Temperature, Salinity, and Origin of the Ore-Forming Fluids at Pine Point, Northwest Territories, Canada, from Fluid Inclusion Studies

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Abstract

Although the Pine Point ore is relatively poor in usable fluid inclusions, some sphalerite crystals from replacements, vugs, and from "colloform" crusts were found to contain primary or pseudosecondary liquid-gas inclusions adequate for study. Most (132 of 133) of these had low freezing temperatures, indicating exceedingly saline brines. The 112 inclusions suitable for filling-temperature determination homogenized at +52° to +97° C. A very small pressure correction must be added to obtain the trapping temperature.

Dolomite crystals from some of the same vugs contain large numbers of primary inclusions, many of which have leaked. The twenty-three that presumably have not leaked had filling temperatures of 90°-100° C, but somewhat lower salinities. Inclusions in late calcite appeared to have similar gas-liquid ratios, but had still lower salinities. The significance of these data lies in the limitations they place on the choice of possible mechanisms of origin of these large deposits. This choice, in turn, may influence the success in prospecting for blind ore bodies. There is general agreement that the deposits are of Mississippi Valley type. Although the high salinities may reflect solution of salts from evaporites, as are now found to the south, the elevated temperatures seem to require deep circulation, perhaps through known faults in the underlying Pre cambrian. The densities of these brines, even at their elevated temperatures, are well above that of fresh, cold surface water, thus restricting the possible modes of circulation during ore deposition.

Introduction

The large deposits of zinc and lead at Pine Point have been described in some detail by Campbell (1966, 1967). The ore occurs as disseminated sphalerite and galena replacements and vug fillings, together with "colloform" sphalerite and coarse galena cavity fillings in solution breccia, at certain stratigraphic horizons within a large, coarsely recrystallized porous dolomite barrier reef of Middle Devonian age. The reef effectively separated the large Elk Point evaporite basin to the south from the open ocean to the northwest. Campbell also showed that although the Pine Point deposits have many characteristics in common with several other Mississippi Valley-type ore deposits, particularly southeast

1 Publication authorized by the Director, U. S. Geological Survey.
Missouri, Austinville (Virginia), Moresnet (Belgium), and Northgate (Ireland), there are notable differences in each deposit. The most obvious similarity between these and all other Mississippi Valley-type ore deposits is the lack of agreement as to origin. This problem of origin (or origins) has been the subject of considerable discussion, and a recent symposium on the subject (Brown, 1967) proves that not only is a consensus far from achieved, but that the various currently held theories still range widely, from essentially magmatic-hydrothermal through "concrete" brines to sea-floor or even fresh-water environments. In view of this range, it seemed desirable to examine Pine Point ores for possible fluid inclusions, which might shed some light on the problem of genesis.

Laboratory Studies

Materials Studied

Eighteen specimens from Pine Point are reported in this study. The specimens included six selected but unlocated specimens of ore from the 1965-1966 mine production, provided through the courtesy of Prof. A. J. Sinclair, University of British Columbia (ER 65-99, -100, -101 and ER 66-3a, -3b, and -4), eight specimens of coarse sphalerite crystals from the Pine Point area, provided through the courtesy of

Fig. 1. Primary inclusions in doubly polished plates of single sphalerite crystals, in transmitted light, showing small vapor bubble (v) in liquid (l). A. Small, isolated inclusion. Freezing temperature \(-24.6 \pm 0.3\)° C; homogenization temperature \(+93\)° C. Specimen ER 65-101. B. Similar to A, but from specimen ER 66-3b. Would not freeze during 20 hours at \(-78\)° C. C. Very large, isolated inclusion, showing apparently large spherical vapor bubble (compare with D). The dark zones are from total reflection at the ends of the wedge-shaped inclusion. Freezing temperature \(-26.2 \pm 0.2\)° C; homogenization temperature \(81 \pm 2\)° C. Specimen ER 66-3a. D. Very large, isolated inclusion similar to C, showing apparently small vapor bubble. Although this inclusion looks as though it should homogenize at a lower temperature than C, it actually homogenizes higher (91° C). The difference lies in this inclusion being flattened, so that area percent is approximately equal to volume percent, whereas the inclusion in C is thicker and three-dimensional, so that the bubble appears to occupy a larger area percent. If the liquid were pure water, these inclusions would homogenize at a considerably lower temperature, but these very saline brines have a much lower coefficient of thermal expansion than water. Specimen ER 66-3a.
TEMPERATURE, SALINITY, AND ORIGIN OF ORB-FORMING FLUIDS

Drs. Neil Campbell and F. S. Hurley, Jr., of Cominco, Ltd. (ER 67-36 through 43), and four specimens collected at the mine in 1967 by Dr. Louis Mody of the National Museum of Canada (ER 68-1a and b, 5, 8, and 10). Details on these specimens are given in the Appendix. Additional specimens that yielded no usable inclusions are not listed. One or more doubly polished plates, in the range of 0.1 to 1.5 mm thick, were cut from each.

Although these plates were relatively poor in usable fluid inclusions over 100 two-phase inclusions (liquid plus gas) were found that are believed to be mainly of primary origin (Roedder, 1967b; see also Figs. 1 and 2). A few may be pseudosecondary, resulting from the healing of fractures in a crystal during its growth. In addition, homogenization temperatures were obtained on one group of apparently secondary inclusions (about 100). Hard pyritobiumen is found on the walls of many of the vugs and there is oil staining in some of the nearby rocks (Campbell, 1966), but no evidence of organic matter was found in any of the inclusions.

Ore Fluid Salinities from Freezing Temperatures

After selection, the bubble in each inclusion was checked for sensitivity and direction of movement in a thermal gradient as an indicator of compositional variations in the fluid (Roedder, 1966). In all but one sphalerite specimen (ER 65-100) the bubbles that were free moved up a thermal gradient, toward a source of heat or the illuminated portion of the field.

Each of the specimens containing suitable inclusions was then examined on the freezing stage (Roedder, 1962) to estimate the salinity of the inclusion fluids. Considerable difficulty was experienced in freezing the inclusions. Many persisted as unfrozen, supercooled liquid at −78° C for periods of 1/2, 2 and even 20 hours, but all appeared to freeze in 10 minutes at −196° C (boiling liquid N₂). The determinations of the freezing temperatures of the inclusion fluids (Fig. 3) were not very accurate, due in part to the low temperatures involved, but mainly to difficulties in seeing ice crystals in optically rather poor material. A few of these results have experimental uncertainties as large as ±1° C, or as small as ±0.1° C, but most have an uncertainty of ±0.3° C.

Only 94 of the 154 inclusions shown in the lower part of Figure 3 had ice as the last solid phase to melt on warming. At the liquidus the remaining 60 (enclosed in the box in Fig. 3) had strongly birefringent rods and/or plates, with indices of refraction well above that of the solution. These are tentatively identified as NaCl·2H₂O, but could well be any of a number of other birefringent hydrates. Many of the inclusions having an NaCl·2H₂O (?) liquidus had only an estimated 5 or 10 volume percent of crystals present at −37° C, that dissolved only at temperatures as much as 25° higher, indicating a rather steeply sloping liquidus surface for this crystalline phase. This is true for NaCl·2H₂O in the pure system NaCl-H₂O, and presumably also is true for NaCl·2H₂O in the multicomponent natural systems that must be involved here. As the composition is unknown, it is impossible to estimate the salinity in weight percent of salts with any accuracy, but as a rough approximation, the freezing temperatures for pure NaCl solutions are given on Figure 3. These salinity comparisons are applicable only to inclusions with an ice liquidus. It should be emphasized also that the wide range in freezing temperatures for inclusions with an NaCl·H₂O liquidus may well correspond to a comparatively small range in brine concentrations (all greater than 23 percent), as the slope of the liquidus for this compound is generally steep.

Some of the inclusions in calcite, with bubbles so small that fracture might be expected on freezing, were run while immersed in oil in a miniature double-windowed cell inside the regular cell of the cooling stage. This technique prevents the entry of acetone, and hence permits reasonably accurate determinations even on inclusions that do fracture on freezing.

Freezing studies on the two aberrant inclusions in ER 65-100 showed that they contained brines only half as concentrated as the rest (Fig. 3).

2 Although all the "sphalerite" specimens exhibit some irregular birefringence, indicating deviation toward wurtzite, even those with "high" birefringence are believed to be mainly sphalerite.
Fig. 3. Plot of freezing temperatures and homogenization temperatures of fluid inclusions from the Pine Point deposit. All inclusions are believed to be primary or pseudosecondary, except for one group of secondary inclusions marked "S." Individual inclusions are indicated by a dot; an accompanying number and a line through the dot signifies that the indicated number of inclusions gave identical results, within the experimental uncertainty. A vertical bar indicates the range of values for the specified number of inclusions, with the mode indicated by a horizontal line. Three inclusions had superheated ice, under negative pressure (Roedder, 1967a); as these results are for metastable equilibrium, with the true freezing temperature an unknown amount lower, they are indicated with arrows pointing down. All heating runs resulted in homogenization in the liquid phase, and no pressure correction has been added, although it is probably small. Those freezing runs outside the box had an ice liquidus; those inside the box had an NaCl·2H₂O (ref—see text) liquidus. For comparison, the freezing temperatures for pure NaCl solutions are indicated on the left, from 0% to 23% (saturation). Not plotted are: 1) several inclusions that obviously leaked on freezing; 2) several inclusions whose bubbles disappeared into opaque areas during the heating runs, and 3) one inclusion in specimen ER 66–3b that homogenized at 108° C. This last result was included in the previously published abstract of this paper (Roedder, 1967d), but is now believed to be a result of leakage.
Ore Fluid Temperatures from Homogenization Temperatures

After the freezing runs, homogenization temperatures were determined for some of these same inclusions (Fig. 3) using a Leitz model 350 heating stage. In addition, a number of similar inclusions from other parts of the same samples were used. The effects of temperature gradients in the stage were minimized by essentially leveling off the temperature after each increment, and through the use of organic melting-point standards in capillary tubes placed on the stage with the sample chips. The major problem, however, was not calibration but the optical quality of the material. The rather low aperture afforded by the heating stage design makes it impossible to get light into many inclusions in sphalerite that appear perfectly transparent with a high power condenser and no diaphragm. Strong oblique illumination from above or below, using a flexible fiber optics illuminator, helped reveal the bubble in some cases, but most of the homogenization data of Figure 3 probably have an uncertainty of ±2°–3° C. As these deposits probably formed at rather shallow depths, the pressure correction that should be added to the homogenization temperature to get the trapping or formation temperature probably is only a few degrees.

Following the homogenization determinations, each inclusion was checked for leakage by either a repeat run, or by remeasuring the size of the bubble at room temperature, or both. Some of the inclusions failed to regain their bubble on cooling following homogenization.

One notable feature of these homogenization runs was the relatively wide variation in homogenization temperature for various inclusions even in the same sample, when considered in the light of the low overall temperatures. Although similar variation in homogenization temperatures can also be caused by necking down after trapping (Roedder, 1967b), the present results are believed to represent real variation in the formation temperatures.

Comparison with Previous Estimates of Ore Fluid Temperatures

Other than generalizations based on the type of occurrence, only three lines of evidence have been used by others to estimate the temperature of deposition of the ore body at Pine Point. Two of these yielded higher temperatures than found in the current work. Folinsbee and others (1965) measured the iron contents of sphalerites and state that they yield “Kellerud temperatures” of 360° to 140° C. More recent work of Barton and Toulmin (1966) has shown, however, that for the equilibrium assemblage pyrite-sphalerite, the iron content of the sphalerite may vary rather widely as a function of the fugacity of sulfur, and that the “sphalerite thermometer” for such assemblages is not yet calibrated.

Campbell (1966, p. 958) reports that traces of liquid petroleum occur in the limestones overlying the ore horizon, and in the surrounding coarse dolomite, but that in some vugs in recrystallized dolomite in the ore area only a hard pyrobitumen is found, in part as small glossy globules adhering to the walls of cavities. He reports that this material melts at temperatures “well above 100° C,” and suggests that due to higher temperatures in the ore area, the volatile fractions were stripped from the petroleum, leaving this residue. This must have occurred after the recrystallization of the dolomite, and possibly during ore deposition. This is an ingenious thermometric technique that would be expected to yield a minimum temperature, as the globules are presumed to have been liquid when they adhered to the walls of the vug.

There are, however, several possible sources of error in the use of such melting as a thermometric point which would tend to overestimate the minimum temperature. First, most such materials melt over a range, and have a “softening point” appreciably below the “melting point.” Actually, many show a more or less continuous decrease in viscosity with increase in temperature, and hence the “softening point” and “melting point” can be defined only in arbitrary terms based on standardized but empirical laboratory procedures. Nature had much time available, as much as 10⁶ or 10⁸ times greater than that of the laboratory experiment, to permit surface tension forces to pull these masses of viscous material into spheres⁴ at temperatures well below that at which they appear to melt. Second, if the hot solutions passing the globule were able to extract the more volatile, low-melting “plasticizers” from the liquid bitumen globule, it is possible that they could continue to do so even after the globule had hardened, as diffusion of small organic molecules to the surface of such a solid might still take place. Third, the original oil globules in the ore zone were, by definition, subjected to a different chemical environment than the others in neighboring rocks. Chemical reactions between fluid and oil, such as oxidation or catalytic polymerization, might have increased the viscosity of the droplets of oil without temperature necessarily being a factor in the process.

The most recent estimate of ore fluid temperatures is based on isotopic evidence. Folinsbee and others (1967) conclude, from a study of the oxygen and carbon isotopes in the primary limestone, the dolomite host and from gangue calcite and dolomite intergrown with the ore minerals, that the ores formed at a temperature of “about 100° C,” in agreement with the inclusion data presented here.

⁴ As they were probably immersed in brines, they were effectively in a zero gravity environment.
Metastability

In both freezing and homogenization runs, there was notable evidence of metastability (reluctance of the system to nucleate new phases). Not only did some of the inclusions fail to nucleate ice at temperatures certainly well below their true freezing temperature, but several (dolomite ER 66-3a, and sphalerites ER 66-3b and ER 68-1b) failed to re-nucleate a vapor bubble after it had been eliminated by expansion on freezing, resulting in metastable "superheated" ice under high negative pressures (Roedder, 1967a). As such data represent metastable equilibria, they yield only maximum temperatures, but these are compatible with the stable equilibrium results. The last ice crystal in the inclusion in dolomite melted at $-14.2^\circ \pm 0.4^\circ$ C into a stretched solution without a vapor bubble, under negative pressure, but adjacent inclusions that had regained their bubbles melted at $-19.8^\circ$ C. Similarly, the inclusion in sphalerite ER 66-3b (without a bubble) melted at $-20.9^\circ \pm 0.3^\circ$ C, whereas the ice in two other inclusions (with bubbles) in the same sample melted at $-27.2^\circ \pm 0.5^\circ$ C. Other inclusions failed to re-nucleate a vapor bubble on cooling after it had been eliminated during a homogenization run. Whether they result from a cooling run or a heating run, such inclusions contain a metastable, stretched fluid under negative pressure, with too low a density. This may persist for days or perhaps for geologic time.

Each of these instances of metastability is caused by the sluggishness of nucleation of a new phase—ice or vapor—under conditions where it should be present and stable. Although metastability occurs more commonly in small systems, the inclusions in these samples display it more often than inclusions of similar size from other environments. The most likely explanation for the greater incidence of metastability is the greater rarity, in these inclusions, of spurious solid nuclei in the solution, on which the new phases may form. It appears that the fluids trapped in these inclusions must be exceedingly free from such nuclei, as might be expected for fluids that have percolated very slowly through rocks.

Summary of Laboratory Results

Primary fluid inclusions in crystals of sphalerite from the ores at Pine Point have very low freezing temperatures, corresponding to very saline brines. Only a few exceptions were noted, most of which were in a pale yellow coarsely crystallized sphalerite that has replaced earlier fine grained, "colloform" sphalerite (ER 68-1b). Although no chemical analyses have been made, the presence of crystals believed to be NaCl·2H$_2$O in many of these inclusions at low temperatures verifies the high salinities.

The absence of visible crystals of NaCl, along with the above data, indicates the presence of other salts in addition to NaCl. The inclusions have homogenization temperatures in the range of about 50$^\circ$ to 100$^\circ$ C, and the temperature of trapping (i.e., the temperature of growth of the host crystals) was probably only a few degrees higher. Inclusions in individual specimens exhibit a range of as much as 30$^\circ$ C. The frequent occurrence of several types of metastability in the inclusions during the laboratory work indicates that these brines were exceedingly free from various solid nuclei in suspension, and in this respect were much cleaner than normal surface or ground waters.

Inclusions in dolomite contained somewhat less saline fluids trapped at about the same temperature range. Inclusions in coarsely crystallized late calcite appeared to have similar gas-liquid ratios, but contained much less saline fluids.

The nature of the available material precluded any attempt at correlation between salinity and homogenization temperature of individual inclusions. But if mixing of hot brines with cold surface waters is involved, as suggested below, this correlation should be observable. It is also possible that a more extensive study, using specimens of known spatial and sequential relations, might shed some light on the circulation patterns during mineralization.

Origin of the Ore Deposits

Structural Evidence

There have been only a few discussions of the genesis of these specific, rather recently developed deposits. However, Campbell (1966) has pointed out the similarities between Pine Point and a number of other Mississippi Valley-type deposits, particularly in Europe, that have been discussed at some length, and to which a variety of modes of origin have been assigned (Brown, 1967). There seems to be adequate field evidence that the ore at Pine Point was deposited epigenetically in an exceedingly porous, brecciated dolomite, with at least some control of the fluid flow and the site of deposition by faults. Campbell (1966, 1967) believes that the ore fluid movement was controlled by large faults in the Precambrian basement (approximately 300 m below) that parallel the reef. These faults, essentially quiescent since the Precambrian, bear some post-faulting mineralization similar to Pine Point where they are visible in the shield area 75 km to the east, and their projections have been traced under the Paleozoic cover to Pine Point. In fact, Campbell states that the drilling program that resulted in the discovery of the main Pine Point ore body, and many other smaller ore bodies (also blind), was set up on
this basis. Beales and Jackson (1966), and Jackson and Beales (1967), however, believe that the mineralization and dolomitization are not connected with the major Precambrian faults, but may have been controlled by very minor faulting parallel to these trends. They propose that the ore formed as a result of mixing of hypersaline waters carrying lead and zinc as chloride complexes, from the compaction of a shale sequence, with hydrogen sulfide-bearing waters from a porous carbonate complex, with the plumbing controlled by minor faults and the porous zones of the reef. Campbell (1966) and Davidson (1967a) point out, however, that the reef would have had to have been thoroughly lithified, dolomitized, coarsely recrystallized, and brecciated before the shales were completely compacted.

Isotopic Evidence

The isotopic composition of the lead in the galena at Pine Point is not the anomalous "J-type" of some Mississippi Valley-type deposits, but ordinary lead as could have been derived from the mantle about 250 million years ago (Folinsbee and others, 1965; Baadsgaard and others, 1965; Robertson and Cumming, 1966). It is also true, however, that this same type of lead could be derived from surface weathering, underground leaching, or metamorphism of any segment of the earth's crust that had maintained overall ratios of U/Th/Pb similar to the mantle. Thus the lead isotope evidence is at least compatible with the idea of deep circulation or source.

Isotopic studies of sulfur from the Pine Point area (Baadsgaard and others, 1965; Evans and others, 1965; Folinsbee and others, 1965, 1966, 1967; Robertson and Cumming, 1966) are particularly revealing, in that there is a strong enrichment in the heavy isotope, making direct derivation of the sulfur from a magmatic source rather unlikely. Folinsbee and others (1966, 1967) show that the sulfur in the ore is isotopically very similar to that of the anhydrite from the Elk Point basin evaporites, but differs considerably from that in the minor syngenetic or dia-genetic sedimentary sulfides in the rocks away from the ore body, and from that in the pyrobitumen. Thus it seems feasible that the sulfur came from solution of the anhydrite and relatively complete reduction of the sulfate to sulfide. Several mechanisms for this reduction have been suggested. Bacterial degradation of sulfate to sulfide is effective, and can occur at surprisingly high temperatures. Although thermochemical data indicate that various organic compounds should reduce sulfate to sulfide in water solution at surface temperatures (Barton, 1967), the rates are so low that they are almost unmeasurable in the laboratory. In addition to the separate organic phase (pyrobitumen) present at Pine Point during ore deposition, the work of Zarrella and others (1967) would suggest that hydrocarbons were probably present in solution in the brines in at least the parts-per-million level. It is thus possible that both sulfur (as sulfate) and the heavy metals could have been carried in a single fluid, and precipitated as metallic sulfides when and where slow reduction of the sulfate took place, from either bacterial or simple chemical action. Such a mechanism would eliminate the need for invoking mixing of two fluids, as proposed by Beales and Jackson (1966) and Davidson (1967a), although the concept of mixing presents some interesting possibilities, such as the addition of magmatic heat and metals to interstratal brines, and seems necessary to explain some other features detailed below.

Fluid Inclusion Evidence

The various data from fluid inclusions cannot prove a certain origin for a given deposit, but do place severe limitations on the mechanism of ore deposition which could have been operative. Any theory of origin, if it is to stand, must be compatible with the inclusion data, or the data must be refuted. Detailed documentation of the validity of fluid inclusions as samples of the ore fluids has been presented in two recent papers, one dealing with ore deposits in general (Roedder 1967b) and the other with Mississippi Valley-type deposits in particular (Roedder, 1967c), and will not be repeated here. The possibility that the inclusions studied might represent merely fluids present during recrystallization at some later time, after original deposition of the sphalerite as a colloidal gel, is dealt with (i.e., dismissed) in the following paper in this issue, on "colloform" texture (Roedder, 1968). The general problem of possible remobilization of the ore minerals in such deposits after original deposition is also discussed elsewhere (Roedder, 1967c). It is important to note that the only sphalerite that appears to have been remobilized—the pale yellow coarsely crystallized material in specimen ER 68-1b (Fig. 3)—has much less saline fluid inclusions than the bulk of the sphalerite, and the salinity is comparable to that found in inclusions in obviously late cross cutting calcite veins in the same specimen.

Entirely apart from the structural and isotopic evidence at Pine Point, the inclusion data alone would seem to be adequate to eliminate the need for further consideration of certain suggested modes of formation of such deposits involving fresh surface waters, or syngenetic deposition from sea water in shallow lagoonal or back reef environments. There is apparently abundant field evidence of shallow water during the formation of the host reef rock, and the high salinities could be derived from the evaporation
of sea water, but the high filling temperatures exclude any normal lagoonal environment for the ore itself.

The possibility of a syngenetic origin, with the metals and heat (and the salts in the fluids?) brought to the reef by volcanic exhalations, cannot be excluded, but the spatial and temporal localization of the ore deposition at the reef would be extremely fortuitous. More important, no volcanic rocks are reported in the sequence (Norris, 1965).

The possibility of a conventional magmatic-hydrothermal ("telethermal") origin for these deposits, with the ore fluids derived from below, seems unlikely in view of the high salinities found. Inclusions containing definitely magmatic fluids that are strongly saline do occur, but are most characteristic of relatively high temperature deposits such as those of tin, tungsten, molybdenum, and the porphyry copper. When inclusions in related lead and zinc deposits from the same areas are examined, they are found to contain much less saline brines, for example, at Bingham, Utah (Roedder and Creel, 1966). Even if the strongly saline fluids at Pine Point could be obtained from a distant magmatic source, a mechanism is also needed to permit them to be transported and cooled without dilution, or with dilution only by strong brines. Furthermore, as pointed out by Beales and Jackson (1966), a precipitation mechanism must be invoked that does not involve simple reaction with wall rock and change in T, P, Eh, or pH, as the fluids must have penetrated hundreds of meters of carbonate sequence before forming ore, and there are not even open space fillings of ore minerals in the barren strata between masses of ore.

The high salinities and low temperatures of the inclusions (compared with normal epithermal lead-zinc ores of established magmatic affinity) suggest deposition from hypersaline formation waters, as are frequently found in sedimentary basins, particularly those containing evaporite sequences. At the time of reef formation the huge Elk Point evaporite basin was forming to the south. Although the basin proper only came within 200 km of Pine Point (Campbell, 1966, Fig 1, or 1967, Fig. 2), the rocks at Pine Point now contain anhydrite and hence may well have had some salt beds. Thus it may not even be necessary to invoke pressure filtration through shales to obtain the high salinities. Davidson (1966a, b) has presented a rather well documented theory explaining the movement and redeposition of heavy metals in sedimentary terranes via high-chloride brines from the solution of evaporite sequences, and recently (1967a, b) has elaborated on this concept as it pertains to the Pine Point deposits. Although the data from fluid inclusions corroborate this theory, they must be considered as necessary but not sufficient evidence.

The inclusion evidence seems to introduce a problem concerning the mechanism to drive the dense metal-bearing brines up through the deposit, porous as it apparently was at the time of ore deposition. If surface waters have percolated down through the sedimentary pile, dissolving salts and metals on the way, and penetrated deep enough to become heated and channeled by the Precambrian faults before moving up to the reef where they formed ores, how can these dense fluids displace cold surface waters at a density of only 1.00 g/cm³?

The density of the ore fluids at the time of ore formation can be estimated from the inclusion evidence. The depression of the freezing point of the inclusion fluids of approximately 25° C (as in the sphalerite) corresponds to approximately 25 weight percent of salts in solution, or roughly 4.5-molal NaCl equivalent. The most dilute fluids in the calcite correspond to approximately 1-molal NaCl equivalent. Data on densities and thermal expansions of various brines (Ellis, 1966; Unterberg, 1966; Fabuss and others, 1966) show that a 2.5-molal NaCl solution must be heated to 163° C before thermal expansion decreases the density to 1.00 g/cm³, and even a 1-molal solution must be heated to 95° C before its density drops to 1.00 g/cm³. Extrapolations from these data would place the density of the brines that deposited the sphalerite at about 1.15-1.20 g/cm³ at 100° C, and even the most dilute brines found at Pine Point (in the calcite) would have a density at 100° C equal to that of cold surface waters. If a simple hydraulic drive is postulated to have moved these brines up through the faults and reef, even without friction, the fresh water column needed to support the saline brine column must have been 15 or 20 percent higher. As there are only relatively small elevation differences in this area at the present time, and there is no indication of any great differences since the Paleozoic, the hydraulic regimen at the time of deposition of these ores is not at all obvious. The problem is further complicated by an unknown thermal gradient (and hence density gradient) in the "recharge" fluids, and an unknown depth at which they dissolved salts and hence became dense.

Davidson (1966a, b) indicates that dense saline brines may have spread out laterally for great distances around saline deposits. Although this rather surprising concept has led to a charge of "armchair speculation," simple quantitative considerations of the permeabilities, density differences, and geologic times involved make the concept seem very realistic indeed. In fact, if one speculates that dense brines from the Elk Point evaporite basin had spread north
as far as Pine Point by gravity and saturated all the rocks, a driving mechanism to make them flow upward through the reef zone might easily be based on relatively small temperature differences alone. Thus the thermal expansion of a nearly saturated NaCl brine (26 weight percent; Unterberg, 1966) is such that the hydrostatic pressure at the base of a column maintained at 300 m height decreases approximately 1 atmosphere for each three Centigrade degrees increase in temperature.

The thermal gradients in the Pine Point area at the time of mineralization can never be known with certainty, but as heat can be moved through porous rocks much easier by water flow than by conductivity, it is probable that the movement of water controlled the geothermal gradient. The inclusion homogenization temperatures of 51°–97° C require either deep circulation of originally cold surface waters, as might be expected if circulation involved major faults in the underlying crystalline basement, or a contribution of heat by the addition of possibly magmatic waters from below. Under a "normal" geothermal gradient (with no flow of water) depths of 3,000 m would be required for temperatures in the range of 80°–100° C, and still greater depths of circulation are needed if cool surface water must be heated to these temperatures. Campbell (1966, p. 959) reports that a temperature of 87° C was encountered at a depth of 420 m (1,375 feet) in a well drilled into the basement along the southwest projection of the same major fault that underlies Pine Point, so abnormally high geothermal gradients exist at least locally along the fault at present.

Many of the "colloform" sphalerite crusts from Pine Point (particularly ER 65–99) and some other similar deposits have a microscopic, regular (periodic) color banding with individual dark and light layers alternating (Roedder, 1968). These bands or "varves" are tentatively interpreted as a result of an annual change in the conditions of deposition. If the very saline fluids at Pine Point resulted from ground water solution of the Elk Point evaporites far to the south and its subsequent underground movement northward, it is reasonable to expect that all traces of any original annual variation in chemistry or temperature of the influent would be leveled out by mixing enroute. From this it would seem necessary to invoke some local mixing process at the ore body, whereby the relatively uniform ore-bearing brines from the south are continuously mingled with local surface waters of variable composition or amount. Variations in the amount of this fresh water might yield the differences in salinity, and temperature, noted even in adjacent inclusions. Indeed, these differences are difficult to explain otherwise. As most of the inclusions in sphalerite are very saline, the amount of fresh surface water would have to be small. In addition to possible annual variation in the amount of diluting water, it is reasonable to expect that the composition would change over an annual cycle, particularly the amount of organic matter (iron surface and soil), and the amount of free, dissolved oxygen (as a function of influent temperature). Some such variations as these presumably caused the observed color changes in the banded sphalerite.

If these "varves" in the sphalerite are truly annual in origin, it is possible to place some limits on the time for ore deposition. Thus if one assumes that the total ore deposition consists of approximately 7 cm of such "varved" crusts on the numerous breccia fragments—a hazardous guess at best with such multiply brecciated and crustified material—with an average thickness of 7 μm per pair, a total time of about 10,000 years would be involved. This amount of time would be adequate to form the main ore body as described by Campbell (1966) (20 million tons of 7 percent zinc) if the total flow of ore fluid through the entire ore body was only 10 gallons per minute, and it precipitated 5,000 ppm of zinc (Roedder, 1960; Czamanske and others, 1963). Lower concentrations of zinc would require proportionately greater flow rates.

Conclusions

The freezing and homogenization temperatures of primary inclusions in the Pine Point ores show that they formed from exceedingly saline brines, very free of solid particles, at temperatures in the range of 50°–100° C. Although the inclusion evidence precludes certain proposed mechanisms of origin for such deposits involving fresh water or sea water, it is not presently adequate to prove which of the other possible mechanisms was actually involved. A sedimentary origin (interstratal brines) seems likely for the salts in solution, and for the sulfur of the ore. Presumably the ore metals were leached from the rocks penetrated (sedimentary and/or crystalline basement), and circulation was deep enough to result in the elevated temperatures. The inclusion evidence does not reveal the cause for deposition of the ore body, but is compatible with several of the mechanisms that have been proposed. In particular, it is

6 Although the colors are the normal yellows, oranges, reds, and browns usually assumed to be due to iron substituting for zinc in the sphalerite, the color of these bands cannot be correlated with iron content (Roedder and Dwornik, 1968).

7 For comparison, the Salton Sea brines contain 790 ppm Zn and 84 ppm Pb (Skinner and others, 1967, p. 318). Lebedev (1967) reports analyses of as much as 5 ppm Zn and 77 ppm Pb in high chloride oil field waters in the USSR, which are currently depositing 300 tons of lead per year (Davison, 1967b).
suggested that an upward flow of hot, metal-bearing brines mixed with a small amount of relatively fresh, cold surface waters in the vicinity of the ore deposit. This mixing may explain the precipitation of the ore, the range in salinity and homogenization temperatures, and the minute, regular color banding seen in some of the sphalerite.

Acknowledgments

I am indebted to Prof. Sinclair and Drs. Campbell, Hurley and Mody for the ore specimens, as detailed under “Materials studied.” John P. Creel, U. S. Geological Survey, prepared the excellent doubly polished sample plates and made the rather difficult freezing temperature determinations, and Steven Battrille made some of the filling temperature determinations. The manuscript has profited from a careful reading by Prof. Sinclair, and by E. T. McKnight, P. Toulmin 3rd, and P. M. Bethke, U. S. Geological Survey. I also wish to acknowledge frequent and stimulating correspondence with the late Prof. C. F. Davison.

Appendix—Specimen Descriptions

ER 65–99. Massive “colloform” sphalerite with individual layers in various shades of yellow, red, and brown, and some purplish gray, in plate 0.09 mm thick. Birefringence, low; extinction, fibrous. Contains numerous tiny inclusions too small for further study with present techniques, but does show interesting details in the “colloform” texture (Roedder, 1968).

ER 65–100. Massive “colloform” sphalerite crusts over irregular masses of crystalline dolomite. Color, yellow to almost opaque dark reddish brown in plate 0.243 mm thick. Birefringence, moderate; extinction, fibrous. Two small, flat, possibly primary inclusions were found in the sphalerite.

ER 65–101. Botryoidal “colloform” crusts of fine-grained, radial sphalerite crystals, showing numerous minor bands or layers. Color varies from pale yellow to orange in plate 0.040 mm thick. Birefringence, moderate; extinction, fibrous. Some bands are white in reflected light and almost opaque in transmitted light due to fine grain size. Co-deposited galena crystals are much coarser. The botryoidal top surface of the sphalerite consists of coarser euhedral crystals projecting into vugs. Some of these single crystals have occasional clear purple bands, irregularly distributed but outlining former crystal faces. Four small primary inclusions were found.

ER 66–3a. Coarse (1–3 mm) sphalerite crystals, strongly zoned yellow to dark reddish brown in plate 0.42 mm thick, embedded in gray crystalline dolomite, and lining vugs, along with pearly rhombs of dolomite. Birefringence, moderate; extinction, coarse to fine mosaic. Galena crystals, which partly fill vugs, have been deeply etched and rounded. Numerous good primary inclusions are found in the sphalerite and dolomite. (Figs. 1 and 2.)

ER 66–3b. Vuggy, banded crust of zoned pale yellow-brown to dark red sphalerite crystals in plate 0.24 mm thickness; no dolomite was visible. Birefringence, moderate; extinction, mosaic. Euhedral crystals lining vugs have several small, primary inclusions. (Fig. 1B.)

ER 66–4. Calcite, 4-cm cleavage fragment, from high-grade ore pile. Of unknown relation to ore, but probably later. White, varying to yellow where relatively free of inclusions. Contains many primary inclusions, most of which appear to have leaked. Eigh having an apparently uniform gas-liquid ratio were selected.

ER 67–36. Sphalerite vug filling; crystals as much as 4 mm long. Color, zoned pale yellow to orange and purplish gray in plate 1.5 mm thick. Birefringence, high; extinction, coarse mosaic.

ER 67–37. Sphalerite vug filling or replacement; euhedral crystals as much as 2 mm long. Color, very strongly zoned, with dark patchy reddish brown cores and almost white margins in plate 0.18 mm thick. Birefringence, moderate; extinction, mosaic. Also contains some “colloform” finely banded masses that have fibrous extinction.

ER 67–38. Sphalerite vug filling or replacement; euhedral crystals as much as 4 mm long. Color, very strongly zoned, with dark patchy reddish brown cores and white to purplish gray margins in plate 0.10 mm thick. Birefringence, moderate; extinction, mosaic.

ER 67–39. Sphalerite crystals as much as 6 mm long, as vug filling or replacement. Color, uniform yellowish brown in plate 1.1 mm thick. Birefringence, high; extinction, fine mosaic.

ER 67–40. Sphalerite vug filling; euhedral crystals as much as 6 mm long. Color, pale yellow to dark yellowish brown, irregularly banded, in plate 1.1 mm thick. Birefringence, moderate; extinction, coarse to fine mosaic.

ER 67–41. Sphalerite crystals as much as 5 mm long in massive sulfide, one foot from dolomite. Color, pale yellow to irregularly yellowish brown in plate 1.4 mm thick. Birefringence, moderate; extinction, coarse to fine mosaic.

ER 67–42. Sphalerite vug filling or replacement; euhedral crystals as much as 5 mm long. Color, patchy, banded very dark brown cores and rims, elsewhere pale yellow to almost white in plates 0.19 mm thick. Birefringence, moderate; extinction, very coarse to fine mosaic.

ER 67–43. Sphalerite vug filling or replacement, crystals as much as 3 mm long, also considerable pyrite. Color, patchy zoned pale yellowish brown to almost white in plate 1.4 mm thick. Birefringence, moderate; extinction, very coarse to fine mosaic.

ER 67–43. Same sample, calcite.
ER 68-1a. Concentrically banded sphalerite botryoid 4 cm in diameter. Individual bands vary from pale yellow to dark reddish brown in plate 0.10 mm thick. Birefringence, moderate; extinction, coarse mosaic. The non-banded core consists of pale yellow sphalerite crystals about 0.5 mm, enclosing numerous pyrite (?) cubes, many of which have tufts of thin opaque subparallel needles projecting approximately perpendicular to each face. The two presumably primary fluid inclusions run were in the deep red brown and pale yellow outer bands.

ER 68-1b. (Same specimen as ER 68-1a.) Multiply banded, very fine grained dark yellowish brown to opaque white sphalerite, in plate 0.33 mm thick, with odd lens-shaped masses of very clear pale yellow sphalerite containing many inclusions. These lenses are single sphalerite crystals with low birefringence and irregular extinction. They appear to have replaced similar shaped masses of white, opaque porcelaneous sphalerite. The inclusions in sphalerite run from this plate were possibly primary groups in these pale yellow lenses. Thin cracks cross cutting the entire sample are filled with large single calcite crystals containing numerous large primary inclusions, three of which were run.

ER 68-5. Multiply banded botryoidal sphalerite varying in color from pale yellow to dark brown in plate 0.07 mm thick. Inclusions run from this specimen were in transparent coarse, pale yellow, almost perfectly isotropic sphalerite that has partly replaced a band of almost opaque white porcelaneous sphalerite.

ER 68-8. Coarsely crystalline rosette of dark brown sphalerite tetrahedrons up to 1 cm on an edge, which grew in part contemporaneously with dolomite crystals. In a plate 0.40 mm thick this sphalerite is irregularly colored dark reddish brown. Some very thin needles of an unknown opaque mineral, completely embedded in this sphalerite, are curved into almost circular multiple loops. The core of the rosette is a 5 mm mass of coarse sphalerite crystals of pale yellow color with purple streaks and some reddish brown bands paralleling crystal faces; this is coated in turn with dolomite crystals. Both sphalerite types show strong birefringence, and very coarse to fine mosaic extinction. All inclusions run in this specimen were from the inner, pale sphalerite (see also specimen ER 68-10).

ER 68-10. Very similar to ER 68-8. The pale colored inner zone shows some anomalous green colors in crossed polarizers. Only inclusions in the outer zone (yellow to reddish brown in plate 0.20 mm thick) were run from this specimen.

U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C. 20242,
April 17; May 6, 1968

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