INTRODUCTION

Although this volume includes discussions of many types of deposits in sedimentary and volcanic rocks, fluid-inclusion evidence is most abundant and pertinent in the Mississippi Valley-type of deposit (and, to a lesser extent, in the Kuroko type); hence, data from these deposits are emphasized here. Only a small part of the inclusion literature deals with such deposits. Much of it deals with ore samples, either from vein deposits obviously associated with igneous intrusions ("magmatic hydrothermal"), or from quartz crystals in veins of metamorphic to quasi-igneous origin (particularly the large Russian literature — see Ermakov, 1950). In addition, particularly in recent years, studies of silicate melt inclusions in terrestrial, meteoritic, and lunar samples have provided data on the liquid lines of descent for various magmas. The principles are generally applicable, however, to any deposit in which the constituent minerals have grown from a fluid medium — gas, liquid, or melt. Because of the lack of suitable sample material (as described below), very few studies have been made of fluid inclusions in most of the other types of ore deposits covered in this volume. Usable material may eventually be found in at least some of these and could provide exceedingly important data on ore genesis, data that are in part otherwise simply unavailable.

"The origin" of the Mississippi Valley-type of ore deposit, using the type term in its most general meaning, has been the subject of an extensive, in part heated discussion, only a small part of which comes from problems of exactly what types of deposits are to be included. The range covered is well illustrated in the volume stemming from a symposium on the genesis of stratiform lead—zinc—barite—fluorite deposits held at the United Nations in New York in 1966 (Brown, 1967). In an excellent review and sequel to this volume, Brown (1970, p. 104) summarized eleven distinctive characteristics of these deposits, as they are found in the three main districts in the Mississippi Valley proper (see Sangster, Chapter 9, Vol. 6).

Other apparently similar deposits in the United States and throughout the world differ most drastically from these characteristics in terms of the isotopic composition of the lead. Brown therefore suggested (1970, p. 117) that the broad class of Mississippi Valley-
type deposits might be divided into three categories, based on the presence of normal type, B-type, or J-type lead. These three leads yield model ages that are, respectively, approximately correct, “too old”, and “too young”.

These differences are particularly significant in discussions of “the origin” of these deposits, in that they are one of the most obvious indications that there can hardly be only one mechanism of origin. Indeed, one of the most important causes for differences of opinion as to genesis is that there must have been a multiplicity of mechanisms operating in the various specific deposits. One does not need to go to isotopic studies to see this, however; the tremendous range in gross composition of the individual deposits, from essentially pure Pb with only traces of Zn, F, and Ba, to those with essentially pure Zn, to mixtures containing major amounts of all four (and other) elements, suggests that there had to be significant differences in the chemistry and perhaps in the mechanism(s) operating.

Most ore deposits represent the results of one ore or more processes in which an ore element is dissolved from a (presumably) dispersed or dilute source area, transported to the future site of the ore body, and deposited there in a relatively concentrated form. The many theories of origin of the Mississippi Valley-type ores differ among themselves in part as to the source or sources chosen for the ore elements. The term “ore element” used here includes not only the obvious metals Pb and Zn (and to a minor extent, Cu) but also the F and Ba that are even more highly concentrated. Thus, the production of the Illinois–Kentucky district, reported by Grogan and Bradbury (1968), is Pb, 60,000; Zn, 200,000; and CaF₂, 10,000,000 tons (ratio 1/3/170). Other districts are equally biased, but toward high barite or high Pb. The sources to be considered are listed in Table I. Each of these eight has been put forward as the major source or as a significant contributing source.

It is very important to realize that as long as the fluids can move through distances measured in kilometers (e.g., 1 km equals 30 years flow at 1 μm/sec), during geologic time, the source need not be enriched. As a good approximation, each part per million of an element in a rock corresponds to about 10,000 tons of that element per cubic mile of

<p>| TABLE I |</p>
<table>
<thead>
<tr>
<th>Proposed sources for the ore elements in Mississippi Valley-type deposits</th>
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<tr>
<td>1. Seawater (and hence originally from weathering of rocks)</td>
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<tr>
<td>2. Leached from sedimentary rocks or muds in place</td>
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<tr>
<td>3. Expelled from sedimentary minerals, particularly from shales, during diagenesis</td>
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<tr>
<td>4. Expelled from recrystallizing metamorphic minerals</td>
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<td>5. Leached from metamorphic rocks in place</td>
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<tr>
<td>6. Leached from igneous rocks in place</td>
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<tr>
<td>7. Expelled directly from crystallizing magma</td>
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<tr>
<td>8. Volcanic exhalations (via fumaroles, hot springs, etc.)</td>
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rock (or 2400 tons/km²). Thus the extraction process can remove enough metal to make a big ore deposit from geologically reasonable amounts of very dilute source materials; geology kindly provides such vast amounts of materials and time that the extraction (and concentration) processes can be (and probably are) exceedingly slow and inefficient.

Central to any understanding of the processes of dissolution, transport, and redeposition of the ore elements is the nature and origin of the responsible fluid — the ore-forming fluid. Because fluid inclusions provide us with samples of that fluid, the physical and chemical data obtained from their study supply useful information toward an understanding of the entire process.

A variety of sources has been suggested for the ore fluids forming the Mississippi Valley-type deposits, as listed in Table II. Also, some theories of origin invoke combinations of several sources for the fluids, i.e., mixing. This mechanism, involving separate sources for metal- and sulfide-bearing fluids, was first detailed, for the Pine Point deposits, by Beales and Jackson (1966; see also Jackson and Beales, 1967); Hoagland (1973) has since applied it to the Central Tennessee deposits. It is also important to note that the divisions in Table II, as in Table I, are based on rather indistinct boundaries. Thus, there may well be a continuum between sea, connate, compaction, and metamorphic water (White, 1957; Noble, 1963), and several varieties may be combined in the water evolved from a subduction zone.

Obviously there must have been a much larger volume and weight of ore fluid than the resultant ore itself; the ore fluid, therefore, must not only be transported from the site of dissolution to the ore body, but many successive volumes must pass through the site of the ore body in sequence. The volume of this ore fluid will bear a simple inverse relationship to the concentration change (input minus output). Thus, if this concentration change is only 1 ppm, 1 million times more fluid than ore is required, and at 100 ppm, 10,000 times more fluid. These volumes may seem large, but when examined in geological terms they are not unreasonable. Even when geologically very small segments of time are assumed for ore deposition (Roedder, 1960), the flow rates required are low (<1 μm/sec) and the quantity of flow is also reasonable (e.g., 10 gallons/min (= 38 l/min) to form the main ore body at Pine Point: Roedder, 1968a, p. 447).

**TABLE II**

Proposed sources for the fluids responsible for dissolution, transport, and deposition of the ore elements in Mississippi Valley-type deposits

1. Meteoric (surface) waters (+ deep circulation and heating to form "hydatogenic" fluids)
2. Seawater (+ evaporation to cause enrichment in salts)
3. Connate and compaction fluids in sediments (+ dissolved evaporites)
4. Metamorphic waters, expelled during dehydration reactions
5. Magmatic waters, evolved from crystallizing magma ("magmatic–hydrothermal" or "telethermal")
Fig. 1. Diagram showing the interrelations between time, flow rate, and concentration change (incoming minus outgoing fluid) needed for the deposition of $10^8$ tons of 10% ore in a stratum 4 km$^2$ in area and 10.7 m thick. The rock is assumed to have a bulk density of 2.34 and a bulk porosity of 10 vol%, and the liquid a density of 1.0. The shaded area is the geologically most probable range of conditions under which most Mississippi Valley-type deposits formed. Adapted from Roedder (1960).

In Fig. 1, the interrelations of the three variables, concentration change, flow rate, and deposition time, are illustrated graphically on a log–log plot, for a very large hypothetical tabular deposit of a $10^8$ tons of 10% ore (Pb, Zn, or any other element). The model has been set up for flow perpendicular to the beds for simplicity; in nature most of the flow has probably been parallel with the beds, but the numerical results will be identical.

The central crosshatched area on this diagram represents what the writer believes to be the geologically most reasonable range of these variables for the formation of most Mississippi Valley-type ore deposits. The right- and left-hand limits of this area are based on rather arbitrary guesses as to the maximum and minimum flow rates to be expected in such sedimentary terranes (see below under section “Types of data available: rate of movement”). The lower and upper limits of 10 and 1000 ppm concentration change (i.e., amount of precipitation) are based on data from fluid inclusions (Roedder, 1972) and brine analyses (White, 1967; Carpenter et al., 1974). The diagonal time limits are chosen somewhat arbitrarily at 1000 and 10 m.y. on the basis of several lines of evidence (Roedder, 1968a, p. 447; 1969, p. 807; 1971a, p. 786; Brown, 1971, p. 568; Lavery and Barnes, 1971; Leach, 1973; Skinner and Barton, 1973). Other data may result in these boundaries being moved one way or the other, but it seems unlikely that they can be moved very far. Thus, the single neutron activation analysis for zinc in inclusions in fluorite from southern Illinois giving the highest heavy metal content ever reported from inclusions (Czamanske et al., 1963) would move the upper boundary up to 10,000 ppm.
at a maximum, assuming that complete precipitation of all heavy metals occurs. Similarly, White (1971) has suggested that the ore fluids at White Pine, Michigan, flowed for $10^6-10^8$ years. Regardless of the position chosen for the boundaries, the diagram gives the quantitative relationships between the variables.

In addition to the multiplicity of possible sources for the elements and the transporting fluids, the fluid may follow a wide variety of possible pathways, i.e., “structural control”, both on a regional scale and within the space of the deposit itself. Thus, for long distances, major faults, unconformities, bedding planes, and porous horizons have been proposed; within the confines of the ore body itself, an even wider assortment of features may control the flow, including caverns, joints, solution collapse or tectonic breccias and breccia pipes, reefs, and fossil stream channels.

Some have suggested that diffusion in a static fluid might be involved in the localization of the ore (e.g., by precipitation at the ore bed setting up concentration gradients). In the model shown in Fig. 1, however, even if we assume a complete transfer of all zinc from the sediments above and below to the ore bed, and an original Zn content of 100 ppm in these sediments, the average distance that the Zn atoms would have to diffuse would be over 2.5 km. Thus diffusion might aid the transport of ore metal, but hardly seems adequate by itself in this example.

The final unknown in the process is the actual cause for deposition. Here also many possibilities have been proposed, including mixing of waters, changes in T or P, loss of gases, reaction with country rock, internal changes within the liquid itself (e.g., sulfate being reduced slowly by organic compounds in solution), and biological activity.

The possible combinations of these variables in the construction of a theory of origin for a given ore body are almost infinite, and the evidence to select or discard any given concept or model is frequently nebulous, almost always ambiguous, and sometimes completely lacking. Fluid inclusions provide one more line of evidence that has too frequently been ignored. Inclusions are no panacea for ore-deposition problems, but they do provide a surprising amount of evidence, sometimes otherwise unavailable, with a minimum of ambiguity. Thus they provide data on the density, temperature, rate of movement, pressure, salinity, and composition of the ore fluids.

The purpose of this chapter is to examine the evidence from fluid inclusions and how it is obtained, evaluate its significance and limitations, and show how it can be used to place limitations on the possible mechanisms of ore transport and deposition. The various data from fluid inclusions alone cannot determine the origin or origins of stratiform ores, but (regardless of this origin), the data place severe limitations on the mechanisms of ore deposition which could have been operative. Any theory of origin must be compatible with the inclusion data, or the data must be refuted, if the theory is to stand. It is important to note that the selection of possible mechanisms of origin, and the elimination of impossible ones, is of more than academic interest. These decisions can be all important in the selection, and in the success, of exploration procedures to be used for these deposits.
LITERATURE SOURCES

There is no single source book in English on fluid-inclusion research. A review of the extensive Russian work (Ermakov, 1950) is available in English translation but is now rather obsolete. A short semipopular article (Roedder, 1962b) provides a brief review, and a discussion of fluid-inclusion evidence concerning ore deposition in general is available (Roedder, 1967a). A summary of the world literature on all aspects of the composition of inclusions is also available (Roedder, 1972). Abstracts of the scattered world literature (including particularly the large volume of articles in Russian) have been published each year since 1968 in a series of privately printed volumes entitled Fluid Inclusion Research – Proceedings of COFFI, available at cost from the present writer. Although perhaps half the world literature on fluid inclusions is in Russian, very few of these Soviet publications deal with deposits of the type covered by the present volume. Furthermore, many of them pertain to studies using a method (decrepitation) that has not found favor in the West.

ASSUMPTIONS ON WHICH FLUID-INCLUSION DATA ARE BASED

There has been little dispute since Sorby’s classic paper (1858) about what assumptions must be made in fluid-inclusion research, but debates have been heard on the validity of these assumptions. The use of fluid inclusions as evidence of the nature of the ore-forming fluid, and the environment of ore deposition is based on the following major assumptions (for a more detailed discussion of these and other assumptions, see Roedder, 1967a):

1. If a crystal of an ore mineral (or a gangue mineral known to be cogenetic with ore) grows from a fluid medium, irregularities in the growth process can, and usually do, cause the trapping of small amounts of this medium within the crystal.

2. The fluid trapped is a representative sample of the ore fluid at the moment of trapping.

3. Significant quantities of material are neither lost nor gained from the inclusions after this trapping.

There is little argument concerning the validity of the first assumption, as many natural crystals provide convincing proof of trapping by various types of irregularities; perhaps the most lucid examples come from the Mississippi Valley deposits (e.g., Roedder, 1965, 1972). Such inclusions are called primary because they form at the same time as the surrounding host crystal. There are many different criteria for establishing a primary origin for a given inclusion, and these vary widely with the individual sample or deposit. The specific criteria used are normally given in each published report (see also Table III).

Along with these primary inclusions, however, other inclusions may be found that were trapped at some later time, during the spontaneous healing of fractures. These
secondary inclusions not only contain a later fluid, possibly millions of years later, which may have no connection with the ore fluid, but they are also very common, frequently far more common than primary inclusions. Inclusions along healed fractures (e.g., along cleavage directions in fluorite or sphalerite) are not necessarily secondary, however; evidence indicates that many if not most of them in Mississippi Valley-type deposits, although appearing to be secondary, are actually formed by fracturing and rehealing during the growth of the host crystal (e.g., Roedder, 1965, figs. 18, 19; Roedder et al., 1968, figs. 12–15). Such inclusions are termed pseudosecondary. In practice, data from pseudosecondary inclusions are found to be identical with those from equivalent primary inclusions (i.e., those trapped at the same time), but data from true secondary inclusions may be very different. The criteria for distinguishing the three types of origin are summarized in Table III.

Proof of the validity of the second assumption is a little more difficult, but supportive evidence in the literature on fluid inclusions is extensive. Certainly, there are differences between the bulk of any fluid and the fluid at its interface with any other phase. These equilibrium boundary layer effects are believed to extend out into the fluid too short a distance (tens or hundreds of Ångstroms) to be significant in present-day experimental inclusion studies. Nonequilibrium conditions, in which crystal growth is more rapid than diffusion in the fluid, may yield very much thicker nonrepresentative layers, but such rapid growth does not generally occur in geological environments. The only discordant notes here are some data reported by Barnes et al. (1969), indicating that the fluids trapped in some synthetic inclusions were slightly more dilute than the bulk of the fluid in the experiment. To my knowledge, no one has attempted corroboration of these results. One other situation which almost certainly invalidates the second assumption is the presence of an inhomogeneous fluid — liquid plus a gas, another liquid, or suspended solids. This very limitation turns out to be useful, as detailed beyond.

The third assumption, concerning leakage, was once thought to cause a major problem in the interpretation of all inclusion data (Skinner, 1953) but has since been shown to be of little consequence, except in a relatively few, generally recognizable situations, e.g., inclusions in barite (Roedder and Skinner, 1968). In addition to these three basic assumptions, each specific type of application of inclusion data involves additional assumptions that will be mentioned in the individual sections. One other general assumption should be mentioned, however, concerning the problem of possible reworking of the material in the deposit. Brown (1970) pointed out that although fluid-inclusion evidence on Mississippi Valley deposits was widely quoted and generally believed in North America, many students of this type of deposit in Western Europe, and particularly in France and Germany, tend to ignore the inclusion data, under the assumption that it gives no information on the original ore fluids. As will be shown later, the fluid-inclusion data, if true, preclude several of the low-temperature and syngenetic concepts of origin most generally held in Europe. Some small part of these problems may arise simply from different usage of terminology by various researchers, but there still remains a major difference
TABLE III

Criteria for primary vs. pseudosecondary vs. secondary origin for fluid inclusions, summarized in part from Roedder (1967a, pp. 519–523)^1

I. Primary
A. Criteria based on occurrence in a single crystal with or without evidence of direction of growth or growth zonation.
   1. Occurrence as a single (or a small three-dimensional group) in an otherwise inclusion-free crystal, e.g., Roedder, 1965, fig. 10; Roedder, 1972, plate 6.
   2. Large size relative to that of the enclosing crystal, e.g., with a diameter ~ >0.1 that of crystal. Occurrence as multiple relatively large size inclusions is an even more valid criterion. Large size in three dimensions is the most obviously valid criterion.
   3. Isolated occurrence, away from other inclusions, for a distance of ~ >5 times the diameter of the inclusion.
   4. Occurrence as part of a random, three-dimensional distribution throughout the crystal, e.g., Roedder and Coombs, 1967, plate 4, figs. A, B.
   5. Disturbance of otherwise regular decorated dislocations surrounding the inclusion, particularly if they appear to radiate from it, e.g., Roedder and Weiblen, 1970, fig. 9.
   6. Include daughter crystals (or accidental solid inclusions) of the same phase(s) as occur as solid inclusions in the host crystal or as contemporaneous phases.
   7. Occurrence associated with a group of solid inclusions.

B. Criteria based on occurrence in a single crystal showing evidence of direction of growth.
   1. Occurrence beyond (in the direction of growth), and sometimes immediately before extraneous solids (the same or other phases) interfering with the growth, where the host crystal falls to close in completely. (Inclusion may be attached to the solid or at some distance beyond, from imperfect growth, e.g., Roedder, 1972, plate 1).
   2. Occurrence beyond a healed crack in an earlier growth stage, where new crystal growth has been imperfect (e.g., Roedder, 1965, figs. 18, 19; Roedder et al., 1968, fig. 15).
   3. Occurrence between subparallel units of a composite crystal, e.g., Roedder, 1972, frontispiece upper right.
   4. Occurrence at the intersection of several growth spirals, or at the center of a growth spiral visible on the outer surface.
   5. Occurrence, particularly as relatively large, flat inclusions, parallel to an external crystal face, and near its center (i.e., from "starvation" of the growth at the center of the crystal face), e.g., much "hopper salt".
   6. Occurrence in the core of a tubular crystal (e.g., beryl). This may be merely an extreme case of previous item.
   7. Occurrence, particularly as a row, along the edge from the intersection of two crystal faces.

C. Criteria based on occurrence in a single crystal showing evidence of growth zonation (as determined by color, clarity, composition, X-ray darkening, trapped solid inclusions, etch zones, exsolution phases, etc.).
   1. Occurrence in random, three-dimensional distribution, with different concentrations in adjacent zones (as from a surge of sudden, feathery or dendritic growth), e.g., Roedder, 1965, fig. 11.
   2. Occurrence as subparallel groups (outlining growth directions), particularly with different concentrations in adjacent zones, as in previous item.
   3. Multiple occurrence in planar array(s) parallel to a growth zone, e.g., Roedder and Coombs, 1967, plate 4E. (Note that if this is also a cleavage direction in this crystal, there is ambiguity.)

D. Criteria based on growth from a heterogeneous (i.e., two-phase), or a changing fluid.
   1. Planar arrays (as in C-3), or other occurrence in growth zones, in which the composition of inclusions in adjacent zones are different (e.g., gas inclusions in one and liquid in another), e.g., Roedder et al., 1968, fig. 9.
   2. Planar arrays (as in C-3) in which trapping of some of the growth medium has occurred at
TABLE III (continued)

points where the host crystal has overgrown and surrounded adhering globules of the immiscible, dispersed phase (e.g., oil droplets or steam bubbles).

3. Otherwise primary-appearing inclusions of a fluid phase that is unlikely to be the mineral-forming fluid, e.g., mercury in calcite, oil in fluorite (Roedder, 1972, plate 9, fig. 2) or air in sugar (Roedder, 1972, plate 9, fig. 4).

E. Criteria based on occurrence in hosts other than single crystals.

1. Occurrence on a compromise growth surface between two non-parallel crystals. (These inclusions have generally leaked, and could also be secondary).

2. Occurrence within polycrystalline hosts, e.g., as pores in fine grained dolomite, cavities within chalcedony-lined geodes ("enhydros"), or as crystal-lined vugs in metal deposits or pegmatites. (These latter are the largest "inclusions", and have almost always leaked.)

3. Occurrence in noncrystalline hosts (e.g., gas bubbles in amber; vesicles in pumice).

F. Criteria based on inclusion shape or size.

1. In a given sample, larger size and/or equant shape.

2. Occurrence in euhedral crystals, projecting into vugs (suggestive, but far from positive — see Roedder, 1967, p. 523).

II. Secondary

A. Occurrence as planar groups outlining healed fractures (cleavage or otherwise) that come to the surface of crystal (note that movement of inclusions with recrystallization can disperse — Roedder, 1971b, fig. 11).

B. Very thin and flat; in process of necking down.

C. Primary inclusions with filling representative of secondary conditions.

1. Located on secondary healed fracture, hence presumably refilled with later fluids (Kalyuzhnyi, 1971).

2. Decrystallized and resealed following exposure to higher temperatures or lower external pressures than at time of trapping; new filling may have original composition but lower density.

III. Pseudosecondary

A. Occurrence as with secondary inclusions, but with fracture visibly terminating within crystal, e.g., Roedder, 1965, figs. 18 and 19; Roedder et al., 1968, figs. 12, 14 and 15.

B. Generally more apt to be euhedral and of negative crystal shape than secondary inclusions in same sample (use with care).

C. Occurrence as a result of the covering of etch pits cross-cutting growth zones (Roedder, 1972, plate 1, fig. 8).

1 These criteria are in part only suggestive, and must be applied with care, as there is considerable chance for ambiguity.

between paleokarst, sabkha, lagoon, and similar environments at essentially surface temperatures (although perhaps sunheated) and the 150°C or higher reported for inclusions from many Mississippi Valley-type deposits. Although rarely discussed in any detail in the literature, the crux of the "reworking" problem lies in exactly which reincarnation of the ore deposit one is referring to as the origin. If an ore body is formed from fluids at one set of P—T—X conditions (and presumably contains inclusions representative of such conditions), and then is completely reworked (i.e., all crystals are dissolved and reprecipitated via a different fluid medium), then the new inclusion data will give only the P—T—X parameters of the reworking process (Bernard, 1973, p. 53–55). The necessary assumption here is that primary inclusions reveal the conditions of formation of the host crystal
where we see it now, and obviously can tell us nothing of any previous deposit. Recognition of the possibility of such former deposits would then become a field problem rather than an inclusion problem.

In this connection, Bernard (1973, p. 54) has made the point that fluid-inclusion specialists sample only the late recrystallized idiomorphic ore minerals. As a result they get \( P-T-X \) data corresponding only to the fluids present during the last recrystallization of the ores, under conditions of deep burial, whereas the original fine-grained ores formed from fresh waters under near-surface conditions. It is true that good primary inclusions are easier to find, more photogenic, and larger, in the coarser crystals from any deposit; hence, these have received the most attention. The new crystal containing the inclusions may have formed by growth at the expense of immediately adjacent crystals via an intergranular pore-fluid (i.e., typical recrystallization), or by direct free crystallization from a moving mass of liquid that had previously dissolved other crystals at some distance. The fuzzy line between “recrystallization” and “reworking” (or “remobilization”) depends upon the interpretation of this distance. In either case, the inclusions represent samples of the fluid from which the present host crystal actually formed. If any fluid inclusions containing earlier fluids were present before, they would be effectively dispersed and lost by either process.

The writer believes that this argument is refuted by the inclusion evidence itself, as well as by the field data. Many examples in the literature on inclusions verify that the tiny inclusions in very fine-grained ores have salinities and homogenization temperatures as high as those of the coarse crystals (e.g., Roedder, 1967b, 1968a; 1971a). Also, the very tiny inclusions found in fine-grained ores, although frequently too small to use for homogenization studies, still show visually similar gas/liquid ratios; only the very tiniest inclusions may remain single phase, and these are believed to be metastable (Roedder, 1971b). If the hot saline inclusions are a result of later reworking, this would require that every sample, from every Mississippi Valley-type deposit studied, has been recrystallized in the presence of hot saline fluids; this would seem to require a very unlikely coincidence. On the other hand, the writer knows of no data to show that any primary inclusions in any Mississippi Valley-type deposit were either filled with fresh water or were formed at surface temperatures. The only possible exceptions are some barite deposits that may well have been reworked by surface waters.

CLASSIFICATION OF INCLUSIONS

In addition to the threefold classification of inclusions by mode of origin discussed above, into primary, pseudosecondary, and secondary, many attempts have been made, particularly in the Soviet literature, to set up an all-inclusive classification of inclusions. Thus, Ernakov (p. 18 in vol. 2 of Fluid Inclusion Research – Proceedings of COFFI, 1969) has set up 21 classes of inclusions based on composition and origin, and had earlier
established another widely used classification based on the relative proportion of the phases present (Ernakov, 1950, p. 28, in translation). Classifications are only useful, however, if they result in elucidation of principles by organizing an otherwise confusing mass of data, reveal otherwise hidden relationships between categories, or provide insight into the nature of otherwise unknown samples. Unfortunately, most inclusion classifications are not very useful in practice, as they require more knowledge about the inclusions than one has, or consist of categories based on arbitrarily chosen numerical ratios of phases present (e.g., division at 25, 50 and 75% gas). These ratios are part of a continuum and cannot generally be measured accurately anyway. Most particularly, in spite of many explicit statements in the literature to the contrary, there is no real physical, chemical, or genetic significance to the division “line” at 50/50 gas/liquid at room temperature.

LABORATORY TECHNIQUE

As is all too common in most scientific literature, the important practical aspects of fluid inclusion research are usually omitted in the reports and have to be learned by each individual worker “by experience” (i.e., at a considerable waste of time). Each type of inclusion data requires a specific type of technique and has its own set of problems. Some of these are given under the individual headings in the succeeding section (“Types of data available”), and many others, particularly those dealing with various aspects of determining the composition of fluid inclusions, are detailed elsewhere (Roedder, 1972) and need not be repeated. A few of the more common and basic problems are covered in the following section, as there is no single general reference work on inclusion laboratory technique.

Sample selection

The selection of material to be studied is one of the most important aspects of fluid inclusion research. Optimum material will vary, of course, with the specific study, but for normal optical determinations, the optimum would be large, clear, euhedral zoned crystals of an ore mineral, such as sphalerite, protruding into vugs. If all the ore minerals are opaque, transparent gangue minerals growing contemporaneously with the ore minerals can be used, but obviously the significance of the data obtained is a direct function of the validity of this determination of contemporaneity. Far too often, mere association in the hand specimen is assumed to establish contemporaneity; this assumption is generally invalid. Even in intimate intergrowth and incrustation relationships, there are difficulties in establishing which minerals were in what type of equilibrium with each other (Barton et al., 1963). The common occurrence of complex paragenetic sequences of various ore and gangue minerals, clearly established by textural features of crustified ores, is proof that fluctuations took place in the ore fluid of such a nature or magnitude that the mineral assemblage being deposited changed with time. Under such a situation, it is
hazardous to extrapolate from one mineral to another (e.g., from a transparent gangue mineral to an opaque ore mineral). Even the common occurrence of crystals of an ore mineral within a crystal of gangue mineral does not prove contemporaneous deposition of the two; when examined with care (e.g., Poty, 1969; Grigor'ev, 1965), such solid inclusions frequently are found to have grown by themselves, at a time when the enclosing host mineral was not precipitating. Truly contemporaneous growth of two crystals in contact with each other yields the characteristic ribbed "compromise-growth surface" (Grigor'ev, 1959).

Large crystal size merely increases the probability of finding adequate criteria for establishing fluid inclusion origin (Table III), as well as the probability of finding the larger inclusions that are easier to study. On occasion, crystals less than 1 mm are found to contain adequate inclusions, but these are difficult to prepare for study.

It is not unusual to find that the vagaries of inclusion formation have resulted in some samples having much better inclusions than others, and it is simply not possible to predict what material will be good. As there are usually far more samples than can be properly prepared in polished plates, time can be saved by careful hand-specimen study with a low-power binocular microscope to find those areas or individual crystals that are most likely candidates for further study. Cleavage plates are particularly useful. A coverglass stuck on which an index liquid that matches the mineral helps in looking into imperfect crystal faces or cleavage surfaces. The larger inclusions in clear crystals can be readily seen with a hand lens, but lack of such inclusions should not exclude the material from further study. Less transparent minerals can be crushed and examined in a matching index liquid. Small crystals are also best examined in a bath of matching index liquid; for this purpose the writer cements thin rings of glass (2–5 mm sections cut from glass tubing) onto ordinary glass slides with epoxy. The crystals to be examined are placed in the ring, and index liquid added until the reflection from the top surface shows a change from concave to very slightly convex. A coverglass is then placed on top and is held in place by capillarity. (Too little liquid results in a bubble which invariably lies over the grain; too much can also cause trouble.) These slides can be used also for handpicking grains under the binocular microscope for further preparation by filling with index liquid to the point where the meniscus is flat, eliminating the need for a coverglass. As only an approximate match is needed, several inexpensive liquids suffice: kerosene of \( n = 1.45 \) (for fluorite); "HB 40 oil" made by the Monsanto Chemical Co., Wilmington, Delaware, adjusted with kerosene to \( n = 1.55 \) (for quartz); and \( \alpha \)-monobromonaphthalene of \( n = 1.64 \) (for olivine). Methylene iodide saturated with sulfur \( (n = 1.788) \) is a rather inadequate liquid for sphalerite-(there is no inexpensive matching liquid). For groups of tiny grains, ordinary liquid mounts with a coverglass suffice. When a single tiny grain is to be examined, however, it is easiest to put it in a tiny three-sided "corral" of appropriately thin wire under the coverglass. It can then be manipulated for observation from various directions using a probe tipped with a single tapering camel's hair, inserted under the coverglass in the open side of the corral (Roedder and Weiblen, 1970, p. 808).
Cutting and polishing

The cutting and polishing of doubly polished plates suitable for microscopy require more care than is generally given to these steps. Optical examination of inclusions, particularly under the less-than-optimum optical characteristics of heating and cooling stages, is sufficiently difficult without being penalized by additional problems from poor sample polish, which causes serious image degradation. For ordinary microscopy (but not for heating or cooling); a coverglass with a closely matching index liquid is a poor substitute for a good polish.

Plates are usually prepared by cutting a slice in the optimum direction for the specific sample. This should be done with a thin continuous-rim diamond cutoff wheel and water coolant. These wheels can be obtained in a variety of grits and grades for cutting various materials. This type of wheel causes much less fracturing of the surface adjacent to the saw cut than occurs with the standard notched-edge diamond blade used in thin-section preparation. The thinner the blade the less pressure is needed in the cutting and the less sample is lost, but the more chance there is of blade breakage. For small crystals, and for cutting wedges out of prepared slides, the writer uses a blade 0.015 inch thick and 5 inch in diameter. The quality of the polish, especially the top surface, is particularly critical. (For details on polishing techniques, see Cameron, 1961; Saager, 1967; Allman and Lawrence, 1972.)

Thin crusts of crystal druses and fragile or porous samples are best prepared by coating or embedding in epoxy (under vacuum if necessary) and curing, grinding down to the point where a maximum amount of the desired crystals are intersected, and then polishing. This polished surface is cemented to a slide with a soluble cement and a second parallel saw cut is made. After the grinding and polishing, the cement can be dissolved to provide a doubly polished plate suitable for heating or freezing. Before reducing the thickness of any section by grinding, it is best to examine it with a “temporary polish” in the form of a coverglass and matching index liquid. In this way, one can frequently recognize a large inclusion that is near the surface and that can be saved only by grinding and polishing from the opposite side. A fine matt surface on the lower side of the plate can be tolerated with good inclusions but makes difficult inclusions impossible.

All impregnating and cementing materials must be chosen with the nature of the sample and its final use in mind. Thus, many epoxies can stand both the heating and cooling operations necessary for samples from low-temperature deposits, and hence, if the stage permits, the sample plate can be left on the glass slide during these operations. This is particularly important with very dark sphalerites that must be cut into very thin (and, hence, fragile) plates. If at all possible, however, the sample plates should be removed from the glass slides before heating or cooling runs. If balsam or Lakeside is present during heating-runs at ~150°C, even just as films in cracks, it will creep out over the surface, spoiling the optics, and will fog the stage windows. For several reasons, the writer prefers to complete all normal microscopy with the plates still cemented, mark the parts
on which runs are to be made, and then remove them by cutting out a wedge of sample (and glass slide) with the diamond saw, holding the slide in the hand rather than in a clamp. The cuts are made so as to place the desired inclusions near the point of the wedge, to permit several chips to be placed in the heating stage simultaneously, still mounted on the glass wedges, all within a radius of several millimeters. To keep the thermal mass to a minimum, a coverglass can be substituted for the glass slide (pers. comm., R.E. Bennet, Jr.).

A record should be kept of what impregnating and cementing materials were used, and the maximum actual sample temperature attained during preparation. Some curing procedures on some epoxies form thousands of tiny spherical immiscible liquid inclusions in the cured resin, many of which are complete with a moving vapor bubble (Roedder and Weiblen, 1970, p. 801). When these occur in the excess epoxy at the edge of the sample, they are harmless, but when they occur in nearly invisible films of epoxy within cracks in the plate, they can appear to be indigenous to the sample. Also, as the hot plate temperatures needed (and even more so, the higher temperatures generally used) for the thermoplastic cements such as Canada balsam and Lakeside 70 are well above the homogenization temperature of the low-temperature inclusions characteristic of some Mississippi Valley-type deposits, such inclusions will be either lost through decrepitation, or will have become stretched and hence yield grossly misleading results (Larson et al., 1973). Bubbles in the cementing materials should be carefully avoided, as they generally spoil the plate for photography, and if numerous, they confuse the eye in searching for suitable inclusions.

The thickness of the doubly polished plate must be appropriate for the stage to be used and for the particular sample. Plates that are too thick prevent adequate illumination and usually result also in degraded images from birefringence or in the superposition of other inclusions, cracks, etc., upon the image being examined. They also are slower to equilibrate in the heating stage. On the other hand, plates that are too thin present less actual volume of mineral for examination, for a given amount of sample preparation. Average material is usually suitable at \( \sim 1 \) mm thickness, but if a dark and a clear mineral are present together (e.g., sphalerite and quartz), the quartz should be scanned when the slide is still thick, or the slide can be polished and cut in half at this stage and only half ground down for the darker material. Very dark sphalerite may require doubly polished sections of less than standard thin-section thickness (<0.030 mm); warpage in the cement can be a serious problem here. Standard thin sections are satisfactory for examination for very tiny inclusions only, as all larger inclusions are necessarily lost in preparation. Further, as inclusions even in the center of the section are at maximum only 15 \( \mu \)m from a normally rather roughly prepared surface, they are apt to either have leaked or to leak during heating (Roedder and Skinner, 1968).

*Choice of inclusions and problems in microscopy*

This is the single most critical step in all inclusion studies and, hence, must be handled
with utmost care. The difficult problem here is generally that of verifying the primary origin of the inclusions. Pseudosecondary and secondary inclusions are frequently run along with the primaries, but they should be specifically selected, *in advance*, as examples of these types (see Table III for criteria for distinguishing).

An additional problem is presented by occasional inclusions that differ visually in their phase ratios from the bulk of the inclusions, either in gas/liquid ratio or in the presence or nature of “daughter crystals” precipitated from the liquid after trapping. Generally, such visually divergent inclusions will be found to have grossly different homogenization temperatures. The problem lies in deciding whether they are valid samples of pre-existing fluids (e.g., formed from rapidly changing or inhomogeneous fluids), or whether they have been made divergent by some secondary later process and, hence, should be eliminated from the group to be run. If they are valid but are eliminated under the assumption that they have been altered, valuable information is lost; conversely, good data from valid inclusions are confused and diluted with grossly misleading numbers. The main secondary processes that must be considered when one is presented with such divergent inclusions are: (1) leakage (natural or laboratory induced); (2) later refilling; and (3) necking down.

Leakage occurs in nature for a variety of reasons but is usually related to some deformation of the host crystal, causing cracks. These cracks are not always visible, as they must be an appreciable fraction of a wavelength of the light to affect it. Leakage from such fracturing is fairly evident when a series of primary-appearing, but divergent, inclusions (often empty of all liquid) occur as a planar array through a group of otherwise uniform primary inclusions. In thin sections, inclusions within a few μm of the top or bottom surfaces are frequently empty, particularly if their contents had been under high pressure. Overheating of inclusions beyond their homogenization temperatures, whether from later dikes (Lokerman, 1965) or in the laboratory (Roedder and Skinner, 1968; Larson et al., 1973) can build up high pressures and cause decrepitation or stretching, particularly of the larger inclusions. Freezing can also cause similar damage if the vapor bubble is small. “Later refilling” is a special case of leakage in which fracturing and rehealing of the inclusions occurs in the presence of a later fluid, under a different set of conditions. The opened inclusions will thus retain their original shape and spatial arrangement but will yield a different homogenization temperature.

Necking down is the process whereby a long thin or flat inclusion spontaneously reduces its total interfacial energy by selective solution and redeposition, to yield two or more separate, smaller, more equant inclusions of the same total volume (Roedder, 1972, plate 10). Nothing is lost or gained from the system as a whole, but if a phase separation has occurred previous to the necking down, the separated inclusions will differ in phase ratios and homogenization temperatures (Roedder, 1962b, p. 45 in original). The writer believes that necking down occurs commonly in nature, but that it generally takes place near the original trapping temperature. As such, it is probably responsible for much of the scatter of results that is apparent in any careful thermometric studies (Roedder, 1967a, pp. 534 and 558; Roedder et al., 1968, fig. 13). In the laboratory one must be alert to
recognize the existence of necking down. When it has been interrupted while in progress, the long tails between inclusions are easy to see. After sufficient recrystallization, however, it may only be recognized by the adjacent occurrence of two or more inclusions that are divergent in opposite directions (too much and too little vapor relative to other nearby inclusions), and sometimes by abandoned daughter crystals, left surrounded by host crystal.

It is important to keep in mind that the apparent gas/liquid ratio is strongly affected by inclusion shape, so inclusions that appear to be different may have identical homogenization temperatures. A visual estimate of the gas/liquid ratio is normally used to guide the heating-stage operation. Thus, if the inclusion with the smallest ratio looks as though it would homogenize at 150°C, one may be tempted to set the heating stage to level out at 125°C and to creep up from there. However, the coefficient of expansion of water solutions varies inversely with the salinity, so an inclusion filled with pure water at 150°C can have a bubble at room temperature that is double the volume of one that was filled with saline brine at 150°C.

It is particularly important to spend enough time on microscopy before any runs are made. Not only will additional time frequently yield inclusion data not recognized at first, but a more careful search will almost always result in finding bigger, clearer, or more obviously primary inclusions than were found at first. This is particularly important because the optical images with the heating stages are so much poorer than with normal microscopy. It is especially important with freezing work, as ice is much more difficult to see than a bubble. Although the temptation is great to start immediately with high magnification, this is very wasteful of time. The entire plate should be scanned at low power, then at intermediate power before “homing in” on individual inclusions at high power. The location of particularly good inclusions seen during the scanning should be noted, of course, but the assumption should always be: “There are probably other, better, inclusions”. It is also imperative to view at low power before assigning a primary or secondary origin to a given inclusion, as many of the critical features (faint traces of fractures, alignments with other inclusions, vague growth banding, etc.) are only visible at low power. On the other hand, high magnification is absolutely essential for all small inclusions and for small daughter phases in larger inclusions. In this connection, it is important to note that optical data from inclusions too small to run on heating or cooling stages may still provide valuable corroboration of the meager quantitative data from a few larger inclusions, and in some samples, such optical data may be all that are available from certain zones. The writer uses a 100X oil immersion objective (plus 12.5X oculars) regularly in his own microscopy and would recommend it as the most important single special tool for inclusion work, second only to a good microscope. If its depth of focus is inadequate to reach a desired inclusion, try turning the sample plate over and focusing through the bottom.

Lighting is an important consideration in searching for good inclusions. If the plate is very clear and transparent, and contains rare small inclusions, these are best found by
closing the substage diaphragm down to a very small diameter; this shows up small inclusions over a considerable depth of focus. When searching for good inclusions in samples that are crowded with inclusions, cracks, or solid debris (and for close examination of any given inclusion), the diaphragm should generally be wide open. The eliminates much of the troublesome superposition of images.

Birefringent minerals should always be examined with one polarizer in place, set parallel to a vibration direction of the sample. This eliminates the annoying double images seen when looking deep into a mineral of low birefringence, and visible at almost any depth in calcite. The polarizer should be set parallel to the ordinary ray on highly birefringent, uniaxial negative minerals such as the rhombohedral carbonates, unless the inclusions are very close to the surface. This is because the extraordinary ray image is severely distorted and fuzzy. (As the ordinary ray in these minerals has a much higher index of refraction, this also permits one to focus significantly deeper into the section and hence brings more of the sample within range of the oil immersion objective.) If coverslips have to be used, it is best to use the thinnest possible grade (“00”), to obtain the maximum depth of focus into the sample.

Faint growth-banding in colored minerals can sometimes be enhanced by the use of a wedge interference filter, adjusted to give maximum visual contrast between adjacent bands. Growth-banding and other planar features with which inclusions may be associated are best viewed first at very low power on a binocular microscope, where the working distance is large enough to permit tipping the plate up at high angles. Samples containing solid opaque inclusions outlining growth-bands should be viewed alternately in transmitted and reflected light; for this purpose two foot switches, one for each light source, are particularly convenient, as they leave the hands free (P.M. Bethke, personal communication, 1971). Growth-banding that is otherwise invisible may sometimes be revealed vividly when the plate is viewed under cathodoluminescence. Poty (1969) made effective use of radiation coloration from intense X-ray dosage to reveal very fine growth-banding, otherwise invisible, in quartz plates.

Relocating an inclusion, particularly a small one in a large plate crowded with inclusions, can be very frustrating. The writer uses a combination of rough sketches (starting at actual size) to show the approximate location, plus photographs or sketches of the area as seen through the microscope at one or more stages of magnification. It is important to record at which point in any such series of sketches one switches from the erect image as seen by the naked eye to that of the inverted image seen through the microscope, as this difference can cause much confusion on returning to the sample at a later time. Mechanical-stage vernier coordinates can be used if the section is still mounted on a glass slide. Poor reproducibility in the position of the slide when seated against the stops in the stage, and backlash in the stage mechanism, may make such coordinates useless at high magnification. To avoid loss of valuable data, each stage in disaggregation of a plate (sawing, breakage, etc.) should be well documented, so that interrelationships of inclusions to each other and to growth zones can be reconstructed. Not infrequently a sketch can be more
useful than a photograph, because it can readily show features such as inclusions at slightly different levels that cannot be simultaneously photographed and can delete the clutter of unwanted and confusing detail that the camera insists on seeing. Record photographs of special inclusions should be made before running in case they decrepitate and are lost.

*Heating stages and their operation*

It is comparatively simple to set up a homemade heating stage on the microscope, and many different models have been described (Roedder, 1972, pp. JJ27–JJ28). Surprising as it may seem, however, a really satisfactory solution has not yet been achieved. It is very difficult to obtain an adequately high, known, and controlled temperature in a sample under such conditions that an objective of adequately high magnification and resolution, and adequately convergent transmitted illumination, may be used and still permit flexibility and speed in operation. The major problem with most heating stages is the working distance needed for the objective lens on the microscope. In order to keep the objective out of the heat, long-working-distance lenses must be used. Most commonly these are objectives designed for use with the universal stage, and as they must be used here without the hemispheres, the effective magnification is considerably below their normal rating. The optical quality under such conditions is also far from optimum. It is frequently better optically to use an ordinary objective of lower magnification, with higher magnification oculars, than the universal-stage objectives. The writer seldom uses oculars less than 12.5×, and frequently goes to 20× oculars, in order to get magnification and still use long-working-distance objectives. The resolution is poor, but this is not too serious with moving black bubbles.

At the time of writing, two commercially available heating stages appear to be the most appropriate for inclusion studies. The Leitz 350 stage is the most commonly used; some of its limitations have been discussed elsewhere (Roedder et al., 1968, p. 341). The other is a new combination heating and freezing stage, based on a design by B. Poty of Nancy, France, and manufactured by R. Chaix, Nancy, France; the writer has not had the opportunity to try this stage.

The operation of any heating stage must be done with care and constant consideration of the possible sources of error, as it is surprisingly easy to get beautifully consistent, reproducible, but incorrect numbers. One of the major problems comes from the difficulty in minimizing thermal gradients within the sample chamber (they can never be eliminated). The necessarily large temperature gradients between the small hot chamber and the cold microscope stage, objective, and condenser, at most only tens of millimeters away, make significant gradients within the sample chamber almost inevitable. These gradients should (and do) change with sample size, shape, and placement, as they are a function of the thermal conductivities of the metal, glass and sample, and of the effectiveness of hot-air convection in the chamber. If thermocouples are used, heat flow along thermocouple lead wires can be a serious source of error, particularly if the wires are thick (Larson et al., 1973).
Perhaps the most difficult problem is that of calibration. Normally the writer uses tiny crystals of organic compounds of known melting point, provided commercially for this purpose (Arthur H. Thomas Company, Philadelphia, Pa.). These standards may be individually sealed into short segments of thin-walled capillary glass tubing and placed on the stage between or beside the sample chips. Because most impurities lower the melting point and cause it to occur over a range of temperature, the melting of the last crystal should be used. Additional crystals of a given melting point standard, sprinkled beneath and on top of the sample plates, may yield some surprising data on thermal gradients. All calibrations should be made with a stage and sample geometry (and heating schedule) as close as possible to that used with the unknown samples. As the standards cannot experience the identical gradients that exist in the samples, errors in the measurements will still take place that will vary greatly with the equipment and technique.

Although dynamic methods are commonly used to obtain homogenization temperatures (i.e., using a continuously increasing temperature — sometimes as much as 3–5°C/min), this technique probably yields very large errors. It is far preferable to effectively level off the temperature of the stage after each temperature increment, as the thermal gradients under static heat-flow conditions will generally be much less than those under dynamic conditions.

To check on the possibility that inclusion leakage during the run may cause erroneously high homogenization temperatures, it is best to measure the diameters of the gas bubbles before and after the run, using a graduated ocular in the microscope. These measurements may be in arbitrary units, as only changes are of importance. A useful substitute check on leakage is the duplication of homogenization temperature on a second run. Such duplication is a necessary but not sufficient check, as overheating of inclusions above their homogenization temperatures, particularly the low-temperature inclusions in soft minerals characteristic of the Mississippi Valley-type deposits, can cause permanent stretching of the inclusion walls. They then yield duplicable but seriously erroneous homogenization temperatures (Larson et al., 1973). This source of error can be avoided by making all desired determinations on the low-temperature inclusions first, before attempting to homogenize the higher-temperature inclusions in the same plate.

The point of homogenization is taken as the temperature at which the bubble disappears. There is a semantic problem here that can cause difficulty. Most fluid inclusions consist of only liquid plus vapor, and so the temperature at which the bubble disappears is the temperature of homogenization. If daughter crystals are also present, they may not have dissolved completely at this temperature and hence, it is not a true temperature of homogenization for the inclusion. Confusion can be eliminated by the use of “L–V homogenization” (or “liquid–vapor homogenization”), and “complete homogenization” whenever ambiguity might occur.

Homogenization usually occurs suddenly, because of surface tension, when the bubble has been reduced to 1–2 μm diameter, introducing a minor error that can be ignored (Roedder, 1971b, p. 328). The behavior of any daughter crystals should also be noted.
On cooling after homogenization, the temperature at which heterogenization (i.e., formation of a bubble) occurs should be noted, particularly if the temperature at homogenization had been rising, as the true temperature of homogenization, under equilibrium static conditions, should fall between these two. If the homogenization temperature was low (i.e., the bubble at room temperature was very small), heterogenization may not occur even on cooling to room temperature because of metastable stretching of the inclusion liquid (Roedder, 1971b). If many different inclusions are being followed simultaneously, or if there are rapid changes, as in critical phenomena or in the solution of multiple daughter crystals, a dictaphone can be used during the observations, to avoid loss of continuity of observation.

Probably the most frustrating aspect of all fluid-inclusion study is the problem of illumination in the heating or cooling stages. Large inclusions that appear clear and have only thin black lines at their boundaries will usually be usable even in poorly designed heating stages that severely limit the angle of convergence possible for the light. Most inclusions, however, that require the use of strongly convergent light (i.e., the high power condenser) for ordinary microscopy will appear opaque or almost so in the nearly collimated lighting that results from the common heating-stage design. The more collimated the lighting, the broader the dark borders around inclusions (from total reflection at the inclusion—mineral interface). This effect is most bothersome in high index minerals such as sphalerite, in which it is not uncommon to find that perhaps only one inclusion out of ten selected for running can actually be used in the stage. Even if the black border is not very broad, the small bubble will frequently disappear in these dark areas. Such inclusions should be checked at higher temperatures, however, as the bubble generally moves about much more actively when it gets very small, and hence it may reappear. (Stretching may yield similar behavior — see Larson et al., 1973). The most effective remedy (other than finding better inclusions) is the use of a flexible fiber optics illuminator. By bringing the light in from beside the objective (above the stage) or from below the stage, it is generally possible to find some position where the bubble can still be seen. The 1/8 inch by 24 inch light guide is best, because of its flexibility (American Optical Co., Space Defense Division, Southbridge, Mass.). It is often most effective if the normal transmitted light beam is blocked.

Cooling stages

The problems in design and operation of a cooling stage are more difficult than those for a heating stage. Most commercial cooling stages, except the newly designed Chaix stage mentioned above, are for metallurgical use, in reflected light. Several different stages for inclusion use have been described in the literature (Roedder, 1972, p. JJ28), and some of the problems in their use have been discussed (Roedder, 1962a). Mississippi Valley-type inclusions commonly show gross supercooling and other metastable phenomena that can lead to serious errors if not recognized (Roedder, 1967c, 1971b). As freezing is less
apt to damage inclusions than homogenization (unless they contain low-salinity fluids and small bubbles), it is generally best to make freezing runs on a given sample before heating runs. If only a few determinations need be made, the writer recommends a manually controlled freezing cell (Roedder, 1962a, p. 1051).

TYPES OF DATA AVAILABLE – MISSISSIPPI VALLEY-TYPE DEPOSITS

Inclusions have yielded at least some data on each of the following features of Mississippi Valley ore fluids: density, rate of movement, pressure, temperature, gross salinity, pH, noncondensable gases, isotopic composition, and nonvolatile ions in solution. When inclusions are studied from various parts of zoned crystals, or from various minerals in a previously established paragenetic sequence, it is frequently found that changes took place in the ore fluid with time, particularly in composition and temperature (e.g., Roedder et al., 1968; Roedder, 1971a). For this reason it is important to view the data from any given deposit in this larger context, to see if there is a correlation of the occurrence of changes in the mineralogy (e.g., mineral assemblage, or the size, crystal habit, or color of a given mineral) with changes in the fluid-inclusion data. Note that such correlations do not necessitate a cause and effect relationship. Many studies of magmatic hydrothermal deposits have been made showing such correlations (e.g., Ernackov, 1950). Although obvious mineralogical changes have taken place during the deposition of the Mississippi Valley-type ores (e.g., the district-wide changes in calcite crystal habit in the Upper Mississippi Valley district, Heyl et al., 1959, p. 100), the correlative changes in the fluid inclusions are generally less abrupt or may not even be recognized. One should always be alert to the possibility of such changes, however, and hence to the hazards of assuming equivalence of data from different parts of a given deposit.

Density

Unlike the estimates of pressure and temperature, fluid inclusions permit reasonably accurate and unambiguous estimates of the density of the ore-forming fluids, and there does not appear to be any other source for such information. If the relative volumes of the liquid and gas phases are determined at room temperature (by using geometrically regular inclusions), and if the salinity is known (from freezing data), the density of the originally homogeneous fluid can be calculated. Thus, simple linear intercepts of the phase boundaries on long tubular inclusions give an approximate phase ratio, and thin flat inclusions can be photographed or sketched onto paper, using a camera lucida and the relative volumes of liquid and vapor obtained with a pantoagraph or (much more easily) by cutting out and weighing the two “phases” on a good balance. Although these methods can be highly precise, their accuracy can be very poor when the inclusion walls are not truly parallel, as is commonly found. Inclusions with an appreciable third dimension can
also be measured, but the errors involved become much larger unless a universal stage is used. At first glance, it appears that the volume of the spherical gas bubble could be obtained accurately, from its diameter, but that the volume of the liquid phase (total inclusion volume minus gas-bubble volume) would be inexact, except in very geometrically regular inclusions whose volumes can be assumed to consist of the sum of measurable cylinders, cones, pyramids, or prisms. Unfortunately, however, although it is true that the inclusion volumes are inexact, the volume of the spherical gas bubble may also be inexact, because of the negative lens effects of a curved inclusion wall. This may cause an error of as much as 50% in the estimate of the bubble volume in minerals of high index of refraction, such as sphalerite (Roedder, 1972, plate 11, figs. 7, 8). Volume changes from external or internal pressure, and from thermal expansion of the host, are negligible compared with the effects of composition and inaccuracies in phase-volume measurement. With rare exceptions, the overall inclusion fluid densities (i.e., the density of the fluids at the time of trapping) for Mississippi Valley-type deposits are found to be greater than 1.0, and frequently are as high as 1.1 g/cm³. This is because the room-temperature solutions have densities reaching a maximum of about 1.2, and there is about 10% of vapor of effectively zero density. The most important point here is that this overall density (i.e., the density of the hot fluid that was trapped) is greater than 1.0, as this controls the direction of hydraulic gradients of the hot ore-forming fluids against fresh cold meteoric and ground waters at density near 1.0. The room-temperature density of the liquid phase must be estimated from the salinity (as determined on the freezing stage), or if chemical analyses have been made, it can be measured experimentally on synthetic fluids of such composition. Brown (1942) has shown that even very small compositional differences may result in density differences that can be significant in surface-water circulation patterns. However, it should be noted that the density increase from dissolving 1 wt.% salt would be cancelled out by a 30°C rise in temperature.

Rate of movement

Except for possible surges from large-scale solution collapse of the wall rock (as in East Tennessee, Roedder, 1967b, pp. 352–353), the ore fluids are believed to have moved very slowly at the site of deposition. Several lines of evidence support this, the first two of which are based on metastable equilibria:

1. All published freezing studies of fluid inclusions in Mississippi Valley ore and gangue minerals report gross supercooling on the microscope freezing stage. This is taken to signify a complete freedom from such solid nuclei in suspension as are present in surface waters; these nuclei in surface waters normally preclude more than 10°C supercooling, whereas many inclusions in Mississippi Valley-type samples require supercooling of 20–40°C below their equilibrium freezing temperature before they will freeze (Roedder, 1962a, 1963, 1968a, c). (Daughter crystals of NaCl and other phases generally do not act as nuclei for ice.)
Data from Mississippi Valley-Type Deposits

(2) If the expansion on freezing in the microscope cold-stage eliminates the vapor bubble, it should re nucleate as the ice melts to form more dense water, but in many Mississippi Valley-type samples, metastable superheated ice occurs, at high negative pressures — as much as 1000 atm negative pressure. At such negative pressures, ice is in equilibrium (metastable) with water at temperatures as high as +6°C (Roedder, 1967c), because of the failure to nucleate a vapor bubble. This is a much larger negative pressure on a liquid than has ever been recorded before in extensive studies of laboratory liquids, and just as with item (1), this metastability requires that the inclusion liquid be exceptionally clean and free of suspended solid nuclei.

(3) Crystals of ore and gangue minerals growing in open fractures or vugs may contain crystals of other phases that nucleated and grew simultaneously, but they are very clean and free of inclusions of clay or other debris that might have been carried in suspension, as are found in some magmatic—hydrothermal veins (Barton et al., 1971).

(4) The inclusions and other microscopic features reveal exceedingly minute regular oscillatory growth bands in several Mississippi Valley ores and related types of occurrences. If these bands are truly annual varves as suggested (Roedder, 1968a, b; 1969; Leach, 1973), they indicate crystal-growth rates in the range of only 10 μm/year and hence suggest very quiet conditions, fluid flows being in the range of perhaps one μm/sec over tens of thousands of years, unless the concentration change (amount precipitated) is very low (<1 ppm, see fig. 1).

Although they do not concern inclusions, several features observed in the field also suggest relatively slow flow rates. Included here would be the following:

(1) Although some crystal growth anisotropy from fluid movement has been found (Stoiber, 1946; Kesler et al., 1972) such anisotropy is generally minor or absent.

(2) The large size and perfection of the crystals in some deposits.

(3) The obvious vertical settling of most nuclei in open fracture fillings, as in the East Tennessee district where the sphalerite crystals are found almost entirely on the lower sides of even steeply inclined fractures, apparently as a result of sphalerite nuclei forming in the fluid and settling to the bottom. Bastin (1931, p. 39) presented similar evidence for the vuggy Illinois fluorite ores.

(4) The relatively great distance between individual crystals of a given phase in some mines (this indicates only that little spontaneous nucleation took place, hence very little supersaturation, hence very slow growth, and hence very slow flow rates; Roedder, 1971a, p. 786).

Pressure

The information available from inclusions as to the pressure of deposition is meager but may still be useful. Several features permit the placing of rough lower limits. Although boiling has occurred in some magmatic—hydrothermal deposits, as evidenced by the presence of low-density primary inclusions that had been filled with steam as well as
others filled with hot liquid, such evidence is not found in Mississippi Valley-type inclusions. Thus, we know that the hydrostatic pressure was always greater than the vapor pressure of the solutions present at the inclusion-homogenization temperatures. At a homogenization temperature of 150°C, pure water has a vapor pressure of 3.7 bars over atmospheric and hence would require a minimum of 37 m of hydrostatic head of cold water (at 1.0 g/cm³) to keep it from boiling. Gases, such as methane in solution, would of course raise this minimum. If the water over it were heated to the boiling point throughout, the column would be lighter and this minimum head would have to be higher (40.9 m); if the solution were saline, its vapor pressure would be slightly lower, requiring a lower head (28.5 m for 20% NaCl; Haas, 1971).

The inclusion evidence places no upper limit on the pressure at the time. However, if another, independent (and correct) thermometer were available, the difference between this temperature and the homogenization temperature would be a true “pressure correction” and would permit a valid estimate of the pressure. Such an independent thermometer would have to be very accurate. Thus the compressibility of 20% NaCl solution, at 150°C, is so small that even 3,300 m of hydrostatic head on it would only cause a pressure correction of 25°C (Klevtsov and Lemmler, 1959). Bethke and Barton (1971, p. 160) have shown, for example, that the distribution of Mn between galena and sphalerite can be combined with $P-V-T$ data on fluid-inclusion fluids to give both pressure and temperature within surprisingly narrow limits.

Another rough lower limit is established by the presence of gases under pressure (mainly methane), dissolved in the brines of inclusions in many Mississippi Valley-type ores. Thus, when these are opened on the crushing stage, the gas bubble expands approximately twenty fold (Roedder, 1970b, fig. 4). If this represents strictly the expansion of the gas in the bubble itself, the twenty fold volume change would correspond to approximately 20 atm pressure. The true pressure in the bubble is undoubtedly lower than this, as much gas can be contributed to the bubble from the liquid. The solubility of methane in these brines at geologically reasonable pressures is probably about one volume of gas/volume of liquid, and because distances for diffusion are small, only 10–100 μm, degassing can occur very rapidly. On the other hand, the pressure necessary to keep this gas in solution at the elevated temperature of trapping, although unknown, would be much higher.

Another potential source of data on pressure is present in the many deposits that contain inclusions of liquid petroleum as well as brine. There is abundant inclusion evidence that the ore-fluid brines frequently contained suspended immiscible globules of petroleum-like liquids and that these oil globules stuck to growing fluoride surfaces and, hence, were trapped preferentially. On cooling after trapping, these “oil” inclusions form a shrinkage bubble just as do the brine inclusions, and homogenization temperatures can be determined on a heating stage (see next section). They usually give lower homogenization temperatures than adjacent presumably coeval brine inclusions (Freas, 1961; Roedder, 1963, p. 175; 1971a, p. 785). This is a result of the much higher compressibility of
oils than brines (approximately four fold), causing a much larger pressure correction for the oil inclusion than for the brine. If independent data on the relative compressibilities of the two fluids were available, both pressure and temperature of trapping could be obtained. In any such application, care should be taken to avoid material in which spontaneous decomposition reactions have taken place within the oil inclusions, as has occurred in some inclusions in Illinois fluorite (Roedder, 1962b, p. 40 in original).

**Temperature**

The temperature at the time of fluid trapping, and hence the temperature of a particular ore fluid, can best be obtained from optical determination of homogenization temperatures of primary two-phase, gas-liquid inclusions in ore or in gangue minerals known to be coeval with ore. Although there are many serious problems in the use of homogenization temperatures for geological thermometry, particularly for deposits formed at high temperature and pressure, most of these problems are minor for samples from low-temperature stratiform deposits. In addition, the temperature corrections needed for the effects of hydrostatic pressure are small and fairly well known. It should be noted, however, that the added basic assumption here—that the reported measurements are correct—is not always valid because of various problems in sample selection and measurement technique. When care has been used, the values obtained are probably the most precise and accurate in the field of geologic thermometry. Large numbers of such homogenization determinations have been made, particularly on Mississippi Valley-type deposits in the United States (Table IV). In summary, they show that during the ore-forming stage, temperatures were generally 100—150°C and rarely were as high as 200°C. Temperatures of late-stage, calcite-depositing fluids in many deposits were less than 100°C.

As inclusions are heated, the internal pressure builds up, and for those homogenizing in the liquid phase, dP/dT increases abruptly at the point of homogenization. Further heating causes the internal pressure eventually to become greater than the tensile strength of the host, and it bursts. This is the basis for the decrepitation technique of geothermometry. The coarsely crushed sample is heated at a specified rate and the frequency (and/or magnitude) of decrepitation is detected with a microphone and suitable electronic amplification and averaging techniques, and plotted vs. sample temperature to form a decrepigram. Although there are many serious problems in both theory and practice with this technique, the temperature of decrepitation of any given inclusion is a function, in part, of the temperature of homogenization. It is also a function of a series of other factors that in part cannot be controlled. As a result, the difference between these two temperatures can be large and either positive or negative. However, as a result of the relative incompressibility of water solutions in the low-temperature range, decrepitation in Mississippi Valley-type samples tends to occur only a small temperature increment above the homogenization temperature. The amount of this overshoot varies appreciably with the nature of the sample, but is commonly at least 20°C. As decrepitation can be
<table>
<thead>
<tr>
<th>District, mine, or occurrence</th>
<th>Homogenization temperature, °C</th>
<th>Freezing data</th>
<th>Reference</th>
</tr>
</thead>
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<td>maximum</td>
<td>accepted best range or value</td>
</tr>
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<td>110</td>
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<td>194*6</td>
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<td>74*5</td>
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<tr>
<td>Upper Miss. Valley, Pb–Zn</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*1 See original reference for details on samples, locality and geology; only data on sphalerite, fluorite, or barite are listed unless otherwise stated; no data on decretation listed.

*2 Data on known secondary inclusions are excluded.

*3 Given only where appropriate.

*4 As –21.1°C is the minimum liquidus temperature (eutectic) in the system NaCl–H₂O, temperatures below this must have salts other than NaCl.
TABLE IV (continued)

*5 Late calcite only.
*6 This has been shown to be incorrect — see Larson et al. (1973).
*7 This inclusion had a NaCl · 2H₂O liquidus, hence, it was very strongly saline.
*8 Some as high as −10° had a NaCl · 2H₂O liquidus and hence were very strongly saline.
*9 Data only on fluorite cogenetic with barite.
*10 Oil inclusions.
*11 Estimated, from tiny oil inclusions in sphalerite and brine inclusions in associated carbonates.
*12 Estimated, as all inclusions are full of liquid at room temperature.
*13 This temperature obtained only on calcite and barite; sphalerite temperatures were 108—115°.
*14 Values in parentheses are salinities (NaCl % equiv.).
*15 Low values obtained on barite.
*16 Possibly the same brine that formed the northern Arkansas zinc district?
*17 These homogenization temperatures are believed to be approximately 30°C too high, because of thermal gradients in the heating stage (R.W. Potter, personal communication, 1974).
performed in the field and on opaque materials as well, however, it is useful as a *qualitative* field tool, particularly on low-temperature deposits. The writer has serious doubts that it can ever be calibrated to yield accurate data, free of subjectivity, on the temperatures of homogenization (or formation).

A necessary corollary of the slow flow and deposition rates and the large volumes of liquid passing any given point in the ore is that a considerable volume of rock in the vicinity of the ore body must have been heated to the temperatures recorded in the inclusions. The heat capacity of water is so high that the fluid from six complete changes of the water in the pores of a rock with only 10% porosity has a total heat capacity greater than that of the rock. As such, any temperature differences will soon be levelled, and hence the inclusion temperatures cannot be considered to represent merely some local late-stage recrystallization environment, as some have argued.

**Gross salinity**

The salinity of the ore fluid is most easily determined from the equilibrium freezing temperature of fluid inclusions (Roedder, 1962a, 1963). This is the depression of the freezing point for the trapped solution and is so determined that metastable phenomena such as superheating or supercooling are not involved. There is obviously some uncertainty in estimating the salinity from the depression of the freezing point for mixed salt solutions. However, the gross composition of these salts is fairly well known and uniform (see below). The conversion of freezing points to salinities (in weight percent mixed salts) can be determined experimentally by freezing a synthetic fluid simulating the inclusion fluids. Such data have been verified by actual quantitative analyses of inclusions for salts and water, as mentioned below.

In summary, the salinity of Mississippi Valley ore fluids usually exceeds 15 wt.% salts, and frequently exceeds 20% (see Table IV), yet daughter crystals of NaCl are almost never found, implying appreciable amounts of ions other than Na and Cl. It is important to note also that several details of the freezing work prove the presence of at least some salts other than just NaCl, even though this is usually the main salt. One such detail is that pure NaCl can only lower the freezing point to $-21.1^\circ\text{C}$ (Roedder, 1962a, fig. 4), yet many inclusions have a lower freezing temperature.

**pH**

It would be very desirable to know the pH of the fluids in inclusions at the time of trapping. If these values could be obtained at room temperature, together with inclusion composition, extrapolations to the temperature and pressure of formation might be possible. The pH at room temperature can be obtained by calculation, e.g., by using analytical results for $CO_3^{2-}$ and $HCO_3^-$. Direct measurement is possible only with large inclusions, which can be broken into and absorbed onto indicator papers under a low-power micro-
scope. If gases are evolved when the inclusion is opened, gross changes in pH can occur almost instantly. An extensive literature in Russian concerns such procedures (Roedder, 1972, p. JJ39), but only one modern attempt has been made in the Western world (Erickson, 1965; pH about 7.5, on samples from Upper Mississippi Valley lead–zinc deposits). Another procedure for determination of inclusion pH is that of crushing the host mineral in water and measuring the pH of the slurry. Hundreds of such measurements will be found in the Soviet inclusion literature (Roedder, 1970a), but for several reasons, in particular the effects of various mineral surfaces, loss of gases, and the several-thousandfold dilution, the writer believes that they are practically worthless (Roedder, 1972, pp. JJ38–JJ41).

Noncondensible gases and organic matter

Although very little information is available on noncondensible gases and organic matter, it could be of considerable import to problems of the chemistry of ore deposition. Thus, unless the mixing of two fluids is assumed to take place, one is faced with the difficult task of possible simultaneous transport of sulfur and metals in a given fluid. Organic matter should, in general, reduce sulfate to sulfide, although these reactions are apparently very slow. Barton (1967) has proposed that the Mississippi Valley-type ore metals have been transported by a fluid bearing organic matter, and in which the sulfur was present as sulfate; slow reduction of the sulfate in this nonequilibrium solution avoids the problems of simultaneous transport of sulfide and metal in the same fluid. The solubility of methane alone in 50,000-ppm brines is adequate to provide, at saturation under pressures equivalent to a depth of only 1,000 ft. (Duffy et al., 1961), reducing capacity to form about 2 g S²⁻/l of brine. In addition, many subsurface waters are known to be saturated with respect to methane (Buckley et al., 1958), and studies with the crushing stage (Roedder, 1970b) reveal appreciable gas in solution, presumably mainly methane. In contrast, magmatic hydrothermal fluids also contain methane, but usually in much smaller amounts, which could well be from simple inorganic equilibrium reactions in the system C–H–O.

In addition to the obvious methane, a surprisingly high percentage of Mississippi Valley-type ores contain small amounts of a yellow-brown, fluorescent oily fluid, which, when a sample is crushed, smells strongly of petroleum. This is present as separate fluid inclusions, as immiscible globules in primary and secondary brine inclusions, or in larger quantities as seeps in the mine workings. In some samples, this fluid has degraded spontaneously, inside the inclusions, into a dark-brown viscous phase and a colorless low-viscosity liquid. (and sometimes a birefringent crystal as well). The two liquid phases are immiscible; the darker one has an amazingly selective preference for only certain crystallographically oriented surfaces on the walls of the approximately spherical inclusions in fluorite (see Roedder, 1962b, p. 40 in original; 1972, plate 9). The colorless fluid flashes into vapor when the inclusion is opened and hence probably consists mainly of light hydrocarbons.
Organic materials in solution may be of importance to several aspects of the origin of Mississippi Valley ores. In addition to the reducing capacity of the methane mentioned above, the oily phase, present as immiscible globules in the brine and the rather surprising amounts in solution (Price, 1973), would have been a continuing internal source for reductants of sulfate to form sulfide. In some deposits some semisolid organic debris may also have been present in the solutions (e.g. Hansonburg, New Mexico; Roedder et al., 1968, figs. 9–11), and it is important to remember that the most effective reductants are probably used up as a result of this fact, and hence are not found on analysis. Many other organic compounds may be present. Thus, the oxalate ion was present in at least some connate brines, as the mineral whewellite (CaC$_2$O$_4$ ⋅ H$_2$O) has been recognized in several occurrences. Veitch and McLeroy (1972) found that amino acids in solution greatly increased the solubility of heavy metals in carbonate environments, and Miller et al. (1972) found fatty acids in bedded barites that they believe are from sulfate-reducing bacteria. (This would explain the common occurrence of free hydrogen sulfide in the inclusions in these “fetid” barites.)

**Isotopic ratios**

Practically all the isotopic studies of fluid inclusions have been made in the last decade, and most of these have been on magmatic–hydrothermal-type deposits. Roedder et al. (1963) reported a procedure for obtaining the amount of water, its isotopic ratio of deuterium to hydrogen (D/H), and the chemical analysis of the seven major ions in solution, all from a sample containing several milligrams of water, and they list seven such analyses from Mississippi Valley-type deposits. Hall and Friedman (1963) then used this technique on 33 samples of known paragenesis, from the southern Illinois fluorite–lead–zinc district, and the Upper Mississippi Valley lead–zinc district. The D/H ratios (and the concentration and gross chemical composition of the salts present) are all similar to present connate waters in those formations for the main ore stage, but some late minerals were deposited from fluids of different composition. It may seem that “several milligrams” is a very small sample, but actually this amount of inclusion liquid of verified singular origin is only possible with special types of material, and usually requires much work to obtain. Samples are needed containing large single inclusions, in the 1-mm range, or large numbers of smaller primary inclusions, cut to eliminate most secondaries. The sample size requirements can be expected to decline as techniques improve, but as in all inclusion analyses, the single most important step is that of verifying the origin of the selected inclusions (Roedder, 1972).

The original isotopic signature of the water (e.g., sea or meteoric) can be changed by isotopic exchange with the rocks through which the water percolates only if the exchange is sufficiently rapid, and if there is a significant reservoir present. Oxygen will exchange in geological environments at as low as 150°C (Clayton et al., 1968; Pinckney and Rye, 1972), and rocks contain a large reservoir of oxygen. Hydrogen is probably exchanged
more readily, but the reservoir of hydrogen in the rocks is so very small that it will be controlled by the water composition, rather than the reverse. Thus, even a normal shale contains less hydrogen than would be present in the water filling its pores, but it contains about seven times as much oxygen as the water. Several changes of water could thus exchange the hydrogen of the rock completely, but far more changes would be needed for the oxygen. No oxygen-isotopic determinations have yet been reported for Mississippi Valley-type inclusion liquids, but as the improvements in this technique have been rapid, we may expect more work of this kind. Although it would be of considerable interest, the isotopic composition of the sulfur in the inclusion fluids is not within reach of present experimental methods, considering the available sample size.

*Nonvolatile ions (i.e., "salts") in solution*

The composition of the salts in inclusion fluids can be determined by semimicroanalysis of water leaches prepared from samples crushed under conditions carefully controlled to avoid loss and contamination (Roedder, 1972). The salts are surprisingly uniform among the various districts examined and consist mainly of sodium and calcium chlorides. A typical analysis is shown in Table V. Almost without exception, such analyses show the descending weight percent sequence, chlorine—sodium—calcium—potassium—magnesium—boron. Bicarbonate is probably low. Total sulfur, stated as sulfate, seldom exceeds a few thousand ppm. The value given for total sulfur as sulfate in Table V is a maximum, because an appreciable but unknown amount of sulfur is also contributed by oxidation of the sphalerite during the leaching. Unfortunately the determination of microgram quantities of sulfur is one of the most difficult analytical problems and at present does not permit distinction between the various valence states. Some evidence, however, indicates

<table>
<thead>
<tr>
<th>TABLE V</th>
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</table>

Typical fluid-inclusion analysis: sphalerite, Tri-State district, Oklahoma (Roedder, 1967b)

<table>
<thead>
<tr>
<th></th>
<th>Parts per million</th>
<th>Moles per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
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<tr>
<td>K⁺</td>
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<tr>
<td>Ca²⁺</td>
<td>18,000</td>
<td>0.45</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>2,400</td>
<td>0.10</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>124,600</td>
<td>3.51</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>&lt;3,300</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>B₄O₇⁻</td>
<td>107</td>
<td>0.0007</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>

Total salts 208,000 (does not include heavy metals)
H₂O 792,000 (probably includes approximately 800 ppm CH₄)
DATA FROM MISSISSIPPI VALLEY-TYPE DEPOSITS

that sulfide sulfur must be very low. Most significant, however, is the concentration of salts. The freezing data indicating very strong brines are corroborated by those few analyses in which actual concentrations were determined (rather than just ratios). Analyses of this type are reported for the southern Illinois fluorite—lead—zinc district, the Tri-State lead—zinc district (Kansas—Oklahoma—Missouri), and Santander, Spain (Roedder et al., 1963), and for the southern Illinois fluorite—lead—zinc district and the Upper Mississippi Valley lead—zinc district (Illinois—Iowa—Wisconsin; Hall and Friedman, 1963). Additional studies of this sort are needed on other deposits, but most deposits simply do not provide suitable sample material.

A few preliminary data on inclusions in a sample of fluorite from southern Illinois, obtained by neutron activation (Czamanske et al., 1963), showed unexpectedly high heavy-metal contents. The fluid contained approximately 1% each of copper and zinc, and 0.4% manganese. Pinckney and Haffty (1970) analyzed some other samples from the same locality by atomic absorption spectroscopy and found much lower concentrations (maxima in ppm: Zn 1040; Cu 350; Cl 152,000); the cause for the difference is not known, and it should be resolved.

As sodium and potassium are among the most abundant constituents present in inclusions and may be determined by flame photometry with relative ease, precision, and accuracy, the Na/K ratio is one of the most useful parameters. The fluids that formed the Mississippi Valley-type ore deposits seem to be characterized by much higher Na/K ratios (about 17, by weight) than those having magmatic—hydrothermal affiliations. Even though the Mississippi Valley fluids have very high Na/K ratios and are very similar in many respects to "normal" connate and oil-field waters, the most striking difference is that the inclusion fluids have lower Na/K ratios than the lowest ratio reported in oil-field waters (Roedder et al., 1963). Hall and Friedman (1963) and Sawkins (1968) suggest that the extra potassium may represent a magmatic contribution. Similarly, the Mississippi Valley fluids have lower Cl/\(SO_4\) ratios than subsurface waters (Sawkins, 1968).

With few exceptions, calcium exceeds magnesium, frequently by a large factor. Although little attention has been given it, the Ca/Mg ratio in the ore-forming fluid is of considerable significance in controlling dolomitization. Care is needed to obtain valid determinations of this ratio in inclusions, however, because of contamination from embedded carbonate crystals exposed during crushing. Mississippi Valley-type ores formed from fluids with a rather uniform Ca/Mg weight ratio between 4 and 8, but other types of deposits deviate widely at both ends of this range.

Comparison of fluid-inclusion data from Mississippi Valley-type deposits with those from magmatic hydrothermal deposits

Inclusions in Mississippi Valley-type deposits show surprisingly little variation, whereas those from magmatic—hydrothermal deposits vary widely, although they do have some features that are characteristically in certain ranges for specific ore types.
In density, most Mississippi Valley-type fluids had densities very close to or slightly >1.0, whereas the magmatic fluids, with a few notable exceptions, were significantly <1.0. In this connection, Hanor (1973) has shown that subsurface brines in many areas have \textit{in situ} densities for which the increasing salinity and temperature with depth just compensate, to yield a gravitationally stable column.

In terms of rate of movement, evidence is fairly abundant for very low rates for the Mississippi Valley-type fluids and is rather scanty for possibly much faster flows in magmatic systems (Barton et al., 1971).

The maximum pressure at the time of deposition cannot be determined in most inclusions, but nothing suggests a high pressure for the Mississippi Valley-type (in keeping with the generally low estimates of depth to cover during formation). In contrast, inclusion evidence can be found for the formation of magmatic deposits over a wide range of pressure, from near surface to >1000 atm.

The temperature ranges of formation for the two types overlap, in that Mississippi Valley inclusions generally have homogenization temperatures between 100 and 150°C and rarely as high as 200°C, whereas magmatic deposits cover the entire range from 100 to >500°C and frequently show a range of >100°C for ore minerals in a single deposit. The largest differences found in Mississippi Valley-type deposits are between inclusions in the main ore-stage and those in late calcite, which are always at the low-temperature end, as well as being much lower in salinity.

The salinity, as determined by the freezing-stage technique, is high in almost all inclusions from Mississippi Valley-type ore deposits. It is seldom < 15% NaCl equivalent and frequently exceeds 20%. All examples with <10% NaCl equivalent were from secondary inclusions or very late stage minerals (see Roedder, 1967b, for details on many of the individual deposits or related occurrences listed in Table IV). In contrast, magmatic–hydrothermal deposits have inclusion salinities generally <10 wt% NaCl equivalent, with a few notable exceptions such as the porphyry copper deposits, where boiling may have occurred, leaving brines of >50 wt% actual NaCl (i.e., with large NaCl daughter crystals in the inclusions).

The differences between the inclusions in the two classes of ore deposits are most notable in terms of composition. Mississippi Valley-type ore deposits have formed from fluids that were essentially sodium—calcium—chloride brines, generally containing appreciable methane (perhaps ~800 ppm) in solution and frequently containing droplets of a brownish immiscible oily phase (Roedder, 1967b, 1972). Magmatic–hydrothermal deposits, on the other hand, have formed from a wide range of solution types containing little or no organic matter, but to my knowledge, these never approach the ratios found in the Mississippi Valley-type. Among the major constituents, the ratios Na/K, Na/Ca, and Na/Cl are always much higher in the Mississippi Valley-type fluids. (It is necessary to use ratios for comparison, as the overall concentrations are so different.)
DATA FROM OTHER THAN MISSISSIPPI VALLEY-TYPE DEPOSITS

Many types of ore deposits are included in the subject matter of this volume other than the Mississippi Valley-type deposits, but relatively few studies have been made of their fluid inclusions. The fifteen most pertinent examples are listed in Table VI. The major hurdle in most of these is the problem of finding suitable host material for inclusions in these generally fine-grained ores; when coarse-grained material is found, the relation of its inclusions to the ore is frequently ambiguous. Thus, the high temperatures found for inclusions in Soviet taconites and jaspilites (Sivoronov, 1968) probably refer to a later metamorphic event, and similar explanations might be appropriate for the Witwatersrand (Krendelev et al., 1970).

Fluid inclusions in detrital grains in sediments can give much information on the nature of the source rocks (e.g., Clocchiatti, 1970; Lofoli, 1970, 1971), and hence aid in the solution of structure and correlation problems. Furthermore, recognizable special fluid inclusion types that are characteristic of a specific type of ore deposit, e.g., the very high-temperature, high-salinity inclusions found in porphyry copper deposits, can be used as an exploration tool, since they will persist through the gossan stage of weathering and even into stream sediments (Nash, 1971; Roedder, 1971c).

The origin of the Colorado Plateau uranium ores has been a particularly controversial subject, and if fluid inclusions could be found in these ores, they might help to place some constraints on the possible conditions of origin. Unfortunately, the primary ores are very difficult subjects for inclusion investigation, as they consist mainly of exceedingly fine-grained opaque minerals. One occurrence, however, a pipelike deposit in Permian sediments (Gornitz, 1969), had usable inclusions in calcite, with homogenization temperatures of 60–110°C. The close relation of the calcite to the primary ore minerals is based on the presence in it of solid inclusions of chalcopyrite and hematite.

The Kuroko-type deposits have been the subject of rather intensive geological study, particularly by the Japanese. Ten of these studies involve inclusion work, the data from which show that the fluids responsible for the Kuroko deposits were quite different from those forming the Mississippi Valley-type deposits in that they were similar to seawater in concentration of salts and were much hotter (as high as 310°C; Table VI). The data are very consistent with the model of a marine volcanic environment generally proposed for these ores (e.g., Moteki, 1968; Otagaki et al., 1968; Horikoshi, 1969; Tatsumi and Watanabe, 1971; Kajiwara, 1973), probably including mixing of seawater and meteoric water (Sato, 1968; Sakai and Matsubaya, 1973).

SUGGESTIONS FOR FUTURE WORK

Many of the more obvious avenues for further work on inclusions are implicit in the preceding discussion. In particular, a concerted effort should be made to develop micro-
scope heating and cooling stages that combine better optical characteristics with good control and measurement. The writer is currently attempting to devise a stage using flowing heated (or cooled) gas as the heat-exchange fluid surrounding the sample plate, but many different design avenues should be explored. Refinement of the available criteria for assignment of a primary origin, and the development of new criteria, are both needed and presumably will come from more detailed microscopy.

Fluid-inclusion studies may be expected to contribute increasingly to an understanding of the genesis of several types of very fine-grained ore deposits in sediments, possibly formed during diagenesis, about which there has been much controversy. The Colorado Plateau-type of U—V—Cu ore deposits may seem at first to be an unlikely candidate for inclusion studies. Recent detailed studies, however, of the inclusions in cements in limestones deposited during diagenesis (Nelson, 1973) have shown that careful microscopy on the inclusions in such difficult materials, including the use of cathodoluminescence, can provide valuable information. An important distinction must be made, however, between

**TABLE VI**

Homogenization data on ores in sediments other than Mississippi Valley-type

<table>
<thead>
<tr>
<th>Locality</th>
<th>Type</th>
<th>Mineral examined</th>
<th>Homogenization temperature °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kamoto, western Katanga</td>
<td>Co—Cu in shale</td>
<td>dolomite</td>
<td>55, 120, 200*2</td>
<td>Pirmolin (1970)</td>
</tr>
<tr>
<td>USSR — various</td>
<td>taconites and jaspilites of iron ore deposits</td>
<td>quartz</td>
<td>60—530*7</td>
<td>Sivoronov (1968)</td>
</tr>
<tr>
<td>Orphan mine, Grand Canyon, Arizona</td>
<td>uranium deposit as a pipe in Permian sediments</td>
<td>calcite</td>
<td>60—110</td>
<td>Gornitz (1969)</td>
</tr>
<tr>
<td>Witwatersrand, Blind River and others</td>
<td>uranium deposits in Precambrian conglomerates throughout the world</td>
<td>quartz</td>
<td>60—560*3</td>
<td>Krendelev et al. (1970)</td>
</tr>
<tr>
<td>Japan</td>
<td>cpy.-bearing veins in silicified zone of Kuroko deposits</td>
<td>quartz</td>
<td>*5</td>
<td>Takenouchi and Imai (1968)</td>
</tr>
</tbody>
</table>
### TABLE VI (continued)

<table>
<thead>
<tr>
<th>Locality</th>
<th>Type</th>
<th>Mineral examined</th>
<th>Homogenization temperature °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kosaka mine, Japan</td>
<td>Kuroko-type</td>
<td>quartz of siliceous ores</td>
<td>200–295</td>
<td>Tokunaga (1968)</td>
</tr>
<tr>
<td>Furutobe mine, Japan</td>
<td>Kuroko-type</td>
<td>barite (Keiko)</td>
<td>99–211</td>
<td>Homma and</td>
</tr>
<tr>
<td></td>
<td></td>
<td>quartz (Keiko)</td>
<td>117–190</td>
<td>Miyazawa (1969)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>sphalerite (Ohko)</td>
<td>245</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>fluorite (Ohko)</td>
<td>159</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>barite (Kuroko)</td>
<td>116–212</td>
<td></td>
</tr>
<tr>
<td>Kosaka mine, Japan</td>
<td>Kuroko-type</td>
<td>quartz</td>
<td>225–310*4</td>
<td>Lu (1969)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>sphalerite</td>
<td>190–245</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>barite</td>
<td>120–300</td>
<td></td>
</tr>
<tr>
<td>Kosaka and other mines, Japan</td>
<td>Kuroko-type</td>
<td>siliceous ore</td>
<td>180–290</td>
<td>Tokunaga et al.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>yellow ore</td>
<td>220–290</td>
<td>(1970)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>black ore</td>
<td>80–200</td>
<td></td>
</tr>
<tr>
<td>Northern Japan</td>
<td>various Kuroko-</td>
<td>quartz, barite and</td>
<td>100–265</td>
<td>Ohmoto et al.</td>
</tr>
<tr>
<td></td>
<td>type deposits</td>
<td>sphalerite</td>
<td></td>
<td>(1970)</td>
</tr>
<tr>
<td>Kosaka mine, Japan</td>
<td>Kuroko-type</td>
<td>Upper Kuroko (gn.–sp.–barite)</td>
<td>100–150</td>
<td>Sato (1970)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lower Kuroko (sp.–py.–cpy.–barite)</td>
<td>150–200</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oko (py.–cpy.)</td>
<td>~200</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Keiko (py.–cpy.–qtz.)</td>
<td>200–300</td>
<td></td>
</tr>
<tr>
<td>Shakanai mine, Japan</td>
<td>Kuroko-type</td>
<td>quartz</td>
<td>132–274*6</td>
<td>Enjoji (1972)</td>
</tr>
<tr>
<td>Japan</td>
<td></td>
<td>unspecified Kuroko-type</td>
<td>150–300</td>
<td>Ohmoto (1973)</td>
</tr>
<tr>
<td></td>
<td>deposits</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*1 Bubble homogenized at 140°; last daughter crystals at 240°. A leach yielded a solution with Na/K about 1.4 and (Na + K)/Cl about 0.4.
*2 These are the temperatures of disappearance of three different daughter crystals.
*3 Includes study of the gases evolved on crushing.
*4 Freezing temperatures of −1.5 to −5.3 indicate salinities of <10% (NaCl equivalent). The range of temperature for quartz is interpreted as due to trapping of primary gas bubbles and that of barite to leakage.
*5 Only freezing data given in abstract: −2.7 to −3.4°, corresponding to 5–6% salinity (NaCl equivalent).
*6 Freezing studies show salinity to be 2.4–5.2% salinity (NaCl equivalent) (his page 117).
*7 Temperature range related to degree of metamorphism.

Abbreviations: cpy = chalcopyrite; gn = galena; sp = sphalerite; py = pyrite; qtz = quartz.
what is theoretically possible to achieve with inclusion study and the practical problems presented by available sample materials. In theory, a large number of important questions in sedimentary petrology and ore research can be answered by studies of inclusions, such as primary vs. diagenetic vs. hydrothermal chert (or dolomite), but until new techniques are developed to observe, analyze, and interpret data from inclusions of <2 μm diameter, most such samples are simply not usable.

Another aspect of inclusion study may eventually aid in determining the origin of the heavy metals in the U–V–Cu deposits in sediments. The chemical alteration and leaching of pyroclastic volcanic glass in the sediments during diagenesis has frequently been proposed as the source for the uranium (and perhaps the vanadium) in these ores, but a good chemical mass balance calculation cannot be made because the compositions of the original unaltered glass can only by guessed. If, however, detrital quartz phenocrysts from this volcanic component remain in the altered sediments, these will almost always contain unaltered inclusions of volcanic glass, complete with its original complement of heavy metals. Analysis of such glass inclusions for uranium, particularly, is possible with presently available alpha and fission track techniques, as well as by ion probe. The bulk composition of such inclusions, which is easily obtained by electron microprobe (see Roedder and Wieblen, 1970, and later papers in that series of proceedings volumes), may also be compared with the altered composition to determine what amounts of each major component must have been added to the circulating brines.

Imminent new developments in analytical techniques offer exciting possibilities for the future of inclusion analysis. Neutron-activation analysis is a powerful technique particularly suited to heavy-metal studies, if the problems of contamination and loss in sample preparation can be overcome. It should also be particularly applicable to determining the important ratio Br/Cl, which has genetic significance. New developments in gas chromatography, alone or combined with mass spectrometry, show great promise in studies of the small but important amounts of gases and organic compounds present in so many inclusions. New and more precise analyses for K, Ar, Rb, and Sr may prove of value in understanding some of the problems in using these elements in dating some types of samples (e.g., Rama et al., 1965).

The identification of daughter minerals is important in the study of fluid inclusions, as these minerals represent compounds with which the inclusion fluid has become saturated on cooling. Application of modifications of the new methods of small-particle handling, plus the electron microprobe and the scanning electron microscope, should help greatly. The main problem is the technique of extracting the daughter mineral from the inclusion.

One of the most fertile fields for inclusion study will be the hopefully inevitable refinement in analytical technique to permit the determination of isotopic ratios on much smaller samples than can now be run, as the major hurdle in many isotopic studies is that of preparing samples that contain an adequate amount of inclusion fluid of known origin. It can now be done with relative ease for H, but not for C, O, and S. This is not intended to minimize the significance of the major contributions already made by the study of the
isotopes of hydrogen in fluid inclusions (and of all four elements in minerals), particularly from Mississippi Valley-type deposits. However, these have generally been on rather special types of material from which relatively large quantities of inclusion fluid (i.e., >1 mg) could be obtained. Reasonably accurate ratios for all four elements, determined on the same small inclusion sample, would provide a much more powerful tool for understanding the source and mixing of ore-forming fluids and the chemistry of ore precipitation than determinations of hydrogen alone.

Several problems on the analysis of inclusions remain which cause serious gaps in our knowledge of the chemistry of ore transport and deposition, and for which no new breakthrough appears on the horizon. These are pH, Eh, and the sulfur species present in solution. Although many determinations of the pH of inclusion fluids have been published, the writer believes that most are invalid. Determination of inclusion Eh is even more difficult, and very little is known about it, except via the identification of daughter phases and the gases in solution (Roedder, 1972, p. J140). The third problem, that of the sulfur species present, is a purely analytical problem, in that methods have not been devised to determine submicrogram amounts of sulfate and/or sulfide sulfur. Actually, even the procedures for total sulfur in submicrogram amounts are far from satisfactory. A good method for determining sulfide and sulfate sulfur would provide a measure of Eh, if equilibrium had been obtained.

All three of these determinations would presumably have to be made at room temperature and then extrapolated to the temperature of trapping, using known ionization constants. The possible value of the results to understanding ore transport and deposition are such that a concerted effort is warranted.

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