Fluid Inclusions

Edwin Roedder
Harvard University

I. Occurrence and General Significance
II. Mechanisms of Trapping
III. Composition of the Fluid Trapped
IV. Applications to Geological and Geochemical Problems
V. Special Problems

GLOSSARY

Daughter phase Any new phase, solid, liquid, or gas, formed within an inclusion as a result of the change in pressure and temperature (P–T) conditions from that of trapping to that of observation.
Decrepitation method Procedure for measuring the temperatures at which fluid inclusions explode because of an increase in internal pressure.
Homogenization method Procedure for determining the temperature of trapping of an inclusion, wherein a sample on a special microscope stage is heated until all daughter phases homogenize to a single fluid phase.
Isochore Line in a P–T diagram representing the locus of all points for a fluid of a given composition and density.
Primary inclusion One that is trapped during the growth of the host crystal.
Secondary inclusion One that is trapped by the healing of fractures in the host crystal at some unspecified time after its growth.

FLUID INCLUSIONS are small volumes of fluid trapped within a crystal during its original growth from that fluid, or during subsequent healing of fractures in the presence of fluid. Changes in pressure and temperature from those of trapping to those of observation usually result in the formation of new daughter phases in the inclusion. Thus, water-rich fluid inclusion commonly split to form liquid and vapor phases, and sometimes solid crystals as well. If the original fluid that was trapped was a silicate melt at high temperatures, as in volcanic lavas, the fluid may now be a glass.

The study of fluid inclusions provides a wide range of data, some of which are unavailable from any other source, on the various physical and chemical processes that have yielded the minerals we see in terrestrial, lunar, and meteoritic samples. As a result, they have been of interest and value in prospecting, planetary geology, gemology, volcanology, petroleum exploration, geothermal power, nuclear waste disposal, and even in the siting of atomic power plants.

I. OCCURRENCE AND GENERAL SIGNIFICANCE

Fluid inclusions occur in most natural crystals, because most rocks and minerals, including ores and lunar and
meteoritic samples, formed from a fluid or had a fluid present during later fracturing and healing. Inclusions are generally small. Very few are visible to the unaided eye, and usually the abundance in a given sample increases with decrease in size. In most samples, inclusions <10 μm in size are one or two orders of magnitude more abundant than those >10 μm. In many samples, they are exceedingly numerous. Ordinary white minerals such as common quartz or calcite are white because of the refraction of incident light at the many mineral–fluid inclusion interfaces; it is not uncommon to find as many as 10^9 cm^{-3}. Those crystals of hard minerals that are relatively free of inclusions and other defects and have a pleasing color are called gemstones, and the fewer the inclusions, the more valuable the stone.

A geologist is, in effect, a detective, trying to piece together the events of the distant past through a careful study of the many clues present in the rocks as they are found. Fluid inclusions, although small, provide a remarkable array of such clues, in that they can be made to yield quantitative data on the temperature, pressure, density, and composition of the fluids that existed in the past. These data have proven valuable in many aspects of geology and geochemistry, including the search for ore deposits, and some provide striking visual observations of the various phenomena at the critical point.

Crystals of many substances are grown commercially for use in a wide variety of optical and electrical devices. These applications normally require relatively perfect crystals, as free of defects as possible, and hence the growth conditions must be carefully maintained so that fluid inclusions are not formed.

**II. MECHANISMS OF TRAPPING**

With a few very minute exceptions, all crystals are imperfect, and fluid inclusions constitute one kind of imperfection. A cubic water inclusion 10 μm in size contains ~10^{-9} g of water, or ~10^{13} molecules. It is probable that something resembling a continuum exists between this size imperfection and single water molecules trapped within a crystal, but the bulk of fluid inclusion studies today are of inclusions in the range of 10–100 μm. Much work has been done on the mechanisms of trapping of such imperfections, and although some mechanisms have been well documented in the laboratory, in theory, or in nature, it is probably true that for many natural inclusions, the exact mechanism of trapping is simply not known. A sudden jump in the growth rate of an otherwise “perfect” crystal can yield a feathery or dendritic zone, which can subsequently be covered by solid growth. Hollow or tubular growth on certain crystal faces can similarly be covered. Subparallel growth may trap some of the growth fluid between portions of the crystal. Growth spirals may develop central cavities, or cavities may form between adjacent growth spirals. Another common mechanism involves the enclosure of a grain of another solid phase within the growing crystal; often the enclosure traps some fluid along with the solid.

All the above mechanisms pertain to the trapping of primary inclusions, during the growth of the host crystal. However, in most samples, primary inclusions are much less abundant than secondary ones, formed from the healing of a fracture, as shown in Fig. 1. In fact, many samples contain millions of obvious secondary inclusions and not a single recognizable and verifiable primary inclusion. Secondary inclusions represent samples of fluids present at some time after the growth of the host crystal. They may form minutes, years, or millions of years later, and it is not rare to find that there have been several separate periods of fracturing and rehealing, under changing P–T conditions, from fluids of differing composition. A special type of inclusion, called pseudosecondary, forms by the same process of crack healing, but during the growth of the host crystal. Distinction among the inclusions from various origins and generations in any given sample may require careful and extensive petrography. Some planes of secondary inclusions are plainly evident in most samples, but unambiguous identification of a primary origin, although crucial to many uses of fluid inclusions, is often difficult and sometimes impossible.

**III. COMPOSITION OF THE FLUID TRAPPED**

This aspect of fluid inclusion study is the most important of all, as fluid inclusions provide us with the only actual samples we have of the fluids responsible for, or at least intimately involved in, many geochemical processes in the past. Other than silicate melts, fluid inclusions most commonly consist of a dilute to concentrated water solution of various solutes, with Na and Cl generally predominant, but with variable amounts of K, Ca, Mg, SO_4, HCO_3, CO_2, etc. Others consist mainly of liquid CO_2 under pressure, with various amounts of N_2, CH_4, and other gases and hydrocarbons. Ever since an 1858 seminal paper by H. C. Sorby, often called the father of fluid inclusions, a wide range of methods have been applied to determine the composition of the fluids. The small size of most inclusions, the extremely wide range of possible composition (at least 40 elements have been found in significant quantities), the occurrence in many different host minerals, and the difficulties of avoiding serious loss or contamination during extraction for analysis present a formidable quantitative
A. Nondestructive Methods

Any property of the fluid in an inclusion that can be measured under the microscope may provide at least some compositional evidence. Thus, these features of a liquid phase may be determined and interpreted in terms of probable composition: viscosity, color, wetting characteristics (relative to other daughter phases and the host phase), infrared and ultraviolet absorption, Raman spectra, fluorescence, index of refraction, thermal expansion, temperature of homogenization, critical phenomena, phase changes on heating or freezing, bubble movement in thermal gradients, and many others. Unopened inclusions can be bombarded with electrons, protons, X-rays, or other radiation, and the spectra from their constituent elements or polynuclear species such as CO₂ or SO₄²⁻ can then be detected. Many of these same features can be used in the identification of solid phases in inclusions, but here one has many more possible definitive properties that can be measured or estimated, particularly crystal habit, interfacial angles, extinction angles, elongation, birefringence, and indices of refraction and their relation to crystal orientation. Some data can even be obtained on opaque daughter phases, such as reflected light color, crystal shape, magnetic properties, and the Curie point. Perhaps the two most commonly used properties are the depression of the freezing point of water-rich fluids and the homogenization temperature and triple point of carbon dioxide. The first provides a measure of the solute content, and the second provides a measure of the density and purity of the CO₂ phase.

B. Destructive Methods

Many of the earlier chemical analyses of fluid inclusions are bulk analyses of the inclusions in large samples (100 or even 1000 g). Very few samples of this size can be found in which only one generation of inclusions is present; most will have a mixture of primary and perhaps more than one generation of secondary inclusions, and hence, the analysis of such a mixture is close to meaningless. Those very specially selected bulk samples that do contain essentially only one generation of inclusions present relatively few problems to the chemist in terms of needed sensitivity, as the total mass of inclusion fluid available is ample, but
the most serious problems lie in the step involving the extraction of the fluid from the host mineral without serious loss and/or contamination. Generally, the extraction is done by fine grinding to open the inclusions, followed by leaching with one or more types of solutions and filtration. Major loss of cations to absorption on the host mineral surfaces can be minimized by the addition of a high-valence element that is not expected in the analysis, but the contamination from various sources can be a serious limitation on the usefulness of the results. The leach solutions can be analyzed by inductively coupled plasma, ion chromatograph, ion-specific electrodes, or other procedures.

Such analyses provide the ratios of the various solutes, but not their concentrations in the original fluids. To obtain concentrations, it is necessary to determine the amount of water (and CO₂). For this, somewhat smaller samples may be crushed in a vacuum system that permits the analysis of the amounts of water and other volatile materials, as well as the determination of the isotopic ratios of the oxygen and hydrogen in the water. Following this crushing, the broken mineral grains are leached with water or acids, and the concentrations of released solutes in the original fluids are calculated.

In view of the multiple origins for the inclusions in many samples, much more effort has been expended in recent years on procedures for the quantitative analysis of individual inclusions. Although many of the modern analytical procedures are adequately sensitive for samples in the range of 10⁻⁹ g, the bulk of this 10⁻⁹ g is generally water; the most valuable information pertains to the solutes in this water. Thus, the total mass of a constituent present in the range of 1000 ppm in the fluid would be only 10⁻¹² g, which taxes the limits of sensitivity of some analytical methods. An additional problem is that of obtaining truly duplicate samples for check analyses or for the determinations of other constituents. In spite of these difficulties, a variety of procedures have been developed for quantitative multiple element analysis of individual inclusions. A major development in this direction has been in the methods for quantitative analysis of the gases in individual inclusions, by gas chromatography and mass spectrometry, after release by crushing, or by thermal or laser decrepitation.

IV. APPLICATIONS TO GEOLOGICAL AND GEOCHEMICAL PROBLEMS

A. Temperature Determinations

By far the most common use of fluid inclusions is to obtain a measure of the temperature of past events. H. C. Sorby showed in 1858 that the bubble present in most inclusions represents the differential shrinkage of the host crystal and the fluid that was trapped in it, from the temperature of trapping to that of observation. By reversing this shrinkage on a heating stage on the microscope until homogenization occurs, the minimum temperature of trapping can be determined (Fig. 2). The actual temperature of trapping must be at this temperature or higher, because any and all inclusions trapped along that particular isochore will have the identical homogenization temperature. The dissolution of solid daughter phases on heating also yields a minimum temperature. The true temperature of trapping can only be obtained if some independent estimate of the pressure is available. Several conditions are necessary for this method to be valid, and there are numerous problems in both the measurement itself and in the interpretation of the results, but still, the homogenization method is one of the most accurate and widely applicable geothermometers available.

Temperature determinations on past geologic events are of far more than mere academic value. Many mining companies make use of them in understanding the processes that went on to form known deposits and in the exploration for new deposits; oil companies look at the

![FIGURE 2 Serial photomicrographs of a large primary inclusion in sphalerite (S) from Creede, Colorado, after equilibration at the temperatures indicated. The horizontal bars are oscillatory striations on the cavity walls. On heating, the bubble (v) decreased in volume to the homogenization temperature; this inclusion is said to "homogenize in the liquid phase at 210°C."](image-url)
temperatures of inclusions in core samples from wells to determine, among other things, whether the rocks have been hot enough to generate oil, or so hot that any oil would have been destroyed; geothermal energy companies use them to guide drilling and to determine the potential for a field; gemologists use them to validate the place of origin of gemstones, to distinguish between manmade and natural stones, and to detect laboratory heat treatments made to improve the color of an otherwise less valuable natural stone.

B. Pressure Determinations

Under some conditions, fluid inclusions may provide an estimate of the pressure at the time of trapping, or at least some limits on the possible range of pressure. The various caveats are beyond the scope of this article, and the accuracy of the pressure values obtained differ widely with the specific method used, but they have provided important data on processes that cannot be observed directly. Volcanoes erupt some solid materials along with the molten silicate melt or lava. Pressure determinations on the inclusions in these solids have provided insight into the "plumbing system" of the volcano, and may help eventually in predicting volcanic hazards. Estimates of the pressure and hence depth at which some ore veins have formed have aided in the search for similar veins in otherwise unknown new areas.

Fluid inclusions provide one of the many examples of "pure" scientific research, pursued for what might have been considered purely academic reasons, that turn out to have social value. The siting of nuclear reactors involves careful evaluation of the hazards from various possible geologic processes that might occur after the reactor is in operation. One such process is movement on faults in or near the site. Movement on a fault actually cutting the site could cause major disruption, and seismic action from movement on a fault near the site could also cause damage. Not uncommonly, excavations for major construction projects uncover evidence of faults. When such a fault is found, the geologist is immediately asked to predict the possibility of renewed movement on the fault. This question is not easy to answer. The probability of such renewed movement is assumed to be inversely related to the length of time since the last movement; if fault movement has not occurred for a very long time, the fault can be considered inactive. However, an old inactive fault may look very similar to a recently active one. Fortunately, fluid inclusion geobarometry can sometimes help to place some constraints on the time since the last movements.

In 1974 at the Ginna Project in New York State, fluid inclusions were found in cubic crystals protruding into vuggy cavities along a fault that cut the proposed site. The occurrence of the crystals suggested that they must have grown since the last movement on the fault. An elevated pressure at trapping, shown by thermometric data on the inclusions in the crystals, established a minimum depth below the surface at the time of formation. (The inclusions can be either primary or secondary for this procedure, and in fact, the latest inclusions, the secondaries, are actually the most useful.) Subsequent erosion had removed this much material from the site, so by estimating the rates of denudation, a minimum time since the last movement was obtained. Similar procedures have since been used at several other reactor sites.

C. Density Determinations

If the compositions (and hence density) of the individual daughter phases in an inclusion can be determined, and the relative volumes of the various phases determined by optical measurement (or other procedures), the bulk density of the fluid that was trapped can be calculated. These densities range, for water-rich inclusions, from very low densities of $<0.1 \text{ g cm}^{-3}$ (from the trapping of a dense steam phase) to densities $>1.3 \text{ g cm}^{-3}$ (from the trapping of a strongly saline fluid or hydrosaline melt). Inclusions in many ore deposits have densities near $1.0 \text{ g cm}^{-3}$. Most ores have formed as a result of a hot ore-bearing fluid moving through the earth. One of the problems in understanding the origin of ore deposits (and in the search for others) is in understanding the hydrologic system—what fluid moved which way? Since most rocks near the surface of the earth are saturated with cold, essentially fresh water of density $1.0 \text{ g cm}^{-3}$, it is important to know the density of the ore fluid at the time of ore deposition, and hence which direction convection might have taken. Fluid inclusions provide the only known source of data on the densities of these ore fluids.

D. Compositional Determinations

Two examples from the extensive literature on fluid inclusions will have to suffice to illustrate the application of compositional data to geological and geochemical problems. First, in the study and exploration of a given type of ore deposit, the geologist commonly establishes a model of the process, built on the basis of available data. Ore deposits do not occur randomly; they are the result of transport of the ore metal or metals in a fluid from a dilute source to a site where they are deposited in a more concentrated form, that is, as an ore. The chemical and physical nature of the fluid that transports and deposits the ore is the essential element in any such model. In recent years, there has been a major breakthrough in our understanding of the chemistry of ore metal transport and deposition.
Fluid inclusion compositions have helped to refine these models, as it has become obvious that the chemistry of the ore fluid has been different in various types of ore deposits. Thus, one well-known type of very large copper deposit, the porphyry copper, has involved fluids that, based on inclusion study, were almost always exceedingly saline (commonly as much as 50% salts in solution), very hot (as much as 700°C), and generally two-phase at the time of trapping (i.e., boiling or condensing). Other ore deposits formed from very different fluids. One class of gold deposit formed from very low salinity aqueous fluids, containing much CO₂, at moderate temperature and low pressure. Such model characteristics are sufficiently typical that they are useful in exploration for deposits. During surface weathering of a porphyry copper deposit, all copper may be leached out, but fluid inclusions in residual quartz in the soil or stream sediments may still preserve the recognizable characteristics. Unfortunately, no such set of characteristics is completely limited to a given class of ore deposits, but they may still be used as possible indicators.

Another example of the use of fluid inclusion compositions is found in the studies that have been made in the search for possible sites to store nuclear waste. The basic question is, where in the earth can nuclear waste be stored for thousands of years so that it will not be a hazard to mankind? One type of geological environment that has been considered for nuclear waste storage is the massive salt deposit. Fluid inclusions in such salt play two roles, one beneficial and one detrimental. On the beneficial side, study of the fluid inclusion composition can provide some clues on what processes have taken place in that salt deposit in the millions of years since it formed. These data on the past are of major concern, since the geologist is being asked to predict what may happen to the waste site in future millennia. For example, has there ever been an incursion of fresh groundwater into these beds in the past (and hence might one occur again in the future)? Fluid inclusions trapped from such an incursion would have grossly different solute compositions and isotopic signatures for the water than those from the original evaporated seawater.

On the detrimental side, fluid inclusions in the salt complicate the engineering problems in designing a nuclear waste site. A nuclear waste canister buried in the ground becomes thermally hot from the intense radioactivity of the waste. Such heat, in flowing out into the surrounding salt, set up a thermal gradient. Fluid inclusions in salt in a gradient tend to dissolve the host salt on the hot side of the inclusion and redeposit it on the cold side, and hence, they migrate up the thermal gradient toward the waste canister. Yet salt beds were originally selected for consideration because they were considered to be an exceedingly dry environment. An additional problem comes from the cation composition of the fluids. Ordinary saturated NaCl-H₂O solutions can be expected to be corrosive to the canister materials, but the fluid inclusions in salt normally contain high concentrations of such divalent cations as Mg (as chloride). These solutions may show metal corrosion rates orders of magnitude higher than simple saturated NaCl brines. As a result, if a salt repository is to be used, it may be necessary to engineer the use of very special and expensive canister materials.

V. SPECIAL PROBLEMS

The small size, ambiguity as to origin, and extremely wide range of possible combinations of inclusion constituents and host materials make measurements difficult and the interpretation sometimes uncertain. In addition to these expectable problems, two others are particularly pertinent and of some scientific interest.

A. Leakage and Volume Change

The term leakage in fluid inclusion studies refers to movement of material either into or out of an inclusion. Many lines of evidence have been used to show that in most geological environments, fluid inclusions have not leaked, at least not enough to have measurable effects with present procedures. One special case, however, does seem to be best explained by significant leakage of hydrogen out of fluid inclusions. In many porphyry copper deposits, the fluid inclusions contain solid crystals of hematite (Fe₂O₃) or anhydrite (CaSO₄) or both. Although these might be considered to be daughter minerals, formed on cooling, they do not redissolve on heating the inclusions in the laboratory, as a true daughter mineral should. These may represent new phases formed irreversibly in the inclusion after trapping, as a result of leakage of hydrogen. Disproportionation of water at these high temperatures to form hydrogen and oxygen, followed by outward diffusion of the hydrogen, has apparently resulted in auto-oxidation of original ferrous iron in solution to precipitate hematite, and of sulfide iron to sulfate, to precipitate anhydrite. Several features of the porphyry copper environment might be expected to lead to the presence of hot but oxygenated surface waters in the ore body during the long cooling period, thus providing a hydrogen sink surrounding the crystal, with enough time at high temperatures to permit significant hydrogen diffusion to that sink.

One of the necessary assumptions implicit in any use of fluid inclusions for geothermometry and geobarometry is a constant cavity volume after trapping. Most geological environments investigated apparently fulfill this
requirement within the limitations of modern measurements. However, during metamorphism of large masses of rock in the crust, individual crystals containing inclusions trapped by growth during an early stage may later be subjected to higher pressures and temperatures as the depth of burial increases. In addition, all inclusions trapped at the peak pressures and temperatures must, out of necessity, be subjected to long period of decreasing temperatures and pressures before reaching surface conditions. If the P–T path taken during this cooling follows the isochore for the trapped inclusion fluid, valid data can be obtained from the inclusions. If, however, the path deviates from this isochore, pressure differentials will be set up between the inclusion and the exterior of the host crystal. If the internal pressure is higher, the inclusion may permanently expand (i.e., stretch) and if it is lower, it may permanently collapse; recent studies show that geologically expectable differential pressures can result in such changes, even in quartz, in a few days at high temperatures. The validity of the extrapolation of these results down to the P–T paths encountered most commonly in metamorphic rocks (i.e., possible lower temperatures and pressure differentials, but for much longer times) is still an open question.

B. Metastability

Inclusions are very small systems to consider, even from an atomic viewpoint. Thus, an inclusion 10 μm in diameter containing a 30 wt% solution of a salt may have only $10^{11} - 10^{12}$ “molecules” of that salt; at 10 ppm PbS, it would contain only 25 million “molecules” of PbS, enough to form a crystal only 200 unit cells on an edge. The smaller the system, the more common metastability becomes. Hence, not surprisingly, metastability—resulting from failure to nucleate new but stable phases—becomes a problem that can be observed in (and frequently interferes with) many types of inclusion studies. It is common in samples as found, even though they have had geologic time periods to equilibrate; and it is even more commonly observed in the phase changes during the much shorter time spans of laboratory experiments on inclusions.

Metastability that results from failure to freeze on cooling in the laboratory is almost universal, and can be frustrating, but it normally does not lead to misunderstanding or error. However, one aspect of metastability—the occurrence of metastable superheated ice in liquid-water inclusions at high negative pressures—can lead to serious errors. Although negative pressures are not encountered in many inclusion studies, they are very commonly observed in some, particularly in studies of low-salinity inclusions formed at low to moderate temperatures, in which the vapor phase is eliminated upon freezing and fails to renucleate on warming. In such inclusions, it is not rate to have as much as 1000 atm of negative pressure, resulting in perfectly normal-appearing (but metastable) ice-water equilibria to as high as +6°C, until the spontaneous nucleation of the stable vapor phase results in instantaneous melting of the superheated ice and a return to the stable phase assemblage of liquid + vapor.

SEE ALSO THE FOLLOWING ARTICLES

CRYSTAL GROWTH • CRYSTALLOGRAPHY • EVAPORITES • FLUID DYNAMICS • VOLCANOLOGY

BIBLIOGRAPHY


