalerite-pyrrhotite. There is no textural evidence to suggest reaction between pyrrhotite and pyrite in the Balmat No. 2 mine although in some cases pyrrhotite fills cracks in pyrite.

In determining a temperature of formation then, the following requirements must be met - (1) solid solution equilibrium must be closely established between the phases of interest at the temperature of deposition of the latest phase, (2) the solid solution of the phase analyzed must remain unchanged from the time of deposition through the time of analysis, (3) the components of the solid solution must be accurately analyzed, and (4) the activity of the components of interest in the solid solution analyzed should not be greatly affected by other components present in the phase of interest or in surrounding phases. In the study at Balmat, (3) above is satisfied, (4) is thought to be a reasonable assumption particularly for samples with MnS and CdS contents in the range found, but (1) and (2) are inferred and subject to question. If two solid-solution geothermometers give compatible results, then (1)above is strengthened as to the establishment of equilibrium but perhaps not as to the time of interest. Thus concordant temperature values indicated by the ZnS-FeS phase diagram and pyrite-pyrrhotite phase diagram would indicate that pyrite, pyrrhotite, and sphalerite had all come into equilibrium at some temperature but not necessarily at the temperature of deposition of pyrrhotite (the last of the three phases deposited). Arnold (1958) found good agreement between temperatures derived from the system pyrite-pyrrhotite-sphalerite. On the other hand, Skinner (1958, p. 559) in the Nairne Pyritic formation in Australia, the author in this study, and to a lesser degree Stone (1959, p. 1019) find discordant temperatures indicated by the system pyrite-sphalerite-pyrrhotite. Skinner and Stone thought that the temperature indicated by the FeS-ZnS part of the system was in error to the high side of the true temperature of formation; however, the author feels that euhedral pyrite associated with pyrrhotite may indicate exsolution of pyrite from pyrrhotite so that the temperature indicated by the pyrite-pyrrhotite part of the system may be too low. Further work is needed to establish the validity of the use of sulfide solid solution systems as indicators of temperatures of formation in natural systems. Temperatures indicated in this study should be viewed as representing the best estimate obtainable at the present time and may be subject to revision at a later date.

Arnold shows that two kilobars pressure has no significant effect on the d(102) spacing of pyrrhotite formed in the temperature region below 400°C. The one hexagonal pyrrhotite specimen analyzed from Balmat indicates a temperature of formation of 340°C whereas coexisting sphalerite indicates a temperature of formation of 480°C (no pressure correction) or 550°C (allowing for 3.0 kilobars pressure at the rate suggested by Kullerud, 1953). It is thought that euhedral pyrite associated with pyrrhotite may represent extensive exsolution of pyrite from pyrrhotite.

A number of coexisting pyrrhotite-sphalerite-pyrite samples have been analyzed for iron in sphalerite from three levels in the No. 2 mine and indicate the following temperatures assuming 3.0 kilobars pressure:

Mine Level	Number of Samples	T°C	Range T°C
500L	5	510	70
1100GS	4	520	70
1500GS	9	510	100

When pyrrhotite converts from a hexagonal structure to a monoclinic structure, the (102) reflection splits into two subpeaks. If the wider d(102) spacing of the subpeaks is assumed to represent the hexagonal phase, the temperatures indicated with 3.0 kilobars pressure at the time of pyrrhotite formation are 620°, 540°, 550°, 500°, and 490°C. The apparent agreement between the sphalerite data and monoclinic pyrrhotite data is probably accidental (see Appendix 3D for d(102) spacings). No exsolution laths were noted in the pyrrhotite such as those reported by Arnold (1957) or Kullerud and Yoder (1959).

It was at first feared that the presence of submicroscopic pyrrhotite in sphalerite might account for much of the difference in iron contents observed between sphalerite in pyrrhotite bearing regions and sphalerite in pyrrhotite-free areas. Six sphalerite samples were analyzed by counting in steps of 0.01°2 θ the intensity of iron radiation diffracted from the d(220) lattice spacing in sphalerite (see Appendix 3D). The lattice parameters obtained by the diffractometer study uncorrected and corrected for manganese and cadmium effects (corrections from Kullerud, 1953), are to ± 0.0008Å:

	Lattice Parameter		
Sample Number	a_o uncorrected	a_o corrected	FeS(Wt.%) fluorescent
P12(a, b)	5.419_5	5.418_4	13.5
Q5	5.417_2	5.416_{50}	12.5
R3 (a, b)	5.417_0	5.416_{47}	9.1
T6	5.416_4	5.416_0	8.3
T12	5.414_7	5.414_4	7.9
1N (a, b)	5.411_6	5.411_3	1.8

While the quantitative value for the iron content by diffraction did not agree well with the values obtained by fluorescence, the diffraction analysis ranked the sphalerite samples in the same order of iron content as the fluorescence analysis. Therefore, it is thought that the variations in iron content are real, and further that most of the iron in sphalerite is in the structure and not in submicroscopic defects.

When the total pressure on the solid solution system becomes greater than a kilobar, the pressure term in the temperature calculation becomes important. For sphalerite at Balmat, a pressure correction to temperature of 70° will be added to the temperature indication at one atmosphere. It is thought that one kilobar pressure (or about 25°C) is about all the error expected due to pressure. It is further thought that 12.5 wt. percent FeS is close to the equilibrium value for the FeS-ZnS system in Balmat. The value is probably not more in error than one percent (or 30°C) because the highest FeS values for sphalerite are thought to have appreciable pyrrhotite contamination and the lowest values may be an effect of lack of equilibrium. The best estimate of pyrrhotite deposition then is thought to be 510° ± 50°C.

The range in temperature of the deposition of pyrrhotite is independent of the error in the pressure correction. As given above, it would appear that the range of deposition of pyrrhotite is less than 100° and probably less than 70°C. The conclusion is that the temperature range in the deposition of pyrrhotite is quite small. In all, about 1800 feet of the path of the ore fluid have been examined over a vertical distance of 1000 feet in the No. 2 mine and over 600 feet of parts of several ore bodies in the No. 3 mine. There is no evidence of gradients in temperature either vertically or horizontally. Any variations in solid solution relations can be accounted for by the presence of pyrrhotite disrupting the sphalerite-pyrite equilibrium. With minor exceptions, sphalerite in all the ore bodies of the No. 3 mine contains FeS in the range 2-3 weight percent. If areas of pyrrhotite are avoided in the No. 2 mine and supergene sphalerite is excluded, the bulk of the sphalerite falls in the FeS content range of 6-9 weight percent. If emphasis is placed upon the pyrrhotite bearing areas, the average FeS content of sphalerite on the 1500 grizzly sublevel is the same as on the 500 level. There is no reason to assume that the ores of the 500 level were formed at a higher or lower temperature than the ores of the 1100 grizzly sublevel or the 1500 grizzly sublevel.

It is not clear either how rapidly or in what quantity the ore fluid was introduced; however, small clots of sphalerite have both iron and minor element contents compatible with larger masses near by. The impression gained is that the temperature of the ore fluid was externally controlled, presumably by the temperature of the surrounding country rock.

While there is no evidence of horizontal or vertical temperature gradients during ore deposition, there is evidence that the temperature changed during the paragenetic sequence. Kullerud and Yoder (1959) indicate that the temperature of formation of marcasite is less than 400°C although they do not state what the effect of pressure may be. In a section below, it is shown that information from minor elements indicates that the No. 3 mine was formed at a lower temperature than the No. 2 mine. Thermal gradients in the Grenville metamorphism were apparently small. Engel and Engel (1958) indicate a gradient of 30° between Balmat and Edwards, a distance of 12 miles, at the peak temperature of metamorphism. Such a small gradient could well account for the lack of any thermal gradient for a given interval of the paragenetic sequence in the Balmat ores if the temperature of the ore fluid was controlled by the temperature of the country rock. On the other hand, the formation of serpentine in the retrograde sequence must have taken place at less than 500°C (Bowen and Tuttle, 1949). The maximum temperature at which the serpentine could exist would be governed by how much the $p(H_2O)$ is less than p(total). Thus the difference in temperatures of formation of the bulk of sulfides in the No. 2 and No. 3 mine ores can easily be explained if the temperature of the ore fluid is controlled by the temperature of the country rock, and if the ores of the two mines were formed during different stages of the retrograde metamorphism of the area. Thus it is concluded that the No. 3 mine was formed at a later date than the No. 2 mine although the time span involved was small in comparison to the accuracy of the age dating methods employed.

Engel and Engel (1958) have indicated that the peak temperature of metamorphism in the Balmat area was about 550°, and commented upon the agreement between peak temperatures obtained from the sulfide ore deposits with thermometers examined in the country rock at distances of several miles from the ore body. Thus it would appear that the bulk of deposition of sulfides in the No. 2 mine had occurred at temperatures near the peak temperature of metamorphism of the area. It cannot conclusively be stated that much pyrite and sphalerite was not formed at temperatures somewhat greater than the surrounding rocks (but not likely to be much over 600°C if the pyrite-sphalerite geothermometer applies as a maximum) except for lack of any such evidence. Therefore it seems reasonable to assume that the bulk of the No. 2 mine mineralization occurred between the maximum temperature of country rock metamorphism and the temperature of deposition of pyrrhotite or 510° ± 50°.

Most minor elements in sulfides are found to have highly variable concentrations within the host crystal in individual ore bodies or even within single crystals and polished sections (Burnham, 1955; Rose, 1958). It has been assumed by many that concentrations of minor elements in sulfides are controlled by temperature, a viewpoint that has been seriously questioned and discussed at length by Rose (1958) and to a lesser extent by Edwards (1954, p. 44-47). The concentration of trace elements in a crystalline phase will depend upon the concentration of the trace element in the ore fluid, the temperature of the ore fluid, the extent of reaction, the kind of reaction which takes place between the ore fluid and the crystalline host, by total pressure, and by disruption of the original extent of reaction at some post-depositional period. If the type of reaction involved between ore fluid and crystalline host is ideal solution or if the activity coefficients are known, the distribution of a trace element between two phases will be given by:

$$\frac{X_1^1\ (a_1^1)}{X_1^2\ (a_1^2)} \approx \exp(-\Delta h/RT) \qquad (1)$$

X_1^1 is the mole fraction of component 1 in phase 1

X_1^2 is the mole fraction of component 1 in phase 2

a_1^1 is the activity coefficient of component 1 in phase 1

a_1^2 is the activity coefficient of component 1 in phase 2

Δh is the partial molar heat involved in displacing component 1 from phase 2 to phase 1

T is the absolute temperature at which the transfer takes place.

Equation (1) is given for a particular pressure, but, if the solution takes place at the same temperature but different pressures, Equation (1) will become to first order:

$$K_1/K_2 = \exp\left[(\Delta v)(P_2-P_1)/RT\right] \qquad (2)$$

Δv is the partial molar volume change in displacing component 1 from phase 2 to phase 1

P_1 is the total pressure to which the equilibrium constant K_1 applies

P_2 is the total pressure to which the equilibrium constant K_2 applies

K_1 is the fractionation of component 1 between phases 2 and 1 as given by Equation (1).

It may be that a chemical reaction is involved in the transfer of component 1 from phase 2 to phase 1. In the latter case the equilibrium constant becomes more complicated. An example to be considered might be the transfer of manganese from pyrite to sphalerite. If the manganese simply proxies for iron in pyrite, the transfer might well be governed by solution laws and Equation (1). If manganese is of the form MnS_2 in pyrite and MnS in sphalerite, the transfer would be governed by the equation $\left[MnS_2\right]^{py} = \left[Mns\right]^{sl} + \frac{1}{2}(S_2)$ in which case the fractionation would be given by:

$$\frac{\left[MnS\right]^{sl} (fS_2)^{1/2}}{\left[MnS_2\right]_{py}} \approx \exp(-\Delta H/RT) \qquad (3)$$

where the activity and fugacity coefficients are ignored and ΔH is the heat of the reaction. Equation (3) will also be governed as shown by the fugacity of sulfur and is the type of reaction Barton and Kullerud describe for the sphalerite-pyrite geothermometer (1958, p. 228).

The equilibrium constants between ore fluid and mineral are likely to be even more complicated than assumed so that care must be taken in interpreting trace element data. It should be noted, however, that the concentrations of minor elements in crystalline phases may be controlled by the concentration of minor elements in the ore fluid, but the ratio of a minor element between crystalline phases will not be controlled by the concentration of the minor element in the ore fluid if the crystalline phases have come into equilibrium with each other.

It is concentrations of minor elements that are measured in mineral analysis and little is known about the activity coefficients of a minor element as a function of temperature, pressure, and other components. If the activity coefficient of a minor element is the same in both mineral phases of interest, the equations used assuming ideality will probably still be true. In addition to the assumptions involved above are errors involved in the analytical procedures used in trace element analysis and the fact that Δh and ΔH may not be constant or nearly so for the system studied over the temperature range involved. Thus it is seen that temperatures based upon trace element data should be considered as preliminary values.

In order to utilize the trace element geothermometer, it is necessary to be able to determine the content of a specific trace element in two crystalline phases to a degree usually not obtainable by emission spectroscopy for most trace and minor elements. In the present study, only manganese and copper approach the necessary analytical criteria in two mineral phases, and it may be that averaging several samples of mineral pairs will reduce the error. It will be assumed that trace elements came into equilibrium between pyrite and sphalerite at the temperature of deposition of sphalerite. The partitioning of trace elements between crystalline phases may then be used to determine the relative temperature of formation of sphalerite in the No. 3 mine with reference to the No. 2 mine. In the case where the trace element is in ideal solution in pyrite and sphalerite, division of Equation (1) at temperature ${}^{2}T$ by the equation at temperature ${}^{1}T$ when Δh is constant over the temperature range involved gives the following equation:

$$ {}^{2}T \approx {}^{1}T\,(\ln {}^{1}K_{1})/(\ln {}^{2}K_{1}) \qquad (4) $$

where ${}^{2}T$ is the temperature in $^{\circ}K$ of equilibrium of component 1 in the No. 3 mine and ${}^{1}T$ is the corresponding temperature in the No. 2 mine. ${}^{1}K_{1}$ is the equilibrium constant of component 1 at temperature ${}^{1}T_{1}$ and

${}^2K_1$ is the corresponding equilibrium constant at temperature ${}^2T$.

It may well be that the transfer of a metallic element from an XS to an XS_2 mineral is not a case of ideal solution. It may be that the fugacity of S_2 is involved in the following way:

$$(MnS_2^{py}) = (MnS^{sl}) + \frac{1}{2} S_2: \qquad K_{Mn} = (f_{S_2})^{\frac{1}{2}} (MnS^{sl})/(MnS_2^{py})$$

$$(CuS_2^{py}) = (CuS^{sl}) + \frac{1}{2} S_2: \qquad K_{Cu} = (f_{S_2})^{\frac{1}{2}} (CuS^{sl})/(CuS_2^{py})$$

$$(FeS_2^{py}) = (FeS^{sl}) + \frac{1}{2} S_2: \qquad K_{Fe} = (f_{S_2})^{\frac{1}{2}} (FeS^{sl})/(FeS_2^{py})$$

where the quantities in the brackets are the activities of a particular species in the phase designated by the superscript. The numbers outside the brackets are stochiometric coefficients, and K is the equilibrium constant for the reaction under consideration.

For each one of the reactions given above there will be a corresponding equation given by Equation (3) above. If the three reactions above came into equilibrium at a common fugacity of S_2, then the unknown f_{S_2} term may be eliminated by division of Equation (3) for one species by the equivalent equation for a different species. If ΔH is constant for the reaction over the temperature range involved, the resulting equation in the case of reaction where one unknown must be eliminated becomes:

$${}^2T \approx {}^1T(\ln {}^1K_1/{}^1K_2)/(\ln {}^2K_1/{}^2K_2) \qquad (5)$$

From Table 5, the molar fractionation factor of FeS between sphalerite and pyrite is found to be 0.085 in the No. 2 mine and 0.035 in the No. 3 mine. From Table 7 are obtained data for trace element

Note

The reader is cautioned against any prima facie acceptance of Equation 1 and therefore Equations 3, 4, and 5. These equations are not necessarily valid. However, if the relationship between fractionations of minor elements among sulfide minerals and temperature are similar to those studied by Bethke and Barton (1959, p. 1569), then the argument presented by Equations 4 and 5 will yield a valid approximation of a temperature distribution. In addition, the observed fractionation factors must be demonstrated to be an equilibrium distribution of the element under consideration among the minerals studied. At Balmat, any assumption concerning the equilibrium of minor elements distributed between sphalerite and pyrite is speculative. This material on fractionation factors is presented because Equation 4 appears to be a valid approximation of the relation between temperature and fractionation factor. If this is true, measurements of the distribution of minor elements have broad application to studies of temperature distributions. The procedure, then, is felt worthy of further consideration.

partitions for pyrite and sphalerite based on analyses of pyrite and sphalerite samples obtained from the same polished section. The data for copper were found to be too erratic to be of much use in the present calculation; however, the samples with the highest ratios for manganese also have the highest ratios for copper. With respect to manganese, it was noted that sphalerite from areas containing magnetite had manganese contents below 1000 parts per million; therefore, samples were discarded in which magnetite was present in the polished section. The ratio of concentration of manganese in sphalerite to manganese in pyrite when the sphalerite and pyrite are from the same polished section was found to be 15 in the No. 2 mine and 50 in the No. 3 mine.* From Equation (4) using the equilibrium constants observed, the temperature in degrees of Kelvin at which equilibrium was approached between sphalerite and pyrite in the No. 3 mine was found to be 0.69 that of the No. 2 mine. From Equation (5) using manganese for K_1 and iron for K_2 with the values given above for the equilibrium constants, a temperature for the sphalerite of the No. 3 mine is found to be 0.71 that of the No. 2 mine.

Since it is thought that 783°K describes the temperature of formation of sphalerite in the No. 2 mine, a first approximation of the temperature for the No. 3 mine is 548°K or about 300°C keeping one significant figure.

The temperature of the supergene mineralization is not known. Fryklund and Fletcher (1956) found sphalerite near a post-ore dike

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* An average value may be obtained for the content of manganese in sphalerite from Table 7 and a corresponding value for pyrite regardless of whether or not the pyrite and sphalerite samples come from the same polished sections. When the average values are obtained, a ratio of 24 is found for manganese in sphalerite over manganese in pyrite for the No. 2 mine and a factor of 49 for the No. 3 mine. In this case the temperature is indicated to be 350°C using Equation (5).

developed iron-rich rims in contact with iron minerals (magnetite, pyrite, and siderite). Thus it is known that such oxide minerals can coexist with sphalerites containing significant iron contents. In the Balmat area, sphalerite closely associated with magnetite, hematite, and chlorite is almost snow white (Plate 6a) indicative of an insignificant iron content. Surely the temperatures of formation of the white sphalerite are low, but cannot be stated exactly due to the unknown effects of the fugacity of O_2 on the system sphalerite-magnetite-S_2-O_2. The association of the supergene mineralization with solution cavities might mean that the mineralization occurred at depths not much greater than the bodies are at present in which case the mineralization may have been at much less than $100^{\circ}C$ or even at about the temperatures encountered at present - $15^{\circ}C$.

TABLE 5: The Iron Sulfide Content Of Sphalerite With The Estimated Percents by Volume Of Associated Minerals (B. R. Doe, Analyst)

Sample Number	FeS (wt. o/o)	Possible Contaminants	Sl	Py	Gn	Po	Mar	Mg+ Hm	Gangue
500 Level, Central Ore Body (C), No. 2 mine									
A1	11.9	F-cpy, py	60	30	(0)	-	-	-	10
A2	10.6	F-mar	85	10	-	-	x	-	5
A3	12.3	Clean	50	40	-	-	-	-	10
A4	12.1	Not recorded							
A5	11.4	Clean	70	25	-	-	-	-	5
A6	10.9	Clean	35	5	-	-	-	-	60
A7	12.0	F-cpy	30	40	-	-	x	-	30
A8	12.3	Clean	65	5	-	(0)	-	-	30
A9	9.8	Clean	20	20	(0)	-	x	-	60
A10	10.4	F-cpy	25	40	(1)	-	-	-	35
B1	11.0	Not recorded							
B2	9.1	Not recorded							
B3	8.9	Clean	25	55	-	-	x	-	20
B4	9.2	Clean	40	20	10	-	-	-	30
B5	11.7	A-cpy	85	10	-	?	-	-	5
500 Level, Lower West Ore Body (LW), No. 2 mine									
C1	13.2	S-cpy	30	20	-	(0)	-	-	50
C2	9.6	Clean	80	10	(1)	-	-	-	10
C3	8.6	A-cpy; mg, hm	80	10	(0)	-	-	x	10
C4	7.4	F-cpy	20	40	(0)	-	-	-	40
C5	6.5	S-cpy	20	30	(0)	-	-	-	50
C6	9.6	Clean	65	25	5	-	-	-	5
C7	7.5	F-cpy	40	40	(1)	-	-	-	20
C8	7.1	Not recorded							
C9	7.2	Not recorded							

Sample Number	FeS (wt. %)	Possible Contaminants	Sl	Py	Gn	Po	Mar	Mag +Hm	Gangue
500 Level, Lower Far West Ore Body (LFW), No. 2 mine									
D1	8.7	Clean	30	40	-	-	-	-	30
D2	10.9	Clean	75	15	(0)	-	-	-	10
D3	10.0	Not Recorded							
D4	6.8	Not Recorded							
D5	8.2	Clean	40	15	5	-	-	-	40
D6	-	Mag, hm	25	60	(1)	-	-	x	15
D7	5.8	Clean	75	25	(0)	-	-	-	(1)
D8	7.7	Clean	80	20	-	-	-	-	(1)
D9	7.6	Not Recorded							
D10	7.9	F-cpy	75	5	-	-	-	-	20
1100 Grizzly Sublevel (GS), Central Ore Body (C), No. 2 mine									
F1	7.5	F-cpy, py	25	15	-	-	-	-	60
F2	9.0	S-cpy	35	20	-	-	-	-	45
F3	10.4	F-cpy	30	35	-	-	-	-	35
F4	8.3	Clean	55	15	(0)	-	-	-	30
F5	7.6	F-cpy	15	20	-	-	-	-	65
F7	11.8	C-cpy	65	5	(0)	-	-	-	30
F6	-	F-cpy	20	60	-	-	-	-	20
F8	12.4	A-cpy	75	15	-	-	-	-	10
F9	9.7	Clean	85	10	(0)	-	-	-	5
F10	9.2	Clean	75	10	-	-	-	-	15
F11	8.8	S-cpy	Not recorded						
F12	11.4	A-cpy	65	15	-	-	x	-	20
F13	14.3	A-cpy	20	15	-	-	x	-	65
F14	-	Not recorded							
F15	11.9	F-cpy	75	20	-	-	-	-	5
F16	11.8	Clean	65	25	-	-	-	-	10
F17	11.1	F-cpy	65	1-	10	-	-	-	15
F18	12.7	S-pyrr?	45	5	-	5	-	-	45
F19	-	A-cpy	70	5	5	-	-	-	20

Sample Number	FeS (wt. %)	Possible Contaminants	Sl	Py	Gn	Po	Mar	Mag +Hm	Gangue
1100GS, Central Ore Body (C), No. 2 mine									
G1	10.0	Clean	30	60	-	-	-	-	10
G2	9.8	Clean	35	40	(1)	-	-	-	25
G3	10.8	Clean	80	15	-	-	-	-	5
G4	-	A-cpy	60	20	(0)	-	-	-	20
G5	10.3	Clean	60	20	-	-	-	-	20
G6	11.2	Clean	70	10	(0)	-	-	-	20
G7	10.8	F-cpy	60	30	-	-	-	-	10
G8	10.6	F-cpy	30	30	(0)	-	-	-	40
G9	9.1	S-cpy, py	60	25	(0)	-	-	-	15
G10	-	-	15	35	1	-	-	-	50
G11	10.8	-	45	30	5	-	-	-	20
G12	8.3	Clean	25	50	(1)	-	-	-	25
G13	10.6	-	25	45	(0)	-	-	-	30
G14	9.0	F-cpy	20	35	(1)	-	-	-	45
G15	10.0	F-cpy	50	30	5	-	-	-	15
G16	10.6	F-cpy	30	30	(0)	-	-	-	40
1100GS, Lower West Ore Body (LW), No. 2 mine									
H1	10.0	F-cpy	40	25	5	-	-	-	30
H2	11.4	F-cpy	55	25	10	-	-	-	10
H3	10.4	Clean	35	40	(1)	-	-	-	25
H4	-	-	25	50	(0)	-	-	-	25
H5	8.8	F-py	20	(1)	(0)	-	-	-	80
H6	6.9	Clean	85	15	(0)	-	-	-	(1)
H7	8.7	F-cpy	40	60	-	-	-	-	(1)
H8	8.8	S-cpy	40	40	-	-	-	-	20
H9	7.9	S-cpy	35	30	-	-	-	-	35
H10	8.6	S-cpy	40	20	-	-	-	-	15
H11	-	A-cpy, py	15	70	(0)	-	-	-	15
H12	7.2	A-cpy	40	35	-	-	-	-	25

Sample Number	FeS (wt. °/o)	Possible Contaminants	Sl	Py	Gn	Po	Mar	Mag +Hm	Gangue
H13a	-	A-cpy, py	25	25	-	-	-	-	50
H13b	10.9	F-cpy	85	10	-	-	-	-	5
H14	9.2	A-cpy	60	25	(0)	-	-	-	15
H15	9.8	S-cpy, py	50	(1)	(1)	-	-	-	50
H16	9.6	C-cpy	70	25	(0)	-	-	-	5
1100GS, Lower Far West Ore Body (LFW), No. 2 mine									
I1	6.8	Clean	70	30	(0)	-	-	-	(1)
I2	7.4	Clean	25	70	-	-	-	-	5
I3	-	-	5	80	-	-	-	-	15
I4	8.3	F-cpy	70	25	(0)	-	-	-	5
I5	6.8	F-cpy	80	15	(0)	-	-	-	5
I6	5.7	F-cpy	65	25	(0)	-	-	-	10
I7	6.8	F-cpy	80	10	-	-	-	-	10
I8	6.0	Clean	40	35	-	-	-	-	25
I9	10.7	Hm, mg	85	15	(1)	-	x	x	(1)
I10	7.9	Clean	70	25	-	-	-	-	5
I11	10.9	F-cpy, py	10	85	-	-	-	-	5
I12	8.8	Clean	80	20	(1)	-	-	-	(1)
I13	8.1	Clean	85	10	(1)	-	x	-	5
I14	7.9	S-cpy	50	45	(0)	-	-	x	5
I15	11.0	A-cpy, mg, hm	55	35	(1)	-	x	x	10
1100GS, Upper-Streeter Ore Body, No. 2 mine									
J1	8.5	F-cpy	45	40	5	-	-	-	10
J2									
J3a	8.0	Clean	30	20	5	-	-	-	45
J3b	8.4	Clean	45	20	0	-	-	-	35
J4	8.0	F-cpy	30	30	-	-	-	-	40
J5	6.8	Clean	40	45	(1)	-	-	-	15
J6	6.2	Clean	75	15	-	-	-	-	10

Sample Number	FeS (wt. °/o)	Possible Contaminants	Sl	Py	Gn	Po	Mar	Mag +Hm	Gangue
J7	7.6	Clean	35	45	-	-	-	-	20
J8	11.1	A-cpy	30	50	-	-	-	-	20
1100GS, Lower-Streeter Ore Body, No. 2 mine									
K1	11.9	C-cpy	35	50	(0)	(0)	-	-	15
K2	10.6	S-cpy	50	20	-	-	-	-	30
K3	11.4	Clean	85	15	-	-	-	-	(1)
K4	12.2	C-cpy	50	30	-	(2)	-	-	20
K5	12.3	F-cpy	60	35	-	-	-	-	15
K6	11.4	C-cpy	30	15	-	-	-	-	55
K7	10.5	S-cpy	60	30	-	-	-	-	10
K8	10.9	S-cpy	65	30	-	-	-	-	5
1500GS, Central Ore Body (C), No. 2 mine									
P1	8.0	Clean	Not recorded						
P2	8.7	Clean	55	10	-	-	-	-	35
P3	(8.0)	S-cpy, py	70	20	(0)	-	-	-	10
P4	7.8	Clean	65	20	-	-	-	-	15
P5	7.8	A-cpy	40	35	-	-	-	-	25
P6	8.3	S-cpy	45	35	-	-	-	-	20
P7	9.3	F-cpy, py	65	30	-	-	-	-	5
P8	12.8	S-cpy	30	30	-	-	-	-	40
P9	10.6	Not recorded							
P10	-								
P11	12.7	S-cpy	45	10	(1)	-	-	-	45
P12	13.5	Clean	30	15	-	(0)	-	-	55
P13	-								
P14	10.4	C-cpy	50	25	(0)	(0)	-	-	25
P15	9.4	Clean	35	25	-	-	-	-	40
P16	9.9	F-cpy	30	35	-	-	-	-	35
P17	11.6	F-cpy	45	35	0	(0)	-	-	20
P18	11.4	A-cpy	50	30	-	-	-	-	20
P19	9.6	F-cpy	35	40	-	-	-	-	25
P20	12.2	F-cpy	45	5	(0)	-	-	-	50

Sample Number	FeS (wt. °/o)	Possible Contamination	Sl	Py	Gn	Po	Mar	Mag +Hm	Gangue
Q1	13.9	F-cpy	30	50	-	5	x	-	15
Q2	10.4	Clean	50	25	-	-	-	-	25
Q3	15.8	A-cpy	10	(1)	-	20	-	-	70
Q4	10.4	Clean	70	10	-	-	-	-	20
Q5	12.5	F-cpy	35	20	-	(0)	-	-	45
Q6	12.2	F-cpy	55	35	-	-	-	-	10
Q7	13.6	A-cpy	10	75	-	15	-	-	(1)
Q8	14.1	A-cpy	15	(1)	-	20	-	-	65
Q9	11.4	C-cpy	(1)	5	-	95	-	-	(1)
Q10	10.3	F-cpy	40	40	(0)	-	-	-	20
Q11	9.2	Not recorded							
Q12	8.6	F-cpy	20	15	-	-	-	-	65
Q13	8.8	F-cpy	15	75	-	-	-	-	10
Q14	12.4	A-cpy;mg	50	30	-	-	-	x	20
Q15	9.8	F-py	20	50	(0)	-	-	-	30
Q16	12.0	A-cpy	50	35	(0)	-	-	-	15
Q17	8.8	Not recorded							
		1500GS, Lower West Ore Body (LW), No. 2 mine							
R1	6.4	Clean	Not recorded						
R2	7.6	Not recorded							
R3	9.1	Clean	75	20	(0)	-	-	-	5
R4	6.6	F-cpy	60	25	(1)	-	-	-	15
R5	10.9	Not recorded							
R6	14.0	S-cpy	65	25	(0)	(0)	x	-	10
R7	11.1	Clean	25	35	-	-	-	-	40
R8	7.9	F-cpy	50	30	(0)	-	-	-	20
R9	6.2	Clean	25	25	5	-	-	-	45
R10	11.6	F-cpy	35	40	-	-	-	-	25
R11	9.4	F-cpy	75	15	(0)	-	-	-	10
R12	7.4	Not recorded							
R13	10.1	S-cpy	35	40	(0)	-	-	-	25
R14	10.4	A-cpy;mg	60	30	(1)	-	-	x	10
R15	7.7	Clean	55	25	-	-	-	-	20

Sample Number	FeS (wt. °/o)	Possible Contamination	Sl	Py	Gn	Po	Mar	Mg +Hm	Gangue
1500GS, Lower Far West Ore Body, No. 2 mine									
T1	8.3	A-cpy	55	20	(1)	-	-	-	25
T2	6.8	Clean	20	35	(1)	-	-	-	45
T3	9.0	A-cpy;mg	75	10	(1)	-	-	x	15
T4		mg,hm	70	15	-	-	-	x	15
T5	10.7	S-cpy	70	20	(0)	-	-	-	10
T6	8.3	Clean	95	5	(0)	-	-	-	(0)
T7	7.4	F-cpy	80	10	-	-	-	-	10
T8	7.4	F-cpy;hm	40	55	-	-	-	x	5
T9	8.6	S-cpy	55	30	(1)	-	-	-	15
T10	7.3	S-mg	60	25	(0)	-	-	-	15
T11	8.0	Not recorded							
T12	7.9	F-cpy	65	15	5	-	-	-	15
T13	6.7	F-cpy;mg	75	20	-	-	-	-	5
T14	8.7	F-cpy;mg	85	10	(0)	-	-	x	5
300L, Upper Gleason Ore Body (UGl), No. 3 mine									
1N	1.8	S-py	50	10	-	-	-	-	40
2N	3.1	Clean	40	10	-	-	-	-	50
3N	2.6	Clean	80	10	-	-	-	-	10
4N	2.4	Clean	25	5	-	-	-	-	70
5N	2.8	Clean	80	10	-	-	-	-	10
700Bottom Mining Sublevel (BMS), Upper Gleason Ore Body, No. 3 mine									
6N	2.2	Clean	60	25	-	-	-	-	15
7N	2.3	Clean	75	5	-	-	-	-	20
8N	1.8	Clean	60	20	-	-	-	-	20
9N	3.2	Clean	100	(0)	-	-	-	x	(1)
10N	2.4	Clean	85	5	-	-	-	-	10
11N	3.0	S-cpy,mg	100	(0)	-	-	-	x	(0)
12N	3.0	S-py	95	5	-	-	-	-	(1)
13N	7.1	Clean	90	5	-	-	-	-	5
14N	2.1	Clean	80	10	-	-	-	-	10

Sample Number	FeS (wt. °/o)	Possible Contaminants	Sl	Py	Gn	Po	Mar	Mg +Hm	Gangue
700BMS, Middle Gleason Ore Body (MGl), No. 3 mine									
15N	3.0	Clean	90	(1)	-	-	-	-	10
16N	3.1	S-mg	70	(1)	-	-	-	x	30
17N	3.0	Clean	85	5	-	-	-	-	10
18N	2.9	Clean	85	10	-	-	-	-	5
19N	3.2	S-py	50	(0)	-	-	-	-	50
20N	4.4	Clean	80	5	(0)	-	-	-	15
21N	3.4	Clean	20	(1)	-	-	-	-	80
900GS, Loomis Ore Body, No. 3 mine (Lo)									
22N	3.6	F-cpy, py?	95	(0)	-	-	-	-	5
23N	3.4	Clean	90	-	-	-	-	-	10
24N	2.9	F-py	75	(1)	-	-	-	-	25
25N	4.2	S-cpy	60	10	(0)	-	-	x	30

Sl - sphalerite
Py - pyrite
Hm - hematite

A - abundant
C - common
S - some
F - few
Clean: no danger from contamination

Gn - galena
Po - pyrrhotite

Mar - marcasite
Mg - magnetite

TABLE 5b: Approximate modes of rock samples

Sample Number	Rock Description
cdm 14-j	Equigranular sparsely twinned calcite-90, diopside and quartz 10, sericite (?)-trace.
ps 7-1	Pyritic schist, 75-quartz, 15-pyrite and magnetite, 10-sericite and chlorite, trace apatite.
ps 7-2	Banded gneiss, medium-grained, 70-quartz, 5-apatite and tourmaline, 5-pyrite and magnetite, 10-biotite, 10-sericite and chlorite.
ps 7-3	Banded gneiss, medium-grained, 70-quartz, 15-pyrite and magnetite, 5-chlorite, 5-sericite, trace-apatite, trace-graphite.
fd 7-3	Marble, equigranular, 65-dolomite, 35-diopside.
fd 7-2	100-dolomite, equigranular, coarse-grained, trace-diopside, trace-talc, 0.26 percent by weight graphite.
fd 7-1n	Dolomite-100, equigranular, coarse-grained, trace-talc, trace-graphite.
fd 7-1b	Dolomite-100, equigranular, coarse-grained, trace-serpentine and talc, trace diopside.

VI. PATH AND COMPOSITION OF THE ORE FLUID

Path In the section on the source for the ore fluid, it was concluded that the fluid was originated at great depth. It is not clear what path the ore fluid followed over most of the distance of travel. Because the bulk mineralogies of the No. 2 and No. 3 mines are different, it is thought that the sulfides in the two mines were formed from the same ore fluid at different times or from different sources but similar ore fluids.

Within the No. 2 mine itself, it might be inferred that over the length of the ore body the ore fluid rose upward along the plunge of the ore bodies - 35° south. The same plunge is indicated by the distribution of minerals. In the section on paragenesis, it has been stated that pyrrhotite is only found in certain areas of the mine and principally in the central ore body which plunges upward at 35° to the south. In the lower-west and lower-far-west ore bodies, a study by Doe (1956) indicated zones of sphalerites with high iron content (greater than 10 weight percent FeS) within the zone of sphalerite with intermediate iron content (6-9 wt. percent FeS). An increase of sample number, inclusion of data from an intermediate level, and better correlation with geology supports but modifies slightly the earlier positions of the high iron sphalerite channels.

Two high iron sphalerite channels are correlated on the 500 level, 1100 grizzly sublevel, and 1500 grizzly sublevel and are indicated at "A" and "B" on the maps of this report (Fig. 2, 3a, and 4). The plunge of the channels are somewhat different. The more westerly channel plunges uniformly at about 27-30°, N3-6°W between the 500L and

1100GS. The more easterly channel is more irregular in direction of plunge - 30-32°, N2°W between the 500 level and 1100 grizzly sublevel to N16-20°W between the 1100 grizzly sublevel and the 1500 grizzly sublevel. It is thought that the channels discussed above are representative of the path followed by the ore fluid entering the area during the pyrrhotite stage of the paragenesis. There is some indication of channels of sphalerite with high iron content in the upper- and lower-Streeter orebodies; however, lack of data from levels other than the 1100GS prohibits confirmation.

Ore Fluid It is difficult to obtain even a rough approximation of the composition of the ore fluid because of the large number of variables involved. In general, the number of chemical species in the ore fluid is thought to be large; larger than the number of chemical species associated with the ore. Other difficulties are the lack of conclusive evidence of deposition under either isothermal conditions or conditions under which deposition occurs because the ore fluid is chilled. There is even a great deal of disagreement over whether ore fluids are liquids or gases or both. There is greater disagreement as to how the cations are carried in the ore fluid - in solution or suspension; as sulfides, chlorides, metals; or some sort of complex molecule or ion.

Approaches to solutions of some of the problems on the nature of the ore forming fluid have been presented or summarized by Graton (1940), Holland (1956, 1959), Barnes (1958), Krauskopf (1957, 1959), and Barton (1957). Graton in the most comprehensive analysis to date concluded that the ore fluid must be water-rich and must not be composed essentially of chloride, sulfide, and metal vapors. Krauskopf came to the same conclusion after consideration of more data than were available to Graton. However, Krauskopf (1959, p. 275) differed somewhat from Graton over whether the ore fluid is a gas or liquid. Graton felt that the ore fluid was probably liquid, but Krauskopf says:

> "A highly compressed, water-rich gas at 600° might be expected to serve not only as a gas into which metal compounds could evaporate, but also as an active solvent forcing them into solution."

Krauskopf was speaking of ore deposits in general, but it is necessary for further discussion to consider Balmat in particular. Krauskopf's main objection to chloride gas transport was the very small volatility of copper and silver both in absolute terms and relative to the volatilities of other metal chlorides. While Krauskopf considered the formation of complex ions apparently in water under great pressure, he did not consider the possibility of increased vaporization as complex gas particles. In Balmat, both the contents of silver and copper are very small. The mole fraction of silver in the ore is about 10^{-6} and 10^{-4} or 10^{-5} for copper. In an imperfect fashion, the abundances of silver and copper are such that a chloride system of transport cannot be conclusively eliminated for the Balmat ores.

Holland (1959) has not broached the difficulties of water transport but states:

> "From this study it becomes apparent that the mineral assemblages of most ore deposits are thermodynamically stable at the time of formation, that the position of the fields of stability of ore assemblages shift gradually with changing temperature, and that this change can be interpreted in terms of the cooling of gas mixtures in the carbon-oxygen-sulfur-hydrogen system."

The model of Holland may be used to explain certain mineral assemblages and may well work even if some of the assumptions are not valid.

A train of thought has been developed above which is based on the lack of any evidence of thermal gradients with depth and the temperature of the ore fluid in the Balmat area being controlled externally, probably by the temperature of the country rock. In the latter way, ore genesis at Balmat differs somewhat from the mechanism of a cooling gas mixture outlined by Holland; however, the principles are still the same for the two different thermal mechanisms except that in the case at Balmat replacement was nearly isothermal. One of the most pertinent implications from the calculations of Holland is the pyrrhotite-pyrite relation. If pyrrhotite is later than pyrite at Balmat, then in a falling temperature sequence such as retrograde metamorphism the rate of fall of the fugacity of S_2 with time must be more rapid than the rate of fall of temperature.

The diagrams of Holland (1959) indicate a large range of thermal stability of the pyrite field. It seems doubtful that any pyrite was deposited at a temperature greater than the peak temperature of Grenville metamorphism in the area. Thus for the purposes of calculation the temperature of No. 2 mine mineralization is chosen as $510^{\circ}C$. The probable error in the latter statement ($\pm 50^{\circ}$) has little influence upon the conclusions. The temperature of formation of barite and anhydrite is chosen as $400^{\circ}C$, the maximum temperature of formation of marcasite, and may be in considerable error but again with little effect upon the conclusions.

By applying the model of Holland at the derived and assumed temperatures of formation of ores at Balmat, pyrite deposition implies a fugacity of S_2 less than 10^{-5} atmospheres and greater than 10^{-19} atmospheres. At the start of pyrrhotite deposition in the sequence, the fugacity of S_2 must have fallen below 10^{-19} atmospheres but have been above 10^{-26} atmospheres or native iron would have formed. It is not understood why there is no evidence of pyrite altering to pyrrhotite during the pyrrhotite stage of the paragenesis unless: (1) reaction rates are very slow; (2) the fugacity of S_2 was the equilibrium fugacity for the temperature involved of the reaction $FeS + \frac{1}{2}(S_2) = FeS_2$; (3) pyrrhotite was formed metastably; or (4) the system reacted as if closed. It might be that whole pyrite grains were either altered to pyrrhotite or not altered at all. The fugacity of oxygen must have been less than 10^{-40} atmospheres to deposit pyrite and 10^{-50} atmospheres for pyrrhotite to account for the lack of $FeSO_4$ with the CO_2 fugacities determined below.

The S_2 fugacity for formation of galena would have the same maximum as given for pyrite and minimum as given for pyrrhotite. The fugacity of oxygen indicated is less than 10^{-35} again assuming for the present a CO_2 fugacity of less than one. Sphalerite adds no new restrictions except that the bleached margins of sphalerite in contact with serpentine and talc did not alter to either zinc carbonate or sulfate implying an O_2 fugacity at that stage probably below 10^{-40}. Quartz imposes a restriction. At the 500°C stage, the fugacity of O_2 must have been greater than 10^{-90} atmospheres or quartz should have altered to elemental silicon thus setting a minimum on the fugacity of oxygen. In some areas of the mine there is some sphalerite and pyrite in juxtaposition to calcite. No isometric sulfide was noted other than sphalerite among the non-opaque minerals so that oldhamite (CaS) was not formed from calcite. Further, Holland's Fig. 39 (1959, p. 219) indicates that the fugacity of F_2 must have been less than 10^{-80} atmospheres at 500°C in order to account for the absence of apatite. No estimate may be made on the C $_2$ fugacity.

There is some doubt as to when the anhydrite and barite formed, whether they were formed before the sulfides and reworked or whether they may have been both original constituents of the sediments of the area and deposited in an unrelated form from the ore fluid. None-the-less, calcite and anhydrite are an incompatible pair unless the volatile species are not externally controlled and the same goes for barite. Both barite and anhydrite are found as crack fillings as noted in the section on paragenesis. Both appear to be late in the ore deposits. The resistance of anhydrite to alteration to carbonate through an extensive period of high temperatures in a carbonate section is a relationship of some interest (note gm 10 of Brown and Engel), Fig. 1 this article). Anhydrite and barite are found in juxtaposition to sphalerite and pyrite in certain areas of the No. 2 mine. It will be assumed that the survival of the sulfates with the sulfides is an equilibrium phenomenon no matter what the origin of the sulfates. The late stage survival in the No. 2 mine as demonstrated by textures would indicate fugacities of CO_2 in the late stages of less than 10^{-10} atmospheres in an O_2 fugacity range of 10^{-40} to 10^{-60} atmospheres. In the range above there is no overlap with the pyrrhotite field and to get such an overlap the CO_2 fugacity would have to be less than 10^{-60} atmospheres. Barite in the No. 2 mine is shown to be much more extensive than the macroscopic occurrences would indicate assuming that all the barium in the emission spectrographic analyses is in the barite phase. The alteration of much of the pyrrhotite to marcasite may be a manifestation of the incompatibility of barite and pyrrhotite. If the CO_2 fugacity is higher than is compatible with pyrrhotite conditions, Holland indicates that magnetite or hematite would be the product; however, little is known about the chemistry of marcasite which is the alteration product observed for pyrrhotite.

Holland (1959) has not considered at all the mechanisms needed to transport the cations of the ore. Rather he has dealt with the problem of which solid phase is stable with a given externally controlled assemblage of gas phase fugacities. Further, all the information used in Holland's calculations yields fugacity information which may have only a vague relation to partial pressure in a supercritical mixture of many phases in a highly compressed state. If the Holland model is to be adopted, the application applied to Balmat with the accepted paragenesis would be:

1. A relatively large decrease in the fugacity of S_2 with time (by a factor of 10^{-10} or more). Possible range 10^{-1} to 10^{-26} atmospheres.

2. An O_2 fugacity possibly fairly constant that falls within the range 10^{-40} to 10^{-60} atmospheres.

3. That the fugacity of CO_2 probably was less than 10^{-10}.

Since the structural control of the sulfides rules out the possibility that the sulfide cations could be sedimentary, the question of transport of the cations to the depositional source cannot be ignored.

The gaseous components of the ore fluid determined above give a total fugacity for the ore fluid of approximately the value found for CO_2 which is much less than one atmosphere. Many recommend that the minimum pressure of a fluid phase expected in earth processes is equivalent to or greater than a head of water from the site of the reaction to the surface of the earth. At Balmat then the total pressure of the ore fluid would be expected to be on the order of 10^3 atmospheres. The discordance between expected vapor pressure and the sum of the fugacities found may be explained in several ways: (1) the partial pressure of water in the ore fluid was high (about 10^3 atmospheres); (2) the relationship between partial pressure and fugacity is vague under the conditions of the formation of the ore; (3) the assumption of the magnetude of the total vapor pressure is far too high; (4) the mechanism of determination of the fugacities is grossly in error; or (5) some combination of the above.

It is felt that to assume an ore fluid composed primarily of H_2O causes a major part of the total discrepancy in the vapor pressure. The ore bodies were formed during a period of hydration of the surrounding metasediments - i.e., formation of serpentine and talc from diopside and tremolite. Whether the ore fluid acquired the bulk of the water near the site of deposition or at its source is not known. Many have expressed their doubt as to the ability of water to carry enough metals in solution to form a large ore body. Whether or not the metals that are later deposited as sulfides are present as a solution in water or supercritical H_2O; as molecules, ions, and complex ions; as a suspension of some form; or as a coincidental association is not known. There seems to be no reason to believe at present that the ore fluid that formed the Balmat sulfide ores was anything but a phase composed predominantly of H_2O. It also seems reasonable that the H_2O-rich ore fluid was in the supercritical state during the deposition of the bulk of the ores of the No. 2 mine, but was perhaps a liquid during the deposition of the ores of the No. 3 mine. If it is assumed that (1) the total sulfur content of the ore fluid is within a couple factors of 10 of 0.1 moles/liter, (2) that the conclusions from Holland's (1959) diagrams as applied to the Balmat deposits are valid, and (3) that the pH was nearly neutral at the temperature of interest in the No. 3 mine (5.5), then the diagrams of Barnes (1959, p. 237) would suggest that the sulfur was predominantly in solution as the HS^- ion or possibly as the S^{-2} ion. The HS^- and S^{-2} ions would furnish an opportunity for the sulfides to be in solution as complexes of the bisulfide or polysulfide ions. Apparently the only alternative is that the rates of diffusion of the sulfide species through the ore fluid are very rapid.

Boundary Conditions There is little obvious wall rock alteration surrounding the ore bodies at the No. 2 and No. 3 mines. Serpentine and talc are very widespread minerals and are not restricted to the sulfide ore zone. In the area of mining, chlorite is almost entirely associated with the supergene mineralization. Tremolite was formed before the introduction of the sulfides. The best wall rock effect is noted in the No. 3 mine in the Loomis ore body between the sulfides and the fetid dolomitic marble (fd 7) near the contact of fd 7 with sm 8.

The fetid graphitic marble is bleached from medium gray to white in a zone surrounding the ore from less than an inch in width to as great as eight inches. The bleaching was associated with wall rock alteration by E.R. Lea (personal communication). Four samples of the fd 7 unit were examined for minor elements which included a sample from the bleached zone, from the adjacent unbleached zone, from the contact of fd 7 with sm 6 near the mine shaft, and from the contact of fd 7 and sm 8 on the surface a half mile away from the ore body. Barium and strontium are the minor elements in greatest concentration in the bleached zone whereas manganese seems to decrease as the ore is approached.

The decrease in graphite content may be explained by oxidation:

$$C_s + O_{2_g} = CO_{2_g} \quad : \qquad K = (f_{CO_2})/(f_{O_2})$$

The maximum fugacity of oxygen during the last stages of ore deposition in the No. 2 mine was estimated to be 10^{-40} atmospheres, and the temperature of the formation of sphalerite in the No. 3 mine is estimated to be in the range 300°C to 400°C. The standard free energy of reaction may be calculated from the data of Kelley (1949) and may be utilized in calculating the equilibrium constant of the reaction. The equilibrium constant is 10^{+34} at 300°C and 10^{+29} at 400°C. Using the fugacity of O_2 in the ore fluid as the maximum found for the No. 2 mine, the indicated fugacity of CO_2 is less than 10^{-6} at 300°C and less than 10^{-11} if the temperature was 400°C. Once again the indication is that the fugacity of CO_2 was very small during the formation of the ores.

At Balmat the grain size of the sulfides is related to the individual ore body and not to the position of the sample within the orebody. The more disseminated the type of ore, the smaller the grain size.

Implications of Minor Elements The paragenesis and the distribution of temperature in the ore bodies indicates that the order of deposition of the sulfides was controlled at the source. First the bulk of the iron was released, second zinc and lead, third copper and possibly some iron, next was perhaps barium, and more zinc at the end. After deposition of pyrite, iron was probably continuously removed except during the formation of pyrrhotite. Calcium and magnesium were also acquired by the ore fluid at the site of sulfide deposition. It might be expected that minor and trace elements should also be controlled by the source.

Barium The overwhelming bulk of barium is present as barite, but the few parts per million ppm of barium found in sulfides away from barium areas (for example the No. 3 mine) are probably barium in the sulfides either in solid solution or as fillings of crystal defects. The data for barium from duplicate analyses are so erratic that it should only be considered an estimate of the order of magnitude of the concentration.

Bismuth A few sphalerite samples, mainly in the upper-Streeter ore body of the No. 2 mine, have detectable concentrations of bismuth too great to be accounted for by inclusions of galena. The content of bismuth in sphalerite may reach 100 ppm, but in most samples of sulfides the amount of bismuth found is below the sensitivity of the analytical procedure (about 10 ppm). The amount of bismuth in three specimens of galena from three ore bodies is XO ppm or less.

Cadmium Cadmium is concentrated in sphalerite and is below the limit of detection in other minerals (about 30 ppm). The cadmium content of sphalerite is remarkably constant and varies within the range 1000-2000 ppm for most samples. The average content of cadmium in sphalerite for both the No. 2 and No. 3 mine was found to be 1400 ppm. The latter type of variation could be accounted for by (1) fluctuation of the concentration of cadmium in the ore fluid by a factor of two over the period of deposition, (2) change in temperature with change of cadmium content of the ore fluid, or (3) a change in the activity coefficients at constant temperature due to a change in the bulk composition of the ore fluid.

It is thought that the ores of the No. 2 and No. 3 mines were deposited at different temperatures, but this variation in temperature had no effect on the amount of cadmium found in sphalerite. The narrow range of the content of cadmium in sphalerite has been noted by Burnham (1959). The lack of variation of cadmium in sphalerite throughout a period of deposition involving changes in temperature may prove to be very valuable from several standpoints. Cadmium can be easily used as an index element. Ore bodies may be fairly safely cataloged as to the content of cadmium in sphalerite from very few samples or even one sample. Bethke and Barton (1959) have determined the equilibrium constant for cadmium between sphalerite and galena at high temperatures. The partition of cadmium between sphalerite and other minerals may prove invaluable as a geothermometer. At the temperatures of interest in the formation of ores, the fractionation factor between sphalerite and other minerals may be very large so that the concentration of cadmium in sphalerite would be relatively unaffected by changes in the fraction of sphalerite to the total volume of the ore unless sphalerite is a trace mineral. Precise analysis of cadmium should be well worth the effort.

It is not understood why the content of cadmium in sphalerite should vary so little. One explanation might be that the heat involved in the transfer of cadmium from the ore fluid to sphalerite is very small in which case the equilibrium constant would be approximately one. The latter would explain the lack of variation with temperature. Then it must be still assumed that the content and activity coefficient of cadmium in the ore fluid must be nearly constant during the period of deposition of the ore. While it is true that the ratio of Cd/Zn varies little in sphalerite, there are systematic differences between ore districts.

Chromium Both pyrite and pyrrhotite contain some chromium, and the ore sulfides contain more chromium than does the pyrite of the country rock. The amount of chromium indicated by duplicate analyses is so erratic that it should only be considered an estimate of the order of magnitude.

Cobalt and Nickel There is some indication that sphalerite in the lower-Streeter ore body and parts of the upper-Streeter ore body contains up to 70 ppm cobalt. The sulfides of the No. 2 mine and No. 3 mine are quite low in cobalt compared to many other areas. The content of cobalt in pyrrhotite is less than 3 ppm and averages less than 50 ppm for pyrite. Pyrite from the metamorphic rocks tends to be high in cobalt (up to 1000 ppm) so that the high cobalt value obtained for pyrite in Q7 in the No. 2 mine may indicate that the pyrite from Q7 may have been incorporated from replacement of the marble.

The nickel content of pyrite is about 10 ppm in the No. 2 mine and about 30 ppm in the No. 3 mine. The cobalt content of pyrite is found to be slightly higher than the nickel content. The latter is in accord with the compilations of data on minor elements by Fleischer (1955, p. 1004) for hydrothermal deposits. The nickel content of pyrrhotite is quite uniform at about 100 ppm. Gavelin and Gabrielson (1947) reported that the cobalt content of pyrrhotite in a zinc-rich ore is low. The pyrrhotite from the sphalerite ores at Balmat affirms this statement.

Copper Most of the copper that is found in the sulfides may be contributed by the exsolution of chalcopyrite or by contamination with chalcopyrite. In sphalerite, the relative amounts of chalcopyrite blebs taken in the sampling does not agree well with the amounts of chalcopyrite found by emission spectroscopy. Consequently significant quantities of copper may still be dissolved in the sphalerite. A small amount of copper is thought to be in pyrite (up to a few hundred parts per million). The close association between chalcopyrite and pyrrhotite leaves doubt as to the quantity of copper contamination in the sampling of pyrrhotite; however, the copper content of pyrrhotite may be as low as 10 ppm.

The fractionation factor for copper between sphalerite and pyrite was found to be erratic. The values for 15 samples are given in Table 6. A correction has been applied to the quantity of copper in pyrite by assuming that all zinc found in the pyrite is due to contamination of the sample by sphalerite. The correction is about 0.1 of the value of copper found in pyrite. The large variability of the fractionation of copper between sphalerite and pyrite found in the present study suggests that copper is not very useful for most investigations of the geothermometry on deposits of sulfides. The equilibrium fractionation factor for copper between sphalerite and pyrite is attained with great difficulty and/or easily destroyed at a later date.

Gallium Gallium is contained in sphalerite and is below the detection limit in the other sulfides. The No. 3 mine (lower temperature and later) sphalerite contains ten times as much gallium as the sphalerite in the No. 2 mine ore bodies. The reverse relationship between gallium and temperature of formation has been noted by others (Fleischer, 1955, p. 992), and in this case may indicate that gallium is released late in the paragenetic sequence.

Germanium The relationship of germanium in sphalerite to temperature is similar to but less dramatic than the gallium-sphalerite relationship. The germanium content is in general less than a part per million in all sulfides at Balmat. Corrections for interference from indium are difficult in analyses for germanium by the emission spectrographic procedure used. The data for germanium in an absolute sense should only be considered as an order of magnitude estimation.

Indium Indium analysis is difficult and subject to serious errors; however, sphalerite in the No. 3 mine contains indium at less than 10 ppm for the most part and the sphalerite in the No. 2 mine has very erratic indium values that vary within the intermediate-iron sphalerite ore bodies by about a factor of 100 to 800 and by a factor of 10 to 60 in the high-iron sphalerite ore bodies. Indium in pyrite and pyrrhotite is below the limit of detection. The same difficulty is found in the analyses for indium due to interference by iron and manganese. Thus the data for indium also are only order of magnitude estimations.

Lead Lead contents of the sulfides are thought to be mainly due to inclusions of galena in the samples. Microscopic and macroscopic galena in the No. 3 mine is only observed in a few samples whereas all the sphalerite samples contain perceptible amounts of lead. It may be possible to have about 10 ppm lead in the sphalerite structure. The same may be true for other sulfides as well as for sphalerite; however, the sensitivity of analysis of the high iron minerals is such that the lead content commonly is below the limit of detection in lead free areas. Some of the pyrite in the country rock contained quite high concentrations of lead (up to 1000 ppm) but no galena was observed in polished sections of splits of the samples.

Manganese Many workers have noted a correlation between the concentration of manganese in sphalerite and the temperature of formation of the sphalerite. It is shown above that temperature is only one of the factors that controls the concentration of trace elements in a mineral. Fryklund and Fletcher (1956, p. 242) found only a vague relationship between the contents of iron and manganese in sphalerite in the Star mine of the Coeur D'Alene district, Idaho. A plot of FeS in sphalerite versus MnS in sphalerite from the ores at Balmat looks very similar to that of Fryklund and Fletcher. Manganese is related to iron content with the following range:

$$\mathrm{Mn(wt.\%)} < 0.20 + 0.13\,(\mathrm{FeS\ in\ wt.\%})$$

$$\mathrm{Mn(wt.\%)} > 0.0075\,(\mathrm{FeS\ in\ wt.\%})$$

In general, the sphalerites with the most iron contained the most manganese. Sphalerite with greater than 9 wt.% FeS (with an average of 10.2 wt.%) contained an average of 1.06 wt.% MnS, sphalerite with intermediate FeS contents (6-9 wt.%) averaged 0.48 wt.% MnS, and low-iron sphalerites (from the No. 3 mine with an average of 2.9 wt.% FeS) contained 0.35 wt.% MnS.

If mining districts are compared, those mining districts in which sphalerite contains the most manganese are characterized by sphalerite with the least concentrations of cadmium. This relationship is apparent in the work of Burnham (1959) and Rose (1958). The amount of cadmium found in sphalerite at Balmat (1400 ppm) is relatively low when compared with some other mining districts. The reverse relationship between cadmium and manganese in sphalerite may be explained in several ways. Two explanations might be (1) the mechanism of release of manganese and cadmium from the source are different or (2) the heats involved in the release of cadmium and manganese from the source are of different sign. It has been stated above that the cadmium content of sphalerite appears to be little affected by temperature; so it is inferred that the control must be at the source.

Sphalerites with the highest iron contents are not necessarily indicative of the highest temperatures of formation. Sphalerite at Balmat has the highest iron values where it occurs with pyrrhotite. Thus it is tempting to say that the concentration of manganese in the ore fluid reached a peak during the deposition of pyrrhotite. However, the manganese values in pyrrhotite are very irregular. Pyrrhotite apparently may accommodate up to a few hundred parts per million manganese even if manganese from sphalerite included in the sampling is allowed for.

The fractionation of manganese between sphalerite and pyrite is much more uniform than for copper. It was noted from Table 7 that all but one of the sphalerite samples containing less than 1000 ppm manganese were from the zone of supergene mineralization that contains magnetite. The distribution of manganese and copper between sphalerite and pyrite in 16 different polished sections is shown in Table 6.

Table 6: Fractionation factors of copper and manganese between sphalerite and pyrite

Sample Numbers	Mn(Mol.%) in Sl	Mn(Mol.%) in Py	Mn(Mol.%) ratio Sl/Py	Cu(Mol.%) ratio Sl/Py
A10	1.3_6	0.019_2	71	8
B3	0.28_0	0.019_7	14	10
D1	0.24_4	0.021_4	11	3
G1	0.40_0	0.015_7	25	1.5
J1	1.9_1	0.001_8	1100	> 78
J7	0.27_9	0.023_4	12	13
K7	0.99_0	0.004_5	220	> 5
P4	0.41_7	0.033_4	12	2
Q14	2.1_0	0.10_0	21	0.5
R3	0.29_6	0.002_8	100	> 21
R10b	2.1_0	0.16_2	13	1
T7a	0.10_3	0.03_5	3	4
2N	0.24_4	0.0068	48	8
6N	0.095_5	0.0091	13	3
8N	0.12_2	0.0064	19	18
10N	0.08_5	0.0098	9	4

It is unfortunate that three of the four samples of pyrite analyzed from the No. 3 mine are from areas where magnetite is present. There is the suggestion that magnetite removed some manganese from sphalerite. On the other hand, pyrite from the same samples does not show any evidence of removal of manganese. Thus it is thought that the most representative sample from the No. 3 mine is 2N. If the manganese concentrations of all the sphalerite samples in the No. 3 mine are averaged (excluding those associated with magnetite), the average molar concentration is found to be 0.39 percent. If the same is done for pyrite, a value of 0.0080 mole percent is obtained. An average value of the fractionation of manganese between sphalerite and pyrite is then 0.39/0.0080 or about 50. On the other hand, if the same process is performed on the sphalerite specimens containing intermediate amounts of iron in the No. 2 mine, the fractionation factor of the average sample is found to be 0.78/0.033 or 24.

It will be noticed that in Table 6 there are several specimens that yield a lower fractionation factor than 24 (B3, D1, J7, P4, R10b). Sample T7a is thought to have a low ratio because of the effect of the presence of magnetite on sphalerite. It is thought that a fractionation factor of 15 represents a reasonable minimum value for the distribution of manganese between sphalerite and pyrite at the time of formation of the bulk of the sphalerite. There are four examples in which the fractionation of manganese between sphalerite and pyrite in the No. 2 mine is very large (70-1000). In three of the four cases, the pyrite phase has an uncommonly low manganese value when compared to the larger list of pyrite samples in Table 7. In addition, three of the four samples have higher than normal manganese contents in sphalerite. If the other samples represent a near equilibrium assemblage, then the very high and very low ratios may indicate a disequilibrium assemblage at the time of interest. An alternative is that none of the ratios observed approaches the equilibrium value. Until the mechanism that arrests exsolution and transfer of components between phases is understood better, meaningful conclusions derived from fractionation factors are very limited and should be held in question.

Molybdenum For the most part the concentration of molybdenum in the sulfides is below the limit of detection; however, a few samples from the eastern orebodies do indicate molybdenum contents up to 65 ppm for sphalerite.

Silver Much of the silver found in sulfides is due to contamination by galena; however, a few parts per million of silver may be incorporated in sphalerite. There seems to be less silver in pyrite than in sphalerite; however, the quantities are so low and possible contamination is so high that it is not thought justifiable to apply the trace element geothermometer. There also is some indication that silver is somewhat more abundant in pyrite of the country rock than in the pyrite in the ore. Silver may well be one of the best trace elements to use in further geothermometry investigations if better analytical procedures are used. One galena sample from the No. 3 mine indicated 650 ppm, and two from the No. 2 mine give 1200-1700 ppm.

Titanium Appreciable contents of titanium were only observed in the pyrite of the country rock among the sulfides. The titanium was mainly found in the pyritic schist (ps 7) unit.

Tin The sphalerite of the No. 3 mine contains a few parts per million tin, but other areas are erratic. No tin was observed in other sulfides. The indium-tin relationship as observed in sphalerite at Balmat has been commented upon by Burnham (1959).

Vanadium Vanadium was observed in pyrite of the pyritic schist and pyrite of the region containing sphalerite of a high iron content in the No. 2 mine. Since most of the ore pyrite is thought to be nearly contemporaneous in age, vanadium presumably was added to the pyrite during the pyrrhotite stage of paragenesis. The amounts of vanadium indicated by duplicate analyses are so erratic that in an absolute sense the data are only an estimation of the order of magnitude of the concentration.

Zinc It has been assumed that effectively all the zinc found in the pyrite and pyrrhotite of the ore is contributed by sphalerite contamination; however, analysis of pyrite of the country rock in which sphalerite was not observed indicates that a few hundred parts per million zinc may be incorporated into pyrite. One sample of pyrite from the sm 4 marble unit had 3000 ppm of zinc or an equivalent of 0.45 weight percent sphalerite. This might mean that sphalerite accompanies pyrite in the country rock as noted by Engel & Engel (1959).

Summary Some elements such as silver and cadmium, particularly in sphalerite, are found in quite consistent concentrations in the host minerals. Amounts of these elements in a mineral seem to be little affected by the temperature of deposition of the host mineral, by later geologic events, and by changes in accompanying components or phases.

A much larger group of minor elements such as indium and to a lesser extent manganese show wide variations in the amounts found in sulfides. Further, at Balmat it has been found that a plot of concentration of this type of element in sphalerite against its concentration in pyrite does not give a good straight line or smooth curve. Some of the variation may be explained by the introduction of a new phase from a different ore fluid. An example of the latter is thought to be leaching of manganese from sphalerite by a fairly recent episode of deposition of supergene magnetite and hematite. Another attractive alternative is that equilibrium was not closely approached during crystal growth. However, the concentration of a minor element in a host mineral may also vary because of a varying concentration of the minor element in the ore fluid, a change in the activity coefficients due to change in bulk composition in the ore fluid, or to a large amount of heat involved in the transfer of the component from the ore fluid to the crystalline host. And the fractionation factor may also vary because equilibrium was established at different temperatures in different parts of the ore body or the activity coefficients of the trace element of interest may change at different rates with change in temperature and composition.

Unique solutions to the problems noted above are difficult to obtain and further may be complicated by many different kinds of reactions that take place at grossly different rates. Some reactions may be rapid with equilibrium closely approached over considerable distances. Other reactions may be very slow with equilibrium not even closely approached over very small distances. Thus may be explained sphalerite containing consistent values of iron and cadmium in sphalerite over distances of hundreds of feet whereas indium will vary by several orders of magnitude within the same ore body.

It is thought that the order of paragenesis of the major elements - iron, lead, and zinc - was controlled not so much by temperature at the site of deposition as by the order of release of the elements from the source. If the source of the ore fluid was a crystallizing magma, a reason for the paragenesis is easily imagined. Explanations for paragenesis of an ore fluid coming from a non-crystallizing source are much more hypothetical and will not be discussed further.

TABLE 7: Minor And Trace Elements In Sulfides At Balmat, New York (B. R. Doe, Analyst)

Sample Number	Concentration in PPM By Weight In SPHALERITE												
	Ag	Ba	Bi	Cd	Co	Cu	Ga	Ge	In	Mn	Mo	Ni	Pb	Sn
300L, Upper Gleason Ore Body (UGl), No. 3 mine														
1N[1]	2	150	80	1600	20-	350	200	22	20	650	-	100	15	10
2N	2	5	-	1100	8-	400	150	3-	8	1400	-	5-	4	4
4N	2	4	-	1200	-	400	150	3-	15	2600	-	2-	20	6
5N	1	5-	-	2000	-	250	55	9	3	1000	-	5-	3	3
700 BMS, Upper Gleason Ore Body, No. 3 mine														
6N	2	3	-	1100	-	550	70	10	2	540	-	10-	6-	2
8N	2	4	-	1200	-	~1500	500	3-	2	700	-	10	4	3
10N	4	40	-	1600	-	350	7	-	-	480	-	-	-	-
12N	1	5	-	1500	-	850	25	35	4	1000	-	2-	4	2
700 BMS, Middle Gleason Ore Body, No. 3 mine														
15N	1	6	-	1600	-	~200	90	-	4	850	-	~25	4	3
16N	2	5-	-	1300	-	400	45	-	4	910	-	1	3	4
17N	2	2	-	1600	-	~400	40	8	5	1400	-	1	3	4
19N	2	4	-	1600	3-	550	45	-	~60	5800	-	9	3	4
21N	2	8	-	2000	-	550	200	3-	4	1200	-	-	10	2
900GS, Loomis Ore Body (Lo), No. 3 mine														
22N	2	8	-	1400	-	550	15	10-	4	1300	-	-	4	2
23N	5	4	-	1000	-	300	150	-	35	3800	-	7	70	5
24N	1	1000	-	~1300	-	300	50	3-	15	2400	-	-	10	10
25N	5	15	-	1600	-	1400	45	3-	15	2600	-	-	2500	2

~in duplicate the smaller value was less than one-half the larger value, 5- is less than 5 ppm, 5+ is more than 5 ppm, - the line was not observed.

Sphalerite, Concentration in PPM by Weight

Sample Number	Ag	Ba	Bi	Cd	Co	Cu	Ga	Ge	In	Mn	Mo	Ni	Pb	Sn
500L, Central Ore Body, No. 2 mine														
A2	9	100	-	1300	-	70	10	-	60	4800	10-	-	200	-
A6	8	30	-	1400	-	200	9	-	45	4000	15-	-	65	-
A10	13	12000	-	1400	3-	150	6	-	200	7800	10-	-	1600	-
B1	6	3000	-	1400	-	350	7	4	55	5000	-	-	300	4-
B3	4	~15000	-	~1000	-	300	10	-	~100	1600	8-	-	85	-
B4	28	~6000	-	1600	-	700	1	-	200	7600	-	-	1400	1
1100GS, Central Ore Body, No. 2 mine														
F1, F2	4	20	-	1300	-	150	2	-	35	3700	4-	-	80	-
F4	2	6	-	1200	-	~650	3	-	10	1900	6-	-	~25	-
F15	5	10	-	~1100	-	60	20	-	70	4600	4	-	90	-
F16	3	10	-	1600	-	150	2	-	30	3700	8	-	2	-
G5	4	2000	-	1400	-	100	15	-	20	2600	12-	-	6	-
G1	3	800	-	1400	-	100	4	-	10	2300	8-	-	300	-
G14^1	8	100	-	1200	-	90	8	-	25	3300	-	-	6000	-
G15	32	80	-	1400	-	150	10	-	50	4600	6-	-	19000	-
1500GS, Central Ore Body, No. 2 mine														
P2	2	~8	-	1600	3	200	3	-	10	2200	6-	-	2	-
P4	2	~30	-	1400	-	~55	2	-	15	2400	12-	-	30	-
P5	4	40	-	1100	-	900	3	-	100	5800	7-	-	15	-
P6	8	~10	-	1400	-	800	4	-	50	4600	7-	-	150	-
P7	4	~10	-	1400	-	200	4	-	15	2400	12-	-	30	-
P11	4	~20	-	590?	-	150	4	-	600	16000	30-	-	100	-
P12	2	~20	13-	1800	-	250	6	-	100	5800	10-	-	20	-
P15	4	700	-	1200	-	80	4	-	85	5300	-	-	8	-
P20	6	5000	-	940	-	100	9	-	150	14000	-	-	450	-
Q2	0.9	200	-	1200	-	50	9	-	30	3600	-	-	~30	-
Q4	2	270	-	1400	-	100	16	-	25	4000	-	-	10	-
Q5	0.6	3000	-	920	-	400	10	-	85	4400	-	-	2	-

Sphalerite, Concentration in PPM by Weight

Sample Number	Ag	Ba	Bi	Cd	Co	Cu	Ga	Ge	In	Mn	Mo	Ni	Pb	Sn
Q7, Q8, Q9	2	3000	-	980	-	1400	4	-	70	5000	-	-	3	-
Q12, Q13	1	11000	-	940	-	300	15	-	150	6300	-	-	6	-
Q14	6	10	-	1600	-	40	2	-	900	12000	-	-	1000	-
500L, Lower West and Lower Far West Ore Bodies, No. 2 mine														
C2	12	350	-	1300	-	80	8	-	~20	1800	-	-	1600	2-
D1	2	7	-	1100	-	150	2	-	200	14000	-	-	70	2
D5	13	1000	-	~1200	-	300	4	-	9	1800	-	-	5200	2
D7a[1]	6	750	20	2400	-	150	40	-	3	410	30-	7	750	2
D10	11	8	-	1500	-	250	10	-	2	470	-	6-	170	2
1100GS, Lower West and Lower Far West Ore Bodies, No. 2 mine														
H2	40	700	-	1500	-	90	3-	-	550	11000	-	-	4300	-
H5, H6	3	850	-	1600	-	150	6	-	80	860	-	-	420	2-
H13b	2	5500	-	2500	-	30	4	1-	8	2200	-	-	1-	2-
I7	4	850	-	1400	-	300	2	-	2	680	-	-	60	2-
I13	2	900	-	1500	-	~400	2-	-	4	830	-	-	8	2-
1500 GS, Lower West and Lower Far West Ore Bodies, No. 2 mine														
R3	2	200	15-	1400	1-	80	9	5-	10	1700	-	6-	3200	2
R6	4	70	-	1400	-	75	2	-	550	16000	-	-	240	2-
R10b	4	10	-	1300	-	55	2	-	850	12000	-	-	150	-
R11	8	4000	-	1400	-	150	3	-	15	3000	-	4-	180	2
T6	5	750	3-	1400	-	400	2	~1	~40	1600	-	-	160	2-
T7a	4	10	-	2200	-	90	4	-	-	580	-	-	70	-
T12	12	750	-	1600	-	350	3	-	1	650	-	-	360	2-
1100GS, Upper-Streeter (LEU) Ore Body, No. 2 mine														
J1	18	8000	100	1500	25	300	65	55	350	11000	65	100	3600	50
J3b	0.5	45	3-	1300	-	55	4	2-	100	6800	-	-	2-	3-
J5	2	4000	-	1500	-	200	8	-	55	4600	-	-	75	5-
J6	0.6	25	3-	1400	1-	150	8	4-	5	1100	4	-	1-	2

Sphalerite, Concentration in PPM by Weight

Sample Number	Ag	Ba	Bi	Cd	Co	Cu	Ga	Ge	In	Mn	Mo	Ni	Pb	Sn
J7[1]	0.6	4000	3-	1500	-	100	4	-	8	1600	-	-	4	2-
J8	2	100	5-	1200	-	850	15	-	300	16000	-	-	2	2-
1100GS, Lower-Streeter (LEL) Ore Body, No. 2 mine														
K2	7	90	3-	1400	1	40	4	6	45	4200	-	5	1400	2
K3	6	440	10	1400	2	100	10	6	55	4600	6	10	2200	4
K5	4	30	3	1300	70	70	8	~2	300	9900	-	10	20	3
K7	1	1000	-	1500	-	20	1	-	90	5600	-	-	4	-
*	0.5	3	3	30	3	1	3	3	3	3	3	3	3	2
#	17	25a 45b	?	8.5	?	15	37	?	27	10	?	?	28	?

1 Samples not analyzed in duplicate

* Minimum concentration resolved, average

\# Relative analytical standard deviation in percent multiplied by $(1/2)^{\frac{1}{2}}$ to yield the deviation for pairs, average

a Value of relative standard deviation of pairs for concentration greater than 100 ppm

b Value of relative standard deviation of pairs for concentration less than 100 ppm

Looked for but not found in sphalerite:

Au(2676.0)	La(3245.1)	Pt(2659.5)	Ta(3311.2)	Sb(2877.9)
Be(1650.5)	Nb(3163.4)	Sc(2840.0)	As(2780.2)	Ti(3311.2)

Chromium traces, unstandardized, observed in:

A10, B4, G4, H2, Q2, Q5

Sample			Concentration in PPM by Weight for PYRITE								Possible
Number	Ag	Co	Cr	Cu	Mn	Ni	Pb	Ti	V	Zn	Contaminants
					No. 3 mine undifferentiated						
2N	1	35	75	45	48	50	80	-	-	12000	S-sl
5N	1-	50	~25	160	40	30	-	-	-	10000	S-sl
8N	2	50	50	130	58	20	-	-	-	28000	S-sl
10N	1-	100	200	76	57	20	35-	-	-	26000	S-sl
					500L, Central Ore Body, No. 2 mine						
A3	3	~15	~75	~15	340	-	-	-	50	7300	S-sl
A7	2	70	15	46	140	-	-	-	65-	31000	S-sl
A10	11	13-	350	15	120	-	2800	-	50	2800	Clean
B3	4	30	50	26	100	15-	280	-	65	4200	S-gangue
					1100GS, Central Ore Body, No. 2 mine						
F6	13	~15	9	240	460	-	50	-	65	38000	S-sl
G1	8	20	10-	54	140	-	150	-	50-	20000	S-sl
G5b	7	15	10-	16	130	-	50	-	-	3400	S-dolomite
G12	12	40	~95	31	160	8	2800	-	65	160	Clean
					1500GS, Central Ore Body, No. 2 mine						
P4	10	25	20	25	260	12-	-	-	60	30000	S-sl, Py fractured
P19	12	10-	~8	~12	160	-	250	-	-	2100	Clean
Q7	16	1000	~90	12000	280	40	400	-	65	18000	Py fractured
Q14	51	15	95	90	460	15-	-	-	75	190	Clean
					1100GS, South East Ore Bodies undifferentiated						
J1	8	8-	~20	3-	38	-	1400	-	-	1800	Clean
J7	2	30	45	6	110	15	70	-	-	1400	Clean
K1	4	3-	~20	35-	47	15	75	-	-	300	Clean
K7	2	30	~15	3-	56	30	41	-	-	5500	S-sl

Sample Number	Ag	Co	Cr	Cu	Mn	Ni	Pb	Ti	V	Zn	Possible Contaminants
		Concentration in PPM by Weight for PYRITE									
500L, Lower West and Lower Far West Ore Bodies, No. 2 mine											
C1	2	15	45	25	700	-	35	-	60	14000	Py fractured
D1	8	4-	10-	47	390	-	160	-	85	14000	Py fractured
D6	13	15	100	5	160	-	1800	-	50	18000	Py fractured
D7b	9	~10	20	10	110	-	10000+	-	40-	15000	Py fractured
1100GS, Lower West and Lower Far West Ore Bodies, No. 2 mine											
H4	4	20	30	3-	320	10	600	-	-	9600	S-sl
H11	6	3-	150	36	77	8	350	-	-	3400	Clean
I3	8	12-	250	40	240	10	140	-	-	28000	Py fractured
I11	~16	~7	~200	3-	~80	-	660	-	-	9600	Py fractured
1500GS, Lower West and Lower Far West Ore Bodies, No. 2 mine											
R3	6	8	~15	3-	48	-	2200	-	-	9800	S-sl
R10	12	3-	~25	46	740	-	150	-	-	5500	Py fractured
R13	14	3-	~90	6	380	9	4000	-	-	17000	S-sl
T7	16	~16	200	18	210	-	450	-	-	20000	Py fractured
Country rock, Surface											
sm 4-3	6	1000	15	26	25	1000	-	-	-	200	
sm 4-2	6	250	8	110	10	250	-	250	-	3000	
sm 4-1	8	300	15	85	10	350	-	-	-	~400	
sm 4-4	10	900	15	30	25	600	1000	-	-	100	
ps 2-2	10	300	35	120	240	500	200	1500	270	100-	
ps 2-3	8	300	~10	8	3-	1000	-	300	80	200-	
ps 2-1	5	250	15	20	21	800	-	250	130	100	
rm 15-ff	10	~25	~6	82	75	150	500	700	-	200-	
hpg 1-ff	6	~2500	12-	~80	15	10000+	-	-	-	300	

Sample	Concentration in PPM by Weight for Pyrrhotite										Possible
Number	Ag	Co	Cr	Cu	Mn	Ni	Pb	Ti	V	Zn	Contaminants
A5b	10	3-	10	80	35	100	-	-	-	300	Clean
1100LMS	~75	-	-	440	85	125	-	-	-	900	Clean
1300L	~150	-	6-	2900	250	150	-	-	-	12000	Sl, cpy
P13	300	-	5-	2000	150	150	2000	-	-	13000	Sl, cpy
Q3	~40	-	10	46	70	100	-	-	-	600	Clean
Q8a	8	3-	25	~700	30	150	-	-	-	~200	Clean
Q8b	14	3-	20	2500	200	150	300	-	-	~600	Clean
Q9	4	14-	15	12	15	150	-	-	-	~1200	Sl
*	3	3	10	3	10	10	30	100	30	100	
#	18	21	40	13	8	25	14	?	35	19	

1 Samples not analyzed in duplicate
*Average minimum concentration resolved
#Analytical relative standard deviation for pairs

Looked for but not observed: Au, Be, Cd, Ge, Sc
Present below minimum concentration resolved: As(3000 ppm), Bi(100 ppm), In(100 ppm), Mo(100 ppm) Sb(1000 ppm), Sn(100 ppm), Ti(300 ppm)

ff - fracture filling

Sample	Concentration in PPM for GALENA (E. Godijn, analyst)						
Number	Ag	Bi	Cu	Mn	Sb	Sn	Zn
26N	650	10-	50	X	X	-	1%+
R9	1700	20	10-	-	X	-	0.02%-
F19	1200	12	10-	X	X	-	1%+

TABLE 8: Minor And Trace Element Content Of Some Gouverneur Marble Belt Units (B.R. Doe, analyst)

Sample Number	Mineral	Concentration in PPM for CALCITE and DOLOMITE Ag	Ba	Cr	Cu	Mg	Mn	Pb	Sr	Zn	Level
7 cdm 14-a	calcite	-	400	40	-	5000[1]	660	50	2200[1]	-	1500GS-LW, 2 mine
8 cdm 14-c	calcite	-	650	6	-	5000	2300	65	1800	-	1500GS-LW, 2 mine
9 cdm 14-d	calcite	-	750	4	-	5500	1500	60	1500	-	1500GS-LW, 2 mine
4 cdm 14-e	calcite	-	6000	4	-	3500[2]	920	35	2000[2]	-	1100GS-C, 2 mine
5 cdm 14-f	calcite	-	1500	3	6-	6000	2700	150	1400	-	1100GS-LW, 2 mine
6 cdm 14-h	calcite	-	2500	3	-	2500	490	80	2300	-	1100GS-C, 2 mine
1 cdm 14-j	calcite	-	5000	3	-	7500[3]	1200	45	1600[3]	-	500L-C, 2 mine
2 cdm 14-l	calcite	-	1000	4	-	6000	660	35	1200	-	500L-LW, 2 mine
3 cdm 14-p	calcite	-	100	3	-	6500	930	20	2000	-	500L-C, 2 mine
sm 4-1	dolomite	-	20	-	-	X	810	-	180	-	Surface
sm 4-2	dolomite	-	4	-	10-	X	370	-	100	-	Surface
sm 4-3	dolomite	-	15	-	-	X	450	-	60	-	Surface
sm 4-4	dolomite	-	25	-	-	X	780	-	190	-	Surface
fd 7-lb	dolomite	-	700	-	7	X	240	-	240	-	900BMS-Lo, 3 mine
fd 7-ln	dolomite	0.5-	300	4	40	X	230	100	140	2000	900BMS-Lo, 3 mine
fd 7-2	dolomite	-	9	-	10	X	500	-	140	1000	900L-Lo, 3 mine
fd 7-3	dolomite	-	10	-	-	X	710	-	100	-	Surface

Total Rock	Ag	Ca	Co	Cr	Cu	Mg	Mn	Ni	Pb	Sc	Sr	Ti	V	Y	Zn	Ba	Level
ps 2-2	1	7600	15	130	150	8000	700	100	250	12	250	4500	700	~85	250	2000	Surface
ps 2-3	1	2700	10	35	250	3500	10	170	15	8	9	1500	200	20	90	300	Surface
ps 2-1	0.6	5100	20	40	30	4500	35	210	55	13	40	2500	350	50	80	900	Surface
*	0.5	100	3	2	2	60	4	3	10	4	2	30	3	20	50	2	
#	?	?	?	14	?	4	25	?	23	?	25	?	?	?	?	22	

b- from bleached zone, n- from normal graphitic type marble; *minimum concentration resolved.

Analytical relative standard deviation for pairs of the reproducibility.

1. Mg-5000, Sr-2400; 2. Mg-3500, Sr-2000; 3. Mg-7200, Sr-1600: all by Cu spark analysis
E. Godijn, analyst

VII. GEOLOGIC HISTORY

From the data and geologic relations discussed in the preceding pages, the following geologic history is deduced for the ore deposits at Balmat.

A sulfide depositing ore fluid was derived from a source that had the following properties:

1. Lead was released with nearly homogeneous composition of the lead isotopes. The ratio of U(238)/Pb(204) in the source was close to 9.0.

2. Individual metallic elements were released at somewhat different times.

The ore fluid arrived at the depositional site at about 510°C and deposited the bulk of the sulfides near that temperature after which the temperature of the ore fluid gradually fell with time to about 300°-350°C at the end of primary deposition. The temperature of the ore fluid was at essentially the temperature of the surrounding metasediments.

The fugacity of S_2 fell with time from greater than 10^{-26} to less than 10^{-26} atmospheres; the O_2 fugacity was probably fairly constant within the range 10^{-40} to 10^{-60} atmospheres, and the CO_2 fugacity probably never was greater than 10^{-6} atmospheres. The total pressure at the site of deposition during the formation of the ores was about 3.0 ± 1 kilobar which may mean that the fugacity coefficients of the gaseous components may be much less than one. The ore fluid consisted mainly of H_2O and reached the site of deposition through microbrecciated zones in the marble units.

At first the ore fluid was rich in iron and deposited pyrite as a replacement mainly of dolomite. The dissolved dolomite contributed magnesium and calcium to the ore fluid leaving the depositional site. The ore fluid channels became clogged, and remicrobrecciation of essentially the same area in the No. 2 mine permitted zinc and lead bearing fluid to replace pyrite and more dolomite until the channels again became closed. A new period of microbrecciation opened new channels somewhat offset to the east of but overlapping with the previous channels in the No. 2 mine. Copper-and iron-bearing ore fluid was introduced into the No. 2 mine along the new channels and deposited chalcopyrite and pyrrhotite as crack fillings in pyrite and silicates and as replacements of sphalerite, until the channels again became sealed. Another microbrecciation in the southern part of the No. 2 mine area allowed the introduction of barite and anhydrite. Some pyrrhotite was altered to marcasite.

During the mineralization mentioned above only a little pyrite with perhaps some sphalerite was introduced in the area of the No. 3 mine. Following the rest of the mineralization in the No. 2 mine, a last period of microbrecciation in the No. 3 mine permitted zinc bearing fluids to enter and deposit sphalerite. Only a little sphalerite formed at this time in the No. 2 mine.

The primary sulfide mineralization outlined above occurred during the retrograde metamorphic stage of the metamorphism in the Balmat-Edwards marble belt about 1050 ± 100 million years ago. The span of time involved in the deposition of sulfides is undetermined but short compared to the absolute age of the deposits.

Subsequent to the primary mineralization and before glacial activity, supergene solutions formed solution cavities along zones of macrobrecciation and deposited magnetite, hematite, white sphalerite, chalcopyrite, galena, chlorite, and ilvaite at temperatures less than 140°C.

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APPENDIX 1: Photomicrographs

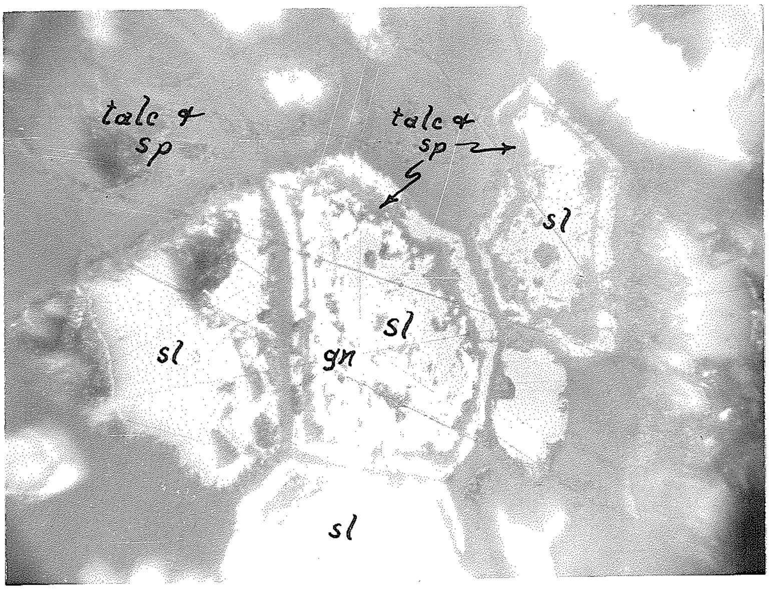

Plate 1a: Colloform structure of sphalerite (sl), talc, serpentine (sp), and galena (gn). (Sample F 19, X320, polished section)

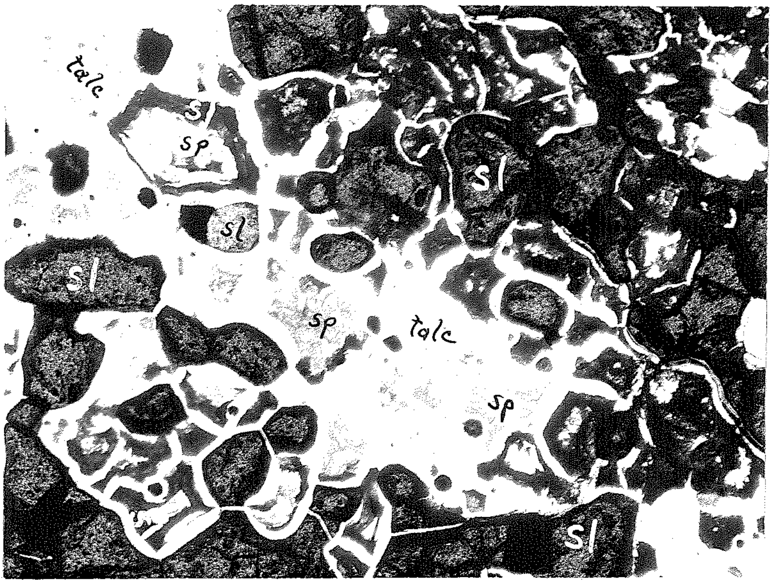

Plate 1b: Colloform structure of sphalerite (sl), talc, and serpentine (sp). (Sample F 9, X30, thin section)

APPENDIX 1: Photomicrographs

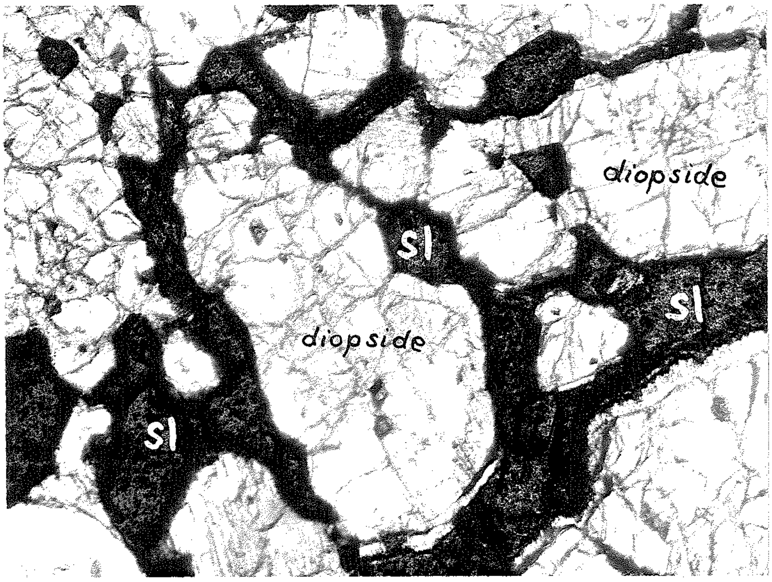

Plate 2a: Sphalerite (sl) deposited around grains of and in cracks in diopside with little or no replacement of the silicate (Sample A6, X40, thin section)

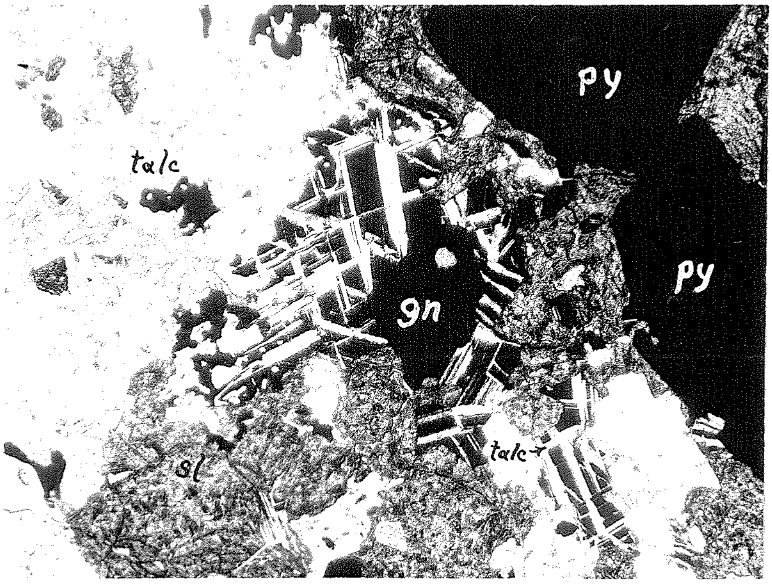

Plate 2b: Talc penetrating along cleavage in galena (gn) (Sample T 14, X40, thin section) with pyrite (py) and sphalerite (sl).

APPENDIX 1: Photomicrographs

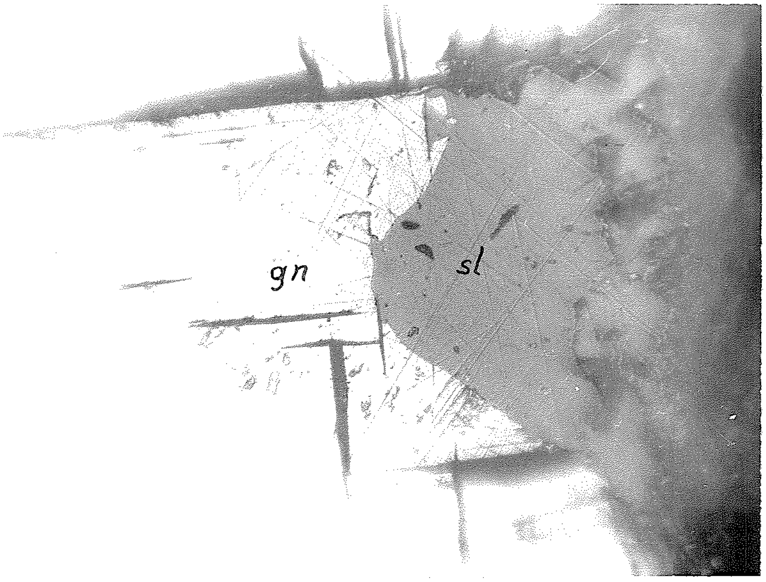

Plate 3a: Sphalerite (sl) penetrating galena (gn) along cleavage (Sample F 19, X320, polished section)

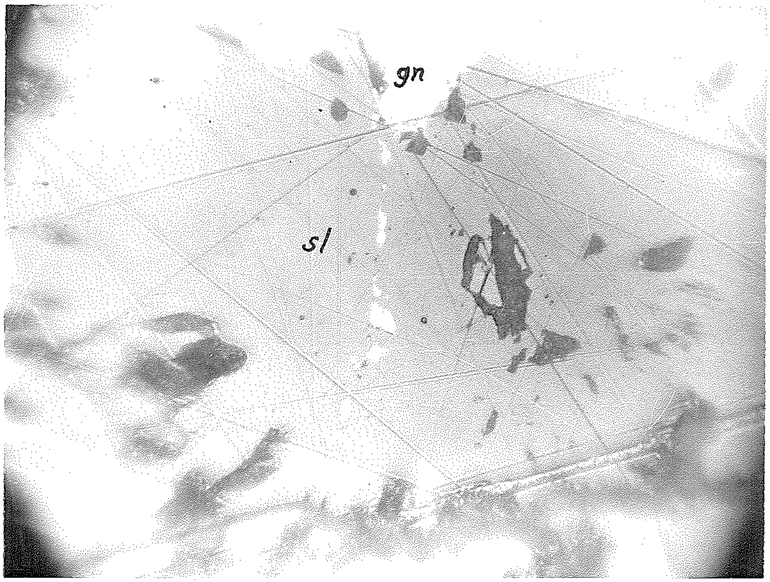

Plate 3b: Discontinuous "veinlet" of galena (gn) in sphalerite (sl) (Sample H 2, X320, polished section)

APPENDIX 1: Photomicrographs

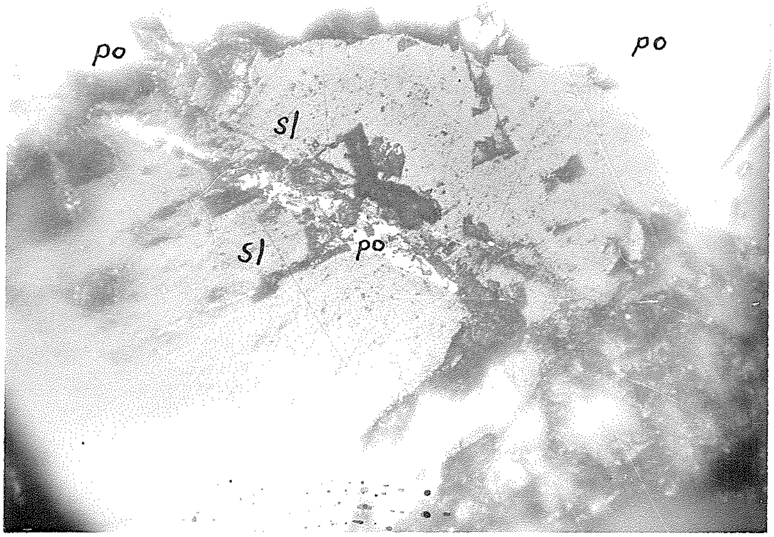

Plate 4a: "Veinlet" of pyrrhotite (po) in sphalerite (sl). The "veinlet" is joined to a large grain of pyrrhotite external to the sphalerite. (Sample Q 8, X320, polished section).

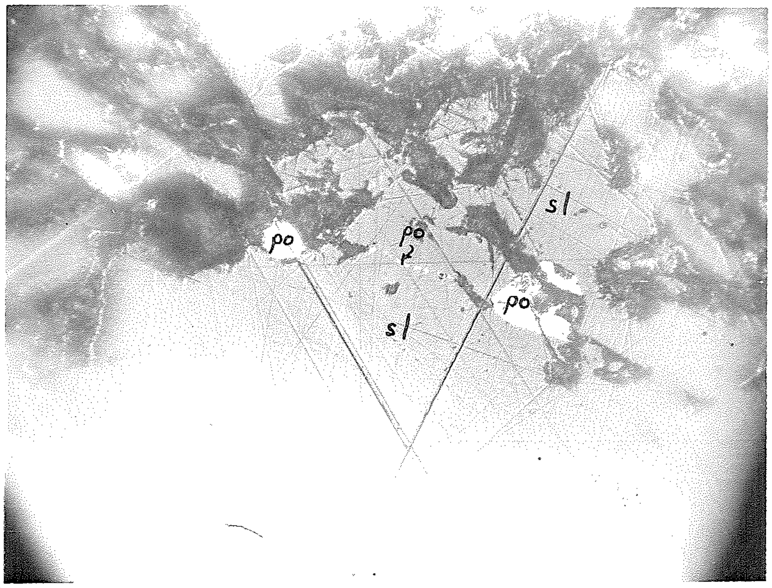

Plate 4b: Discontinuous "veinlet" of pyrrhotite between two blebs of pyrrhotite all enclosed by sphalerite (sl). (Sample F 13, X320, polished section)

APPENDIX 1: Photomicrographs

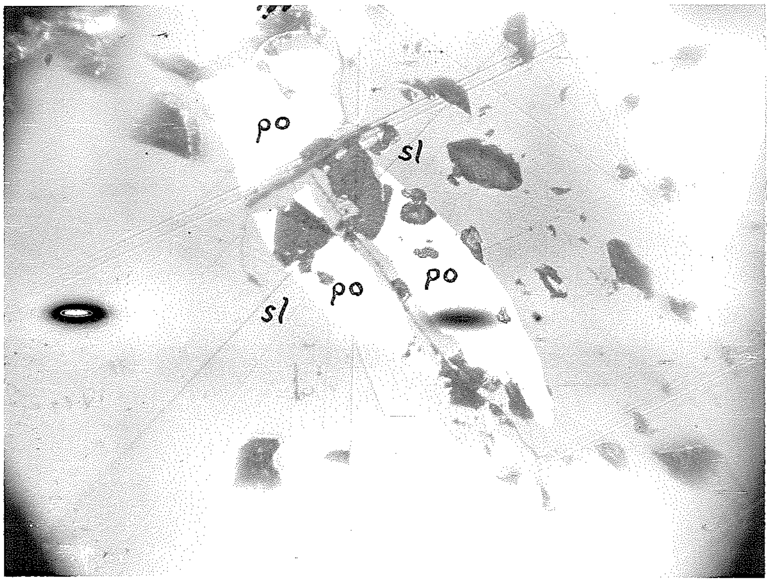

Plate 5a: Sphalerite (sl) replacing pyrrhotite (po) along fractures in the pyrrhotite. Shrinkage cracks are developed in the sphalerite associated with the pyrrhotite. (Sample P 14, X320, polished section)

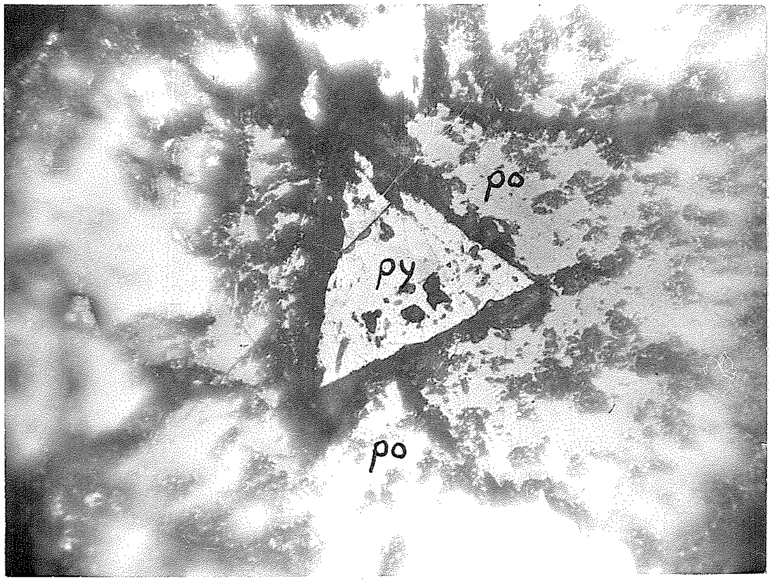

Plate 5b: Euhedral grain of pyrite (py) enclosed in pyrrhotite (po). (Sample P 13, X320, polished section)

APPENDIX 1: Photomicrographs

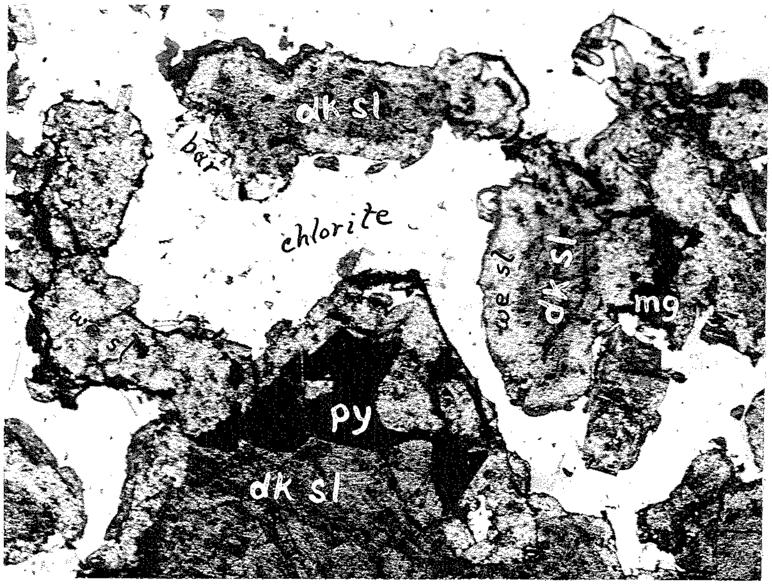

Plate 6a: Dark brown sphalerite (dk sl) with rims bleached white adjacent to chlorite (chl) and magnetite (mg) (Sample T 14, X40, thin section) with barite (bar).

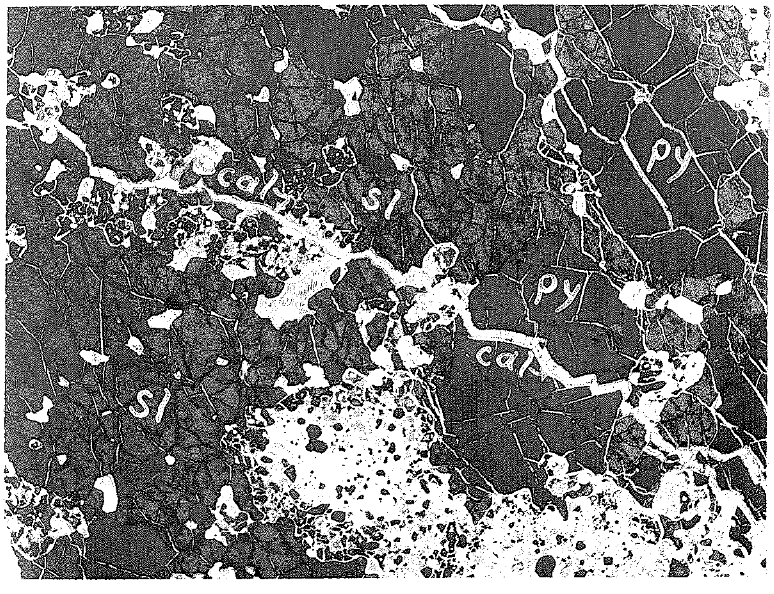

Plate 6b: Fractures filled with calcite (cal) through sphalerite (sl), pyrite (py), talc, and serpentine (sp). (Sample H8, X8, thin section).

APPENDIX 2: Sampling and Mineral Separation

The sampling method used is the point sample method where the sample size is as small as can be utilized in later analysis in the hopes of obtaining values from as nearly an area of homogeneous composition as possible. If it was thought necessary to obtain average values for a unit, multiple point samples were obtained.

Polished sections were made by R. von Huene for nearly all the ore samples analyzed. Sphalerite and pyrite samples were collected from the polished sections by drilling 5 to 20 milligrams of mineral powder with a portable dental drill using an S.S. White No. 2 carbide burr with a diameter of about one millimeter. While drilling, the polished section was observed under 80 magnification in a metallographic microscope with vertical and strong oblique illumination. For sphalerite samples, very small amounts of pyrite, galena, or magnetite turned the powder to a dark gray shade or black color. Gangue minerals turned sphalerite powder white. Chalcopyrite when present as small blebs was too homogeneous in the sphalerite and too small quantitatively to observe a sharp color contrast with chalcopyrite-free sphalerite powder. In pyrite sampling, small amounts of sphalerite showed up brown, gangue white, and galena not at all. The brown color observation of sphalerite on pyrite powder is apparently not as sensitive as at first thought due to the high amounts of zinc observed in many samples.

The area of one polished section is considered a point sample for the purposes of collecting pyrite and sphalerite samples. Sphalerite samples 1-25 (Doe, 1956) were originally collected by hand picking ≠ 40 mesh grains twice under a 3X binocular microscope. Thirteen of the 25 samples were re-sampled and rerun for iron content. Nine of these were in good agreement with the old values. The 13 samples were thought to be particularly suspicious from geological considerations.

Pyrite from the country rock was obtained by hand-picking shiny brass-colored fragments of pyrite. Pyrite from a hand specimen was considered a point sample. Samples of bulk rock from the same hand specimen from which the pyrite was collected were analyzed to determine the possible contaminants in pyrite from other phases.

Carbonate samples were collected by prying a few large grains from a hand specimen with a clean steel needle. The grains were then crushed and examined under 10X magnification for impurities. The grains were in general nearly transparent so that the purity could be easily established. Carbonate samples for lead isotope work were hand specimens from which an outside rind was cleaved with an acid cleaned steel chisel. The handspecimen was then cleaved into pieces weighing about 30 grams each. One piece was selected for analysis.

Galena samples for isotopic work were small cleavage fragments about 0.1 mm on a side pried from a hand specimen with an acid cleaned steel needle. Larger grains for minor element work were pried in the same way from the same hand specimens as for isotopic work. Sphalerite fragments of +40 mesh for isotopic work were collected by hand picking three times under 10X power.

APPENDIX 3A: X-Ray Fluorescence

The iron content of sphalerite was measured by means of the intensity of x-ray fluorescent radiation of iron and zinc by use of a modified Phillip's Norelco x-ray fluorescence spectrometer utilizing a Phillip's gas flow proportional counter with a lithium fluoride crystal grating and a 0.020 inch collimator. The x-ray tube is a high purity tungsten Phillip's FA-60 tube. The tungsten tube is operated at 45kv and 25ma which yields counting rates for the sample size used of approximately 2000 cps. The gas flow counter is operated at 1600 volts. The number of counts taken on the first order iron K_a peak (57.44° 2θ) is 128,000 with background counts (12,800) made at 55.5° and 59.5° 2θ. The second order zinc K_a (90.88° 2θ) is measured by the time needed for 64,000 cts with background of 6,400 cts taken at 89.0° and 93° 2θ. The sample size is 5-10 milligrams. The sample is placed in a well which is pressed into a lucite holder. The time of analysis is about 15 minutes.

Standards used in the procedure are natural sphalerites analyzed by volumetric or emission spectrographic procedures by Doe (1956), Fryklund and Fletcher (1956), and Rose (1958). Splits of samples from Doe, and Fryklund and Fletcher were reanalyzed by volumetric procedures by E. Godijn at the California Institute of Technology (Rose, 1958, p. 88). A straight line is obtained on a log-log plot of Zn/Fe fluorescent intensity against ZnS/FeS weight ratio (see for example Mortimore and Romans, 1953). Once the ZnS/FeS weight ratio has been determined, FeS in weight percent may be obtained assuming that FeS + ZnS + X = 100 percent which when combined with the weight ratio yields FeS = (100 - X)/(1 + wt. ratio) where X is the total amount of other constituents dissolved in the sphalerite and is usually assumed to be zero. In the Balmat ores, the presence of manganese, cadmium and copper in 90 percent of the samples will introduce an error in the FeS determination of less than 0.1 percent of FeS. The presence of any non-iron or zinc bearing contaminants not dissolved in sphalerite will introduce no error.

Rose (1958) determined the actual effects of absorption by manganese of zinc radiation and the fluorescence of copper by iron. At the concentration of manganese and copper encountered in the sphalerites, no effect on the FeS content is expected. After the first 25 sphalerite samples were determined by the fluorescent technique of Doe (1956), the technique was altered to that of Chodos and Rose (1958). The procedure is in brief--ten milligrams of powdered sphalerite are weighed into a flat bottomed circular cavity (1/32" deep x 1/4" dia.) drilled into lucite. The samples are spread to give a roughly even thickness within the cavity. The holder is inserted in the machine and the intensities measured by the constant count technique outlined above.

Differences between the methods employed by Rose and the author are:

1. A set of five standards of various iron contents was run each day in this study intermixed during the running of the unknowns. It was found that the straight line curve of the intensity ratio against the weight ratio would maintain the same slope from day to day but there would be slight vertical adjustments of the curve. In all the standards were analyzed 19 times. Treatment of the data indicated that the relative variation involved if the vertical position of the curve is assumed fixed is ± 3.2 percent with 90 percent confidence. If new working curves are constructed each day, the relative variation in a sample position is reduced to 2.3 percent with 90 percent confidence. Each standard was designated a sample holder so that no holder effect is noted. Rose (1958) did not reconstruct the standard curve each time and reported a coefficient of variation of 3 percent which agrees with the findings of the author for this type of procedure.
2. Rose reports (1958, p. 85) no effect of the sample weight on the Zn/Fe intensity ratios in the weight range 3-15 mg. The author in a separate study found that the effect of sample weight on the intensity ratio may be described as proportional to the amount of iron in the sample in the following way:

$$I(Fe)/I(Zn) = \frac{\dfrac{\bar{p}\; E' I_o^{fe}}{p+b}\overset{(2)}{\left[1-\exp\left\{-xd\left(\dfrac{p}{\cos\theta}+\dfrac{b}{\cos\phi}\right)\right\}\right]}}{\dfrac{\bar{u}\; E\; I_o^{zn}}{u+a}\underset{(1)}{\left[1-\exp\left\{-xd\left(\dfrac{u}{\cos\theta}+\dfrac{a}{\cos\phi}\right)\right\}\right]}} +$$

$$\frac{\dfrac{\bar{u}\; E\; E''}{u+a+b}\left(\dfrac{\bar{a}}{a}\right)I_o^{zn}\overset{(3)}{\left[1-\exp\left\{-xd\left(\dfrac{u}{\cos\theta}+\dfrac{b+a}{\cos\phi}\right)\right\}\right]}}{\dfrac{\bar{u}\; E\; I_o^{zn}}{u+a}\underset{(1)}{\left[1-\exp\left\{-xd\left(\dfrac{u}{\cos\theta}+\dfrac{a}{\cos\phi}\right)\right\}\right]}}$$

where term (1) is the production of zinc radiation by tungsten radiation at the zinc absorption edge, term (2) is the production of iron radiation by tungsten radiation at the iron absorption edge, and term (3) is the production of iron radiation by fluorescent zinc radiation.

u is the mass absorption coefficient of sphalerite for tungsten radiation at the zinc absorption edge.

$\bar{u}$ is the mass absorption coefficient of zinc for tungsten radiation at the zinc absorption edge.

a is the mass absorption coefficient for zinc radiation in sphalerite

p is the mass absorption coefficient for sphalerite for tungsten radiation at the iron absorption edge

$\bar{p}$ is the mass absorption coefficient of iron for tungsten radiation at the iron absorption edge

b is the mass absorption coefficient for iron radiation in sphalerite

$\bar{a}$ is the mass absorption coefficient for zinc radiation in iron d is the density of the sample

x is the sample thickness

E is the excitation coefficient for efficiency in producing zinc radiation for a given intensity of excitation radiation from tungsten

E' is the same for iron by tungsten radiation

E" is the same for iron radiation produced by zinc radiation

I_o^{zn} is the tungsten intensity entering the sample at the zinc absorption edge

I_o^{fe} is the tungsten intensity entering the sample at the iron absorption edge

cos Θ is the angle between the entering tungsten radiation and the direction normal to the surface of the sample

cos ϕ is the angle between the exit radiation and the direction normal to the surface of the sample

In the above equation when $I_o^{zn} = I_o^{fe}$ and $E' = E''$, it is found that a sphalerite containing 4.5 weight percent FeS in thin samples would not have the intensity ratio affected by change in thickness (neutral point) whereas in practice the neutral point is found to be at about 7.5 percent FeS. At FeS concentrations higher than the neutral point, decreasing thickness (or sample weight) would decrease the intensity ratio of Zn/Fe. If the sample thickness is one-half the standard thickness the content will appear greater than the true content by about 2 percent of 20 percent of a sample with 20 percent FeS. The error would gradually decrease to the neutral point. At iron concentrations less than the neutral point the intensity ratio will be higher for a sample weight less than the standard weight so that the apparent FeS concentration will be lower than the true content. While the errors induced are small even for extreme concentrations of iron, they become more important as the fraction of weight of the unknown to standard weight becomes smaller and corrections are quite significant for fractions near 0.1 if the standard weight is 10 milligrams. For best results, samples and standards should be analyzed at close to the same sample weights.

It might be noted that, if the contribution of zinc radiation to iron radiation is ignored, the point where thickness has no effect is raised to 10.8. Since the observed value of the neutral point lies between $I_o^{fe} E' = E''E I_o^{zn}$ and $E'' = 0$, the true efficiency of zinc radiation induced iron fluorescence lies between zero and the value assumed. The theory predicts that a 10 mg sphalerite sample in a sample holder as used should, for all practical purposes, be a sample of infinite thickness; however, actual experiments indicate that 15 mg or greater is a better estimate for infinite thickness. The discrepancy may be due to the fact that the sample cannot be evenly spread over the well so that in some areas the sample is near "infinite thickness" but over most of the area the sample is very thin. The result would be a sample thinner than assumed for a given weight of sample.

3. For undetermined reasons, different lucite holders, cut from the same stock were found to give somewhat different values of the intensity ratio and three of 16 holders gave values greater than 5 percent of the ratio different from the average of the rest and were discarded. The position of the holder in the x-ray beam is only partly the answer. Repetitive analyses in the same sample holder showed that short time variations of ratios during a day are not in excess of one percent of the intensity ratio; yet, different sample holders gave intensity ratios with wells in the same position in the x-ray beam different by as much as 2.7 percent of the ratio which probably accounts for most of the error involved in the daily standard curve. Thus it should be possible to reduce the instrumental coefficient of variation to between 1-2 percent if standards are run with unknowns, the same sample holder or sample holders that have the same bias are used for both standards and unknowns, and if the same weights are used for standards and unknowns.

In the procedure used, the time per analysis including grinding of the sphalerite powder to pass through a 320 mesh and loading of the sample holder is about 15 minutes. Background was subtracted from the peak intensity; however, the well only occupied a small part of the beam so that the background correction is not that of the sample but that of the holder.

In order to determine the reproducibility of the entire procedure including sampling on the concentration of FeS, two samples were collected from each of 14 different hand specimens covering a large range of iron contents. The standard deviation of the results was determined from the range of the pairs as given by Dixon and Massey (1951). A plot of iron content verses range showed that the range of duplicate analyses was independent of the concentration of iron in the sample. It is thought that the contamination of samples by pyrite was a greater effect than the instrumental electronic variations. Assuming normal distribution, the standard deviation (s) is 0.18. There is probably a certain minimum of contamination by pyrite of sphalerite samples, and a somewhat larger value on the average. It is not known what the average level of pyrite contamination is for the samples analyzed but an estimate may be made from sphalerite contamination of pyrite. It is thought that the sphalerite samples on an average are of the same purity as the best pyrite samples since there are no cracks filled with pyrite in sphalerite to counterbalance the cracks filled with sphalerite found in pyrite. If the latter is the case and if all the zinc determined in pyrite belongs essentially to contamination by sphalerite, then the average contamination of pyrite in sphalerite in terms of weight percent FeS would be 0.29 percent FeS by weight. While it may be dangerous to subtract the 0.29 from the content of FeS in any given sphalerite sample, it probably should be subtracted from average values.

APPENDIX 3B: Emission Spectrographic Analysis

The minor elements of sphalerite, pyrite, pyrrhotite, and galena were analyzed by an emission spectrographic procedure modified from Burnham (1955) and Rose (1958). Carbonates and pyritic schists were analyzed for minor elements by the procedure of Chodos and Godijn given in Engel and Engel (1959, p. 1378).

Sphalerite standards were constructed using the following spectrographically pure oxides added to a ZnS phosphor which contained 102 ppm silver by weight as the excitor: As_2O_3, Sb_2O_4, $BaCO_3$, Bi_2O_3, CdO, Co_3O_4, CuO, Ga_2O_3, GeO_2, In_2O_3, Mn_3O_4, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, PbO, NiO, SnO_2. Standards were constructed for 4%, 1%, 0.32%, 0.10%, 0.032%, 0.01%, 0.0032%, 0.001%, and 0.00032%. Silver values were obtained by utilizing the standards of Burnham (1955) along with the calculated concentrations of silver in the 4% and 1% standards constructed for this study. Barium was used as a flux in the formation of the ZnS phosphor but phosphor blanks revealed only perceptible quantities of silver. The pyrite standards used are those of Rose (1958) constructed from a natural pyrite crystal which did not have perceptible quantities of any of the trace elements desired. Pyrrhotite was analyzed as if it were pyrite. Galena was analyzed with reference to standards made from natural galena to which spec-pure oxides were added. The standards contained bismuth so that bismuth values were obtained by the rock analysis method of Chodos and Godijn mentioned above.

The spectrograph, electrodes, wave-length range, photographic plates, plate processing, and plate calibration are as described in Engel and Engel (1959, p. 1379). The excitation is 13 amperes short-circuited. The analytical gap is 4 mm with the central 2 mm focused on a diaphram which is in turn focused on the slit with a vertical cylindrical lens. The exposure is taken with a slit width of 25 microns, and neutral density quartz filters are used to control the transmission of light (60 percent for sphalerite, 100 percent for pyrite). Samples were burned to completion. A two step filter was inserted between the slit and optical bench to give a dark and light portion to each line. A set of standards for the mineral under consideration were burned on each plate.

The electrode charge was a total of 20 milligrams composed of 12 mg of a mixture composed of 90 percent Na_2CO_3, 10 percent SiO_2; 4 milligrams of powdered spec-pure carbon; 4 mg of powdered mineral or standard. A total of 50 mg of electrode charge was prepared at a time and mixed by a Wig-L-Bug for 15 seconds. Over 90 percent of the samples were shot in duplicate. No internal standardization was used. The total energy method was employed. Plates were read on a Jarrel-Ash densitometer as percent transmission except for the high values of manganese, copper, and barium which were timed on an Applied Research Laboratories densitometer for the time of scan below a transmission of 5 percent of the desired line divided by the time of less than 5 percent transmission of a standard iron line.

It has been suggested by Ahrens (1954) that the reproducibility of emission spectrographically determined concentrations should be treated as a log normal function rather than as a function of normal statistics. Ahrens, however, points out that the difference between the two methods of statistics is slight for low relative standard deviations but becomes more important at deviations above 15 percent. The relative standard deviations determined for cadmium, copper, manganese, silver and zinc, assuming normal distribution, are probably small enough to be relatively independent of the type of statistics employed. The relative standard deviation for normal statistics on cobalt, nickel, and lead are probably small enough to quote one numeral followed by a zero or five. The reproducibility of barium and chromium is so poor that it is dangerous to attach any numeral to the value obtained. Barium and chromium are known to an "X" followed by enough zeros to indicate the order of magnitude of the concentration. While the reproducibility of the concentrations of indium and germanium are better than for barium and chromium, difficulties in correcting for interference from other elements are so great that the data are recorded in the same manner as barium.

In this study it is assumed that an unbiased estimate of the relative standard deviation is obtained by multipling the range encountered in analyzing samples in duplicate by 0.886 as suggested by Dixon and Massey (1951). The relative standard deviations are averaged for the total number of samples and multiplied by $1/2^{1/2}$ which furnishes the value for relative standard deviation for pairs of the unstarred samples in the tables. The starred samples were only done once, and the standard deviation may be obtained by multiplication by $2^{1/2}$.

In order to determine the relation of data in this report as to internal consistency and to the work of other workers, Burnham's sphalerite standards (1955) were run as unknowns, six samples from Fryklund and Fletcher (1956) which were also analyzed by Rose (1958) were reanalyzed as unknowns, two samples were done by the rock method, and one sample was repetitively analyzed by the author and also once by Mr. E. S. Lenher at Pennsylvania State University. Cadmium values at the end of a six month period were approximately 30 percent higher as compared to the period when the bulk of the sphalerites were analyzed. The reason for the change is not known, but it does not affect any significant quantity of sphalerites which were all determined within the first month. The sphalerites as determined yield cadmium values about 10 percent higher than by the rock method and by Mr. Lenher's analyses. The same is approximately true of the samples of

Fryklund and Fletcher and the standards of Burnham. In general, the cadmium contents given in this report may be about 10 percent too high.

Comparison of all the data suggests that the indium values given in this report less than 100 ppm may be low by about a factor as great as eight, and germanium values less than 100 ppm may be low by a factor of three. The slopes of the intensity against concentration of In and Ge are found to be greater in this report than in other studies so that the values of these two elements cross from low to high relative to other studies at about 1000 ppm. The reasons for the discrepancy are unknown. Other elements are about the same for all studies.

APPENDIX 3C: Mass Spectrometric Analysis

The mass spectrometer used in this work has been described by Chow and McKinney (1958). The corrections to raw data, precisions, and reproducibility are those of Chow and Patterson (1959). The chemical procedures used to isolate the lead are those of Patterson (personal communication).

In order to obtain the desired beam intensities for lead from galena, it was found necessary to purify the lead. In all chemical procedures either pyrex glassware or teflon ware was used, and all evaporation stages were performed in a nitrogen tank. All chemicals are either redistilled or reprecipitated. The galena (about 25 micrograms) is dissolved in HCl containing a drop of HNO_3. Ammonium citrate and KCN are added. The pH is adjusted to 8.5-9, and the lead is removed by a dithiozone extraction. The lead is re-extracted with dithiozone as before. Organic material is removed by heating to dryness with small amounts of HNO_3 and perchloric acid. The residue is taken into solution and lead is precipitated with H_2S. The lead is loaded onto the filament with a micro pipette.

In the procedure to isolate the lead from blebs in sphalerite, 200 mg of sample were utilized. The sample was taken into solution as above. Ammonia gas is used to neutralize the solution and lead is carried down on iron hydroxide, washed, and re-precipitated. The iron is removed by a double ether extraction. The rest of the procedure is as for galena.

In the procedure to isolate lead from marbles, 30-40 grams of marble are taken into solution in a 400 ml beaker covered with a watch glass. The solution takes from 8-10 hours in a nitrogen tank. The supernatent liquid is poured into a one liter volumetric flask. The residue is transferred to a 100 ml Teflon beaker with a Teflon cover to which 5 gm of perchloric acid are added and then 20 gm of HF and heated at less than 150°C until the HF is gone. The temperature is advanced to get rid of the perchloric acid. The HF-perchloric acid step is repeated three more times. If graphite remains after the last step, the graphite is leached with HCl until no more yellow discoloration of the acid was noted and the solution was added to the volumetric flask. Quadruple distilled water is added until the contents of volumetric flask are brought to the mark. Aliquots were removed for isotope dilution analysis of lead and uranium, and the remainder is treated by the sphalerite procedure. Iron was added as a carrier if needed.

To determine the lead concentration in marble by isotope dilution, lead spike is added to an aliquot from the volumetric flask above. The rest of the procedure is similar to sphalerite.

To determine the uranium concentration in marble, uranium spike is added to an aliquot, a small amount of aluminum nitrate is added, and the uranium is carried down by ammonium neutralization. An ammonium carbonate precipitation is performed followed by a double hexone extraction. The acid-water phase from the second extraction is taken to dryness, and the uranium is picked up in nitric acid and added to the filament by use of a micropipette. The entire procedure from the starting of solution until loading of the filament takes about eight days.

APPENDIX 3D: X-Ray Diffraction Analysis

The lattice spacing of the d(220) of sphalerite and the d(102) of pyrrhotite was measured in two ways. One method was by taking x-ray powder diffraction photographs with manganese filtered Fe(K_a) radiation (wavelength of 1.93597 Å). The second method was by use of a Norelco X-ray diffractometer also using manganese filtered Fe(K_a) radiation. Smear mounts for the study with the diffractometer were prepared on lucite disks. The disks were rotated in the beam of the x-rays. All measurements were standardized against spectrographically pure NaCl. The unit cell edge of NaCl was taken to be that of the U.S. Bureau of Standards measurement at 26°C of 5.6402_0 Å. The d spacings of sphalerite and pyrrhotite were measured relative to the d(220) of NaCl.

In the x-ray diffractometer study, the location of the peak was determined by measuring the intensity of the diffracted radiation in increments of $0.01^\circ 2\theta$. On NaCl, 1600 counts per step were timed and 3200 counts per step on the pyrrhotite or sphalerite. The intensity was recorded on a Berkeley digital recorder and the timing was measured to the hundredth of a second by a Berkeley Universal Counter and Timer. The total time involved per step in the measurement of the intensity was about 100 seconds. The analyses were performed at 25° ± 1°C. The error in the lattice spacing measurements is 0.0003 Å.

The d(102) spacing for the pyrrhotites was found to be:

		± 0.0003Å	
Sample Number	$(\bar{2}02)$ Split a	(202) Peak (in Å) b	Center of peak
A5b	2.058_8	2.052_2	2.056_4
1100BMS	2.062_9	2.052_6	2.057_8
1300L	2.062_3	2.052_6	2.057_3
P13	2.062_4	2.052_3	2.057_1
Q3	2.060_8	2.053_4	2.056_4
Q8	Not split		2.065_2 2.065_6 (102)
Q9	2.059_6	2.052_9	2.056_4

(102) is for hexagonal pyrrhotite
(202) and (202) are for monoclinic pyrrhotite