Changes in Ore Fluid with Time, From Fluid Inclusion Studies at Creede, Colorado

E. Roedder

U. S. Geological Survey, 959 National Center, Reston, Virginia 22092, USA

Introduction

The OH vein at Creede, Colorado, was selected in 1957 as the subject of a detailed and multifaceted study of the environment of ore deposition by a team of geologists at the U. S. Geological Survey (Barton et al., 1971). One of the facets was to be a study of the evidence obtainable from fluid inclusions in the vein minerals and their significance toward an understanding of the environment of deposition. The single most serious hurdle in any such inclusion study is the nature of the available samples. Ideally, they should have identifiably primary inclusions of adequate size, clarity and abundance, distributed throughout a wide range of minerals and recognizable stages in the depositional history of the deposit and over a wide vertical and horizontal range in the vein. In these respects, the OH vein exceeded our fondest expectations.

In the present paper I report only a small part of the larger continuing joint investigation, as an indication of the nature of the data available from fluid-inclusion studies and of the significance of these data as evidence of the environment of ore deposition at Creede and hence possibly at other similar vein deposits.

General Geology

The OH vein is one of a series of steeply dipping epithermal Ag-Pb-Zn-Cu veins of 24 m. y. age in the Creede mining district, Mineral County, Colorado, on the eastern edge of the San Juan Mountains (Barton, Jr., Betchler and Roedder, unpublished data). The mineralization in these veins is essentially fracture-filling, with very little replacement and generally minor hydrothermal alteration of the enclosing rhyolitic welded tuff country rock.
SAMPLE LOCATION AND NATURE

The particular sphalerite sample studied (NJP-X-1-59) came from the 9 level on the OH vein, at present approximately 350 m below the present surface and probably no more than 600 m below the surface at the time of deposition. It is a group of zoned subparallel sphalerite crystals, in which the total depositional thickness is approximately 5 cm. The sample was cut into a series of doubly polished plates, mostly ~3 mm thick; special care was taken to avoid damage to the inclusions. The colour of individual zones in transmitted light varies from almost colourless through yellow and orange-red to brown, in plate thicknesses of 2-5 mm. Analyses of similar zones in other crystals from the deposits show that variation in iron content is the major (but not sole) cause of the colour variation here; the range for these particular zones is from about 0.1 to 3 mole % FeS.

The complex “stratigraphic succession” in this crystal (and other co-genetic crystals from the sampling area) had been previously established by P. M. Bethke and P. B. Barton, Jr., of the U. S. Geological Survey. This was done using many doubly polished plates from a series of crystals, as no individual vug was necessarily a site of continuous deposition throughout the history of the deposit. The criteria used to recognize and correlate zones will be detailed elsewhere (P. M. Bethke and P. B. Barton, Jr., unpublished data). As in any complex stratigraphic correlation, no single criterion is necessarily definitive; hence, they used a combination of criteria, including transmitted light colour and its variability, zones of accidental solid inclusions, birefringence, codeposited minerals, minor-element concentrations and leach zones (i.e. discontinuities), and particularly, the sequence of occurrence of such features. Each leach zone represents a time period when the solutions passing this particular point were no longer saturated with respect to sphalerite; they may well have been or become saturated elsewhere, and deposited sphalerite, before and/or after this point. Vagaries of ore-fluid movement through the tortuous and possibly changing channels of rubble in the vein resulted in large differences in the thickness of given zones, and in the relative thicknesses of the various zones, in individual crystals. Using the procedures listed above, the 5-cm band was subdivided into 20 “stratigraphic horizons” or zones; all 20 zones together make up only the latest quarter of the ore-depositional history at Creede.

NATURE OF THE INCLUSIONS

The inclusions selected were almost certainly primary, mostly irregular and smoothly rounded to subhedral, and in the size range 15 to 450 µm. As these samples have very few planes of pseudosecondary or even secondary inclusions, the possibility of opening and replacement of the former fluid with new fluid at a different set of values for P, T and X is very unlikely. Approximately 10 inclusions (to a maximum of 32) were selected for runs from each of the 20 sequential zones (230 inclusions in all, of which nine leaked during homogenization and had to be discarded). This selection is an important part of the process, as only a very small percentage of the available inclusions could be used. To be selected, an inclusion had to fulfil all three of the following
criteria: (1) good evidence of primary origin; (2) optimum optical quality; and (3) clean-cut evidence of occurrence in a specifically identified zone. The evidence of primary origin generally consisted of the occurrence of large, isolated inclusions, particularly at irregularities in the visible zoning indicating imperfect growth. The optical quality of an inclusion is mainly a function of its shape and the absence of confusing detail in the plate above it. Although the small bubble in an inclusion near its homogenization point can usually be revealed with a fibre optics illuminator, the same is not true with respect to small crystals of ice near the freezing temperature, particularly in sphalerite. As both homogenization and freezing temperatures were to be obtained on the same inclusions, only inclusions with smooth and flat or only gently curving upper and lower surfaces could be used. The problem of identifying with certainty the specific zone in which an inclusion occurs is minimal in sample plates that have vertically oriented broad zones of contrasting features, but becomes very difficult in plates that have strongly inclined thin zones and little contrast. This is particularly true where growth has been irregular and the zone boundaries are convoluted in three dimensions, so that simple tilting of the section relative to the line of sight is inadequate. An additional problem arises from the occasional presence of reentrants, either from solution or growth phenomena, which may result in a given inclusion, formed in such a reentrant, appearing to be in an earlier zone.

After inclusion selection, small parts of the plates, each containing one or more selected inclusions, were cut out for the runs. Some of the zones were represented by samples from more than one plate, or from several places on a given plate.

LABORATORY TECHNIQUE

The homogenization temperatures (all in the liquid phase) were determined with a Leitz model 350 stage, using very slow heating schedules and essentially letting the temperature level off after each increment, particularly near the homogenization point. Calibration was by means of organic-melting-point standards, sealed in vacuum in minute glass capillaries, placed directly on the stage with the unknowns. Use of a very flexible fibre optics illuminator (~3 mm in diameter) from either above or below the stage, permitted observation of the disappearance of the vapour bubble in many inclusions that would otherwise be impossible to use. Duplicate runs on some inclusions and measurements of the vapour bubbles before and after the runs, were used to eliminate the possibly spurious data from the nine inclusions that leaked.

The freezing runs were made using somewhat modified versions of the technique and the circulating, refrigerated-acetone stage described previously (Roozener, 1962). In every run, the freezing temperature obtained refers to the disappearance of ice as a pre-established phase, using a very slow temperature increase near the final stages of the melting. No evidence of crystalline hydrates such as $\text{CO}_2 \cdot 5\frac{1}{4} \text{H}_2\text{O}$ was noted. Calibration was obtained by means of tiny sealed capsules of pure water and $n$-dodecane placed on the stage with the samples.

The possible precision of such temperature measurements will vary widely with the nature of the inclusions, but even the poorest of those used here...
permitted an estimated precision of ±1 or 2°C on the homogenization temperatures and ±0.1 or 0.2°C on the freezing temperatures. The accuracy is much poorer, of course, but is exceedingly difficult to evaluate. The possibility of unintentional operator bias was avoided by making the runs essentially as “blind” determinations, by several operators, over a period of months, without the operators knowing the interrelationships of the individual chips.

RESULTS

The results of these 221 inclusions are plotted in Fig. 1, where $T_H$, the temperature of homogenization, is plotted against $T_F$, the temperature of freezing, for the same inclusion, for each of the 221 pre-selected inclusions that survived the heating without leakage. These results are surprisingly consistent. All inclusions for each given zone, even though they may have been selected from parts of the zone at some centimetres distance from each other in the sections, form very tight clusters on the diagram. The total range for all inclusions is 198 to 269°C ($T_H$) and −3.1 to −7.3°C ($T_F$, corresponding to a salinity of 5.1 to 10.9 weight percent NaCl equivalent).

The loci of the individual groups on Fig. 1, numbered there in the order of their depositional sequence, show that during the deposition of this 5-cm layer of sphalerite, the salinity and temperature first increased somewhat, and then decreased significantly. Superimposed on these general trends, however, are several smaller reversals. Even as these minor reversals are statistically significant, however, and are not just due to experimental error, because each zone's location on Fig. 1 (except zone 3, in which only one suitable inclusion was found) is based on multiple points within the areas outlined. With three exceptions, the data points from one group do not overlap with those from adjacent groups in the sequence. One exception is in zone 4; four of the 21 inclusions selected as being in zone 4 have values for $T_H$ and $T_F$ within the tight cluster of 27 outlining zone 5 on the figure. It is not known whether these four represent a real variation in the fluids during deposition of zone 4, or whether they were actually zone 5 inclusions that only appeared to be in zone 4. The second and major exception is the almost total overlap of the area for zone 5 with that of zone 6. Although the distinction between the host sphalerite for these two zones was fairly obvious, it appears that the fluids depositing this sphalerite changed very little in temperature and salinity. The third exception is a single inclusion, which falls along with the 14 others in zone 11, but was originally identified as being in zone 10. The other four inclusions identified as zone 10 form a tight cluster, so theoretically the small circle for zone 10 as plotted should have a long extension down to overlap zone 11 to include this one inclusion, presumably misidentified as to zone.

The maximum range of temperatures of homogenization for inclusions from any given zone is only 4°C, except for zone 4, in which the range is 6°C, because of the four anomalous inclusions mentioned above. The average range is only 2°C, including the data for zone 4. The equivalent maximum range of temperatures of freezing is 0.6°C, although the average range is only 0.2°C.
In an earlier publication, some preliminary homogenization and freezing data were presented on about 400 primary inclusions from Creede (Röeder, 1965). That work was performed on samples from a series of locations throughout the mine, both near and far from the present sample. However, it was performed before the detailed stratigraphy was worked out; hence, at that time, the 20 zones discussed here were lumped into two zones, a "dark zone" (corresponding to zones 1-14 here), and an "outer yellow-white zone" (corresponding to zones 15-20 here). The measurement techniques used then were also neither as precise nor as accurate as those used now. The ranges found in the early work for the homogenization and freezing temperatures (°C) for the dark and the outer yellow white zones, respectively, were 205 to 265, —4.6 to —8.3; and 189 to 215, —2.95 to —4.0. The equivalent ranges (°C) for the present work (from Fig. 1) would be 241 to 269, —4.7 to —7.3; and 198 to 231, —3.1 to —4.6. The correlation of these two sets of data cannot be exact, as different samples, inclusion selection procedures, and laboratory techniques were used, but both sets of data show a general decline in temperature and salinity with stage of mineralization, from the early "dark" to the later "outer yellow-white" zone.
SIGNIFICANCE OF THE RESULTS

A series of conclusions can be drawn from these results:

1. The variations used to establish the sphalerite "stratigraphy" are paralleled by changes in the ore fluids trapped in inclusions. This parallelism may indicate but does not, of course, require a cause and effect relationship.

2. The fluids forming this deposit did not simply decrease in salinity and temperature with time, as is frequently considered to be implicit under the assumption of eventual quenching and dilution with cold ground water.

3. Even the less distinct boundaries can be significant in that the ore fluids changed appreciably from one zone to the next. These changes are well above experimental errors and generally are larger than the variation within a given zone.

4. The ore fluid changed abruptly at each zone boundary but was constant during the deposition of each zone. This places some constraints on the hydrology of the system and implies that the cause or causes of the sphalerite zonation were surprisingly static throughout the deposition of each given zone, as the variations in $T_H$ and $T_F$ within each zone are small.

5. If such a fine structure is ignored by blind sampling, serious errors can occur in the correlation and interpretation of fluid-inclusion data with the results of chemical analyses of the host and in the assignment of thermal gradients during deposition.

6. Primary inclusions can be recognized adequately in this material. Any pseudosecondary or secondary inclusions would have degraded the consistency seen in Fig. 1.

7. The inclusions have not necked down since they were trapped. If they had, there would be a gross horizontal dispersion of the individual groups on Fig. 1.

8. The experimental techniques used have excellent precision. There is no real proof of the accuracy of these numbers, but the precision is much more important in the present study. As these inclusions were, in all probability, trapped under very shallow conditions, the temperature of homogenization ($T_H$) is essentially equal to the temperature of growth. The maximum estimated pressure correction to be added to $T_H$ to obtain the temperature of formation for these samples is only a few °C.

9. No recognizable difference was noted between large and small inclusions from the same group. This is of interest in that it seems to contradict some experimental data presented by Barnes et al. (1969) that they interpret as evidence that fluid inclusions trap a compositionally nonrepresentative sample of the fluid present.

10. These fluid inclusions obviously did not leak. If leakage has occurred, it would have to have been essentially identical for all inclusions in each given group, an unlikely event.

Much smaller sphalerite crystals in this same mine have probably formed from the same range of fluids, but their size may not permit as detailed stratigraphic assignment of any given inclusion as in larger crystals. Detailed correlation of growth zones from one crystal to another in the same sample and eventually with other samples and other parts of the mine is essential to understanding many aspects of ore deposition, such as the nature of the hydrologic flow in the system, the establishment of the contemporaneity of...
deposition of several different minerals, the chemistry of the ore-forming fluid, and eventually, the cause of the ore deposition.

Acknowledgements. I am very indebted to several of my colleagues on the U. S. geological Survey for help in this work. P. B. Barton, Jr., and P. M. Bethke prepared most of the polished plates, and H. E. Belk in made most of the tedious and very careful heating and freezing determinations. The entire study would have been impossible without the preceding extensive and detailed paragenetic studies by P. M. Bethke and P. B. Barton, Jr., that provided the chronologic sequence, and I have profited from many stimulating discussions with them. I am also indebted to P. B. Barton, Jr., and J. E. Hass for reviews of the manuscript.

REFERENCES


