Fluid Inclusion Studies of Ore Deposits in the Viburnum Trend, Southeast Missouri

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Abstract

Although good material is scarce, 109 small fluid inclusions in sphalerite were studied, at least some of which are probably primary in origin. Most samples came from mines or drill cores in the Viburnum Trend in southeast Missouri.

Metastability was observed frequently during freezing point determinations. Freezing temperatures are mainly in the range −20 to −28°C, corresponding to very saline brines; homogenization temperatures are mainly in the range 94° to 120°C. These sphalerite fluid inclusion data fit into the ranges observed for the ore-depositing fluids in most Mississippi Valley-type deposits, even though the district is different in some respects.

In addition, primary inclusions were studied from the associated, but presumably later, gangue calcite. Fourteen inclusions in Viburnum calcite all contain brines which are much less saline. Most inclusions out of 16 in calcite from three areas in the nearby Old Lead Belt yielded similar low salinities. Twelve inclusions in sphalerite from pyrite-sphalerite-calcite veins in the Precambrian basement beneath the Fletcher mine have trapped hotter, more dilute fluids and hence represent a different mineralization.

Introduction

In 1973 the writer was invited to present a paper on fluid inclusions in the Viburnum Trend ores at a meeting of the North-Central Section of the Geological Society of America at Columbia, Missouri, but no abstract was submitted at that time. At the recent Viburnum Trend Symposium this report was not repeated but it seemed appropriate that the data be reported with the other papers stemming from the Symposium.

Nature of the Samples

Detailed notes on the individual samples are in the Appendix. Although the samples examined looked fairly suitable in hand specimen, they were surprisingly poor in usable fluid inclusions, and some samples, not listed in the Appendix, yielded none. To minimize the uncertainty as to the relationship between the fluids found and the ore-forming fluid, most of the work was done on inclusions in sphalerite, although some gangue calcites were also run, including some from the nearby Old Lead Belt. Paragenetic data on the samples used are rather limited, mainly because of the physical nature of many of the samples themselves. The most obvious evidence for sequential deposition is the common perching of sphalerite crystals on larger galena crystals, and the occasional filling of a sulfide-lined vein or vug with late calcite.

One special feature of the samples used should be noted. The nine core samples containing coarse crystals of sphalerite represent the best available after a search of core from many hundreds of drill holes, yet all nine are either from the very bottom of the Bonnette Dolomite, or near the top of the formations above the Bonnette. None are from the common ore horizons (P. E. Gerdemann, written commun., 1966).

Nature of the Inclusions Studied

Because there are so few inclusions, all suitably large inclusions were run (Figs. 1–4). When more than a few recognizably primary inclusions could be found in a sample, however, obvious secondary inclusions were not run. The origin of many inclusions could not be determined; at least part of these are probably pseudosecondary. Except for one inclusion that was 56 μm long (Fig. 1), all were in the 10 to 25 μm range. All contained vapor and liquid; no daughter crystals were seen.

A brief examination of barite from the Hornsey Bros. mine in Potosi, Missouri (northeast of the Viburnum Trend), showed that it contained many inclusions, as much as 10 percent by volume. These were unsatisfactory for study, however, because there was much evidence of both leakage and necking down.

Experimental Method

Doubly polished plates were cut from each sample, either through the center of single larger crystals, or through the tops of druses of smaller crystals, after embedding in epoxy. Selected inclusions were examined first in a circulating acetone freezing stage (Roedder, 1962), to determine the salinity of the inclusion fluids from the depression of the freezing point. The use of fiber optics illuminator was es-
sential in both freezing and heating runs. To avoid erroneous results from the common metastability due to failure to nucleate ice, the freezing point was always approached from below (i.e., with ice already present). Calibration was achieved by means of capillary tubes containing minute amounts of liquids of known freezing point (Roedder, 1962).

Freezing of the inclusions prior to the actual freezing temperature determination was frequently difficult, because of extensive metastable supercooling. This might be expected for these small, highly saline inclusions, presumably formed from very slow-moving fluids. As shown by Roedder (1962), small inclusions can be expected to show metastable equilibria more commonly than large ones, and slow fluid flow at the time of trapping tends to eliminate the heterogeneous nucleation centers so abundant in normal surface waters. Thus, groups of inclusions in several samples were not frozen after 18 hours at -78°C. Expansion on freezing eliminated the vapor bubble in some of the inclusions, which, upon warming, resulted in metastable superheated ice under negative pressures (Roedder, 1967). As a result, the disappearance of the last ice crystal in these particular inclusions is only a maximum freezing temperature, and the true stable equilibrium freezing temperature may be many degrees lower.

Both the precision and the accuracy of the freezing data obtained are lower than usual because of the small inclusion size and generally poor optical quality. Some of the freezing temperatures were determined only to ± 1°C, but many have a precision (and possibly an accuracy) of ± 0.1°C. Occasionally optical limitations were so severe that only crude freezing point limits could be established. Inclusions in calcite gave particular problems, not only with the metastable superheated ice. As a result of the small bubble size and low salinity, expansion on freezing fractured many of the inclusions, causing leaking in the freezing stage. If this leakage was all outward, the results are probably valid; but if any acetone leaked in, the freezing temperature would be reduced.

Fig. 1-4. Inclusions in sphalerite from the Viburnum Trend. Transmitted plain light. Scale bars in micrometers.

Fig. 1. Sample ER66-51, Viburnum No. 29 mine. Crystal grew from right to left as a subparallel aggregate; the sawtooth growing crystal front fractured and trapped a plane of pseudo-secondary (?) inclusions, and further growth (to left) was essentially free of inclusions. Homogenization temperature 101°-107°C; freezing temperature < -4.2°C (metastable).

Fig. 2. Sample ER66-61, Fletcher mine. Red sphalerite from veins in Precambrian basement. Probably a primary inclusion, with freezing temperature -3.6°C.

Fig. 3. Sample ER66-56B, Viburnum No. 27 mine. Secondary (?) plane of inclusions homogenizing at 112°C and freezing at -10.8°C.

Fig. 4. Sample ER66-55, Viburnum No. 28 mine. “Large” primary inclusion, homogenizing at 120°C and freezing at -28.2°C.
Fig. 5. Freezing and heating results on inclusions from the Viburnum Trend and Old Lead Belt samples. Each square represents data on one inclusion. Solid squares—stable equilibrium data; open squares—metastable equilibrium data (superheated ice, true value lower); L—leaked on cooling stage (true value may be higher); P—primary inclusion; S—secondary inclusion (unlabeled are of unspecified origin). Arrows over two homogenization data indicate true value is some unknown but probably a small amount higher. Results on red and yellow sphalerite in sample ER66-61 are similar. The bulk of the data points have a precision not much larger than the width of the square.
drastically. Such values hence must be considered to be lower limits only.

Following the freezing runs, the homogenization temperatures of some of the same inclusions were determined with a very slow (2–4 hr) heating schedule on a Leitz 350 heating stage. Organic melting point standards were used for calibration (Roedder, 1976). Care was taken to avoid spurious data from stretching of the inclusions (Larson et al., 1973) by always completing measurements on the lowest temperature inclusions first before going on to the higher ones. No special features worth noting were observed in the homogenization runs, except that optical problems permitted determination of only a minimum value for two inclusions; unfortunately, one of these (in sample ER66-61) was one of the higher values obtained in the study. Most of the homogenization results have a precision of ±1°C and an accuracy of probably ±2°C. A few of the samples were examined on the crushing stage (Roedder, 1970) to check on the possible presence of noncondensable gases such as methane.

Results Obtained

The freezing and heating data are summarized in Figure 5. With a few notable exceptions, the freezing temperatures of all inclusions in sphalerite were in the range −20.4°C to −28.2°C, corresponding to very saline fluids. Most of these salinities cannot be expressed in units of percent NaCl equivalent, because the lowest freezing temperature in the pure system NaCl-H₂O is only −21.1°C (at 23.3 wt % NaCl); obviously cations other than Na must also be involved. For example, a 25 percent CaCl₂ solution will freeze at −28°C. Most of the freezing temperatures are higher than −20.4°C. Most of the freezing temperatures higher than −20.8°C (Fig. 5) are either for secondary inclusions or for those that formed metastable superheated ice. The data for samples ER67-15 and ER66-61, however, appear to be valid, indicating that fluids much less saline were present during the trapping of the inclusions in these two samples.

Most of the meager data on inclusions in late carbonate samples (Fig. 5) show that they contain fluids far more saline than ground water, and even more saline than sea water, but less saline than the fluids in the sphalerites. Sample ER57-44 is a notable exception in that four primary inclusions in it yielded very low freezing temperatures (−20.8 to −23.4°C), and even these are only maxima, as they all involved superheated ice.

Relatively few homogenization temperatures were determined. Except for sample ER66-61 from the Fletcher mine, all inclusions homogenized in the range 82° to 137°C. As all other high-salinity inclusions had similar apparent gas-liquid ratios, it is safe to assume that they would homogenize in the same range. Because the gas/liquid ratios in the inclusions in the late carbonates are similar to those in the sphalerites, but the salinity is generally lower, these inclusions would presumably have lower homogenization temperatures than those in the sphalerite.

The mine shaft in the Fletcher mine intersected pyrite-sphalerite-calcite veinlets in the Precambrian basement. Inclusions in this sphalerite (sample ER66-61) were unusual. They contained the least saline fluids (stable freezing temperatures of −2.5 to −3.6°C) and had the highest homogenization temperatures (148° to 152°C).

Crushing tests on calcite from this sample showed gas under pressure of perhaps as much as 20 atmospheres, but, in contrast with data from inclusions in many Mississippi Valley-type deposits, this gas is not soluble in kerosene and hence is not methane. It could be CO₂.

Interpretation and Conclusions

Although the Viburnum Trend deposits have several geological features in common with other Mississippi Valley-type ore deposits, they have some unusual features, in particular, the presence of nickel and cobalt minerals, and of some copper-iron sulfides (see other papers in this Symposium). The fluid inclusion data on sphalerite reported here, although unfortunately very limited in geographic and paragenetic distribution over the district, indicate the same general characteristics for the ore fluids as for those found in most other Mississippi Valley-type deposits: the ores were formed from hot, saline brines that must have contained significant cations other than Na (presumably Ca). Homogenization temperatures range from 94° to 137°C. Although the age of the mineralization is not known (Doe et al., 1975), the depth of cover over the deposit was probably never thick (Thacker and Anderson, 1975), so the pressure correction to be added to these homogenization temperatures is small. Ore fluid movement was presumably slow, as shown by the very common occurrence of metastable equilibria on freezing. The only evidence for paragenetic sequence is that the sampled sphalerites are generally later than galena, but there are no data on inclusions in the galena.

Late carbonate vein and vug fillings formed from much less saline fluids that were not as hot as those that formed the ores. An exception is the calcite filling of a sulfide-lined vug at Bonnerfe in the Old Lead Belt (ER57-44), which formed from fluids just as saline as those forming the sphalerite in the Viburnum Trend.
The most striking exception to all the above data comes from primary inclusions in sphalerite and calcite veins in the Precambrian ridge under the Fletcher mine; these formed from fluids of low salinity, approximately equal to that of sea water. These data, and a few secondary fluid inclusions in this sphalerite that contain highly saline brines, suggest that crystallization of these veins predated the main ore fluid mineralization. Isotopic evidence on galena from these veins bears this out. B. R. Doe has identified this as Precambrian galena (Doe and Delevaux, 1972) on the basis of recent analyses by Maryse Delevaux (U. S. Geol. Survey, Denver).

Because the nine core samples which have typical coarse crystals are stratigraphically restricted to horizons other than the normal ore-bearing horizons, the possibility that they represent atypical mineralization should be considered. However, there is no recognizable difference between the data from inclusions in these samples and those from crystals of sphalerite within the main ore horizons. There may well be minor differences in composition, but certainly the gross salinities and temperatures are similar. In a similar vein, if the samples studied formed by recrystallization of an earlier ore deposit, the inclusion data obtained would represent the fluids responsible for the recrystallization, and not tell us anything about the fluids forming the earlier deposit. Several lines of evidence (Roedder, 1976) seem to preclude this interpretation for the Viburum Trend deposits.

The inclusion data obtained in the present study are similar to those obtained by Leach (1973) on sphalerite from a series of small, high-grade deposits of galena, sphalerite, and barite from the central Missouri barite district to the northwest of the Viburum Trend, and in the northern Arkansas zinc district to the south. Although there obviously must have been major differences in the environment of ore deposition to yield the gross differences in total mass and overall metal content of these several types of ore deposits, I conclude that the Viburum Trend deposits, along with the others, formed from hot, saline, probably slow-moving brines.

Acknowledgments

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REFERENCES


APPENDIX—SAMPLES STUDIED

Note: Sample information in quotes is from St. Joe Minerals Corporation.

ER66-41. "66W56, 1071.8 feet depth. Lamotte-Bonneville contact, Brushy Creek, 19/20. Sample no. 1." Yellow-brown 1.5-cm sphalerite crystals in solid core.

ER66-44. "66W35, 1121.9-1122.0 feet depth. Lamotte-Bonneville contact, 19 zone. Sample no. 4." Yellow-brown 1.5-cm sphalerite crystals in solid core.

ER66-49. "Viburum No. 29 mine, 39 stope, 7-zone Algal reef and tan oolitic dolomite. Sample no. 9." Sample A—galena cubo-octahedra (3-mm) with smaller sphalerite crystals in calcite. Sample B—composite 3-mm sphalerite crystals lining vug. Euhehdral carbonate rhombs are enclosed within single sphalerite crystals.

ER66-50. "Viburum No. 29 mine, 105 stope. Breccia ore. 5 zone. Algal spotted and oolitic dolo-
mide. Sample no. 10." Pale yellow 2-mm sphalerite and 4-mm galena crystals coating breccia fragments.

ER66-51. "Viburnum No. 29 mine, 105 stope. Breccia ore. 5-zone Algal spotted and oolitic dolomite. Sample no. 11." Crust of 2-mm yellow sphalerite crystals.

ER66-52. "Viburnum No. 29 mine, 105 stope. Breccia ore. Sphalerite on 1-1/2" galena cube. 5-zone Algal spotted and oolitic dolomite. Sample no. 12."

ER-66-55. "Viburnum No. 28 mine, zone and stope unknown. Sample no. 15." Disseminated brown sphalerite and galena.

ER66-56. "Viburnum No. 27 mine, stope no. and rock zone unknown. Sample no. 16." Coarse galena coated with small sphalerite crystals, in vug. Sphalerite crystals have (growth?) segments with many extremely narrow, parallel, very deep purple cross bands and enclose carbonate rhombs.


ER66-58. "Federal Division No. 8 mine, 1861 mine map sheet. 7 zone algal dolomite. Sample no. 18." Massive and vuggy crystallized sphalerite.

ER66-59. "Federal Division No. 8 mine, 1668 map sheet. 7 zone, Bonnette Formation. Sample no. 19." Scattered 1-2-mm ruby sphalerite crystals lining vug.

ER66-61. "Veinlets in Precambrian igneous rock, Fletcher mine shaft area. Sample no. 21." Sphalerite is mainly yellow, with large numbers of enclosed bright pyrite cubes, in a matrix of white calcite. Several 0.5-mm grains of sphalerite are dark red.

ER67-15. "Brushy Creek Division, 9 miles south of Bixby, Missouri. Hole no. 67W32; depth 985 feet; Middle Bonnette 5 zone." Euhedral yellow sphalerite crystals on surface of galena (plus carbonate rhombs).

ER67-16. "Viburnum Division, 4500 feet SSW of Bixby, Missouri. Hole no. 67W4; depth 1026.5 feet. Middle Bonnette Formation 5 zone." Brown, 2-mm sphalerite crystals with dolomite and quartz in vug in dolomite.

ER57-44. Calcite, pinkish, filling vugs lined with chalcopyrite and pyrite. 246 stope, probably from 15-bed, St. Joe mine, Federal Division, Missouri (Old Lead Belt). Coll. by E.R.

ER57-48. Late calcite vein, lined with galena crystals. "Tarr Park," Federal Division, Missouri (Old Lead Belt). Coll. by E.R.

ER57-49. Calcite, single-crystal filling vug in massive pyrite. Federal Division, St. Joe mine, 295 stope, Missouri. Coll. by E.R.