FLUID INCLUSION EVIDENCE ON THE ENVIRONMENTS OF SEDIMENTARY DIAGENESIS, A REVIEW

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ABSTRACT

Most sedimentary diagenesis involves recrystallization or overgrowths on original minerals, or the growth of new phases. This new growth may trap fluid as inclusions that provide data not only on the nature, composition, pressure, and density of the fluids present during diagenesis, but particularly on the temperature at which the host crystals grew. As most optical methods of study require inclusions >1–2 μm in diameter, fine-grained products of diagenesis, in the 10–20 μm range, seldom provide useful material. The possibilities of finding inclusions of useful size increase as the size of the host crystal increases. In spite of this limitation, reasonably valid quantitative or qualitative physical and chemical data, both new and from the literature, have been obtained on inclusions from the following specific diagenetic environments: (1) crystal-lined geodes, vugs, and veins in sediments; (2) Mississippi Valley-type ore deposits; (3) carbonate and quartz cements in detrital rocks; (4) saline and sulfur deposits; (5) petroleum reservoir rocks; (6) sphalerite in bituminous coal beds.

Most inclusion temperatures in these and other similar environments range from 25 to 150°C, and most of the fluids are moderately to strongly saline brines which commonly contain petroleum and as much as tens of atmospheres of methane-rich gas. Homogenization temperatures of inclusions in some Mississippi Valley-type ore deposits are higher than 150°C but seldom more than 200°C. It has been concluded that hot, strongly saline fluids have moved through many, if not most, sediments at some time in their history, and that at least part of the diagenetic changes seen have been caused by such fluids.

INTRODUCTION

The environments of diagenesis, when one uses the term in a broad sense, determine the nature of deposits of coal, oil, and inorganic minerals in sediments, and thus are of considerable economic significance in the search for such deposits. Hence all possible sources of potentially useful data on these various environments should be explored. The fluid inclusions that are formed in some minerals during diagenesis provide one such source of data that has not been explored as diligently as it merits. Determination of the origin of the inclusions studied is essential, as many minerals contain several generations, formed at different stages in the history of the sample. For discussions of the origin and significance of fluid inclusions, and the techniques of studying them, see Roedder (1962b, 1972, 1976).

In this review the published literature is summarized, with some previously unpublished data from the author, on six types of samples covering a large part of the spectrum of environments normally included in the term diagenesis. Most of the available data on fluid inclusions from diagenetic environments fall in one of these categories, mainly because these six provide the best sample material, but suitable material may eventually be found in samples from other environments.

CRYSTAL-LINED GEODES, VUGS AND VEINS IN SEDIMENTS

In many areas throughout the world, what were originally soft and porous Paleozoic and younger carbonate sediments have been strongly modified postdepositionally to yield hard, dense crystalline limestones and dolomites. Although the individual sample porosity may be low, such rocks commonly contain open vugs of varying size, sometimes lined with crystals of calcite, dolomite, quartz, fluorite, barite, and celestite. Some also contain sulfides, particularly very coarse sphalerite, and less often galena, pyrite, marcasite, chalcopyrite, wurtzite, millerite, etc. Such localities as Clay Center, Ohio, and Herkimer, New York, have provided spectacular mineral specimens for many collections.

In many of these geodes, vugs, and veins in carbonate rocks, one or more minerals may be relatively rare, so that a mineral collector may consider himself lucky to find one crystal on a given visit, yet this crystal may be well formed, clear, and sometimes several centimeters on an edge. The nucleation and growth of such a large, perfect, crystals of a given mineral, particularly relatively insoluble phases such as sphalerite, requires that both nucleation and growth take place exceedingly slowly, from

1 Much of the literature on inclusions is in Russian; English abstracts (and some translations) of the post-1968 literature cited here will be found in Roedder (1968-onward).

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solutions having a very low degree of supersaturation, under essentially static conditions.

In the laboratory, even very slow precipitation of ZnS from solution usually results in a milky solution that contains many millions of sub-micrometer crystals per milliliter. Yet the distribution of nuclei formed in the fluid in the rocks may have been about one per cubic meter, 9 orders of magnitude less. Furthermore, growth was so slow that there was time for diffusion to occur to these few nuclei through the rock pores, instead of forming new nuclei. Even where the nuclei were more abundant, the degree of perfection of the crystals is sometimes phenomenal, e.g., the Herkimer quartz crystals ("Herkimer diamonds"). There is generally no solid evidence on the specific time at which this slow crystallization took place, except that it was post-lithification, but the widespread occurrence of such crystal-lined vugs indicates the process to be relatively common.

Some indication of the elapsed time involved in the growth may be provided by celestite (Fig. 1A). Crystals from several localities show a microscopic, very regular compositional banding, which has been interpreted as annual "varves," representing variations in the Ba content due to annual variations in the salinity (Roedder, 1969; see also Scherpf and Strübel, 1974). If this interpretation is correct, these celestite crystals grew in \( \sim 10^4 \) years. The solutions from which they grew were hot (\( \sim 100^\circ \) C) and moderately to strongly saline (\( \sim 25\% \) NaCl equivalent). Leach (1973a) has found similar banding in the central Missouri barite district, but reversed, i.e., regular bands of high Sr content in barite.

Some of the more recent studies on inclusions from geodes, vugs, and veins are summarized in Table 1, but many of the entries show special features too complex to tabulate. For example, Touray and Barlier (1975) have been able to correlate the map distribution of the phase composition of multiphase organic-rich inclusions in quartz with the degree of metamorphism of clays and of opaque organic matter in the enclosing rocks (as measured by its reflectivity; see also Barlier, Ragot, and Touray, 1974). Kenvolden and Roedder (1971) report that gas chromatographic and mass spectrometric studies of the organic materials in quartz from calcite veins of unknown age in Precambrian metasedimentary rocks of southwest Africa suggest biological precursors for these components, particularly for the isoprenoid hydrocarbons. The inclusion composition and phase data neither prove nor preclude the inclusion fluids originating during diagenesis of formerly overlying Paleozoic or Mesozoic sediments.

The quartz crystals from Herkimer and adjacent Montgomery County, New York, are in vugs in a crystalline petrolierous dolomite. Inclusions in them contain, in addition to brine, several types of organic matter: high-pressure supercritical mixtures of organic gases (Roedder, 1972, Plate 5); colorless to yellow, highly fluorescent oils; and broken fragments of anthraxolite, a black, organic material with conchoidal fracture that is also found in the vugs with the quartz (Dunn and Fisher, 1954). Individual inclusions may have one or more of these phases, in any ratio, suggesting that all were separate phases at the time of trapping. Small fragments of anthraxolite sometimes are found adhering to the vapor bubble, on the surface of which they move rapidly when minute thermal gradients, caused by asymmetric illumination, result in surface tension differences. The oily liquids show a variety of colors and freezing temperatures (Roedder, 1963, p. 201), and hence presumably indicate a variety of source materials or histories. The physical properties of the gas inclusions show that they also have a variety of compositions, although the major constituents are probably methane and ethane (Roedder, 1963, p. 202; Roedder, 1972, Plate 5, figs. 6 and 7; Rosasco, Roedder and Simmons, 1975). Good compositional data on these, along with homogenization temperatures of cogenetic aqueous inclusions, might permit a valid estimate of the depth at the time of trapping, as it is evident from their occurrence that these were trapped as actual bubbles of gas in the brines from which the crystals grew. Hence these gas inclusions should record the ambient hydrostatic pressure. On warming after being solidly frozen at low temperatures, the water solutions in many of these crystals showed a first melting temperature in the range \(-23\) to \(-27^\circ \) C, and had a NaCl \( \cdot 2\text{H}_2\text{O} \) liquidus; these data indicate near saturation with NaCl, and very little other material in solution (Roedder, 1963). The host rock in the area, the Little Falls Dolomite (Upper Cambrian), is overlain by halite-bearing Silurian formations; hence saturation of the fluids with NaCl is expectable.

Sphalerite, quartz, and fluorite from geodes, vugs, and clay seams in some Paleozoic limestones and dolomites of Indiana were also examined (Table 1; Fig. 1B). The inclusions in these samples contain brines, with freezing temperatures in the range \(-10\) to \(-16^\circ \) C (3–5 molar NaCl equiv.), that have been trapped at \( \sim 100^\circ \) C. These salinities are even greater than modern oil field brines in the state and may represent mixing of strong brines from the adjacent Illinois or Michigan basins with more dilute fluids or ground water (N. R. Shaffer, written commun., 1976). The data on inclusions in fluorite and celestite from similar occurrences
<table>
<thead>
<tr>
<th>Reference</th>
<th>Mineral and locality</th>
<th>$T_H$ (°C)</th>
<th>$T_V$ (°C)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Quartz, various localities</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voznyak, Kvasnitsa, and Galaburda, 1974</td>
<td>Quartz, (“Marmarosh diamonds”), Ukraine, USSR</td>
<td>-0.2</td>
<td>-0.1</td>
<td>Large P incs., some with Hc L and Hc G.</td>
</tr>
<tr>
<td>Lazarenko et al, 1974</td>
<td>Quartz, (“Marmarosh diamonds”), Carpathians, USSR</td>
<td>100</td>
<td>200</td>
<td>Large P incs, some with Hc L and Hc G.</td>
</tr>
<tr>
<td>Cameron, A., 1977</td>
<td>Quartz, veins in Paleozoic Jacksonburg limestone, PA</td>
<td>130</td>
<td>160</td>
<td>Formation includes carbonaceous material, and authigenic albite and 2M muscovite.</td>
</tr>
<tr>
<td>Touray, and Barlier, 1975</td>
<td>Quartz, single xls from septaria and veins, French Alps</td>
<td>115</td>
<td>230</td>
<td>L and G Hc incs. used for $T_H$.</td>
</tr>
<tr>
<td>Karwowski, and Kozlowski, 1973</td>
<td>Quartz, authigenic smoky xls from bituminous ls, Poland; also brown-black calcite</td>
<td>48</td>
<td>190</td>
<td>Yellow L and dark brown bitumen incs. IR spectra showed saturated and aromatic Hcs, and possibly oxidized derivatives.</td>
</tr>
<tr>
<td>Roedder, 1963</td>
<td>Quartz, Montgomery County, N.Y. USNM R1433</td>
<td>+2.2</td>
<td>+3.2 (15)</td>
<td>First melting $&lt;-13°C$; data on Hc L.</td>
</tr>
<tr>
<td>Kvenvolden and Roedder, 1971</td>
<td>Quartz, from calcite veins of unknown age in Precambrian metasediments, South-West Africa</td>
<td>120</td>
<td>160(73)</td>
<td>First melting $-28.5$ to $-20.8°C$, L and G Hc incs. also present.</td>
</tr>
<tr>
<td>Roedder, 1963</td>
<td>Quartz in Paleozoic crystalline dol.; quarry just east of Catasaqua, Northampton County, Pa. (Sample H-Pa-1)</td>
<td>-15.4</td>
<td>-13.4 (26)</td>
<td>First melting $-24.7°C$.</td>
</tr>
<tr>
<td>Roedder, 1963</td>
<td>Quartz, Herkimer County, N.Y. (Sample ER61-26)</td>
<td>-20.1</td>
<td>0.0 (~250)</td>
<td>First melting $-23°C$; some have NaCl·2H₂O liquidus and some contain yellow oil.</td>
</tr>
<tr>
<td>Roedder, 1963</td>
<td>Quartz, Herkimer County, N.Y. (Sample ER61-30)</td>
<td></td>
<td></td>
<td>First melting $-26.7°C$; contains some CO₂</td>
</tr>
<tr>
<td><strong>Ohio localities</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Roedder, 1969</td>
<td>Celestite, Bascom, Ohio (USNM 94965)</td>
<td>68</td>
<td>114</td>
<td>-8</td>
</tr>
<tr>
<td>Roedder, 1969</td>
<td>Celestite, from vug in Paleozoic limestone, Clay Center, Ohio</td>
<td>$\sim$100</td>
<td>$\sim$25</td>
<td>Crystals show annual(?), “varves.” (see Fig. 1A).</td>
</tr>
<tr>
<td>Reference</td>
<td>Mineral and locality</td>
<td>$T_H$ (°C)</td>
<td>$T_F$ (°C)</td>
<td>Notes</td>
</tr>
<tr>
<td>--------------------</td>
<td>--------------------------------------------------------------------------------------</td>
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<td>--------------------------------------------</td>
</tr>
<tr>
<td>Roedder, 1967a</td>
<td>Fluorite, associated with red sphalerite, celestite, and calcite, from vug in Paleozoic limestone, Clay Center, Ohio (Sample ER65-69)</td>
<td>$-100$</td>
<td>$-24.5$</td>
<td>$-23$ (7)</td>
</tr>
<tr>
<td>Roedder, unpub. data</td>
<td>Celestite, Basic, Inc., quarry, Clay Center, Ohio (Sample ER65-71)</td>
<td>$68$</td>
<td>$76$</td>
<td>(4)</td>
</tr>
<tr>
<td>Roedder, unpub. data</td>
<td>Sphalerite, same locality</td>
<td>$68$</td>
<td>$76$</td>
<td>(2)</td>
</tr>
<tr>
<td>Roedder, unpub. data</td>
<td>Calcite, Pugh quarry, Custar, Ohio, in Dundee Formation (Sample ER65-74)</td>
<td>$68$</td>
<td>$76$</td>
<td>(5)</td>
</tr>
<tr>
<td></td>
<td>In part (or all?) metastable.</td>
<td>$-16.0$</td>
<td>$-15.3$</td>
<td>(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-8.5$</td>
<td>$-4.8$</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-5.6$</td>
<td>$-7.0$</td>
<td>(5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-22$</td>
<td>$-14.1$</td>
<td>(17)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-12.1$</td>
<td>$-14.1$</td>
<td>(17)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-0.17$</td>
<td>$-0.17$</td>
<td>(2)</td>
</tr>
</tbody>
</table>

**Indiana localities**

<p>| Roedder, unpub. data | Sphalerite, coarse xls in clay seam in Silurian reefal dolo. (Wabash Fm); quarry at SE$1/4$NE$1/4$ Sec. 19, T. 25 N., R. 2 W., near Delphi, Carroll County, Ind. | $82$       | $83$       | (6)                                        |
| Roedder, unpub. data | $86(4)$                                                                             | $-14.1$    | $-14.1$    | (4)                                        |
| Roedder, unpub. data | $84$                                  | $-12.4$    | $-12.3$    |                                             |
| Roedder, unpub. data | $97(1)$                                                        | $-15.5$    | $-16.6$    |                                             |
| Roedder, unpub. data | $119(1)$                                                            | $-16.6$    | $-16.6$    |                                             |
| Roedder, unpub. data | Barite, occurring with sphalerite as nodules in Sanders Group (Mississippian), quarry at SW$1/4$NE$1/4$ Sec. 5, T. 17 N., R. 6 W., near Waveland, Parke County, Indiana | $97$       | $99$       | (2)                                        |
| Roedder, unpub. data | $120(1)$                                                            | $-11.7$    | $-12.2$    |                                             |
| Roedder, unpub. data | Sphalerite, geode with quartz and dolomite in Harrodsburg Limestone (Mississippian); railroad cut at SW$1/4$NE$1/4$ Sec. 8, T. 9 N., R. 1 E., near Bloomington, Monroe County, Ind. | $83$       | $10.1$     |                                             |
| Roedder, unpub. data | Quartz, same geode as above. Other geodes here have fluorite, millerite, chalcopyrite, barite. | $83$       | $10.1$     |                                             |</p>
<table>
<thead>
<tr>
<th>Source</th>
<th>Description</th>
<th>Data</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roedder, unpub. data</td>
<td>Sphalerite, coarse xls in clay seam in Silurian reefal dolo. (Wabash Fm); quarry at SE1/2NE1/4 Sec. 19, T. 25 N., R. 2 W., near Delphi, Carroll County, Ind.</td>
<td>69 (2) 102 108(11) 109</td>
<td>First melting $&lt;-25.1$ to $&lt;-26.5^\circ$C.</td>
</tr>
<tr>
<td>Roedder, unpub. data</td>
<td>Fluorite, associated with dolomite, from vug in Ste. Genevieve Limestone (Mississippian); road cut at SE1/2SE1/4 Sec. 33, T. 5 S., R. 3 E., near Corydon, Harrison County, Ind.</td>
<td>101 104</td>
<td>First melting $&lt;-23^\circ$C.</td>
</tr>
</tbody>
</table>

**Miscellaneous occurrences**

<table>
<thead>
<tr>
<th>Source</th>
<th>Description</th>
<th>Data</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roedder, unpub. data</td>
<td>Celestite, U.S. Gypsum Co. mine, Sperry, Iowa (Sample ER69-61)</td>
<td>&lt;40</td>
<td>Inclusions full at room temperature.</td>
</tr>
<tr>
<td>Roedder, 1967a</td>
<td>Fluorite from vug, Volga, Iowa (Sample ER65-97)</td>
<td>$-27.5$ $-26$ (8) $-12$ $-2$ (3)</td>
<td></td>
</tr>
<tr>
<td>Jepsen, 1964</td>
<td>Quartz and calcite lining mineralized dinosaur bone, Cleveland-Lloyd quarry, central Utah</td>
<td>43</td>
<td></td>
</tr>
</tbody>
</table>

**Geodes, Iowa**

<table>
<thead>
<tr>
<th>Source</th>
<th>Description</th>
<th>Data</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roedder, unpub. data</td>
<td>Quartz, geode, 11 miles NW of Keokuk, Iowa (ER64-24)</td>
<td>100? $-6.55$ $-1.71$ (9) $-0.37$ $-0.03$ (4)</td>
<td>Not including nine with metastable ice.</td>
</tr>
<tr>
<td>Roedder, unpub. data</td>
<td>Calcite, geode with millerite, Keokuk, Iowa (Sample ER71-5)</td>
<td>&lt;40</td>
<td>Most inclusions full at room temperature.</td>
</tr>
</tbody>
</table>

**Geodes, Kentucky**

<table>
<thead>
<tr>
<th>Source</th>
<th>Description</th>
<th>Data</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roedder, unpub. data</td>
<td>Quartz, geode, Salem Limestone, Boone Hollow, Ky. (Sample ER65-38)</td>
<td>~60? $-19.5$ $-18$ (3)</td>
<td>Not including two with metastable ice.</td>
</tr>
<tr>
<td>Roedder, unpub. data</td>
<td>Quartz, geode, Salem Limestone, Boone Hollow, Ky. (Sample ER62-23)</td>
<td>~60? $-22.8$ (1)</td>
<td>Not including six with metastable ice.</td>
</tr>
<tr>
<td>Roedder, unpub. data</td>
<td>Quartz, probably from weathering of geodes, Douglas Lake, Knoxville, Tenn., just south of dam. (Sample ER65-5)</td>
<td>~2.5 $&lt;-1.7$</td>
<td>Also contains Hc L and G; $&lt;-1.7$ refers to metastable ice.</td>
</tr>
</tbody>
</table>

1Number of inclusions given in parentheses. Range or average given for temperature of homogenization (T_H) and temperature of freezing (T_F) (of water phase except as noted); both types of data on same inclusions where data are on same line.

Abbreviations: P—primary; L—liquid; G—gas; Hc—hydrocarbon; incs.—inclusions; ls.—limestone; dolo.—dolomite; USNM—United States National Museum; Fm—formation; xls—crystals.
in Ohio, and on inclusions in fluorite from vugs at Volga, Iowa, about 100 km west of the Upper Mississippi Valley zinc-lead district, are similar to the Indiana samples (Table 1). Sphalerite is also widespread in the Lockport Dolomite (Middle Silurian) of New York (e.g., see Bassett and Kinsland, 1973), and celestite is common in vugs in dolomite beds of the Pennington Formation (Upper Mississippian) of central Tennessee (Frazier, 1973).

Often the inclusions in barite are the most dilute. Barite is known to dissolve and reprecipitate with surprising ease, and hence inclusions in it commonly represent the latest fluids. Furthermore, barite inclusions tend to leak and to neck down; both phenomena yield erroneous homogenization temperatures. The data reported on barite in Table 1 seem to be based on carefully selected inclusions and hence are believed to be valid.

There have been many suggestions that these scattered occurrences of sphalerite, etc., have formed from the same kind of fluids as the Mississippi Valley ores. The general geological environments and mineralogy are very similar; only the volumes of ore minerals are different. Although the fluid inclusions in these minerals are similar to those in the Mississippi Valley deposits (see following section), in that they were formed from hot, strongly saline brines, with much organic matter, the temperature range and salinity are both a little lower. Many have suggested dilution of hot brines as a mechanism for the formation of the Mississippi Valley-type ore bodies; the present inclusions may reflect more such dilution, but detailed studies of the chemical and isotopic composition of the fluids in inclusions are required to prove such an interpretation.

In addition to the above, numerous geodes in shales and limestones are lined with quartz or calcite and rarely have any sulfides other than pyrite or marcasite. The writer has examined many of these geode minerals, generally with disappointing results, as they are remarkably free of recognizable primary inclusions. In addition, many of the inclusions exhibit metastable superheated ice on freezing (Roedder, 1967b), and hence the true freezing temperature is some unknown amount below the temperature found. Calcite in such geodes, e.g., from the famous Keokuk, Iowa, locality, is commonly the last stage of deposition, and is found to have inclusions filled with only liquid, indicating that it probably grew at <40° C.

The quartz of the geodes from Kentucky has many gypsum crystals embedded in it, and according to C. F. Withington (personal commun., 1965) these geodes started as gypsum-anhydrite nodules and have been replaced, presumably by strongly saline warm brines (Table 1). Fisher (1976) has suggested that these geodes formed during at least two periods of mineralization, and that the distribution patterns are related to the source of the ore fluids of the Central Kentucky Mineral District. The fluid inclusion data on the geodes (Table 1) are compatible with this concept, as the available data on the inclusions from Central Kentucky Mineral District (Roedder, 1967a, 1976) show these deposits to have formed from strongly saline solutions ranging from 60 to 140° C, but mainly ~110° C. Data on carbon and oxygen isotopes in such concretions (e.g., see Hudson and Friedman, 1976) might provide corroboration.

One aspect of inclusions in geodes that is frequently asked about pertains to the very large "fluid inclusions" visible or audible in unopened geodes from various localities. The amplified sloshing sounds made as these natural containers are shaken has attracted the attention of many visitors to mineral shows (Sutton, 1964). Agate geodes containing visible liquid water constitute a collector's item called enhydro, and are found particularly in the soil from the decomposition of basalt in Brazil. Because such geodes have polycrystalline walls, it is expected that they will leak with time, and most museum specimens are either kept in water or coated with impervious coatings to keep them from drying out. The rate of leakage may be very slow; one 10-cm enhydro in the possession of the writer has been steadily losing a few milligrams a year to the laboratory air. As a result of such leakage, the fluid in these geodes has probably been replaced by passing fluids many times since the geodes were first formed, and the present water in them is probably moderately recent ground water. This has been verified by studies of the isotopic composition of the waters (Matsui, Salati, and Marini, 1974).

**MISSISSIPPI VALLEY-TYPE ORE DEPOSITS**

Dunham (1970, p. B133) has pointed out that "ore formation is a minor and specialized process in comparison with the far reaching mineralogical changes brought about in sediments in the course of diagenesis by their formation waters or migratory brines." But fluid inclusions have been studied in more Mississippi Valley-type ore deposits than probably any other type of deposit, largely because such deposits frequently provide excellent sample material, and because the ambiguities in interpretation of the inclusion data are minimum. These many studies are discussed in a recent publication (Roedder, 1976), and need

2 Some additional published studies that are not in this summary include the Viburnum Trend, Missouri (Roedder, 1977a); northern Arkansas (Bennett, 1974; Leach, Nelson, and Williams, 1975); Central Missouri...
not be discussed in detail here, but some generalizations are appropriate.

Perhaps the most striking aspect of the Mississippi Valley-type deposits is the great uniformity of environmental conditions in these various deposits that is evident in the data from fluid inclusions. The data are consistent even though the deposits cover a wide range of elemental composition (e.g., from almost pure lead at Laisvall, Sweden, and southeast Missouri, to almost pure zinc at Friedensville, Pennsylvania, to almost pure fluorite in some deposits in southern Illinois), isotopic make-up (normal lead, B-type lead, or J-type lead), structural setting, geological age, host rock type, etc. All deposits that have been studied, from many places in the world and with almost no exceptions, show that the ore-forming fluids had the following characteristics (Roedder, 1976).

**Density.**—Always $>1.0$ and frequently $>1.1$ g/cm$^3$ at the time of trapping, so they are always more dense than surface waters. These densities are based on measurements of the volumes of liquid and gas at room temperature, and of the salinity of the liquid (from freezing data); with these and the data on the density of similar brines, the present density of the liquid can be calculated and hence the density when the liquid just fills the cavity (Roedder, 1976).

**Rate of movement.**—Very slow, perhaps in the range of a few m/yr.

**Total pressure.**—Low but always greater than the vapor pressure of the brines (i.e., no boiling has occurred), although there may have been gases in solution at pressures as much as 20 bars.

**Temperature.**—Generally 100$^\circ$–150$^\circ$ C, and seldom as high as 200$^\circ$ C (Fig. 1D). (Some of the highest reported numbers were later shown to be invalid; see Larsen et al., 1973.)

**Gross salinity.**—Usually $>15$ wt. % salts and frequently $>20\%$, yet daughter crystals of NaCl are almost never found, implying appreciable amounts of ions other than Na and Cl.

**Organic matter.**—Frequently but not always present, as gases such as methane in solution, immiscible oil-like droplets, and in solution in the brines (Fig. 1E).

**Nonvolatile ions (i.e., “salts”) in solution.**—Highly concentrated solution of mainly sodium and calcium chlorides, with very minor potassium, magnesium, boron, and extremely low sulfur (Rosasco, Roedder, and Simmons, 1975). Heavy metals (Zn and Cu) may be high (Czamanske, Roedder and Burns, 1963).

The source of the brines themselves is not at all clear, although individual brines have been assumed to represent connate, oil-field, compaction, or formation waters. As an example, the Pine Point deposit in Canada has generally been related to the salines of the Elk Point Group (Roedder, 1968). Thiede and Cameron (1975) have shown that three different types of metal-bearing brines might be generated during the history of such a basin: (1) brines residual from evaporation, (2) diagenetic brines released by dehydration of gypsum to anhydrite, and (3) postdepositional brines generated when evaporites are dissolved and leached by circulating ground water. He favors (2) or (3) for Pine Point. In many basins semipermeable membrane filtration may be the main cause for the high salinities. The ratio K/Na is one of the easiest to determine in the laboratory, and the one on which the precision is highest. When inclusions from Mississippi Valley-type deposits are compared with oil field brines, they are found to be similar except for K/Na. The K/Na ratios are all higher (Roedder et al., 1963) than the highest value in the range given for oil field waters by White (1957).

The time of formation of the ore minerals in these deposits is usually not known precisely, but it was generally post lithification and hence certainly should be considered a part of the diagenesis of the enclosing rocks. This view is supported by paleomagnetic evidence placing the time of formation of the ore relatively close to that of the host rock (Beales, Carracedo, and Strangway, 1974). The view that the inclusions in such deposits merely represent fluid present during recrystallization of a preexisting syngenic deposit is discussed and rejected by Roedder (1976, p. 73–76).

An important aspect of the inclusion evidence concerning the environment of diagenesis has yet to be explored. This is the specific nature of the organic material so common in these inclusions. In theory, at least, these materials can provide considerable detail on the thermal and oxidation history that might be read from the variety of specific compounds present (MacQueen, 1976), but care must be taken in such interpretations, as some of the organic inclusions show clear evidence of major chemical reorganization of the compounds present after trapping (Roedder, 1962b, p. 40; 1976, p. 96). Almost no study has been made of the bitumens that occur in some inclusions, yet bitumen can be formed in several ways, and the results commonly can be differentiated (MacQueen, 1976). Still another aspect that may merit further work is the presence and specific nature of any amino acids in inclusions.

(Leach, 1973b,c); Upper Mississippi Valley (McLimans, 1975); North Wales (Smith, 1973); Durham, England, barite (Hirst and Smith, 1974); and possibly south-central New Mexico (Allmendinger, 1974; Beane, 1974).
Mueller (1972) reports finding them among the organic inclusions in the Derbyshire fluorite-lead-zinc deposits. As the various amino acids vary widely in their susceptibility to thermal degradation (Hare and Mitterer, 1969), the assemblage present may provide valuable data on the thermal limits. Fatty acids have also been found in fetid sedimentary barite deposits (Miller, Brobst and Beck, 1972) and may occur, along with H$_2$S, in minute fluid inclusions.

Although many Mississippi Valley-type deposits are believed to have formed at only a few hundred meters depth, some, such as those at East Tennessee, may have formed at much greater depths, and mineralization of this type has been found in midwest oil wells at depths of nearly 2 km.

Although generally considered to be a variant on the normal Mississippi Valley deposit, the barite deposits that are sometimes associated with them are frequently quite different in terms of fluid inclusion data. Necking down and leakage are common problems with barite, but in most deposits, those few inclusions that do look valid (Roedder, 1976) generally have much lower salinities and/or homogenization temperatures than the sphalerite or fluorite in possibly related mineral deposits. As an example, barite from mines and prospects in the Sweetwater barite district of East Tennessee was examined (Roedder, unpub. data). Barite from the Nuns Cove prospect in Sevier County, Tennessee (ER 63-82) showed freezing temperatures of $-0.47$ to $-0.32\,^\circ C$, and some inclusions of organic liquid and gas, and that from the Click Creek prospect, Hawkins County, Tennessee (ER 63-81), showed $-0.15\,^\circ C$ freezing temperatures, corresponding to nearly fresh water. Barite from the Ballard mine contained too many inclusions ($\sim 20\%$ by volume), and hence was porous and no inclusion could be trusted; white barite from many localities is similar in this respect. The associated earlier green and blue fluorite in samples from the Ballard mine (ER 65-103, -106, and -108) had 14 good primary inclusions with freezing temperatures of $-5.6$ to $-10.6\,^\circ C$ (Roedder, 1967a) and homogenization temperatures of 53 to 128$\,^\circ C$ (Roedder, unpub. data).

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**Fig. 1.**—*A*, Two planes of secondary inclusions, formed by the healing of fractures in a celestite crystal from a vug in Paleozoic dolomite from Clay Center, Ohio (sample ER 65-72). The periodicity of the spacing of the inclusions reflects a regularly spaced alternation in the Sr/Ba ratio with a 7.4 $\mu$m thickness per cycle, visible here as faint vertical bars, parallel to (210) of the host crystal. This banding is believed to be a result of annual variations in the salinity of the depositing brines (i.e., they are equivalent to varves; Roedder, 1969). Taken with transmitted, strongly collimated light. Bar = 100 $\mu$m.

*B*, Inclusion in sphalerite from vug in Wabash Formation near Delphi in Carroll County, Indiana (sample no. 1, courtesy N. R. Shaffer). This inclusion, and many others in this material, homogenized at 82–83$\,^\circ C$ and froze at $-14.1\,^\circ C$. Bar = 10 $\mu$m.

*C*, Inclusion in sphalerite from cleats in bituminous coal from the Herrin no. 6 Coal, Knox County, Illinois (sample ER 75-6, L00041, courtesy Illinois Geol. Survey). This inclusion, and others in these samples, homogenized at 94$\,^\circ C$ and froze at $-17.2\,^\circ C$. Bar = 10 $\mu$m.

*D*, Primary negative crystal inclusion in fluorite from the fluorite-zinc-lead deposit at Cave-in-Rock, Illinois (sample courtesy P. B. Barton, Jr.). Most inclusions of this type from this deposit have homogenization temperatures of $-145\,^\circ C$ and salinities of 15–20 wt. $\%$ salts. Bar = 100 $\mu$m.

*E*, Oil inclusion in yellow fluorite from Ozark-Mahoning’s West Green mine, southern Illinois fluorite-Pb-Zn deposits (sample ER 59-57e; F330 from Illinois Geol. Survey, courtesy R. Grogan). This inclusion originally formed as a spherical, immiscible globule of oil that stuck to the growing surface of the host fluorite cube at the bottom surface (see arrow). As the fluorite grew up around it, additional oil droplets in the surrounding brine adhered to the exposed top of the droplet, causing it to develop the neck of the “bottle.” Subsequent cooling from the temperature of trapping ($-150\,^\circ C$) formed the shrinkage bubble (V), and the degradation of the oil precipitated a black asphaltic material that preferentially wet only certain crystallographic planes on the host fluorite wall, yielding black spots with fourfold symmetry (see illustration in Roedder, 1962b, for plan view of such inclusions). The balance of the inclusion fluid is enriched in lighter hydrocarbons; some such inclusions vaporize instantly on opening at room temperature. Bar = 100 $\mu$m.

*F*, Remnant of corner of hopper crystal of halite, embedded in large, single (mainly recrystallized?) halite crystal from ERDA no. 9 borehole, Carlsbad, New Mexico, 2065 foot depth. The hopper growth is outlined by dense, almost opaque, masses of mostly very minute primary inclusions. These contain a strong bittern, not just saturated NaCl. Bar = 100 $\mu$m.

*G*, Three large primary inclusions in recrystallized halite from ERDA no. 9 borehole, Carlsbad, New Mexico, 2569 foot depth. Bar = 100 $\mu$m. These contain a strong bittern with a composition similar to that present in the original, unrecrystallized salt. The two larger inclusions have nucleated a vapor bubble on cooling from the recrystallization temperature (other similar inclusions in this sample homogenized at 43–45 C). The vapor bubble in the larger inclusion (arrow) has a minute (3 $\mu$m) spherical globule sticking to it (see inset photo; bar = 10 $\mu$m); this is possibly an immiscible hydrocarbon, precipitated on cooling (see Price, 1973).
Another aspect of the study of fluid inclusions in Mississippi Valley-type deposits concerns the help they may provide for exploration programs. Every exploration program must be based somewhat on a model of the mode of formation of the type of deposit being explored. If this model is valid, it can greatly enhance the possibility of success by concentrating the exploration effort on the most likely ground (Roedder, 1977b). Fluid inclusion evidence on the Mississippi Valley-type deposits does not suffice by itself to pinpoint which of many suggested models is correct in any given deposit, but it does suffice to eliminate some suggested models and hence help the explorationist. Thus the high salinities and the high temperatures exclude cold surface waters and shallow ocean lagoon waters, both of which have been seriously proposed as the ore-forming fluids for some of these deposits.

CARBONATE AND QUARTZ CEMENTS IN DETRITAL ROCKS

Anyone who has looked at detrital carbonate rocks in thin section is aware of carbonate overgrowths on the grains that commonly act as a cement in these rocks. The small size of these overgrowths is such, however, that they would seem to be a very unlikely place to find usable fluid inclusions. But a study by Nelson (1973) has shown that small but usable primary fluid inclusions can indeed be found in such cements. In a crinoidal biosparite, the Fernvale Limestone (Upper Ordovician), from samples across northern Arkansas, such inclusions show a homogenization temperature range from 85–170°C with a distinct mode in the range 110–150°C. The salinity ranged from 5–25 wt. % NaCl equivalent. These data are very similar to those found for inclusions in the barite-lead-zinc deposits of central and northern Missouri (Leach, 1973a, b), and it is presumed that the cementation fluids and the ore-forming fluids may represent a single episode of fluid flow through these rocks. The possibility of multiple periods of circulation (and cementation) must always be considered (Blatt, 1978).

Another similar application of inclusion data to carbonate rocks is found in the “dolomite problem,” i.e., when did what dolomite form? In some mining areas there are several stages of dolomitization, e.g., Pine Point, Canada (Dunsmore, 1973; MacQueen and Taylor, 1974), and East Tennessee (Wedow, 1974). Freeman (1973) has reported that the fluid inclusions in some epigenetic dolomite-calcite cements show that the fluids forming the dolomite were both hotter and saltier than those forming the associated calcite cements.

Quartz cements may provide similar opportunities for finding inclusions that can delineate the environment of sandstone diagenesis. R. C. Nelson (personal commun., 1975) has studied quartz overgrowths in the Blakely and Crystal Mountain Sandstones (Lower Ordovician) from central Arkansas. Most of the inclusions are trapped at the original grain boundaries of the detrital quartz grains, but some occur within the overgrowth, and considerable care must be used to avoid confusion with the inclusions of the original detrital grains. Homogenization temperatures for inclusions in the overgrowths ranged 97.5–152°C (possibly as high as 175°C). More recently, Pagel (1977) has made use of the inclusions in quartz cements in a study of uranium deposits.

Studies such as these show that fluid inclusions can provide useful quantitative data on problems that heretofore have been plagued by ambiguous, qualitative data. They will generally require extensive and careful microscopy, but the possibilities of getting answers to otherwise intractable problems make the effort worthwhile.

SALINE AND SULFUR DEPOSITS

Saline formations can be very sensitive indicators of diagenesis, as they recrystallize rather readily. Much bedded salt has recrystallized, but it is not uncommon to find within bedded halites single crystals which have very clear multiple chevron-like patterns (Fig. 1F), corresponding to growth zoning parallel to the faces of original hopper crystal cube corners. As these hopper crystals grew on the surface of the brine, and then sank, their orientation is random. When these patterns are examined in detail (e.g., those from the Salina beds at Goderich, Ontario; Roedder, 1963), they are found to be composed of planes of very tiny, liquid-filled inclusions, generally 3–30 μm, but many are <1 μm in diameter and a very few are as large as 300 μm. Some samples have as many as 2 × 10^10 inclusions per cm^3 (Roedder, 1972, p. 43). The wide range of sizes making up a pattern that has remained intact since Salina times places an interesting constraint on the rate of movement of inclusions in the geothermal gradient. Any inclusion in a thermal gradient should move, generally toward the heat source, because of solution on one side and deposition on the other, and large inclusions should move fastest. Unfortunately, numerous factors are involved (e.g., see Anthony and Cline, 1974), but as the original growth pattern has not been lost or even visibly distorted in millions of years in a geothermal gradient, this movement must be exceedingly slow or have a threshold.

When inclusions in halite are studied on the freezing stage, they are frequently found to contain a wide range of compositions, from bitterns with high concentrations of calcium and magnesium to essentially pure solutions of NaCl (Roedder,
1963, p. 182; Roedder and Belkin (1978) have shown that the Carlsbad area of New Mexico provides a notable exception). Such a range is expectable from the normal events in the history of such salt beds. During the original crystallization, evaporation continuously concentrates the more soluble ions such as Ca and Mg into the residual liquids, and unless refluxing is effective, inclusions will be trapped representing various stages in this process. Under diagenesis, formation waters penetrating the recrystallizing halite bed will dissolve the more soluble minerals and gradually flush out residual and grain boundary fluids, until only NaCl (and CaSO₄) remain. Any fluids trapped during subsequent recrystallization or upon the healing of fractures will contain only NaCl (plus any salts originally in the waters passing through).

Analyses of the fluid inclusions in halite have been reported by several workers (see Tables 4 and 6 in Roedder, 1972; Derevyagin, 1973; Kovalyevich, 1975; Petrichenko, 1973; Petrichenko, Kovalevich, and Chalyi, 1974; Petrichenko and Shyadetskaya, 1973; Petrichenko and Slivko, 1973; Sedletskii, Trufanov, and Maisikii, 1973). Several of these studies show large differences in the composition of inclusions in primary salt and in recrystallized material. Although several thousand analyses of inclusions are reported in the literature, for all types of material, the only actual determinations of Eh (−400 to +515 mV) of the fluids have been on inclusions in halite, by Petrichenko and coworkers (see above). He also reports what are probably some of the most valid pH determinations made on inclusions (4.5–6.4), as the inclusions available were huge, and hence minimized the otherwise very serious experimental problems in measurement.

In addition to the major ions Na, Cl, K, Mg, and Ca, several of the minor constituents are useful in understanding the environment of formation. Thus Sabouraud-Rosset (1973, 1974) has found that the Cl/Br ratio in fluid inclusions in gypsum crystals from various types of saline environments varies from 150 to more than 1000, and she has been able to recognize leaching by later waters in some of these environments on the basis of neutron activation analyses for Cl and Br. This ratio is particularly suitable, as it is not apt to be affected seriously by reactions with clays, etc., that can seriously influence other minor elements (Petrichenko and Slivko, 1974). Such reactions particularly affect the ratio K/Mg, and the content of SO₄ ions. Organic matter is also present in the inclusions in many saline deposits, as bitumen (e.g., Kul'chitskaya, 1974), as liquid and/or liquified hydrocarbons, under pressure (e.g., Fig. 1G; also Roedder, 1972, p. 43), and as gas (mainly either CO₂ or methane) under pressures up to many atmospheres (e.g., Bol'shakov, 1972; Petrichenko and Slivko, 1973; Petrichenko, Kovalevich, and Chalyi, 1974). Sometimes the pressure of the gases in the inclusions is enough to make the salt decrepitate either spontaneously or under minor relief of stress, yielding “popping salt” that can become a major hazard in mining (Roedder, 1972, p. 43). There is no consensus concerning the origin of these gases, and they have been termed both syngenetetic and epigenetic. As the composition varies widely from one occurrence of popping salt to another, probably several different processes are involved.

As a result of the rather common occurrence of leakage, necking down, and metastable stretched liquid under negative pressure in inclusions in halite (center inclusion in Fig. 1G; see also Roedder, 1967b, 1971b), temperature measurements by the homogenization method are generally suspect and frequently impossible. Such processes may explain some of the reports of exceedingly high homogenization temperatures (e.g., 240–360°C, Panov, 1975). Gypsum also may give unreliable results (Kul'chitskaya, 1974). However, a few halite deposits have yielded seemingly valid values. Kovalyevich (1975) found that homogenization of sylvite daughter crystals in some primary inclusions in halite from Stebnik in the USSR took place at 38–60°C, whereas secondary gas/liquid inclusions in recrystallized halite homogenized in the range 56–86°C, with the average of 80 determinations 71°C. Petrichenko and Slivko (1973) established that diagenetic alteration of Permian salt in the Donbass took place at ~60°C, and Roedder and Belkin (1978) showed that inclusions in both primary and recrystallized salt in a core from the Delaware Basin (Carlsbad area, New Mexico) homogenized in the range 25–45°C.

For determination of homogenization temperatures with a minimum of ambiguity, other minerals that have formed in the halite beds are generally more tractable. Thus Sedletskii, Trufanov, and Mel'nikova (1971) measured homogenization temperatures of 40–110°C for inclusions in authigenic quartz crystals from Upper Jurassic saline deposits in the Hissar Range, USSR.

One of the most interesting minerals that acts as a recorder of diagenetic conditions in saline deposits is sulfur. Sulfur is found in many saline deposits, where it generally is assumed to have formed as a consequence of bacterial oxidation of organic matter and reduction of sulfate from anhydrite or in the water. There is frequently

³These authors erroneously subtracted 15–20° from these values as a “correction for salinity” to obtain trapping temperatures.
a problem concerning the time at which this action took place, and the fluid inclusions in the sulfur may provide useful input. These inclusions are frequently large, and as there is no reported evidence of inclusions in sulfur leaking, these should provide good material for analysis. The inclusions in sulfur and associated gypsum in the famous Sicilian deposits were so large that they were some of the first inclusions to be analyzed quantitatively and reasonably completely (Silvestri, 1882; Sjögren, 1893). Sjögren found the gypsum to contain a sodium-chloride-rich solution containing 4% salts, but the fluid inclusion in sulfur analyzed by Silvestri contained only 0.1% salts. The latter may be an unfortunate example of an inclusion in sulfur that did actually leak, in view of the very low salinity and the very large size (6 cm³), as large inclusions are much more apt to leak than small ones (Roedder and Skinner, 1968, p. 723).

Yushkin and Srebrol’skii (1965) studied large inclusions in sulfur from the Rozdol and Shorsui deposits in carbonate-sulfate rocks in Uzbekistan, USSR. The inclusions are single phase (i.e., full of liquid) except for a film of bitumen in some. The presence of large single-phase inclusions indicates that the sulfur grew at low temperatures, as even cooling from 40°C will cause a bubble to form in most large inclusions. The fluid released some H₂S when the crystals were crushed, and had a pH of 7–7.5, as determined by the use of various organic indicators. It contained about 6% salts, mainly (Na, K) and Ca chloride, bicarbonate and sulfate. Merlich and Datsenko (1972) found that the fluid in inclusions in sulfur deposits from the Little Carpathians in southern USSR were NaCl solutions, similar to seawater.

Beskorovnyi and Lebedev (1971) studied various minerals from the Gaurdak sulfur deposit which is in a sequence of gypsum-anhydrite-halite rocks in limestone in southeastern Turkmenia. This must be a different type of sulfur deposit, however, as it contains also celestite, fluorite, barite, danburite, hematite, gypsum, calcite, solid bitumens, quartz, sphalerite (high in Hg and Pb), oil, and gas. Early fluorite inclusions homogenized at 130–160°C, but those in late gypsum and calcite homogenized at <50°C.

**PETROLEUM RESERVOIR ROCKS**

Organic matter in contact with fluids moving through a sediment is subject to a continuous series of changes with time, depth, and temperature (Barker, 1972; Macqueen, 1976), as well as surficial weathering (Clayton and Swetland, 1976). However, when the growth of a crystal causes the trapping of an inclusion containing such organic matter, it effectively isolates it from reactions with subsequent external environments. Isochemical changes may still take place, but for reasons that are not clear, they do so only in some inclusions (e.g., some southern Illinois oil inclusions in fluorite; Fig. 1E; Roedder, 1962a, p. 40; 1972, Plate 9, Fig. 2; see also Kvenvolden and Roedder, 1971, p. 1214). Insofar as the environment of trapping can be estimated, or at least delimited, by data on the organic compounds present, these oil inclusions can be useful. Thus, in theory at least, the many changes that take place during the migration and maturation of petroleum should be recorded in oil inclusions trapped at various stages along the way. Very little has been done in this respect, but with the recent tremendous improvement in appropriate analytical techniques, such as microgaschromatography, mass spectrometry, and particularly the combination of the two, the approach has considerable potential.

Organic gases, liquids, and solids have been recognized in inclusions in many samples, and these materials have been characterized to various degrees. The extensive literature is listed or abstracted elsewhere (Table 1; see also Roedder, 1968-onward, 1972) and only a few items can be reviewed here. A pioneering effort in this direction was made by Murray (1957), who reported a detailed mass spectrometric analysis of the molecular constituents in organic liquid-gas inclusions in quartz crystals from vugs in a dolomite core from a gas-productive interval in Mississippian rocks in Alberta. The inclusions contained mainly methane and ethane under pressure, and also included small amounts of many other constituents, but no water. On heating, the two phases homogenized in the gas phase at about 100°C. The problem is how such inclusions can become trapped, as it would seem to require growth of quartz from the hydrocarbon fluid. The fluids trapped in some very thin wedge-like planes of secondary inclusions suggest that oil inclusions are trapped because of preferential wetting of the quartz surface with the oil phase, and growth of the exposed quartz surfaces from the immiscible water phase, so that the cavity full of oil can be enclosed completely, without any of the water phase (Kvenvolden and Roedder, 1971).

In North Derbyshire, England, organic materials of several types have been found associated with lead-zinc-fluorite deposits in Carboniferous limestones. Although these various materials are found there as inclusions, particularly in fluorite, they are also found free, in larger masses, and have been studied extensively in an attempt to determine their origins (e.g., Nooner et al., 1973; Pering, 1973). There have evidently been several stages of selective leaching, transport, and deposition, and possibly recent partial microbial oxida-
tion. This is only one of many lead-zinc-fluorite deposits in carbonate rocks that contain organic matter (see also Table 1). Although some mines have oil or tar actually dripping from the back, others that seem to be free of it have been found to contain measurable amounts (≤100 ppm) in certain minerals, such as sphalerite (Rickard et al., 1975).

Even if no organic phase in the aqueous fluid inclusions is visible, a growing body of evidence shows that very significant amounts of a wide variety of hydrocarbons can dissolve in water or brine (Price, 1973; 1976); these compounds should be looked for. Possibly the “hydrocarbon peaks” frequently seen in mass spectrometric studies of inclusions, that are usually passed off as normal atmospheric contamination, may be in part real. Other compounds, such as amino acids (K. Kvenvolden, personal commun., 1975), should also be searched for that might define better the maximum temperatures to which a sample has been subjected in the past.

Still another application of inclusions in connection with the history of oil-bearing rocks is their use to date the formation of fracture porosity at depth. Currie and Nwachukwu (1974) studied inclusions in mineral fillings of fractures in oil-field formations in Canada. They found that there were ranges of homogenization temperatures, from 45–120° C, which they interpreted as indicating that opening of fractures developed progressively as an accompaniment to tectonism, regional uplift and erosional unloading. They also suggest on this basis that incipient fracture porosity at depth can develop gradually into a network of open fractures under conditions of continued uplift and erosional unloading. The presence of organic coatings on some of the minerals studied suggests the possibility of establishing the time relationship between fracture-porosity formation and oil migration.

One of the most striking convergences of scientific lines of thought has been the rather recent recognition of the similarity of the problems of the petroleum geologist and the minerals exploration geologist in looking for deposits in sediments around the margins of basins. This aspect has been discussed by many (e.g., Dunham, 1970; Macqueen, 1976) and places additional importance on the full characterization of the organic compounds found in inclusions from each of these environments.

Sphalerite in Bituminous Coal Beds

All coals contain at least some sulfides, and because of the environmental significance there has been considerable interest in the nature and origin of these sulfides. Iron sulfides are by far the most abundant and are mainly of authigenic origin (Docter, Kullerud, and Sweany, 1975). In some coals, however, sphalerite is a significant constituent, and as it is a transparent mineral, fluid-inclusion studies on it may yield information concerning the conditions of origin. Leach (1973a) studied inclusions in sphalerite from coal mines in central Missouri and found homogenization temperatures of 80–110° C, and strongly saline brines (>22% NaCl equivalent). As the sphalerite from the adjacent northern Arkansas zinc district had similar fluid inclusions (83–132° C and >22% NaCl equivalent), Leach suggests that these two mineralizations formed from a single episode of fluid flow.

In the northwest part of the Illinois Basin some bituminous coals have very coarsely crystalline banded yellow and purple sphalerite both as vertical veins (“cleats”) and as crystals in clay dikes cutting the coal seams (Hatch, Gluskoter, and Lindahl, 1976; Cobb and Russell, 1976). Fragments of coal are found embedded in the sphalerite. The sequence of color banding is regular throughout a large part of the basin (Hatch, Gluskoter, and Lindahl, 1976). Samples of these sphalerites show many secondary or pseudosecondary aqueous inclusions, and only a very few inclusions that might be primary (Fig. 1C). A group of 25 inclusions from the cleat sphalerite and 19 from the clay dike sphalerite, all from Knox, Peoria, Montgomery and Fulton Counties, Illinois, were selected on the basis of maximum likelihood of a primary or at least pseudosecondary origin, and homogenization and freezing temperatures determined (Roedder, unpub. data). Homogenization temperatures ranged from 90–102° C for the cleat samples (average: 95.7° C) and 82–96° C for the clay dike samples (average: 89.5° C). The freezing temperatures of all samples ranged from −15.6 to −18.9° C and averaged −16.9° C, and all showed first melting at <-26.5° C. The freezing temperature corresponds to about 21% NaCl solutions, but the first melting temperature requires the presence of ions other than Na and Cl (Roedder, 1962a). Although Hatch, Gluskoter and Lindahl (1976) report five generations of sphalerite deposition, no recognizable difference could be detected between the inclusions in the various colors in the present work. However, the distribution of the selected inclusions among the various samples and color zones in them was adequate to detect only gross differences.

The interpretation of these results is not at all clear. Bituminous coal itself is a sensitive indicator of “diagenetic” (low-grade metamorphic) conditions (Walenczak, 1974). Bostick (1973, and personal commun., 1976) has shown from coal petrography that the high-sphalerite coals of the Illinois Basin were never subjected to long-continued burial temperatures above 40–65° C, and any
anomalous temperature events on the order of 100° C could have lasted only 1-3 million years. Thus the maximum temperatures from the inclusion data and the coal petrography data may not be in conflict.

There is an interesting possibility of a connection between the fluids depositing this sphalerite and those forming the sphalerite in the Upper Mississippi Valley zinc deposits ~150 km to the north. The homogenization temperatures found in the Upper Mississippi Valley zinc deposits by earlier workers (see Roedder, 1976, Table IV) range from 75–121° C, and freezing temperatures of ~20° C (Roedder, 1967a). These fluids were thus in the same temperature range but somewhat more saline than those in the coal beds. But recent studies by McLimans (1975) showed homogenization temperatures for inclusions in early sphalerite in the zinc deposits higher than those in any other recorded Mississippi Valley-type ore deposit in the world (150–210° C). Even this large a difference does not preclude a genetic connection, however, as it is expected that the zinc-depositing brines eventually would cool and become more dilute from flowing through cooler rocks and the addition of ground water. As pointed out by Hatch, Gluskoter and Lindahl (1976) from the color banding, the deposition of this sphalerite was a basin-wide event, making it evident that large-scale fluid movements must be involved.

**SUMMARY**

From all the above data on six seemingly very different environments, it is apparent that most environments of sedimentary diagenesis, at least those recorded by fluid inclusions, involved the presence of hot, saline brines. Although many deep basins now contain hot saline brines, particularly below 3 km, some geologists are reluctant to accept such an environment for the thinner piles of cratonic sediments. Admittedly, little evidence of such brines may be visible in the usual outcrop, once the brines have been replaced with surface water, as most of the minerals present are relatively inert. But the inclusions present in the minerals can and do preserve evidence of these hot brines for geologic time. The presence of such hot fluids under pressure in present-day sedimentary piles, and their migration, whether it be due to compaction or other gradients (Magara, 1973; Price, 1975), is exceedingly important to an understanding of both ore and oil deposits.

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**Fig. 2.** Temperature-depth relations with various geotherms. For comparison, the boiling curves for water (0%) and 25 wt. % NaCl solution are given.
FLUID INCLUSION EVIDENCE

As the maximum depth of cover of many of the formations from which the samples were obtained is generally low, this raises the question, what was the geothermal gradient at the time of deposition? Figure 2 shows a series of linear geothermal gradients. From this figure, and the available estimates of depth of cover for the various samples described above on which homogenization data have been obtained, it is evident that those in the upper temperature ranges, particularly those over 150°C, must represent very high gradients at the time of trapping.

The heat capacity of brine is so high relative to that of rock that movement of the brine is of great importance in any thermal calculations. Thus a sediment having 10% porosity (Clark, 1966) has less than six times the total heat capacity of the much lighter brines (assuming 20% NaCl) filling the 10% pores. Hence relatively few recharge of the fluids in the pores could bring the rock to the temperature of the entering fluids, and with higher porosities the process would be even more effective. Diment et al. (1975) show that over much of the interior of the United States, the present vertical heat flow is \( 1.5 \times 10^{-6} \) cal/cm² s. This rate of heat flow (from conductivity) is about the same magnitude as would be obtained from vertical fluid flow rates, assuming normal porosities, in the range of 30 cm/yr (A. H. Lachenbruch, personal commun., 1976). Thus even a very slow upwelling of hot brines can be effective in increasing the thermal gradient of the region, as long as it continues. It may be that the minerals sampled for fluid inclusions are a biased sample, enriched in those from higher gradient areas, perhaps for the very reason that such rising, cooling fluids have caused the precipitation of the host (ore) minerals. Even such slow flow rates can cause the transport of surprisingly vast amounts of material in the available time (Roedder, 1976, p. 70).

The magnitude of the homogenization temperatures found for some Mississippi Valley-type deposits and the high geothermal gradients they require have caused some to look for novel sources of heat, in particular exothermic reactions. Thus Bush (1970), Dhannoun and Fyfe (1972), and Dunsmore (1973), among others, have suggested the reduction of SO₄²⁻ by petroleum (either bacteriologically or direct chemical) as a source of heat as well as the sulfide ion for precipitation of the ores. This is seemingly a very happy solution to the dilemma of simultaneous transport of sulfur and metal in a single solution, as well as the high thermal gradients, as the reaction is admittedly exothermic. However, even with a very liberal choice of chemical and geological parameters, the possible temperature rise of the passing fluids from this reaction can only be a small fraction of one degree—several orders of magnitude too low (Roedder, 1971a). Significant temperature rise could be achieved only if solid anhydrite and hydrocarbons were permitted to react in place, i.e., neither carried by the brines, but then the disposal of the resulting H₂S becomes a problem, particularly as this will retard further bacterial action.

The salinity of the fluids in most deep sedimentary basins generally increases with depth, frequently at such a rate that the effect of salinity on the density is just sufficient to counteract the opposite effect of increasing temperature (Hanor, 1973). The densities of the fluids trapped in the fluid inclusions in these materials, when corrected for expansion up to the temperature of homogenization of these inclusions, are also found to be usually a little more than 1.0 g/cm³. Thus the fluid column is gravitationally stable, but subject to possible turnover if perturbed, as by erosion or by additional heat from a deep intrusive. It is tempting to suggest that the Mississippi Valley-type deposits may represent exactly those areas where such disturbance and convective turnover occurred in the past.

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