Ancient Fluids in Crystals

When a mineral crystallizes out of a brine, some of the brine is trapped in small "fluid inclusions." Thus the inclusions provide samples of a solution that may be more than a billion years old

by Edwin Roedder

The geologist works like a detective in attempting to reconstruct the events of the remote past from the evidence of the present. Unlike the detective, however, he works with events that occurred millions or even billions of years ago, and the clues he has to piece together are unusually meager. It is well known that most sedimentary rocks formed in sea water; it is less commonly recognized that most other geologic processes in the apparently solid crust of the earth, including the formation of most ore deposits, have taken place in a bath of salty water. Droplets of these ancient mother liquors, preserved in the form of "fluid inclusions" in many rocks and minerals, are clues to such processes. Although the droplets are minuscule, they enable the geologist to tell a number of things about the events of the past that would otherwise be completely hidden. These tiny samples of fluids long since gone from the face of the earth have been known for almost 150 years, but they still conceal many secrets and merit much more investigation.

Just about any crystal, natural or manmade, that is grown from an aqueous solution will have fluid inclusions. They are easily seen in a clear quartz crystal. Ordinarily the crystal will have a clear tip, but its base will show faint whitish streaks. A 10-power glass will generally resolve these streaks into innumerable separate liquid inclusions, each containing a tiny bubble. Most of them will look black, because light entering them is trapped by total reflection at the walls, but a few may be flat enough to transmit light clearly. The photomicrographs that illustrate this article were made by light transmitted through polished mineral plates and nearly perpendicular to the planes of somewhat flattened inclusions.

In size fluid inclusions range from a diameter of probably less than one micron (a thousandth of a millimeter), below the limit of resolution of the light microscope, to a few centimeters. Inclusions bigger than a millimeter in diameter are rather rare; those in the centimeter range are museum pieces. Most of them contain a water solution of various salts, in concentrations ranging from nearly fresh water to highly concentrated brines. Most also enclose a bubble of gas. When the bubble is small enough to respond to statistical irregularities in the number of molecules striking it, and is free of the inclusion walls, it can be seen to wander continuously in a jerky Brownian movement. It is fascinating to watch such a bubble under the microscope and to think that it has been nervously pacing its cell for perhaps a billion years. Some inclusions have one or more crystals in the liquid; some are composed of two immiscible liquids; a few, of gas alone. In extremely clear crystals a careful microscopic search may be required to find even a single inclusion. Ordinary white minerals such as quartz and calcite may have as many as a billion inclusions per cubic centimeter. Although fluid inclusions in natural crystals are a welcome source of information to the geologist, they may produce disfiguring flaws in gem stones. In artificial crystals intended for use in electronic circuits inclusions are serious defects.

Careful studies of both synthetic and natural mineral specimens have shown that inclusions can be created in several different ways. One of the most common is by dendritic, or branching, growth of a crystal. When this is followed by a solid, perfect growth that covers the imperfect region, portions of the fluid from which the crystal was growing are trapped in the open spaces. Anything that temporarily halts or slows the growth of a small part of the crystal, such as another mineral grain, a globule of an immiscible liquid or a gas bubble, may also cause trapping of fluid. Inclusions made in this way are called primary, because they form simultaneously with the enclosing crystal.

Even more common are secondary inclusions, which originate in the rehealing of cracks in a crystal. The additional surfaces exposed by a crack in an otherwise perfect crystal represent an increase in the energy stored in the crystal. If the crystal is immersed in a liquid in which it is even slightly soluble, healing starts immediately, returning the structure to a lower energy state. Moreover, if the crack is a curving fracture, the atomic planes exposed are not the normal crystal planes but surfaces of even higher energy and therefore higher solubility; the processes of solution and redeposition rapidly generate a system of two-dimensional dendritic crystals that join together and eliminate most of the new surface [*see illustration on page 41*]. At first the resulting inclusions still have a high surface energy and resemble a family of amoebae with a flair for geometry. In time they smooth out; material is dissolved from the jutting, convex portions and even from the flat walls and is deposited in the concave areas. Two competing but exceedingly weak forces decide what will be the ultimate goal of this process: either an approach to the smallest amount of surface, yielding a spherical inclusion, or an approach to the lowest-energy surface, yielding a faceted negative crystal inclusion. Perhaps the composition of the liquid is involved, since a single crystal may show both types of inclusion, although as separate groups.

Primary inclusions, then, constitute a sample of the fluid in which the crystal grew, whereas secondary ones contain
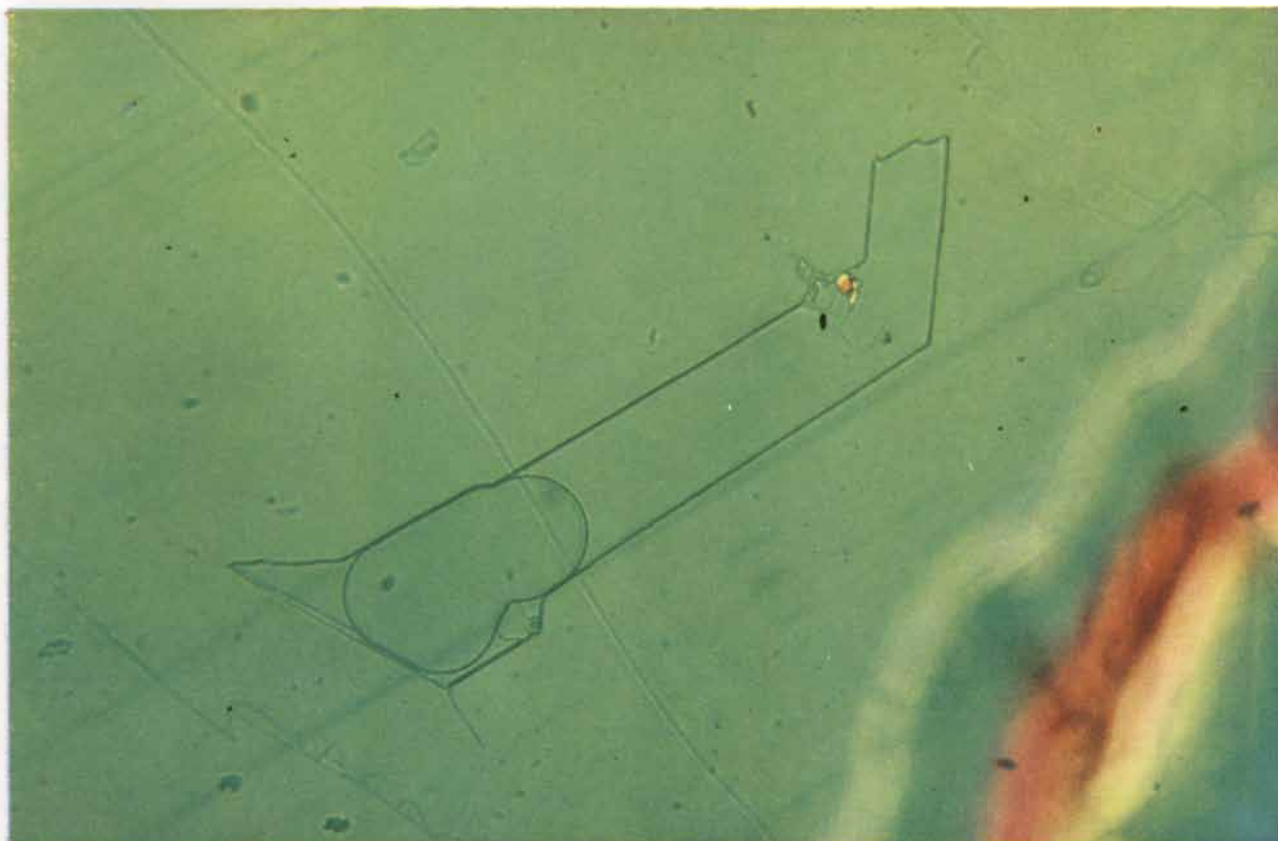
INCLUSION IN TOPAZ, magnified 198 diameters in this photomicrograph, is straight-edged area at center. Rounded area is gas bubble; the rest is saline water. Small reddish spot is a crystal that grew in inclusion; other daughter crystals are also visible.
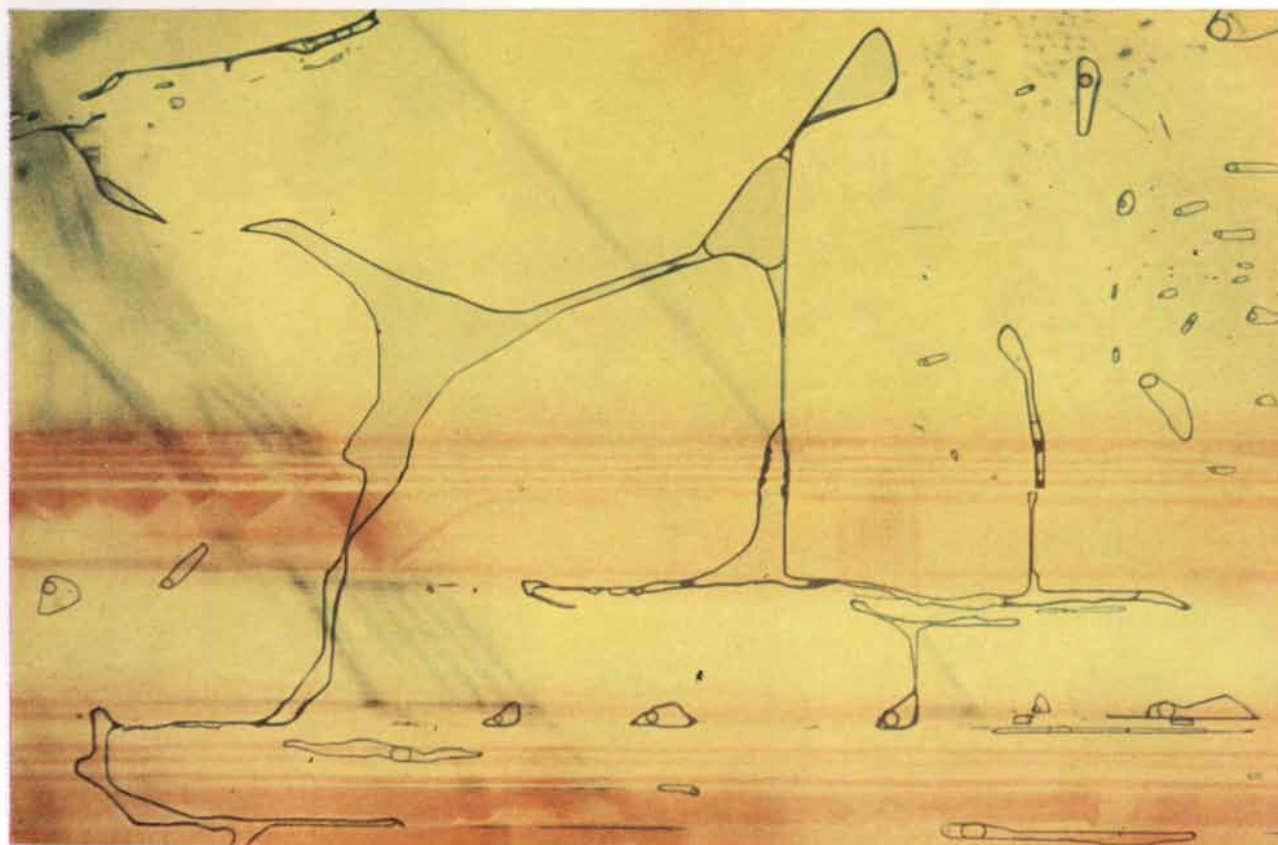
INCLUSION IN SPHALERITE extending over most of this photomicrograph of a polished plate is magnified approximately 46 diameters. Surrounding it are numerous smaller inclusions. Each of the inclusions consists of saline water and a rounded bubble of gas.
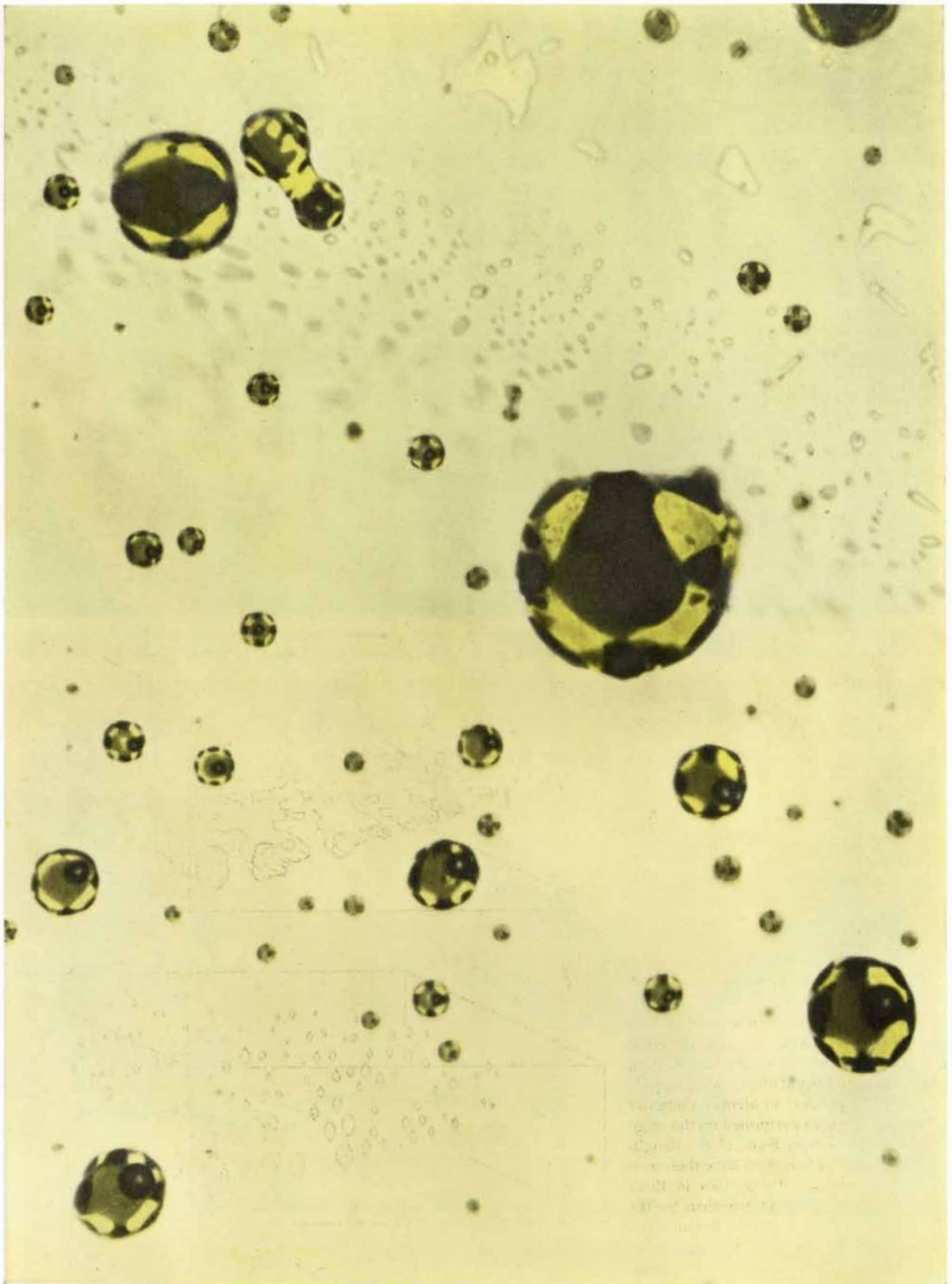
PETROLEUM INCLUSIONS in fluorite, magnified 266 diameters, have undergone degradation into several phases since the time of crystallization. A globular mass with four darker appendages is a phase that preferentially wets certain surfaces, thereby appearing to divide the lighter phase into four quadrants. The dark circle in each inclusion is a bubble of gas under high pressure.

fluids that bathed the crystal at some later time. The great abundance and widespread occurrence of fluid inclusions indicate that many geologic processes went on in an environment where every crack and pore was filled with liquid. Those rocks that do not contain fluid inclusions—meteorites and certain types of igneous and metamorphic rocks—were formed under special water-deficient conditions. The time elapsed between the trapping of primary and secondary inclusions in a given crystal can be quite short in geological terms; there is considerable evidence that many secondary inclusions actually were trapped in fractures that occurred while the crystals were still growing. On the other hand, the crystals in many rocks and veins have been sheared one or more times by earth movements that took place ages after the original formation. Large numbers of tiny inclusions were trapped in the shear planes when they rehealed. Thus adjacent inclusions may differ greatly in age.

The composition of the fluids in inclusions has been studied by a variety of methods. With the rare large inclusions it is possible simply to drill into them, draw out the fluid and analyze it, as Sir Humphry Davy did in 1822. To obtain enough material for chemical analysis from smaller inclusions the mineral sample is crushed, which opens a large number of inclusions. Then the powder is leached with water, and the salts are separated from the crushed mineral by filtering or by electrodialysis, in which the ions are forced through permeable membranes by an electric current. Although 100 billion small inclusions of brine may be opened in grinding a 100-gram sample, they usually yield only a few milligrams of soluble salts. As a result it is necessary to take particular care to avoid contamination during extraction and analysis.

Some inclusions contain solid crystals in their fluid. Generally these daughter minerals formed by crystallization from the saturated liquid after it was trapped. It is often possible to identify daughter minerals by tests performed on the stage of the microscope. Some of the daughter-mineral crystals even have their own fluid inclusions with bubbles in them and, as in the case of Jonathan Swift's celebrated fleas, so on ad infinitum. The most common crystals turn out to be sodium chloride, as is shown by such evidence as their shape, their behavior in polarized light, their small increase in solubility with temperature and their odd behavior at subzero temperatures.
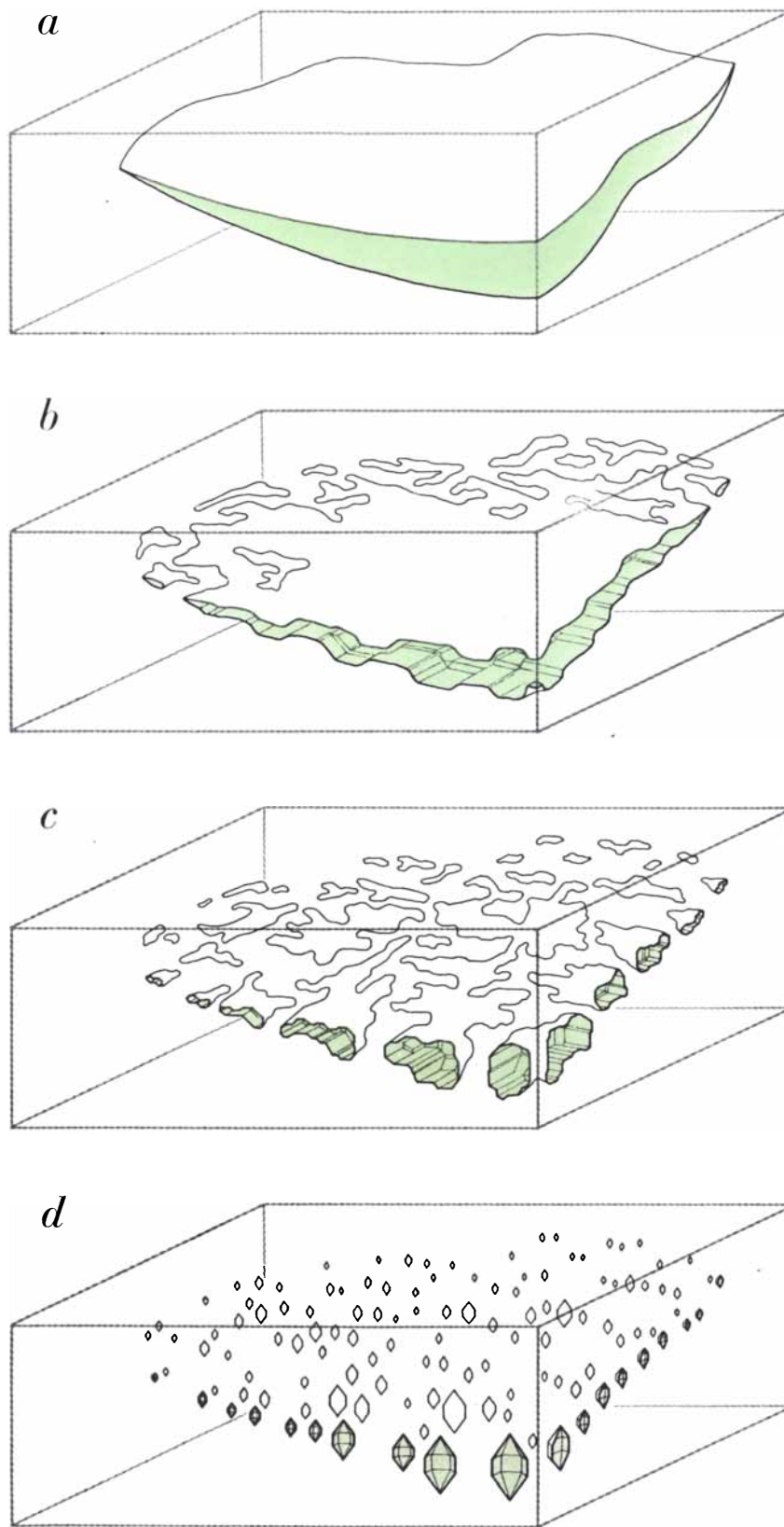
SECONDARY INCLUSIONS form in the fracture of a crystal (a) embedded in a liquid (color). Solution and redeposition of material from the liquid on the fracture surfaces results in dendritic growths (b), which meet and close off small volumes of liquid (c). These gradually lose surface area and become rounded masses or hollow negative crystals (d).

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The finding is consistent with the fact that sodium chloride is the major saline ingredient found by analysis in most inclusion fluids. In fact, the amounts of sodium chloride, as crystals and in solution, in the fluid inclusions in many rocks are adequate to explain the known chloride content of the rocks. This was long considered a mystery because no ordinary rock-forming mineral could take chlorine into its crystal structure.

To determine the complete chemical composition of a few milligrams of inclusions, including the concentration of salts, the author and his colleagues in the U.S. Geological Survey laboratories have used a combination of methods. Small portions of the mineral, containing specific inclusions, are cut out and crushed in a high vacuum. The evaporated water and other gases from the inclusion fluids are collected and analyzed both chemically and isotopically. The crushed sample is then leached with about 10 cubic centimeters of very pure water, filtered through a special low-contamination filter and analyzed for eight to 10 elements by sensitive photometric methods. When the amounts of water and salts are known, the original concentrations of salts in the inclusions can be calculated. In general the most abundant ions are sodium and chloride, with lesser amounts of calcium, potassium, magnesium, sulfate (SO_4^-), carbonate (CO_3^-) and bicarbonate (HCO_3^-). Usually only traces of other elements are found. Both concentration and composition vary widely from one type of occurrence to another. Even single crystals from some ore deposits show significant changes in the composition of
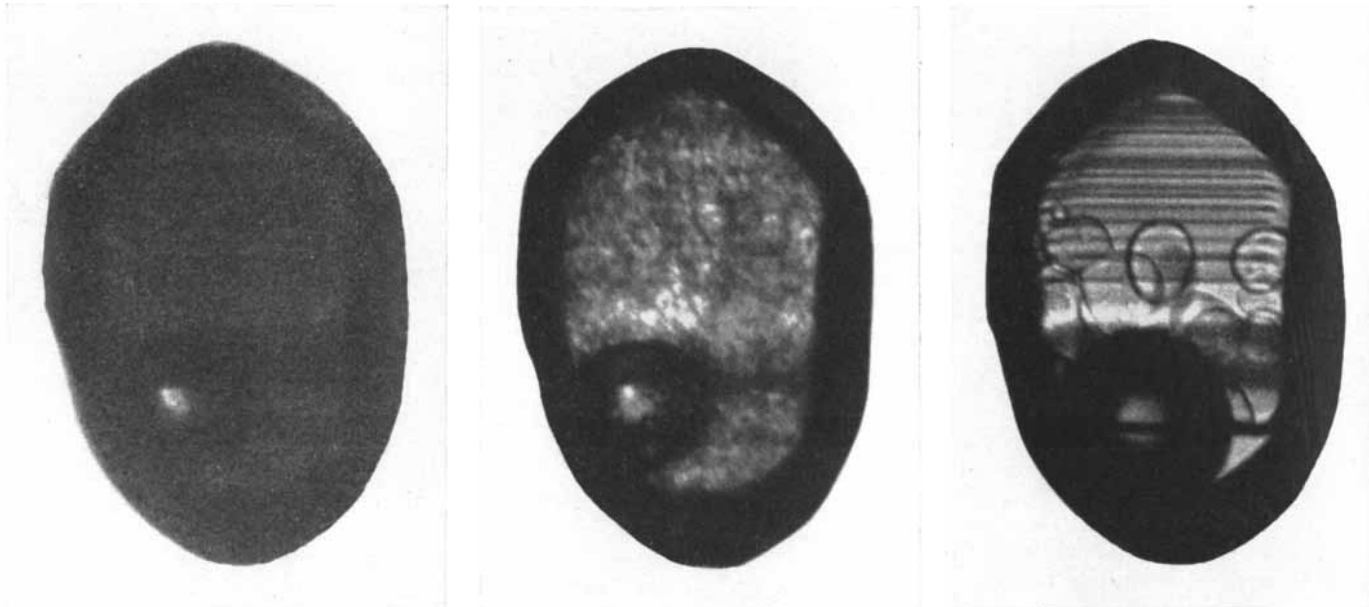
FREEZING AND HEATING are employed in the analysis of inclusions. These photomicrographs show a liquid inclusion in sphalerite at — 29.5 degrees centigrade (*frozen solid*), — 28.5 degrees, — 3.65 degrees and — 3.15 degrees (*completely melted*). This inclusion would be said to have a "first melting temperature" of — 29 degrees and a freezing temperature of — 3.15 degrees. Horizontal
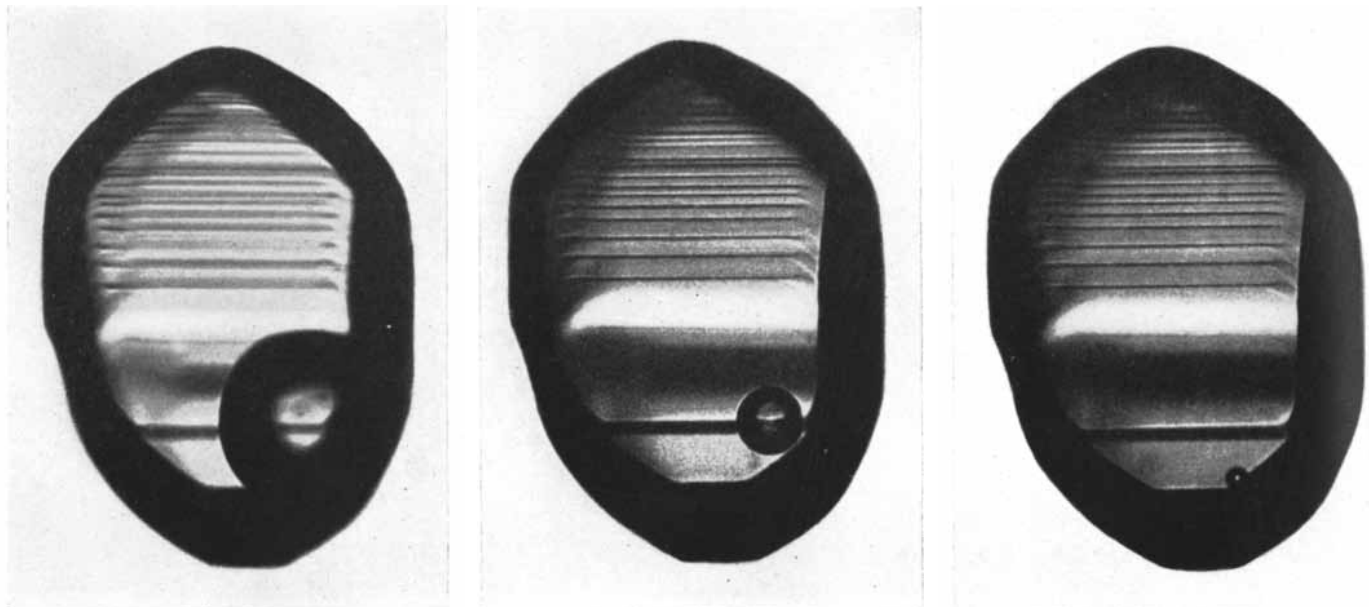
"FILLING" TEMPERATURE is that at which the liquid in an inclusion expands to fill the volume (i.e., the gas bubble disappears). Except for pressure corrections it is generally taken as the temperature at which the inclusion formed. The temperatures are

inclusions from one growth zone to the next, indicating changes in the nature of the ore-forming fluid during the formation of the crystal.

The procedure just described requires several milligrams of inclusion liquid—far more than can be obtained in uncontaminated form from many samples. In order to get information on the approximate concentration of salts in single inclusions as small as 10 microns in diameter (a billionth of a gram in weight) the author has devised a freezing stage for the microscope. The only

lines are striae on inclusion's inner walls. These micrographs, those below and those on following pages were made by the author.

130, 204.7, 209.8 and 210 degrees. The magnification in both sequences is 242 diameters.

property that depends on concentration, and that is measurable in such small inclusions, is the depression of the freezing point of the fluid. The higher the salt concentration, the lower the freezing temperature. In the author's laboratory this temperature is determined by freezing the inclusion solid, then gradually warming it while watching it through the microscope. The granular mass of solid crystals of ice and salt in completely frozen inclusions is essentially opaque. As it warms up, a small amount of liquid appears abruptly at the first melting temperature—the temperature at which the first of the various solid components melts. This fluid wets the grains of ice and salts, causing the opaque mass to become translucent. With further increase in temperature more of the solids melt until only one tiny ice crystal remains. The temperature at which it finally melts is the freezing temperature.

Theoretically this should also be the temperature at which the first ice crystal forms on gradual cooling, but it is not. All inclusions exhibit the phenomenon of supercooling; that is, they must be cooled considerably below their freezing point before the growth of ice crystals starts. This is true even for inclusions containing salt crystals or other crystals. Most small inclusions will remain as supercooled liquid for hours and even weeks at 30 to 40 degrees centigrade below their freezing temperatures; some, such as the inclusion in emerald shown at bottom left on page 46, have failed to freeze after a week at liquid nitrogen temperature (-196 degrees C.). The strong brines in the emerald were finally frozen after 21 days at -78 degrees. Their first melting temperature was -60 degrees, which generally indicates a high concentration of calcium chloride.

The drastic supercooling in inclusions is apparently due to the absence of extraneous particles suitable for nucleating ice crystals. Such particles are quite common in normal surface waters and in rain and snow [see "The Growth of Snow Crystals," by B. J. Mason; SCIENTIFIC AMERICAN, January, 1961], but the fluids in inclusions were generally of much deeper origin and moved at slow rates, so that practically all particles had been eliminated by one process or another before the fluids were trapped.

In 1823 the Scottish physicist Sir David Brewster described a "remarkable new fluid found in the cavities of rocks." By careful microscopy he found its index of refraction to be less than that of water, its thermal coefficient of expansion to be 30 times that of water, and he

noted that it did not mix with water or wet the walls of the cavities. Later workers found that some bubbles of this liquid in otherwise water-filled inclusions could be made to sink or float in the water by adjusting the temperature. Identification of the remarkable fluid had to wait 46 years until the discovery that carbon dioxide can be liquefied. Then it became apparent that the properties Brewster had observed were precisely those of liquid carbon dioxide. The material has since been found in many crystals from certain types of geological environment.

Considerable pressure is required to liquefy carbon dioxide: at 31 degrees C., the highest temperature at which it can be liquefied at all, the pressure must be 73 atmospheres, or more than 1,000 pounds per square inch. The author has verified the magnitude of such pressures in carbon dioxide inclusions, using an adaptation of a method devised by the French mineralogist Georges Deicha. With the help of a vernier micrometer eyepiece on the microscope, the diameter, and therefore the volume, of the bubble of liquid carbon dioxide can be estimated in cubic microns (trillionths of a cubic centimeter). Then the sample is slowly crushed between heavy glass plates immersed in oil. During the process it is under continuous observation with the microscope, lighted from below through the plates. When a crack reaches the inclusion, the liquid carbon dioxide vaporizes and expands tremendously—nearly 400 volumes. The resulting bubble is big enough to measure quite accurately. As little as 10^{-14} (a hundred-trillionth) gram of liquid carbon dioxide will form a gas bubble several microns in diameter, readily visible in the microscope.

At high temperatures water and carbon dioxide mix in all proportions, and such mixtures are sometimes trapped as fluid inclusions. At lower temperatures the mutual solubilities are very low, and an inclusion that was originally a homogeneous, mixed fluid separates into two immiscible fluids, one rich in carbon dioxide, the other rich in water. On dropping still further to some temperature below the critical 31 degrees, the carbon dioxide phase separates into a liquid and a gas, giving a total of three phases. Hundreds of inclusions in a healed crack will all be divided in the same proportions, meaning that they must have been trapped as a homogeneous fluid at high temperature. On reheating they all pass in reverse through the phase changes described above. When they freeze, these inclusions develop large,
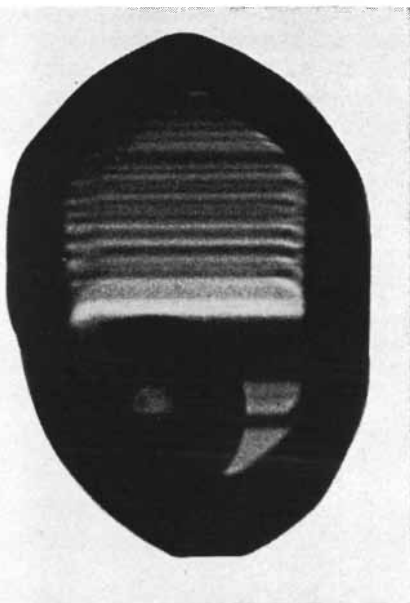
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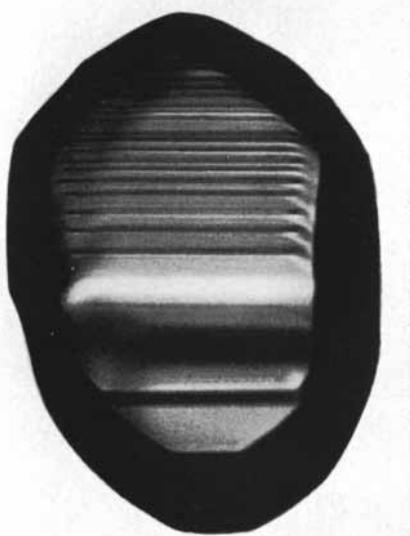
almost invisible crystals of the interesting and improbable-looking compound $8CO_2 \cdot 46H_2O$, in which 46 water molecules form a kind of cage with cells for eight carbon dioxide molecules. Since these crystals are usually stable below about 10 degrees, they probably occur naturally in mixed inclusions of water and carbon dioxide in the rocks of cold climates.

In a few crystals the author has found different ratios of two immiscible fluids in neighboring primary or secondary inclusions. This is clear evidence that the two fluids were present as distinct phases while the crystals were growing. For example, there were minute bubbles of highly compressed carbon dioxide in the slightly salty water solution from which a mercury deposit in Alaska formed, and they were trapped in various ratios with the water. Globules of

yellow petroleum are common in the strongly saline brines trapped as both primary and secondary fluid inclusions in the Kentucky-Illinois fluorite and zinc ores. Globules of dense organic gas were present in the liquid that gave rise to the well-known and beautifully clear quartz crystals from Herkimer, N.Y. Although generally trapped along with some brine, on occasion some gas stuck to the surface of the growing crystal and was enclosed without brine.

Not all the bubbles that are found in inclusions consist of carbon dioxide. Most of them, in fact, are water vapor. These minute gaseous cavities make possible one of the most intriguing applications of inclusions to geological problems: they serve as recording thermometers, registering ancient temperatures. More than a century ago the

English geologist Henry Clifton Sorby suggested that vapor bubbles result from shrinkage of the liquid in originally full inclusions that were trapped at high temperatures and then cooled. A simple inspection of the bubbles in various samples provides qualitative confirmation of the idea. Inclusions in rocks known from independent geological evidence to have formed at relatively low temperatures have small bubbles or none at all; inclusions in rocks formed at high temperatures have large bubbles. Sorby went further than this. He reversed the process of shrinkage by warming inclusions gradually, watching them under the microscope. Eventually the bubbles disappeared. The temperature at which each one vanished—the "filling" temperature—he took to be the temperature at which the inclusion had originally been trapped millions or even billions of years ago.
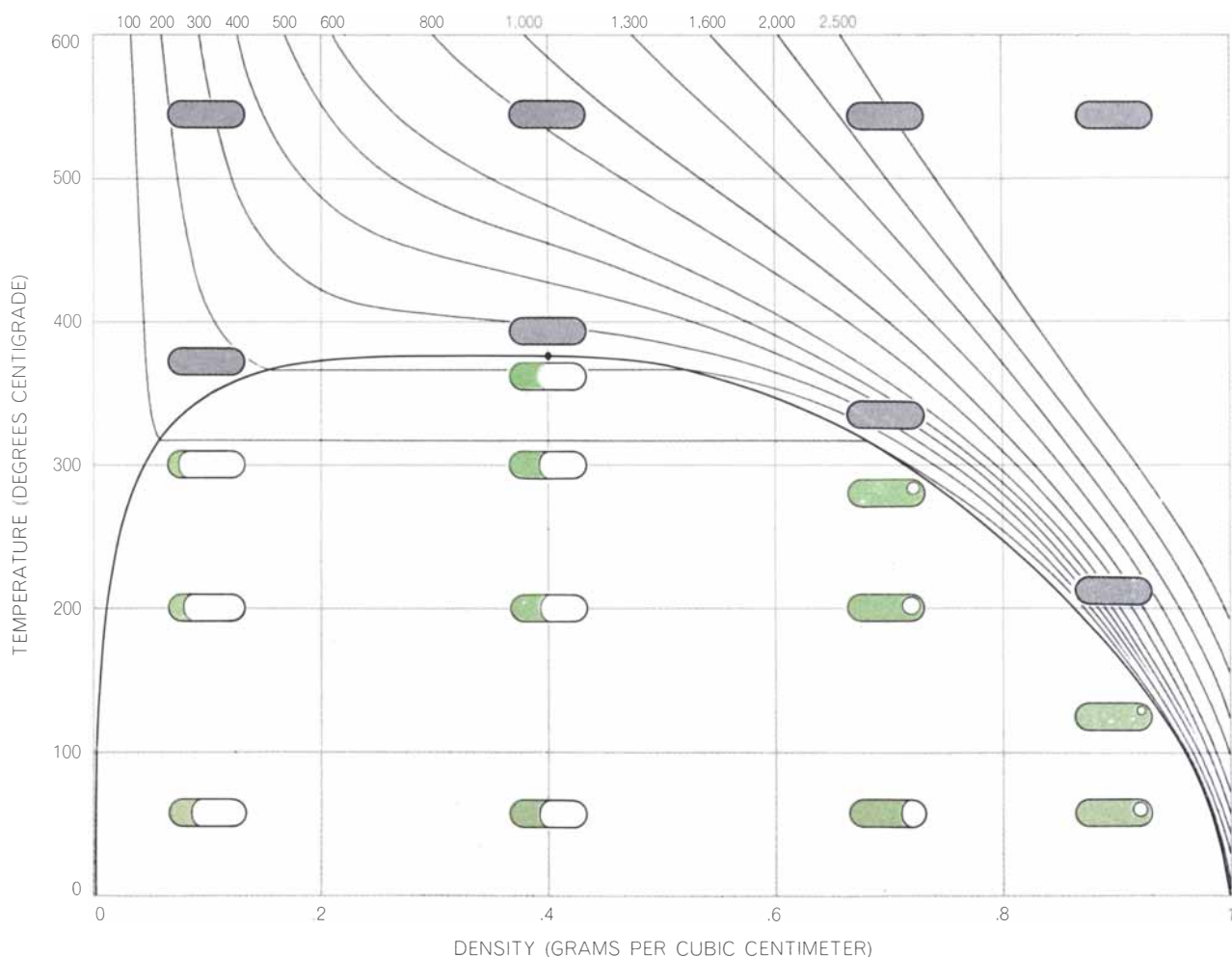
THERMAL BEHAVIOR of four inclusions (*four vertical rows of* "*capsules*") that have different liquid-to-gas ratios is superimposed on the phase diagram for pure water. Numbers at top indicate atmospheres of pressure. The density of each inclusion is the volume of liquid (*dark color*) at 0 degrees C. divided by the volume of the inclusion. The liquid-to-gas ratio tends to change with temperature; at a certain temperature for each inclusion the two phases become a single homogeneous fluid (*gray*). In an inclusion with a density of .4 the ratio remains unchanged; at the critical temperature (*dot on solid black line*) the curved meniscus (*dotted line*) between the phases suddenly fades and disappears. The inclusion is now a supercritical fluid (*i.e., no amount of pressure alone will cause it to liquefy*). The black curve separates two-phase (*light color*) from single-phase region; salts in solution will generally raise the curve.

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Some minerals have primary inclusions with large bubbles and secondary inclusions with small ones, indicating that the temperature dropped after crystallization; many crystals with distinct growth zones show lower filling temperatures for primary inclusions in the outer, last-formed zones than for those in the core. Crystals of daughter minerals present in inclusions dissolve on heating and thus may also be used as geological thermometers, giving minimum temperatures of trapping.

Sorby's experiment gives the true temperature of formation only if the liquid was at its boiling point when it was trapped. In that case the slightest shrinkage would have produced some vapor. If, however, the liquid was under more than sufficient pressure to prevent its boiling, it would have had to cool enough to relieve the excess pressure before it could begin to shrink and form vapor. Accordingly the temperature at which the vapor disappears on warming would be lower than the trapping temperature. From other geological evidence it is often possible to estimate the depth at which the rock sample was formed and therefore the pressure on the liquid. Where this is known, the apparent filling temperature can be corrected to give the true value. There is some evidence that occasionally fluid may leak into or out of inclusions, and that the recrystallization of inclusions with the passage of time may sometimes result in anomalous filling temperatures, but generally these situations can be recognized. One particularly useful check on the whole procedure comes out of studies of the inclusions in synthetic crystals, such as quartz, made under known high temperatures and pressures. These inclusions fill at the correct temperatures.

At room temperature the vapor pressure of water is very low and so a vapor bubble in an inclusion is practically a vacuum, like the "bubble" of mercury vapor at the top of a mercury barometer. This was first discovered by Davy, who pierced some large inclusions while the crystals were immersed in oil and found that the oil was drawn in and the bubbles contracted greatly. In many inclusions on which the author has performed the same experiment the bubbles disappeared completely and instantaneously, indicating that they must have contained considerably less than 10^{-14} gram of noncondensable gases—less than a billion molecules.

When an inclusion with a bubble is heated, the pressure in it—the vapor pressure of the water solution—increases
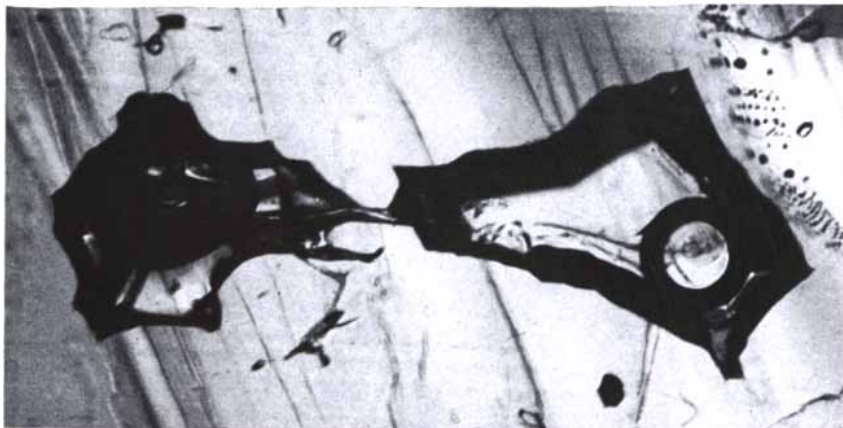
SINGLE INCLUSION in topaz at a late stage in the process of "necking down" is magnified approximately 57 diameters. The two parts, one of which contains a large gas bubble and daughter-mineral crystals and the other a small bubble, are still connected by a thin tube.
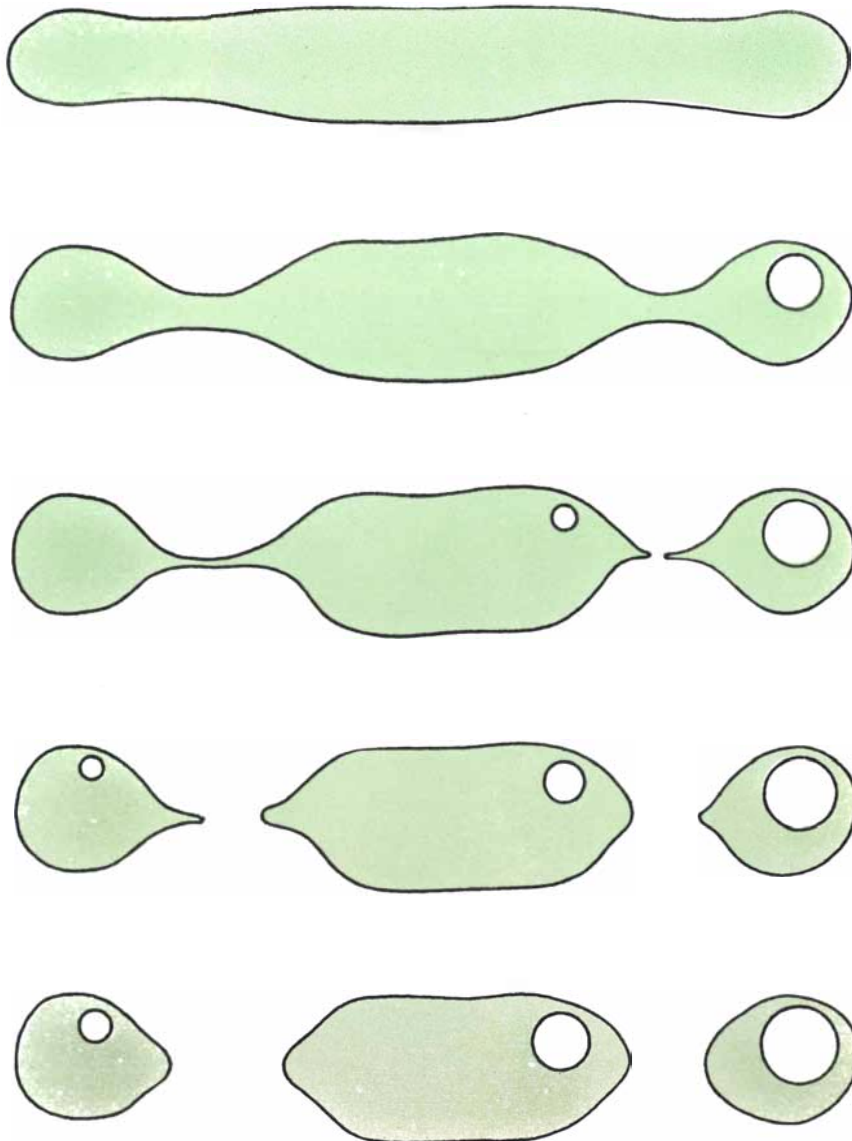
NECKING DOWN of an inclusion with time from its original state (*drawing at top*) into three inclusions (*bottom*) is depicted. Each stage occurs at a higher temperature than the one below it. If reheated to determine temperature of formation (*see lower illustration on pages 42 and 43*), one at right would yield too high a value; the others, too low. If the process occurred while crystal was at formation temperature, all would give correct value.

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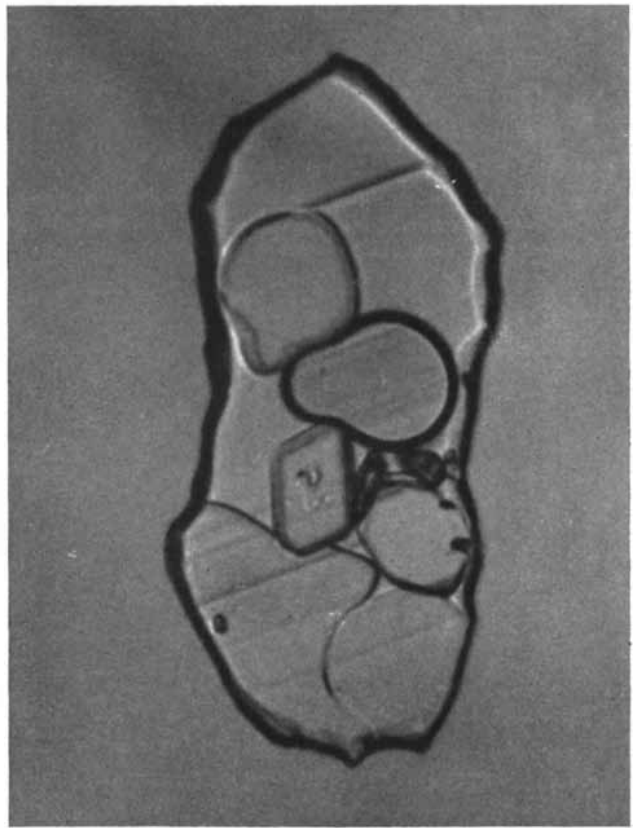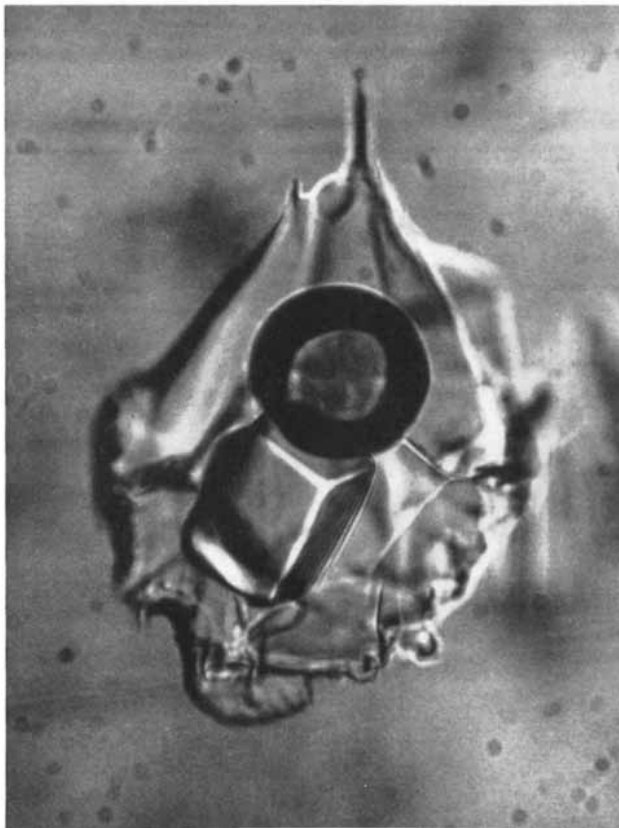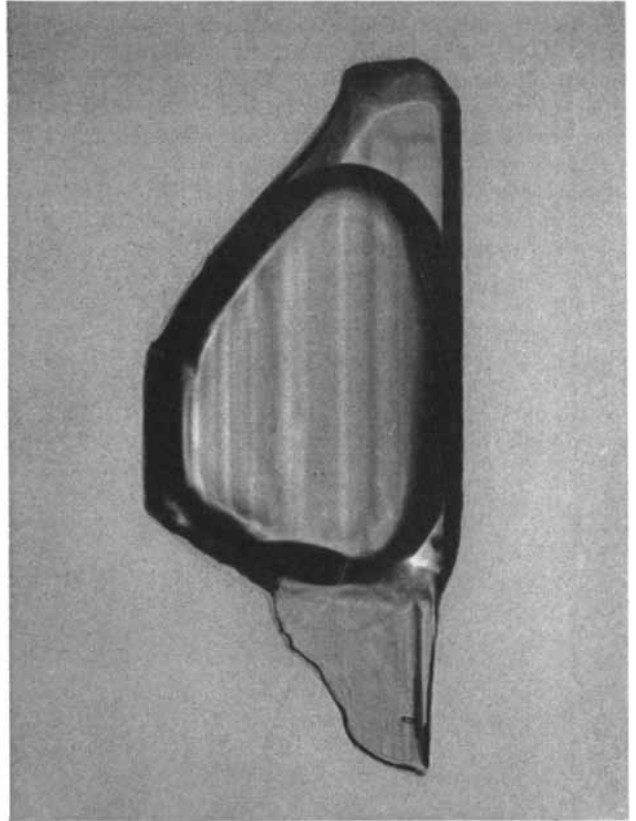
NUMBER OF PHASES in an inclusion varies. The black oblong area at center of micrograph at top left is liquid metallic mercury in calcite. At top right is a two-phase inclusion, in an aquamarine crystal, consisting of a large gas bubble and a smaller volume of liquid above it. The three-phase inclusion in emerald at bottom left consists of a cubic crystal of salt and a carbon dioxide bubble under pressure, both surrounded by a strong brine. At bottom right is a multiphase inclusion, from a magnesite crystal, with a pear-shaped gas bubble, a liquid phase and six solid phases. Respective magnifications of the micrographs are 27, 277, 520 and 366 diameters.

rapidly, reaching one atmosphere at 100 degrees C., 15 atmospheres at 200 degrees and 218 atmospheres at 374 degrees, the critical temperature above which water cannot exist as a liquid. The build-up of pressure in large inclusions, or in planes of many small ones, can cause a series of little explosions that make the sample decrepitate, or crackle. If the more compressible gas bubble disappears before the critical temperature is reached, the pressure increases even faster and decrepitation becomes more probable.

In 1870 the German petrographer Ferdinand Zirkel used decrepitation to demonstrate the presence of sodium in inclusions. The experiment is an elegantly simple one that anybody can do. A sample such as a sliver of ordinary white quartz is held in a clean, blue Bunsen burner flame. As the crystal decrepitates one can see tiny, bright flashes of yellow light signaling the explosion of microscopic quantities of sodium-laden steam in the flame. Measurements made in the author's laboratory indicate that as little as a ten-billionth of a gram of sodium will yield a flash visible to the unaided eye.

In 1948 a group of workers at the University of Toronto hit on a way to make decrepitation experiments more quantitative. H. S. Scott, P. A. Peach and F. G. Smith recorded the number of explosive sounds at various temperatures by placing a microphone at the end of a tube containing granules of the mineral sample. The peaks in these "decrepigrams" are taken to represent the filling temperatures of various homogeneous groups of inclusions. Many U.S. geologists have questioned the significance and interpretation of the recordings, but the method has been enthusiastically adopted in the U.S.S.R. In fact, the study of fluid inclusions in general has been much more actively pursued in the U.S.S.R. than it has in this country.

One of the most important geologic processes, from man's point of view, and one of the least well understood, is the formation of ores. There must have been a number of different mechanisms whereby metals were removed from dilute sources (rock or magma), transported and finally deposited as a concentrated mass. In many cases water solutions were involved, and here inclusions have been able to offer invaluable help in reconstructing the narrative.

Perhaps the most difficult problem is to understand how minerals, which in general have low solubility in water, were carried by the fluids in concentrations large enough to produce ore deposits. They must have combined with other materials in complex ions yielding higher solubilities, but the nature of many of these complexes is not known. Their formation would partly depend, however, on the salts that were present in the fluids. Therefore the analysis of inclusions may throw some light on the whole chemical cycle involving the formation and transport of the complexes and the conditions under which they eventually broke down, causing the precipitation of ores.

Some rich ore bodies appear to have separated as a result of boiling in rising hot fluids. Inclusions provide the only evidence as to the density of the fluids. Such information might thus help to predict the "bottoming" of the ores—an abrupt pinching off at a certain depth.

Inclusions can help the geologist in many ways in his task of understanding geologic processes long since discontinued, an understanding that is essential to the intelligent search for ores. As Sorby wrote in his classic paper on fluid inclusions, "there is no necessary connexion between the size of an object and the value of a fact, and . . . though the objects I have described are minute, the conclusions to be derived from the facts are great."
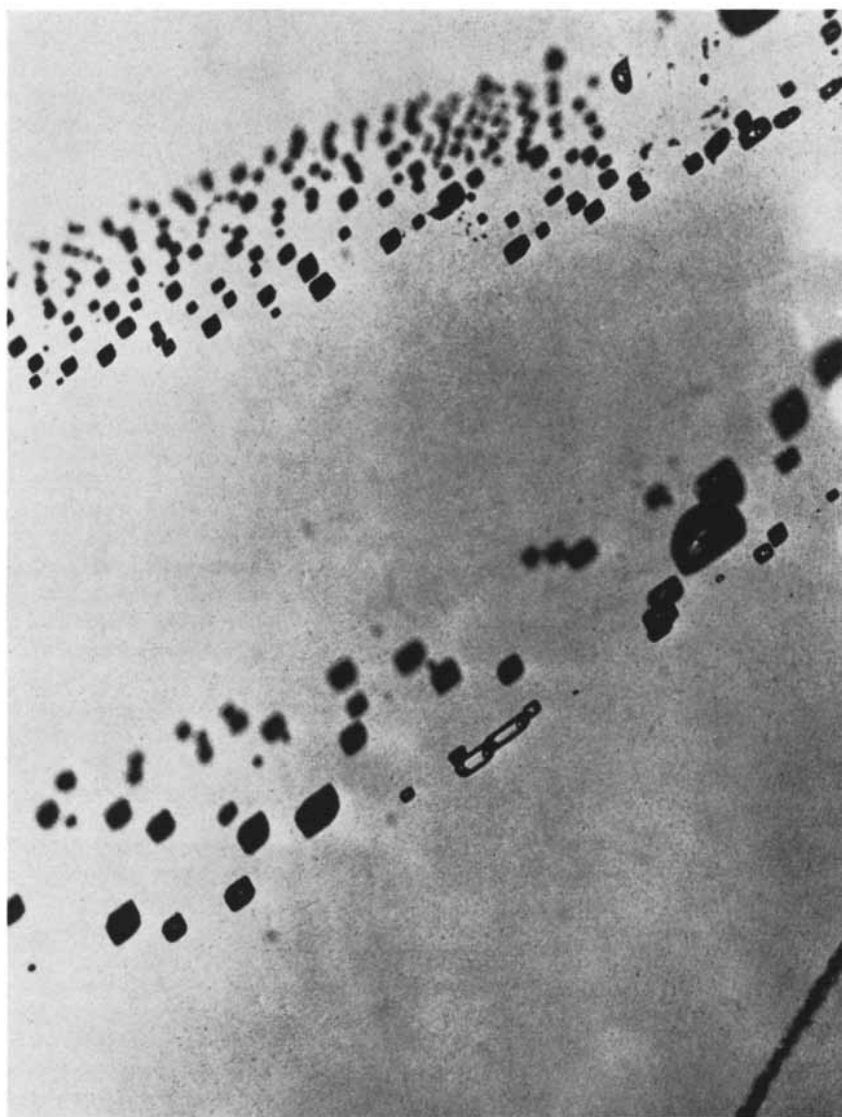
TWO HEALED FRACTURES in quartz (magnified 14.8 diameters) contain numerous secondary three-phase inclusions. Phases can be seen in the flattened pair of inclusions at center that resemble paper clips: liquid (*light oblong areas*) and gaseous carbon dioxide (*two adjacent light circular areas*), and saline water (*tiny light area at upper right*).