

## Variation of Iron Sulfide Content in Sphalerites of Mississippi Valley Deposits

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Geothermometry has long been an inexact field because of the problem of multiple variables. The use of liquid inclusions for determining temperatures of mineral deposition most nearly approaches the ideal method for low and medium temperature ranges. The corresponding science of geobarometry, is even less well developed.

Liquid inclusion temperature data on sphalerites of the Mississippi Valley deposits is extensive. Kullerud (7) has shown by means of a detailed investigation of the FeS-ZnS system at high temperatures that the solubility of FeS in sphalerite is a function of the temperature of formation. (The incorporated iron causes an increase in cell dimensions directly related to the amount of iron introduced.)

Pressure correction data are available for both the correction of liquid inclusion temperature determinations and those of the FeS-ZnS system.

The purpose of this investigation was to determine the FeS contents of Mississippi Valley sphalerites and compare them with liquid inclusion temperature values. It was hoped that the work would shed light on pressures of low temperature FeS-ZnS temperature determinations, and on the variability of iron content within the sphalerites of Mississippi Valley deposits.

Specimens of sphalerite, previously studied by the liquid inclusion method, from the Upper Mississippi Valley district, Wisconsin-Illinois (1), the Deardorff mine, Cave-in-Rock district, Illinois (5), and the Miami-Picher district, Oklahoma (9) were made available to the writer for this study. X-ray spectroscopy was chosen as the method of determining iron content because of the small amount of sample required in this technique and its high accuracy in the anticipated range of iron content.

### Previous Work — Liquid Inclusions Studies

Bailey and Cameron (1) reported temperatures ranging from 121° to 75° (uncorrected for pressure) for the sphalerites of the Upper Mississippi Valley district. Their results suggested that, in general, temperatures declined progressively during sphalerite deposition. From study of the liquid inclusions in the Deardorff mine in the Cave-in-Rock district Freas (5) reported liquid inclusion temperature values of 103° to 84° (uncorrected for pressure) for sphalerite. Schmidt (9) studied sphalerite from the Miami-Picher district and found liquid inclusion temperature values ranging from 120° to 83° (uncorrected for pressure). The techniques employed in these investigations and an evaluation of the liquid inclusion method were given by Bailey and Cameron (1). The reader is referred to their paper.

<sup>1</sup>Material in this paper formed a portion of a master's thesis prepared under the direction of Professor E. N. Cameron at the University of Wisconsin, 1959-1961.

### FeS-ZnS Geothermometer Studies

The sphalerite from the districts named above varies considerably in color and shade, commonly within a single specimen. Sphalerite specimens consisting of successive bands are generally lighter toward the centers of veins but reversals are not uncommon (Fig. 1). The variations in shade have been considered to be due to variations in iron content. Kullerud (7) gave FeS-ZnS temperature values for a group of specimens from Mississippi Valley deposits. The values suggested much higher temperature ranges for sphalerite deposition than indicated by liquid inclusions (up to 245°, uncorrected for pressure).

Similar studies using the FeS-ZnS geothermometer have been made by Fryklund and Fletcher (6) and Benson (3). Bradbury (4) has made spectographic determinations of sulphide minerals from the Upper Mississippi Valley district that augment this study. His Fe values determined for six sphalerite specimens from the Bautsch mine are in agreement with the results of this study.

### General Geology — Upper Mississippi Valley District

This district is located primarily in the southeastern corner of Wisconsin but extends into the adjacent states of Iowa and Illinois. The area is underlain by gently dipping Ordovician limestones, dolomites and shales. The mineralized section is approximately 400 feet thick.

Structural variations consist of minor west-trending anticlines, subsidiary elliptical folds striking east-northeast and northwest, and local faults with displacements up to 50 feet. The ore deposits appear to be controlled by the smaller subsidiary folds that have been accentuated by solution thinning of the carbonate beds. The deposits are separated into "top run" and "bottom run" types. The latter are composed of disseminated and vein ore bodies in the lower section of the mineralized zone. Vein ore bodies are termed "pitches" where they follow steeply-dipping fractures and faults, and "flats" where they occur along bedding plane fractures and faults.

Galena and sphalerite constitute the major ore minerals. Lesser amounts of chalcopyrite, gold, millerite and silver have been found. The major gangue minerals are calcite, dolomite, marcasite, pyrite and quartz. Barite and akermanite are present. More detailed descriptions of the district are to be found in Bailey and Cameron (1) and Behre et al (2).

### Deardorff Mine, Cave In Rock District

The Deardorff mine (W. L. Davis-Deardorff mine) lies northwest of the town of Cave-in-Rock in southeastern Illinois. The district is underlain by gently dipping Mississippian and Pennsylvanian limestones, shales and sandstones. Igneous dikes are present in one part of the district, but do not appear to be related to the ore deposits. Economic mineralization is largely limited to a stratigraphic interval of 200 feet within the Mississippian limestones. The deposits occur in favorable horizons, most abundantly where these horizons are intersected by joint fractures and pre-mineral faults. Small synclines, probably caused by solution thinning and collapse breccia, mark many of the bedding replacements deposits.

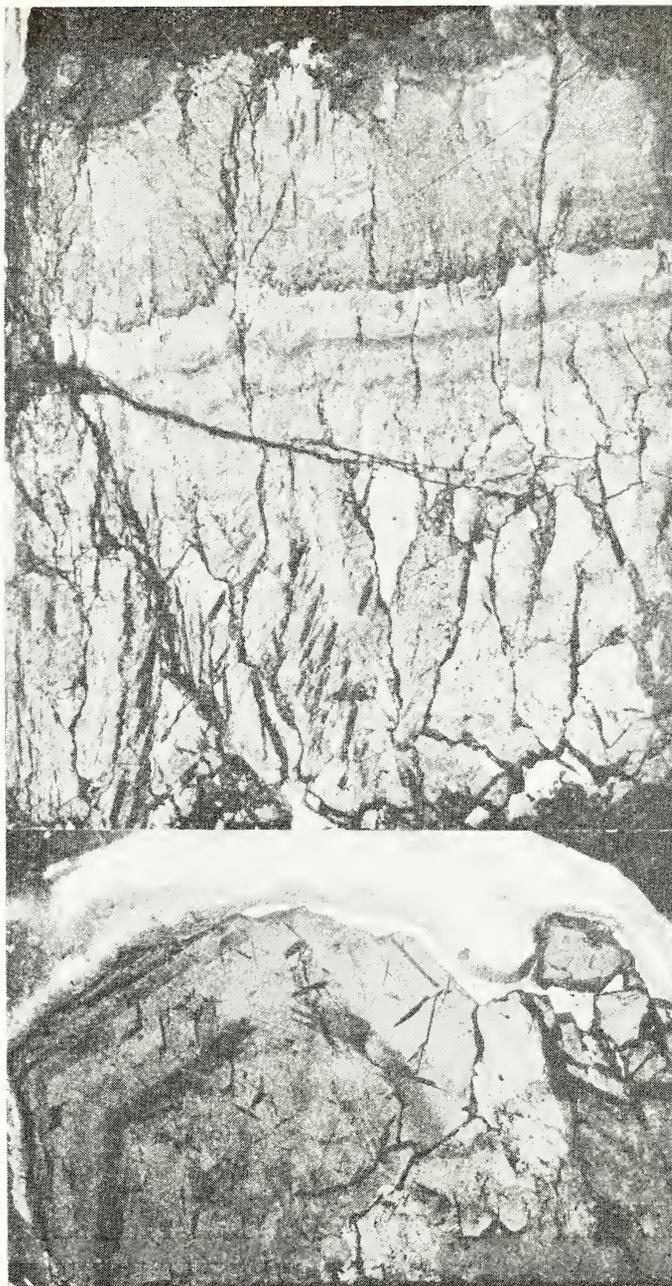


Figure 1. Photograph of a polished section of banded sphalerite from the Liberty mine, Wisconsin. 4x, transmitted light.

Figure 2. Photograph of a polished section of discontinuous banding sphalerite from the Deardorff mine. 4x, transmitted light.

In addition to fluorite, for which the district is noted, the Dear-dorff mine produces important quantities of galena and sphalerite. Figure 2 illustrates typical sphalerite from this mine. Accessory and gangue minerals include calcite, quartz, barite, chalcocite, pyrite, marcasite, witherite, strontianite, cerussite and malachite. A more detailed account of the geology is to be found in Weller et al (11).

#### Miami-Picher District

The Tri-State region, of which the Miami-Picher district is the southwestern part, is made up of several scattered mining centers in an area 125 miles long and 50 miles wide at the intersection of Missouri, Kansas and Oklahoma.

The deposits occur in a stratigraphic interval of 400 feet within the flat lying Boone formation of Mississippian age. The mineralized beds consist of limestone, shaly limestone and chert. The primary structural feature of the district is the Miami Trough, a 40-mile-long synclinal depression trending east-northeast that is only 1,000 feet wide with less than 200 feet of vertical displacement. A few deposits occur along the trough. Most mines lies southeast of the trough, however, beyond its structural limits but well within the zone of intense fracturing and brecciation. The deposits commonly have a linear trend following steep fractures or irregular solution channels. Blanket deposits occur in favorable beds. Gangue and ore minerals replace the limestone of favorable beds leaving the chert relatively unaffected. The chief ore minerals are sphalerite and galena. The chief gangue minerals are dolomite, jasperoid and calcite. Accessory minerals include marcasite, chalcocite, pyrite, enargite, and barite. For further details of the district geology see Behre, et al (2).

#### Results

Table 1 is a summary of the results obtained in this study. Specific observations based on this data include:

1. The Miami-Picher district sphalerite liquid inclusion temperature values range from 80° to 115° but the FeS% does not exceed 0.14%. This suggests that the amount of FeS present during the formation of sphalerite may have been very low and that significant variation in FeS content could not take place. The small amount of pyrite contemporaneous with this sphalerite is in agreement with a low iron environment of deposition.

2. The data from the other areas sampled indicates only the crudest tendency for FeS content to decrease with decreasing temperature.

3. Correlations of FeS percentages and the shade of sphalerite within individual specimens from the Upper Mississippi Valley District is reasonably good but not without inconsistencies.

4. Correlation of a set of layers in several specimens of sphalerite occurring at different locations in one mine by means of iron content determinations seems feasible.

TABLE 1  
 Summary of Liquid Inclusion Temperature Values and FeS Weight  
 Percentage Determinations for Sphalerite

Mine	Andrews	Upper Mississippi Valley Bautsch	Liberty	Deardoff	Miami-Picher	Total
Number of specimens	6	7	8	6	15	42
Number of samples	30	24	27	17	23	121
Number of samples with FeS weight % values	27	22	25	17	23	114
Number of samples with temperature values	13	18	18	7	17	73
FeS Weight % values						
Minimum and maximum	0.12-2.08	0.10-2.20	0.10-1.02	0.61-0.92	0.04-0.14	
Average	0.64	0.82	0.39	0.74	0.08	
Liquid inclusion temperature values (°C).						
Minimum and maximum	75-103	69-110	73-98	82-128	80-115	
Average	91	94	86	92	100	

### Conclusions

Based on the FeS determinations and the related liquid inclusion temperature data, the following statements and conclusions can be drawn.

1. The FeS% in this study of 114 samples of sphalerite taken from 40 specimens ranged from 0.04% to 2.20% by weight. The maximum FeS content for sphalerite formed at a temperature of 138° in equilibrium with FeS<sub>2</sub> was estimated by Kullerud to be about 3.7% (6). Later corrections by Skinner and others (10) suggest that even this figure may be too low. Thus the FeS content of the studied specimens gives no indication of temperatures higher than those given by liquid inclusion determinations and to this extent the data on FeS contents serve to support these determinations. The darker bands of the Upper Mississippi Valley district for which there are no liquid inclusion determinations are 0.4% to 0.5% higher in FeS% than the bands giving maximum measured temperature values. This increase, about one-fourth of the total temperature variation, suggests that the temperature of formation of sphalerite of the darker bands would be near the 128° maximum found by liquid inclusion study.

2. Kullerud's FeS% determinations of sphalerite samples from Mississippi Valley type lead-zinc deposits are at variance with the determinations made in this study. Seven of his ten determinations exceed the maximum values found in this study and range up to 6.22%. Furthermore, these high values are not supported by the liquid inclusion data. Quite possibly contamination of the sphalerite samples with small amounts of included pyrite may account for Kullerud's anomalously high values.

3. The poor correlation of the FeS% and the liquid inclusion temperature determinations in a given sample does not permit the establishment of any direct fixed relationship between the two even for individual mines and precludes the possibility of pressure determinations based on these two lines of inquiry in this study.

4. The FeS% of the sphalerites in the deposits studied are not dependent upon temperature of formation as shown by the lack of direct correspondence between liquid inclusion temperature values and the FeS%. This is not surprising in that there is no evidence that sufficient FeS was available in solution to saturate the sphalerite lattice. Kullerud gives the presence of pyrrhotite as positive evidence for such conditions of saturation, but pyrrhotite does not occur in these deposits. Kullerud and others (8) have experimentally determined the curve for equilibrium with pyrite. This curve is sufficiently higher than the ZnS-FeS curve at moderate temperatures permitting considerable variation in FeS content independent of temperature and dependent only on the amount of iron available in relation to sulphur. The evidence gathered from this study suggests that the use of FeS content variation of sphalerite as a precise geological thermometer, especially under low temperature conditions, is subject to question because of factors (chiefly abundance of FeS ion) other than temperature controlling the variation.

5. The lack of significant FeS% variations and any apparent relationship between probable temperature of deposition as shown by liquid inclusion data in the Miami-Picher district suggest that there was insufficient FeS available to enter the lattice of the sphalerite in amounts much above 0.14% regardless of the ability of the lattice to take up more FeS.

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