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Fluid Inclusions in Gemstones: Valuable Defects

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Fluid inclusions are small volumes of ancient fluids found within many gems. They occupy various types of defects or imperfections that have formed in the crystal during the otherwise more perfect crystal growth that is the prime characteristic of gems. Inclusions may be trapped during the growth of the host crystal (primary inclusions) or during the healing of fractures in the crystals at some later time (secondary inclusions). Both types of inclusions provide data on the environment of formation and history of gemstones that can be useful to gemology.

This paper summarizes: 1) the formation of fluid inclusions, 2) changes that take place after trapping, 3) types of data that can be obtained from the inclusions, 4) available published data on fluid inclusions in peridot, quartz, topaz, emerald (including some unpublished data), and diamond, and 5) some of the possible uses of such data.
Inclusions sous une Meilleure Illumination

Les inclusions fluides sont de petites quantités d'anciens fluides trouvés dans un grand nombre de gemmes. Elles occupent diverses sortes de défauts ou d'imperfectios, qui se sont formés dans le cristal pendant la plus parfaite croissance qui est la principale caractéristique des gemmes. Les inclusions peuvent être trappées pendant la croissance du premier cristal (inclusions primaires) ou pendant la suture des fractures dans les craux plus tard (inclusions secondaires). Ces deux sortes d'inclusions nous fournissent des données sur l'environnement de la formation et l'histoire des pierres précieuses, ce qui peut être utile pour la gemmologie.

Nous avons donc un résumé sur: 1) la formation des inclusions fluides, 2) les changements subis après être trappées, 3) les données qui peuvent être obtenues par les inclusions, 4) les données disponibles qui ont été publiées sur les inclusions fluides du peridot, le quartz, l'émeraude (ainsi que d'autres non publiées) et le diamant, et 5) quelques possibilités d'utiliser ces renseignements.

FLIESENDE EINSCHLÜSSE IN EDELSTEINEN—WERTVOLLE STÖRONGEN

GASFÖRMIGE-UND FLÜSSIGEIT S IN EINSCHLÜSSE IN EDELSTEINEN—WERTVOLLE STÖRÜNGEN

GASFÖRMIGE-UND FLÜSSIGEIT S EINSCHLÜSSE SIND GERINGE MENGEN EINER RESTFLÜSSIGEIT, DIE IN DIELEN EDELSTEINEN VORHANDEN SIND.

SIE BESETZEN VERSCHIEDENE TYPEN VON STÖRÜNGEN UND UNREGELMÄSSIGKEITEN IM URSTÄLLE WÄHREND DES SONST REGELMÄSSIG UERLAUPENDEN KRISSLWACHSTUMS, DAS ANSONSTEN DAS HAUPTMERKMAK EINES EDELSTEINES IST.

EINSCHLÜSSE ÜBEN WÄHREND DES WACHSTOMS ENTSTEHEN UND WERDEN DANN ALS PRÄMIÈRE EIN EINSCHLÜSSE ULASSIFIZIERT. ENTSTEHEN SIE ETWAS SPÄTER, ZEITGEMEIT MIT DEN HEILUNGRISSEN, BEZEICHNET MAN SIE ALS SEUONDÄRE EINSCHLÜSSE.

BEIDE ÜLASSEN VON EINSCHLÜSSEN ENTHALTEN WICHTIGE INFORMATIONEN ÜBER DIE ENTSTEHUNGSGESCHICHTE DES EDELSTEINES FÜR DEN GEMMOLOGEN.

ZUSAMMENFASSGEND WIRD DARSTELLT.

1) DIE ENTSTEHUNG VON GASFÖRMIGEN—UND FLÜSSIGEITSEIN EINSCHLÜSSEN
2) ÄNDERUNGEN NACH DER ENTSTEHUNG.
3) INFORMATIONEN, DIE AUS DIESEN EINSCHLÜSSEN GEWONNEN WERDEN ÜBEN.
4) VORHANDENEN DATEN ÜBER GASFÖRMIGE-UND FLÜSSIGEIT S EINSCHLÜSSE IN PERIDOT, QUARTZ, TOPAS SMARAGD UND DIAMANT (DIES BEINHALTED BISHER UN VER ÖFFENTLICHTE DATEN)
5) MÖGLICHE ANWENDUNGS GEMEITE DIESER DATEN.
ジェムストーン中の液体インクルージョン

液体インクルージョンは、多くのジェムストーン中にみられる、小滴状の残存液体である。液体インクルージョンは、結晶生成中に形成される、種々の空隙部又は歪などに分布していくもので、ジェムストーンの主要な特質となっている。

液体インクルージョンは、主結晶の形成中にその生因のあるもの（第一次液体インクルージョン）と、主結晶の形成中程の終わったあとフラクチャーの発着などで生じるもの（第二次液体インクルージョン）との2つのタイプがある。

どちらの種類のインクルージョンも、結晶形成中の環境、又は宝石学上、有効なジェムストーンの歴史を知る資料として役に立つ。

ここでは以下のような事がらの要約がされている：1）液体インクルージョンの形成について。2）生成された後における変化について。3）インクルージョンから得られる資料の種類について。4）ベリアルド、クォーツ、トパーズ、エメラルド（中には未公表のものもあるが）、ダイアモンドにおける液体インクルージョンについての公表されている資料について。5）このような資料の使い方について。
Fluid Inclusions in Gemstones: Valuable Defects

Gems vs. Mineral Specimens

Perhaps the most basic difference between a gem crystal and an ordinary crystal or specimen of the same mineral lies in the degree of perfection of the crystals. No crystal is truly perfect; the imperfections in gem-quality crystals range from the atomic level, involving a single or just a few atoms, to those huge 0.1 mm imperfections involving 100 million million atoms, that are visible with the 10x eye loupe. Mineral collectors prefer flawless crystals, but most are pleased to find a crystal that contains hundreds of imperfections, each a thousand times larger in volume (~1 mm in width).

Most of the imperfections or defects that make the difference between a ruby crystal selling for $5 as a mineral specimen and another much smaller ruby crystal, of the same color, worth $50,000 as a gem, are inclusions of foreign substances, solid, liquid, or vapor. The mineral specimen may have billions of such inclusions in each cubic centimeter, whereas the gem will have perhaps thousands or even millions. Most such inclusions are less than 1 micrometer (μm) in size (one-thousandth of a millimeter) and hence are tiny specks essentially unresolvable under the light microscope. These small inclusions may have a relatively minor effect on the quality of a gem unless they are present in exceptional numbers, which may cause a turbidity or milkiness from the scattering of light. The small fraction of all inclusions that are larger than 1μm are more important in affecting the quality of a gem. Most such inclusions consist of transparent materials—gases, liquids, or crystals—and are embedded in a transparent host; however, the sometimes very large changes in index of refraction at these many interfaces result in the reflection and refraction that make the difference between the clear gem ruby and the translucent ruby mineral specimen.

Inclusions are not the only difference between gems and mineral specimens. Most crystals in mineral collections, particularly those embedded in a matrix, contain many fractures formed at some time since their growth. Fractures are common at an average spacing of 1 mm. Such close fracturing is so characteristic in mineral specimens that when the spacing of fractures becomes more than a few millimeters in otherwise relatively inclusion-free material, the crystals may be termed “glassy”; when the spacing is still wider, the crystals are termed “gummy.” The natural healing of similar fractures has yielded many of the fluid inclusions found in most minerals.

In this paper, I discuss only those inclusions that contained a fluid (liquid or vapor) at the time they were trapped, even though they may now contain solids. Many other inclusions in gemstones were trapped as solids that the host crystal grew around and enclosed, or that precipitated within the crystal during cooling. The study of such solid inclusions is very important in gemology, for many of the same reasons as the study of fluid inclusions. I have not dealt with such solid inclusions, however, and leave the discussion of this field to those who have (see the adjoining paper by H. O. A. Meyer; also Chikayama 1973).

The Formation of Fluid Inclusions

Primary Inclusions

Fluid inclusions are defects in crystals, which may be formed by a wide range of processes that cannot always be identified unambiguously. Most natural crystals have grown from a fluid (the term “fluid” includes both water solutions
and silicate melts). Anything that interrupts or interferes with the otherwise perfect growth of flat, smooth crystal faces can cause the enclosure of some of the fluid from which the crystal is forming, yielding a primary inclusion (Figure 1). Perhaps the most common cause of imperfections that result in the trapping of inclusions is too-rapid growth. Different crystals, and even different faces on the same crystal, can grow by a variety of mechanisms, but regardless of the mechanism involved, if the growth rate is increased, the size and abundance of the imperfections increases. (By imperfections, I refer to any deviation from a perfect single crystal, bounded by flat faces, with no reentrants.) Very fast growth usually results in the addition of the new material only to crystal edges or corners and hence normally yields feathery, skeletal, or dendritic crystals (e.g., snow). Subsequent solid growth may cover such porous materials, trapping many fluid inclusions. One of the major problems in the commercial growth of large single crystals for optical or electronic use (and to a smaller degree, for gem use) is that of obtaining high growth rates without serious sacrifice of crystal quality (i.e., perfection). Even with precision laboratory control of the several variables involved, success in the growth of relatively flawless crystals of some synthetics may require growth rates to be held down to less than one centimeter per month. Nature was not concerned with maximizing production yield and may well have used vastly less efficient processes of material transfer over much longer times. Thus, some mineralogical and geological evidence suggests that at least a few and perhaps most of the large crystals seen in mineral collections grew over much longer periods of time, tens of thousands of years or more (e.g., Roedder 1969, 1971a; Woods et al. 1981). Gemstones, because they are even more perfect crystals, may have grown even more slowly. At present, we really have no way of knowing.

Perhaps the slowest growth rates of all are those for gems that have formed in metamorphic rocks, e.g., the gem-bearing gneisses and granulites of Sri Lanka (Dahanayake and Ranasinghe 1981; Munasinghe and Dissanayake 1981).

Figure 1. Diagram showing some of the mechanisms by which primary fluid inclusions may become trapped. In A, rapid feathery growth is covered by later solid growth. In B, a dislocation in a crystal etched out during partial dissolution of the crystal, is later covered by new growth. In C, inclusions are trapped between or at the centers of growth spirals. In D, subparallel crystal growth traps fluid. In E, disturbed growth in the vicinity of a fracture in the surface of a growing crystal results in trapping of primary inclusions. In F, enclosure of any foreign object on the surface of a growing crystal may include some of the growth fluid as well.
Instead of growing as free crystals, protruding into the fluid from which they grew, most crystals in metamorphic rocks have grown in an essentially solid medium, by migration of some or all of the constituents to the surface of the crystal nucleus via diffusion through the other crystals, along grain boundaries, or through a fluid film in the grain boundaries. The space for the enlargement of any given crystal is formed by the dissolution or shoving aside of adjoining crystals. As a consequence of growth under such conditions, the resulting gem crystals may have many solid inclusions but no fluid inclusions. Studies in other metamorphic terranes suggest that formation of the mineralogical assemblages in some gneisses and granulites may have taken millions of years (e.g., Hollister and Crawford 1981).

During very slow growth, any extraneous solid particles present in the growth fluid beside the growing crystal face may be pushed out of the way, but more rapid growth will frequently lead to the enclosure of such particles as solid inclusions. When the growing crystal closes in over the top of the solid, it may also trap some of the fluid growth medium (Plate 1, photos 1 and 2). Large fluid inclusions may be trapped in the reentrants between rapidly growing zones, e.g., between adjacent “growth spirals.” Similarly, subparallel growth of adjacent segments of a single large crystal can result in the enclosure of fluid. The subparallel growth can take place as a result of fracturing of the crystal during growth or an increasing mismatch of adjoining parts, as in some curved crystals. Some crystals may grow with numerous long tubular cavities arranged perpendicular to one face (e.g., in beryl, these normally lie parallel to the hexagonal axis). Covering of such tubes can result in trapping of tubular inclusions (Plate 1, photo 3), which are sometimes extremely thin and needlelike (Plate 2, photo 13).

The long tubular inclusions in beryl mentioned above may also form by an etching process. Imperfections in crystals result in a higher energy state than that of a hypothetical perfect crystal. Lines of dislocations in a crystal cause localized strain and hence a high local strain energy. If a crystal having such regions of strain is etched carefully in the laboratory, the points of emergence of the dislocation lines at the surface will form etch pits, because the strained, higher energy material is more soluble. Such etch pits are also seen on some natural crystals. If the strain along the line of dislocations is sufficiently high and the etching long and slow, long etch tubes can form (Nielsen and Foster 1960). Covering of these by later growth could also yield long tubular fluid inclusions.

Secondary Inclusions

As mentioned above, most natural crystals, as found, contain cracks. When a doubly-polished plate or a gemstone is cut through such crystals, these cracks are visible as curving or planar surfaces that are opaque in transmitted light under the microscope because of total reflection, if their curvature (or tipping of the sample) results in a sufficiently low angle of incidence for the light. They are less visible if filled with a medium other than air and will be almost invisible if the filling medium has nearly the same index as the gem. Such cracks normally represent only the latest episode of stressing and cracking that the crystal has undergone. Usually it has been cracked at other times in the past, in the presence of a fluid that has healed the fractures by crystal growth from opposite sides, joining to make the crystal solid again. Planes of secondary fluid inclusions are formed when small amounts of this fluid become trapped by the healing process (Figure 2; Plate 1, photo 4). This fracturing and healing can take place at any time after the original crystal growth—it could be a minute later, or a billion years.

The fluid in the fracture is normally a water solution, so one may ask why so many cracks in natural crystals have not healed, as they have all been immersed in ground water beneath the surface of the earth for at least many thousands of years before being collected? The healing will take place only if a fluid is present in which the crystal is at least slightly soluble, thus permitting dissolution and redeposition of the mineral
along the crack. Gem minerals are essentially insoluble in cold ground water, but deep in the earth, where temperatures are higher and where various salts are in solution in the water, the solubilities, although perhaps vanishingly small, are still adequate to permit the cracks to heal in the large amounts of time available.

Hence, secondary inclusions in gems, though they may have been trapped at lower temperatures and pressures than were the primary inclusions, will generally not have been trapped at surface conditions. All gradations exist, however, between healed fractures for which the temperature and time have been adequate to cause recrystallization of the trapped fluid inclusions into faceted negative crystal cavities (see Plate 1, photo 4) and dry, empty "recent" fractures now filled with air or with whatever grinding, polishing, or optical test fluid was last in contact with the open crack. The drawing of arbitrary boundaries and the assigning of names such as "veils," "fractures," etc., in such a gradational series is important but difficult at best. In theory, the only really definitive boundary line is that between those fractures that are naturally sealed and those that are open. Even here, there can be ambiguity. Thus, if a fracture forms during the growth of a crystal, yielding a pseudosecondary plane of inclusions (this can take place for a wide variety of reasons and is far from rare), it can be covered over with new growth, trapping a flat or curving sheet of fluid (Figure 2b). If time is inadequate for fracture healing before cooling takes place, such a large but very thin and flat fluid inclusion can persist indefinitely. The fluid contents could be lost in gem cutting, however, and the result would appear as a "recent" crack. The decision whether a fracture is indeed sealed presents an even greater problem, and I know of no simple solution. The problem is compounded by the inherent difficulty in even seeing a fracture whose width is a small fraction of the wavelength of the light used.
Changes in Fluid Inclusions
After Trapping

Phase Changes

Usually a homogeneous uniform fluid is trapped as fluid inclusions in the growing crystal, but most fluid inclusions seen in gems now contain more than one phase. The most common phase assemblage is a liquid plus a vapor bubble. As shown in 1858 by Sorby, the vapor bubble normally arises from the differential shrinkage of the host crystal and the fluid. The crystal “bottle” shrinks a very little on cooling from the temperature of trapping to that of observation, but the fluid shrinks much more; the bubble results from this difference. Generally, the greater the amount of cooling, the larger the bubble. The various types of fluid that can be present in fluid inclusions have widely different properties, however, so visual estimates of the relative proportions of vapor bubble and liquid can only provide a crude estimate of the amount of cooling (Roedder 1981a). Various other “daughter phases” can form from the fluid on cooling. The two most commonly found in gems are liquid CO₂ and NaCl crystals, but many other phases, including some very rare and even new minerals are also found. Some inclusions have so many daughter crystals present (e.g., plate 1, photo 5), that a question immediately arises—how does one know that these are actual daughter minerals formed from the liquid after trapping and not just accidental solid inclusions (i.e., a group of solid grains) that were trapped along with the liquid? Unless metastability interferes (Roedder 1971b), the best evidence to settle this question is the presence of the same assemblages of phases in each of several inclusions in the same group (e.g., plate 1, photo 6).

Shape Changes

Many, perhaps most, fluid inclusions do not now have the shape they had at the instant of trapping. Inclusions having relatively large surface areas, such as flat plates or thin tubes, tend to become more equant in shape with time, by the same processes of dissolution and redeposition described in the formation of secondary inclusions from the healing of a fracture. A thin tubular inclusion may thus change to become a row of more nearly spherical inclusions (Figure 3). This process, called “necking down” may take place over a long time period, but only at high temperature and pressure, deep in the earth. If any new phases have formed in the original inclusion before the necking down splits the inclusion into two or more separate inclusions, the overall density, phase ratio, and composition of the resulting individual inclusions will differ (Figure 3, and plate 1, photos 7 and 8). Necking down can even leave daughter crystals apparently isolated in the host mineral (plate 1, photo 9).

Types of Data that can be Obtained from Fluid Inclusions

Temperature of Trapping

Sorby (1858) showed that if a mineral that has inclusions of liquid plus vapor is heated while being observed under a microscope, the temperature at which the expansion of the liquid phase just eliminates the bubble (the homogenization temperature, Th) can be determined precisely; this temperature is a measure of the temperature of trapping (Tt). Actually, this is true only if the pressure at the time of trapping was just equal to the vapor pressure of the fluid, i.e., the fluid was just about to boil. If the pressure from the overlying rocks is greater than the vapor pressure, a pressure correction must be added to Th to get Tt. In high-pressure, high-temperature geological environments, such as those under which some gems were formed, this added “pressure correction” can be several hundred degrees Celsius; an independent estimate of the pressure is needed to evaluate its magnitude. Even with this limitation, fluid inclusions provide one of the most accurate and certainly the most generally applicable of the many geothermometers (Roedder 1979a). Primary inclusions in the various zones of zoned
crystals provide a record of the changes in the mineral-forming process, and each plane of secondaries yields the temperatures of a later episode of cracking and healing. Fluid inclusions provide the geologist-detective with an avalanche of clues on the geological events of the past: a single cubic centimeter of white quartz or calcite may have a billion fluid inclusions, each a two-phase assemblage of liquid and vapor bubble, each one of which provides us with evidence on the temperature of an event or process in geological history (the sealing of the inclusion) that may have taken place (and ceased) a billion years ago.

**Pressure of Trapping**

A surprisingly wide range of methods has been proposed and used to estimate the pressure of formation from fluid inclusions. A discussion of these methods is beyond the scope of this paper, but it is sufficient to warn here that many of these methods have been shown to be erroneous in concept or application (Roedder and Bodnar 1980). The best estimates place the formation of most gemstones (except diamonds and peridots) in the outer 5–10 km of the earth’s crust.

**Composition of the Fluid**

Fluid inclusions are particularly important in the study of various geological processes, as they are samples of fluids formerly present in the earth’s crust—the fluids from which many minerals crystallized, or with which they were later in contact and possibly reequilibrated. Except for some currently active geologic processes, fluid inclusions are the only samples we have of these fluids. Most inclusions, however, are far too small for quantitative chemical analysis by even the most sensitive modern methods. Thus, a single inclusion 10 μm in diameter contains a total of about $10^{-9}$ g of material. Most of this $10^{-9}$ g will normally be H$_2$O and/or CO$_2$, but our major interest lies in
1. Fluid inclusion formed as a result of imperfect closure of host halite (H) around solid inclusion of anhydrite (An). The liquid (liq) is a saturated water solution with vapor bubble (v). The halite growth direction was probably upward, as shown. Sample ER 64-157, Winnfield salt dome, Louisiana; partly crossed polarizers.

2. Solid inclusion of quartz (O) in fluorite (F). The growth of the fluorite was upward as shown; as it grew around the quartz, it enclosed some liquid (liq) which now contains a vapor bubble (v). Sample ER 63-170, Hansonburg, New Mexico.

3. Tubular fluid inclusion in aquamarine. Although originally trapped as a homogenous low-density fluid, the inclusion now contains about 31% liquid, 69% gas, plus a few small grains of daughter minerals. Sample ER 62-1, unknown locality in Brazil.

4. Three curving planes of secondary inclusions in slightly smoky quartz (rock crystal), representing the healing of three cracks (see Fig. 2). Each inclusion is a slightly distorted, double hexagonal pyramid, its axis aligned parallel to the a axis of the host quartz, and containing liquid water, liquid CO₂, and gaseous CO₂, similar to inclusions shown on Plate 2, photos 1 and 2. Sample ER 61-28b-1, Volta Bala, 36 km E of Topázio, (formerly Jardimópolis), Teófilo Otoni, Minas Gerais, Brazil.

5. Multiphase fluid inclusion in transparent magnesite, showing liquid (liq), vapor bubble (v), and 14 daughter crystals, at least 7 of which are different phases. Two of the daughter crystals are isotropic, but 6 of the small and at least 1 of the large crystals are anisotropic (see arrows). Sample ER 62-4, Brumado, Bahia, Brazil.

6. Plane of pseudosecondary (?) multiphase fluid inclusions in transparent magnesite. Inclusion shown in photo 5 is from this same sample and plane. Each inclusion contains at least seven different daughter crystals and a small bubble. Within the limits of available observational techniques, each inclusion other than the very smallest visible here appears to contain the same assemblage, indicating trapping of an originally homogenous fluid containing more than 50% solids by weight.

7. Necking down of an inclusion in halite that will eventually result in three inclusions, two without bubbles and the third with none. Sample ER 64-112, Salar Grande, Chile.

8. Necking down of long tubular inclusions in amethyst. The vapor bubble (v) has been trapped in the smaller inclusion; the other inclusion contains only liquid. Amethyst from an unknown locality in North Carolina.

9. Plane of pseudosecondary inclusions in quartz, showing an early stage in the process of necking down after daughter minerals have precipitated. Highly birefringent daughter crystals (U) and a large halite daughter (H), coated with a film of brine, are nearly isolated from each other and have been isolated from the bulk of the fluid of the inclusion (out of this field of view). Necking down has caused individual parts of the original inclusion to be sealed off at various stages in the process, resulting in another isotropic cube with a coating of liquid (x) and two apparently "low-temperature" inclusions, containing very small vapor bubbles (y). Sample ER 63-84Q, Muizo emerald mine, Colombia, courtesy of Banco de la Republica, Bogota.

10. Inclusions in olivine from olivine nodule. Isolated, presumably primary inclusions of silicate glass (s) containing small shrinkage bubble and opaque daughter mineral occur with two liquid CO₂ inclusions (c) showing characteristic dark borders and large, faint, rapidly-moving vapor bubble. Inclusion in upper right shows all three phases; CO₂ in it homogenizes in the gas phase at 30.91 ± 0.02°C. A plane of secondary CO₂ inclusions crosses the bottom of the photo. Sample ER 63-33a, from 1801 Kaupulehu flow, Hualalai, Hawaii.

11. Olivine grain from olivine nodule, showing many planes of sharply faceted secondary inclusions, outlining healed fracture planes. Although these appear opaque, they are actually transparent (see next photomicrograph). Same sample as previous photomicrograph.

12. Photomicrograph of fluid inclusions in olivine from ultrabasic nodule in basalt, showing basaltic (?) glass (gl), liquid CO₂ (lc), and gaseous CO₂ (v). The two CO₂ phases homogenize in the liquid phase by the slight warming caused by absorption of infrared (IR) light on removal of the IR filter on the microscope light. During the growth of later fracturing and healing of the host olivine, at an estimated depth of 18-23 km and 1,200°C, the CO₂ was present as homogeneous supercritical gas bubbles in the basaltic, CO₂-saturated melt. Sample ER 63-33, 1801 Kaupulehu flow, Hualalai, Hawaii.

13. Two photomicrographs of an olivine grain, embedded in oil of n = 1.64 on the crushing stage, proving the presence of highly compressed gases (CO₂) in the inclusions. Pressure was applied, perpendiculat to the plane of the photograph, by glass plates. This caused cracking and release of gases. The explosively evolved bubbles come from the inclusion indicated by the arrow in the left photomicrograph. Sample ER 63-33a, olivine nodule from 1801 Kaupulehu, Hualalai, Hawaii.

14-15. Typical behavior of large inclusions of essentially pure CO₂ in sapphire, at nearly the critical density of filling. The small triangles on the large inclusion and the two dark bands across the small one are markings on the walls of the inclusions. Because of absorption of infrared light from the microscope light, the meniscus between CO₂ liquid (lc) and CO₂ gas (v) becomes fainter as their densities approach each other as they homogenize at about 31°C (photo 14). Such light absorption obviously cannot be perfectly uniform, so even under static conditions, new bubbles of vapor form continuously in the liquid and move to the cooler main vapor bubble. (See arrows in photo 15.) The large inclusion homogenized in the liquid phase by a fading and shrinkage of the vapor bubble, indicating the fluid density to be slightly greater than the critical density; the faint meniscus in the small inclusion simply faded away, indicating the fluid in it to be almost exactly at the critical density. The difference in filling density responsible for such a difference in behavior may be very small. After homogenization, slight undercooling of the stretched fluid (now a supercooled, subcritical fluid) results in a sudden splitting into faint vapor bubbles and liquid (for additional details, see Redder, 1972, Plate 6). Sample from U.S. National Museum (Natural History), a 10.2-carat cut blue gem sapphire from Yogo Gulch, Montana.
the minor constituents in this fluid: Na, K, Ca, Mg, SO₄, Cl, Br, etc. These individual constituents will make up perhaps 10⁻¹⁰ to 10⁻¹³ g each, orders of magnitude too small for quantitative analysis except in a relatively few special cases.

The ordinary light microscope, however, can provide a surprising array of qualitative and even semiquantitative data on the chemical composition of inclusions even smaller than 10 μm (Roedder 1972), with a relatively small investment of time. In addition, practically all these tests are nondestructive, a particularly useful aspect in the study of gems.

Some Examples of Fluid Inclusions in Gems and Their Associated Minerals

Limitations on the Areas Covered

Relatively few detailed studies have been made of fluid inclusions specifically in gemstones, but many studies have been made of the inclusions in nongem-grade crystals of gem minerals from localities that have produced gemstones. These studies are not always recognizable as being related to gems. Thus, although gems are not mentioned in most studies of fluid inclusions in the mineral tourmaline, many of the geological occurrences in which this mineral is sufficiently transparent to permit inclusion studies (e.g., Roedder 1968, 1972) are potential or actual sites for gem tourmaline. In the following pages, I use some of my own published and unpublished data on inclusions from the very few gem occurrences that I have studied as examples of the sorts of information about gems that can be garnered from inclusions. Additional details are available on many of these samples (Roedder 1963, 1972). These studies make it obvious that a wealth of useful data can be obtained by simple microscopy. Gemologists the world over should become aware of what fluid inclusions look like and what they can tell us. If nothing else, knowledge of the fascinating data available from fluid inclusions might help to sell what would otherwise be considered merely a flawed stone.

Peridot (i.e., Olivine)

Although most large gem peridots come from a single locality on an island in the Red Sea, I have studied them only from other localities, where the crystals are smaller but in part still gem quality. These peridots are from the olivine nodules that have been brought up to the surface from deep in the earth by the eruption of certain types of basaltic lava, as at Hawaii and other localities all over the world (Roedder 1965). Many of these nodules are believed to have come from the earth's mantle. When such olivines are examined, they are usually found to contain at least some solid inclusions of black opaque spinel. The host olivine has apparently grown from a very hot (~1,200°C or 2,200°F) fluid silicate melt, similar to the lavas that brought the nodules to the surface. In many respects, when this fluid is trapped as an inclusion, it behaves like the water solutions trapped in most ordinary inclusions; on cooling it shrinks more than the host mineral, and a "vapor" bubble forms in the larger inclusions, representing the difference in shrinkage (plate 1, photo 10). (The relative volume of this bubble will also be affected by crystallization of olivine onto the walls; Roedder 1979b). Although such silicate-melt inclusions look like their aqueous counterparts, the fluid that was trapped will now be a glass, and hence the "vapor" bubble (generally a vacuum) will be motionless. In the larger inclusions of this type, if cooling has been sufficiently slow, this glass may have crystallized in part.

These silicate-melt inclusions may be found in olivine from practically all localities. However, another entirely different type of inclusion is present in most of these samples, frequently as secondary planes (plate 1, photo 11). If the sample is not too warm, each such inclusion will contain a moving bubble in a liquid (plate 1, photo 10), because the inclusion is filled with dense carbon dioxide and not a silicate melt. At low magnification, under ordinary microscope lighting, which tends to be rather highly collimated, the large difference in index of refraction between olivine (n ~1.64) and CO₂ (n usually
<1.2) may cause these inclusions to appear opaque (plate 1, photo 11). At higher magnification, when a condenser having a high numerical aperture is used, the moving bubble in these inclusions becomes clear. A few inclusions contained some silicate glass on the walls as well (plate 1, photo 12), indicating that both silicate melt and CO$_2$ were trapped.

Because pure CO$_2$ has a critical temperature of 31°C (88°F), no liquid CO$_2$ can exist above 31°C; if the specimen is warmed to a temperature greater than 31°C and the bubble persists, the inclusion probably does not consist of CO$_2$. (Small amounts of other gases in the CO$_2$ can lower this critical temperature greatly and others can raise it, though seldom more than a few degrees.) If the average density of the CO$_2$ phases in the inclusion is >0.4 g/cm$^3$, the liquid will expand on warming and will eliminate the vapor bubble (homogenize) at some temperature ≤31°C. If the density is 0.4 (the critical density), the bubble will remain, but the meniscus between liquid and vapor will become faint during heating and will disappear suddenly at the critical temperature. For a rather wide range of densities, the homogenization temperatures are all very close to 31°C, so that very slight changes in temperature will cause major changes in the phase ratio of liquid to vapor. One indication of this is the sensitivity of the phase ratio to the intensity of the microscope lighting and to the presence or absence of an infrared (IR) filter in the microscope light. CO$_2$ adsorbs infrared very efficiently, so the inclusion (but not the olivine) is heated by the light. The CO$_2$ phases in the inclusions shown in plate 1, photo 12, become homogeneous instantly if the IR filter is removed from the light and become heterogeneous (i.e., the bubble reappears) almost as quickly when the filter is replaced. A very good IR filter is needed (or the microscope stage must be rather cool), or all CO$_2$ inclusions will stay homogeneous and hence will appear empty.

The presence of liquid CO$_2$ plus gaseous CO$_2$ at near 31°C means that the pressure within these fluid inclusions as we look at them at room temperature is ~70 atmospheres (1,030 pounds per square inch). Hence, if we crush a grain containing such inclusions in oil under the microscope, the gases will practically explode into the oil. Plate 1, photo 13 illustrates this crushing procedure. All the bubbles shown in the photograph came from the gas enclosed in the one small inclusion that was opened by the break (marked with the arrow in the left photo). By measuring the approximate volume of the inclusion and the volume of the bubbles evolved, we find the expansion to 1 atm. was about 350 times—approximately correct for liquid CO$_2$. (Similar CO$_2$ inclusions are also found in some sapphire but were probably trapped at much lower temperatures and hence lower pressures—plate 1, photos 14 and 15.)

Abundant indirect evidence (as well as some actual measurements) indicates that the host basaltic lavas generally erupted at ~1,200°C, at which temperature the pressure in the inclusions must have been much more than 70 atm. Minor extrapolation from the P-V-T data of Shmonov and Shmulovich (1974) indicates that a typical CO$_2$ inclusion that now has a total density of filling of ~0.8 g/cm$^3$ (like those in plate 1, photo 12, based on optical measurements of the relative volumes of liquid and gaseous CO$_2$ present at subcritical temperatures) had an internal pressure of ~5,500 atm. (81,000 pounds per square inch) at eruption (Figure 4). Some of these inclusions have a density >0.90 g/cm$^3$, corresponding to pressures of ~7,000 atm. These pressures correspond to those expected under basaltic liquid at 18–23 km (11–14 miles) depth.

These pressures represent the depth at which these particular inclusions were trapped. However, these inclusions are mainly of secondary origin, outlining healed fracture planes. Good evidence indicates that most of the larger primary inclusions of CO$_2$ in these samples were formed at still higher pressures, at still greater depths, and have decrepitated (spontaneously exploded) during eruption. Some of this decrepitation took place at 18–23 km depth, and the new inclusions that formed by the healing of these fractures at that depth, or less, have persisted. Most inclusions (primary or secondary) that formed at greater depth had too much pres-
Plate 2 Captions
(All scale bars 100 μm as noted)

1-2. Photomicrographs of one inclusion of a large group of probably pseudosecondary inclusions in pegmatitic smoky quartz, all showing a uniform ratio (at 24°C; photo 1) of liquid water solution with NaCl equivalent, estimated from the freezing temperature of -2.5°C, liquid CO₂ (lc) and gaseous CO₂ (v). Homogenization of the two CO₂ phases takes place in the liquid phase at 27.65°C (photo 2); at much higher temperatures, probably above 350°C, only one homogenous "gas" phase is present, containing all the CO₂, H₂O, and NaCl. Sample ER 61-28, Volta Bala, 36 km. E. of Topazio (formerly Jardimopoles), Tegid Otoni, Minas Gerais, Brazil.

3. Photomicrograph of plane of inclusions in quartz. Each inclusion contains a cube of halite, which dissolves at 196°C, and a vapor bubble, which homogenizes at 308°C. Sample from a cavity in gneiss at Bitsch power plant, Valais, near Brig, Aar massif, Switzerland. photograph and data courtesy Drs. Bernard Poty (Nancy, France) and Hans Stalder (Bern, Switzerland).

4. Photomicrograph of plane of probably pseudosecondary inclusions in topaz (T), parallel to (001), each containing a large vapor bubble (approximately 35% by volume) in the low-salinity liquid, and a very small daughter crystals. (For example, see arrows; in other inclusions these crystals are hidden.) These crystals are unidentified, but are recognizable different phases. U.S. National Museum (Natural History), specimen 96595, Rukuba tin mine, Nigeria.

5-6. Photomicrographs of two planes of inclusions in a topaz crystal, only a few millimeters apart, that have trapped two entirely different fluids. In each plane, all inclusions apparently have a uniform ratio of phases, and all appear to have the same phases, but the ratio of gas-bubble to other constituents differs greatly between the two planes. The small but plainly visible differences in gas-bubble ratio between adjacent inclusions (particularly in photo 5) may be only apparent and may come from irregularities in the third dimension, or they may be real and stem from bubble nucleation before necking down took place. The differences between the inclusions shown in photos 5 and 6 may be a result of differences in the confining pressure at the time of trapping. These and other inclusions in the sample contain at least 16 daughter minerals, presumably all different phases, plus liquid (liq) and vapor (v). Ten daughter crystals are seen to be birefringent (see photo 7); these may be as many as five opaque phases. All the inclusions are strongly flattened parallel to the (001) cleavage and may be primary pseudosecondary in origin. Lyakhov (1966) gave X-ray powder-diffraction data on six of the 14 different solid phases he extracted from inclusions in morion from these same pegmatites, including hydrous ferrous chloride, FeCl₂·2H₂O.

The two crystals shown at the right end of photo 5 have an index of refraction very appreciably less than that of the enclosing liquid (liq) which, in turn, has an index of refraction less than the enclosing topaz (T). These specific daughter minerals have not been positively identified, but various low-index fluoride minerals such as cryolite (n=1.34) and avogradrite (K,Ca)BF₄ (n=1.32) have been reported in the extensive Russian work on such daughter minerals. Sample from Volynia, USSR, loaned by Dr. Bernard Poty, Nancy, France.

7. Photomicrograph of a large multiphase inclusion in the same topaz sample as photos 5 and 6, viewed in plain light (left) and with crossed polarizers, set to place the enclosing topaz (T) almost at extinction (right). Presumably some of those that appear isotropic are not, but merely have their extinction parallel with those of the enclosing topaz.

8. Photomicrographs taken at +27.5°C (left) and +10.0°C (right) of multiphase inclusions in emerald (E), showing relatively small vapor bubbles (v) and large daughter crystals of halite (h) in saturated brine (lw). The bubbles contain CO₂ gas at high pressures, as shown by a crescent-shaped fillet of liquid CO₂ (lc, right photo) that evaporates into the bubble when warmed to room temperature. Sample ER 63-139b, Chivor emerald mine, Colombia, courtesy of Banco de la Republica, Bogotá.

9. Photomicrograph of a fluid inclusion of liquid (liq) in emerald (E), containing vapor bubble (v) and several daughter minerals, taken at room temperature. This is one of many inclusions containing the same assembly. Cube h is halite, cube s may be sylvite, and x is an unidentified isotropic phase that recrystallized after freezing. Granular mass with high relief (v) nucleated on freezing and remained on return to room temperature. Sample ER 63-139b, Muzo emerald mine, Colombia, courtesy of Banco de la Republica, Bogotá.

10. Photomicrograph of large three-phase inclusion in quartz. In addition to the dark vapor bubble (v), a large daughter crystal of halite (h) grew from the liquid (liq), in very close contact with the quartz walls, sealing off a small part of the liquid phase (at left). The index of refraction of the cube of halite (1.544) is very close to that of the surrounding quartz (Q) in this orientation, making the contacts almost invisible. (See arrows.) This provides one definitive proof that these daughter crystals and presumably those similar crystals in the associated emeralds, are indeed halite. Sample ER 63-84Q, Muzo emerald mine, Colombia, courtesy of Banco de la Republica, Bogotá.

11. Photomicrographs of inclusions in emerald (E), showing an isotropic daughter crystal of apparently hexagonal outline (actually is an octahedron) that is believed to be halite, plus vapor (v) and liquid (liq). Why this particular halite daughter (and some others) should be an octahedron rather than a cube is unknown. Sample ER 63-139b, Muzo emerald mine, Colombia, courtesy of Banco de la Republica, Bogotá.

12. Photomicrograph of a cluster of multiphase inclusions in emerald. The amoeboid mass in the center right is all one large inclusion containing a black vapor bubble (v) and a large daughter crystal of halite (h; enlarged in photo 14). Several tubular inclusions with the same phases are shown at bottom of photo; in photo 13 they are shown enlarged. Sample ER 61-6, from an unspecified locality in Colombia.

13. Enlargement of the group of tubular inclusions shown at bottom of photo 12. Each contains one or more crystals of halite (h), a small anisotropic grain (b), a gas bubble (v) with considerable CO₂ under pressure (see photo 8), and a very strongly saline solution (l) containing other ions in addition to NaCl. In the two partly overlapping very thin, acicular inclusions (1) and (2), the darkest band is vapor, liquid is lighter, and the NaCl crystal (in contact with the emerald walls), is bright and almost invisible (this is shown particularly effectively in inclusion 2). Inclusion 3 is an all liquid inclusion, presumably formed from necking down of the larger inclusion visible in photo 12.

14. Enlargement of part of the halite daughter crystal visible in photo 12, showing many fluid inclusions in the daughter crystal, some containing liquid and vapor in various ratios (arrows), as a result of growth at various stages during the cooling of this emerald or of necking down of larger amoeboid inclusions, or both.
sure to last at surface pressure and 1,200°C and have been lost. Thus, the inclusion sample we have is strongly biased, but it still gives us a valuable relict of a former high-pressure environment. It also tells us that basaltic magma was CO₂-saturated and that a separate CO₂ phase was present beneath our feet at these great depths, all over the world. Such CO₂ may have been involved in the formation of carbonatites, in the explosive intrusion of kimberlites, and even in the origin of diamonds.

**Quartz (Citrine and Smoky)**

Most of the extensive literature on fluid inclusions has dealt with inclusions in quartz, though the quartz is seldom of gem grade, and is generally from metallic ore deposits. Quartz crystals are common in so many different geological environments that a very wide range of types of fluid inclusions can be found in them. Thus, quartz crystals formed in vugs in dolomite beds at low temperature, such as the "Herkimer diamonds" from Herkimer County, New York, have inclusions of strongly saline brine, colorless supercritical gas mixtures (methane, ethane, and some higher hydrocarbons), yellow petroleum, and fragments of a brittle black asphaltic solid "anthraxolite." Most gem-grade quartz comes from veins or quasi-pegmatitic masses in metamorphic rocks. Only two examples are given here, both from well-known deposits.

The pegmatitic or quasipegmatitic quartz-crystal deposits of Brazil have supplied much of the free world's radiograde and gem-grade quartz for years. Plate 2, photos 1 and 2, illustrate one of the most common types of fluid inclusion found in these crystals—mixed CO₂-H₂O. Inclusions such as this, large enough to see the liquid CO₂ with a simple hand lens, are rel-
atively common. The CO₂ liquid and gas phases homogenize from the warmth of the hand, while one watches. This inclusion is one of many probably pseudosecondary inclusions, all lying in a plane. When such a sample is warmed, particularly above 31°C, the possibility for explosive decrepitation is excellent. In fact, one museum quartz crystal with such inclusions spontaneously decrepitated and broke the glass case.

The fluid present during the healing of the fracture that trapped the inclusions shown in plate 2, photo 1 was similar to that from which many of these crystals grew—a mixture of water, salts, and much CO₂. I can only estimate the temperature (>350°C?) at which the CO₂ and the water phase (as in photo 2) would homogenize, as the sample would probably decrepitate far below the temperature of homogenization. When cooled and rewarmed this inclusion follows a complex series of stable and metastable routes (Roedder 1963, p. 191–195).

Plate 2, photo 3, shows inclusions in quartz from an Alpine cleft in the Aar massif in Switzerland. Most of the mineral samples from the Alps contain inclusions consisting of H₂O, CO₂, CH₄, and NaCl, in a wide range of ratios and densities, depending on the local geology, the pressure, and the temperature; many major studies have been published on these interrelations. Thus Bernard Poty and Hans Stalder (personal communications, 1973) have noted that anhydrite, presumably representing the remains of evaporite beds, occurs near this locality and may represent the source of the high salt content in the inclusions. Although these inclusions homogenize at 308°C, the pressures during Alpine metamorphism were high enough for the inclusions to have been trapped at considerably higher temperatures. No CO₂ is visible in these inclusions, but considerable CO₂, sometimes together with much CH₄, is commonly present in the inclusions from many of the Alpine cleft minerals.

Topaz

The inclusions in topaz are a pleasure to work with, because most are flattened parallel to the cleavage, making the various phases plainly visible, even simultaneously in a series of fluid inclusions. Most topaz has grown from hot dilute to relatively concentrated water solutions of various salts, frequently containing CO₂ as well. Thus plate 2, photo 4, shows a plane of probably pseudosecondary inclusions in a gemmy blue topaz from a Nigerian tin mine. The depression of the freezing point of the liquid in these inclusions (−2.8° to −4.7°C, for various planes of inclusions; Roedder 1963) indicates that the salt content of the water solution is in the range 4.6 to 7.4 wt.%. The homogenization temperature (unmeasured) would probably be >350°C.

The most common occurrence of topaz is as one of the last minerals to form in vuggy granite and pegmatite, presumably from the last bit of residual liquid left after the crystallization of the great bulk of granitic igneous rock bodies. As such, these fluids can be expected to contain a wide range of those elements that do not fit well into the crystal structures of the major rock-forming minerals of the granite. Most ores of Be, Li, Sn, W, Rb, Cs, Nb, Ta, and Mo are apparently related to such late-stage fluids, as are the ores of some of the commoner metals. Along with these elements, Cl, F, CO₂, and, of course, H₂O are also concentrated in these residual liquids, because they also do not fit in the structures of the ordinary rock-forming minerals. The result is that these fluids deposit a very complex group of minerals, called the "rare-element pegmatites." All gem-quality topaz, tourmaline, aquamarine, kunzite, and many others come from such a pegmatitic environment (Roedder 1981b). As might be expected, the solutions trapped in the fluid inclusions also are complex mixtures of many elements and hence may form a wide range of daughter minerals on cooling.

The most striking examples of such multi-phase inclusions in topaz are to be found in crystals from the "Zanorsh" or "chamber" pegmatites of Volynia in the Ukraine and the Kayib pluton in northern Kazakhstan in the USSR. In these pegmatites, crystals of fluorite and topaz
as much as 1 m long, along with other phases, line central cavities as large as 200 m$^3$ in volume (N. P. Ermakov, personal communication, 1960). The fluid inclusions in these minerals are more complex and fascinating than any others I have seen. Pegmatites having generally similar mineralogy occur elsewhere in the world, but I am unaware of any others of the "chamber" type, and I have not seen any comparable inclusions elsewhere, though many if not most pegmatites have not been examined for inclusions. The intriguing inclusions in these pegmatites have helped to provide the impetus for an extensive series of Soviet publications on fluid inclusions in general and daughter minerals in particular (see references in Roedder 1972).

A remarkable assortment of exceedingly rare and frequently water-soluble daughter crystals, sometimes 10 µm or more long, such as villiaumite (NaF), hydrous ferrous chloride (unnamed: FeCl$_2$.2H$_2$O), borax (Na$_2$B$_4$O$_7$.10H$_2$O), teepoleite (Na$_2$B$_4$O$_7$.2NaCl.4H$_2$O), cryolite (Na$_3$AlF$_6$), and avogradrite (K,Cs)BF$_4$, has been found in the fluid inclusions of such pegmatites (see plate 2, photos 5–7, and references in Roedder 1972). Even though some of these are highly water soluble, and these rocks have been bathed in ground water for thousands or even millions of years, they have been preserved for us because they were in single-crystal "bottles." I am sure that many new minerals are yet to be recognized and described among such daughter minerals. It is fascinating to consider that huge crystals of such daughter minerals probably were also formed in the central chamber of these pegmatites and have since been leached away by ground water. These central chambers, which represent the largest-of-all "fluid inclusions," were enclosed by polycrystalline rocks, not by a single crystal, and hence have leaked. A 200-m$^3$ "fluid inclusion" of this sort originally could well have had such phases as rare-mineral daughter crystals many meters long!

Most of the inclusions in such topaz crystals are secondary (or pseudosecondary), in healed cleavage fractures. Considerable controversy exists in the Russian literature over the problem of recognition of possible primary inclusions in these crystals, but regardless of origin, the inclusions shown preserve for us samples of some rather strange fluids previously existing in the Earth's crust. Fault movements have presumably affected the pressure during the formation of these pegmatites, as evidenced by major differences in the density of filling of various planes (plate 2, photos 5 and 6). Still another type of fluid was present at some other time in the history of these samples; it forms two-phase inclusions, consisting of a large vapor bubble and liquid, with no daughter phases.

**Emerald, Colombia**

Colombia supplies a major part of the world's emeralds, mainly from the Chivor and Muzo mines. Much has been written on these occurrences (e.g., Johnson 1961; Feininger 1970; Beus and Mineyev 1974; Escobar and Mariano 1976), but the complexities of the deposits, plus the difficulties of access, have resulted in some conflicting statements. Quite obviously, a thorough coordinated study of the deposits is in order, starting with detailed field mapping of the regional and local geology, as well as investigations of the mineralogy and geochemistry. I have made some miscellaneous observations and obtained some quantitative data on Colombian emeralds, most of which have not been previously published, and will put these data on record here to aid future workers who may want to study the deposits.

The solid inclusions in emeralds from Colombia are abundant and fascinating, and much has been published on them, particularly by Gübelin (1953, 1957), and more recently by Fujisaki (1976) and others. However, most reports on the fluid inclusions have been descriptions, without numerical data, of the "three-phase-inclusions" (i.e., solid, liquid, and gas), that are so characteristic of Colombian emeralds (Gübelin 1953). In 1963, I reported on the low-temperature behavior of about 50 primary inclusions in a 1-cm crystal "probably from El Chivor mine" (p. 173). (Because of the extensive illegal mining
and trading of Colombian emeralds, the exact source of many specimens is frequently ambiguous. In that publication, I stated (p. 203) that “The behavior ... remains in part inexplicable and is presented here as a challenge to other investigators”; to my knowledge, this challenge has not been accepted. I found that the main phases in the inclusions were halite daughter crystals (15 volume percent; identified by a variety of unambiguous tests), NaCl-saturated solution (74 percent), and gas (11 percent). Only at low temperatures could a fourth phase be seen, <1 percent by volume of liquid CO₂ as a crescent-shaped filament between the gas bubble and the water (plate 2, photo 8). The amount of this liquid CO₂ varied rather widely from inclusion to inclusion. Although probably present in all, the liquid CO₂ was only visible in strongly flattened inclusions. A fifth phase, a small mineral grain of high birefringence and high index, is present in most inclusions. The liquid CO₂ froze when subjected to liquid nitrogen temperatures, and melted at about the −56.6° triple point for CO₂; when the specimen was warmed, the last liquid CO₂ evaporated into the vapor phase at temperatures ranging from ∼ −33° to +8.1°C, indicating a wide variation in the CO₂ pressure at the time of trapping of the various inclusions. (Some other Colombian emeralds show liquid CO₂ even at room temperature; one from Muzo showed homogenization of the two CO₂ phases, into the gas phase, at +26.9° ± 0.1°C; this corresponds to a CO₂ density of ∼0.4 g/cm³.)

One of the most inexplicable parts of the behavior of these inclusions (particularly that of the larger inclusion shown in plate 2, photo 13) is the extreme reluctance of the salt solution to freeze. Thus, one week at liquid-nitrogen temperatures (−196°C) did not suffice. Some, but not all, the inclusions in this sample eventually froze; the temperature of first melting (the temperature at which visible liquid forms between the dry crystals/of salts and ice) was found to be between −63° and −58°C, and the last recognizable ice crystal melted at −34°C. Such temperatures require the presence of substances other than just NaCl and H₂O, which would yield a first-melting temperature of only −21°C. Among ordinary materials, only CaCl₂ can yield temperatures below −50°C, but even the combination of CaCl₂ and NaCl will only yield −52°C, so still other constituents must be present. Thus, the fluids from which these particular emeralds grew was an extremely saline solution of Ca, Na, and Cl, and unknown amounts of other ions, plus CO₂.

One of the daughter crystals frequently seen in inclusions in emeralds from Muzo, Colombia, has optical properties that resemble those of the rare cerium fluorocarbonate mineral parasite found in the same veins with the emeralds; hence, this crystal had been tentatively identified as parasite (Roedder 1972, plate 2, Figure 2). This same inclusion (plate 2, photo 9) was later examined by Raman spectroscopy (Rosasco and Roedder 1979). In this procedure, an intense beam of visible light from a laser is focused into the inclusion, and the resulting scattered, very weak Raman radiation, of shifted wavelengths, is collected and analyzed spectrographically. The spectrum of the daughter mineral showed that although it is still an unknown, it is not parasite. Only one strong broad band, at approximately 200 cm⁻¹, was observed from the daughter crystal. In contrast, spectra from a parasite crystal from the same vein, measured in the Raman microprobe, showed many peaks, none at 200 cm⁻¹. The strongest peak was a triplet near 1,100 cm⁻¹, which arises from the symmetric stretching vibrations of the three CO₂ groups (parasite is (Ce, La)₂Ca(CO₃)₂F₂).

These frequencies, if they had been present in the spectrum of the daughter crystal, would easily have been observed. Because of the strong fluorescence of the host emerald, no bands of the daughter crystal could be identified in the OH-stretching region above 3,000 cm⁻¹. The identification of this daughter crystal is hampered by this fluorescence and also by the lack of an extensive library of Raman spectra of minerals. A second isotropic cubic daughter mineral, in the same inclusion, gave no Raman spectrum, in accord with its earlier identification as halite, which should show only a weak second-order Raman spectrum.
The spectrum obtained from the 40 \(\mu\)m vapor bubble in this inclusion showed strong peaks for \(\text{CO}_2\), as was expected. A crude estimate based on the intensities of these peaks suggests a pressure of at least several atmospheres. The water surrounding the daughter mineral was evidenced by broad peaks from the bending (\(\sim 1,650\ \text{cm}^{-1}\)) and stretching modes (\(\sim 3,400\ \text{cm}^{-1}\)) of \(\text{H}_2\text{O}\). Spectra of the brine showed no dissolved \(\text{CO}_2\), \(\text{HCO}_3^-\), or \(\text{CO}_3^{2-}\). The absence of such species in the brine suggests that their concentrations are probably less than a few thousand ppm.

A sharp band at \(\sim 2,330(\pm 5)\ \text{cm}^{-1}\), evident in the spectrum of the host, was assigned to \(\text{N}_2\) in the emerald. This band was quite intense, and a very crude estimate suggests a concentration perhaps 3–10 times the maximum reported by Scalanc (1959) for beryl samples (238 ppm). Also, a relatively strong band at \(\sim 3,610\ \text{cm}^{-1}\) observed in the host spectrum is assigned either to substitutional \(\text{OH}^-\) or to trapped molecular \(\text{H}_2\text{O}\) in the emerald. Many emerald varieties have been found to contain \(\text{H}_2\text{O}\) or \(\text{OH}^-\) (see references in U.S. Dept. Commerce, 1973).

The temperature of formation of the Colombian emerald deposits has been the subject of much controversy. The host beds (carbonaceous shale and siltstone, limestone and dolomite, largely albited; Escobar and Mariano 1976) show little or no evidence of an alteration zone from the passage of the emerald-depositing solutions. Some writers have expressed surprise at this and have suggested that the emerald may have formed at low temperatures, even though the inclusions indicate relatively high temperatures, from simple visual estimates of the phase ratios. If the hot emerald-forming solutions permeated the entire mass of the beds, however, there should be no evidence of local alteration around the emerald veins themselves. Beus and Mineyev (1974) reported extensive leaching by hydrothermal solutions and indicated that the emeralds are of "hydrothermal low-temperature origin."

I have attempted to obtain the temperature of homogenization (Th) on 47 primary inclusions in a thin plate cut from a dark green, inclusion-rich crystal from Chivor (sample ER 63-83), supplied through the courtesy of Banco de la Republica, Bogotá, Colombia. (The inclusions in samples said to be from Muzo were generally very similar in appearance.) After careful microscopy to establish that these inclusions were indeed primary (for criteria, see Roedder 1981a), the sample was heated in a microscope heating stage, along with adequate calibrations.

On heating, the bubbles decreased in size and the crystals dissolved. Most of the birefringent crystals dissolved by about 300°C, most of the NaCl crystals dissolved by 330°C, and most of the inclusions that did not leak had only very small vapor bubbles at 355°C, the limit for this particular stage. All larger inclusions formed fractures to the surface and leaked, some explosively. This leakage was recognized by a sudden reversal in the gradually diminishing size of the bubble as temperature increased. Sometimes only part of the contents were lost, leaving a large bubble, but others were emptied completely, leaving only the undisolved salt crystal behind. Most such decrepitation took place in the range 250°–300°C. As is commonly found in inclusion work (and readily explicable), the smaller inclusions do not decrepitate as easily; many of these withstood the 355° run and returned to the same appearance and phase assemblage on cooling.

The conclusion is that this particular emerald crystal from Chivor formed at temperatures well in excess of 355°C. How much in excess depends on how much higher temperatures will be needed to complete homogenization of the inclusions and on an added correction for pressure at the time of formation. This pressure correction can be evaluated for magnitude on the basis of geological field evidence only, but it cannot be negative and may be large. Thus, if this crystal grew under the 6,000 m of sediments suggested by Escobar and Mariano (1976), the pressure correction, assuming a sediment density of 2.5 g/cm³, would be 163°C (Potter 1977), and even greater depths of overburden have been proposed by others. The presence of the lesser amounts of other salts and \(\text{CO}_2\) will have relatively minor effects on this pressure correc-
tion. The inclusions in the other samples of emerald, as well as those in parsite, calcite, and quartz (e.g., plate 2, photo 10) from Chivor and from Muzo, give every indication of being identical with those in this sample and hence probably formed similarly.

The amount of data on the history of a given sample that can be recorded in the fluid inclusions is thus very large; much more extensive and detailed studies of the inclusions in the emeralds and associated minerals from the several deposits will be needed before we can achieve a fuller understanding of how these gems formed. Even some aspects of the cooling history of the deposit are sometimes recorded. Thus, some of the larger daughter crystals of halite in inclusions in these emeralds contain fluid inclusions themselves (e.g., Roedder 1972, plate 2, Figure 6), recording the conditions of growth as that daughter crystal formed while the sample cooled, just as the host inclusion records the conditions of growth of the host emerald. The largest halite daughter crystal found (plate 2, photos 12 and 14) has hundreds of liquid or liquid-plus-vapor fluid inclusions in it, each recording some event in the slow cooling of this sample from the high temperature of formation to surface temperatures.

Diamond

Whenever one speaks of fluid inclusions in gemstones, the inevitable question from the audience is about fluid inclusions in diamonds. Minerals from certain metamorphic rocks, particularly those that have crystallized in a water-deficient environment, are generally free of aqueous fluid inclusions, as are those from most meteorites and many, but not all lavas. Thus aqueous (or CO₂-rich) fluid inclusions are generally not found in materials believed to have formed deep in the earth, such as diamonds and the minerals of the eglogites, with the notable exception of the CO₂ inclusions in the minerals in the olivine nodules brought to the surface with many alkalic basalts (see discussion of peridot, above). Bauer and Spencer (1904, p. 119) and Schlossmacher (1932, pp. 348–51) referred to fluid inclusions containing liquid water, liquid CO₂, and/or gas, in diamond. These and similar statements have been widely quoted and re-quoted ever since, but unfortunately the criteria used for phase identification are never stated. Sutton (1928, p. 42) called these statements “a favorite myth.” Melton and Giardini (1981 and several earlier papers) have obtained gases during the crushing or carbonization of diamonds, but although they use the term “fluid” to refer to these materials in the diamonds, they present no evidence of an actual fluid phase in the diamonds studied. The abundant solid inclusions in diamonds have been extensively studied and provide exceedingly valuable data on the conditions of diamond formation, but I have examined many inclusions in diamonds, including the sample described and illustrated by Eppler (1961, Figures 19 and 20), and have not seen any recognizable liquid, CO₂ or otherwise.

Usefulness of Inclusions

Although fluid inclusions in a gem are imperfections in a material that is prized mostly for its perfection of crystallization, they are not completely negative features. They represent samples of either the fluid from which the crystal has grown, or that in which it was bathed at some later time. As a result, the study of inclusions in gemstones can provide valuable information on the environment of formation of the gems or their subsequent geological history. Such information may be useful in many ways.

Understanding the Environment of Formation of Gems

The selection of a region, locality, or specific spot for prospecting for any given natural deposit, be it metals or gems, can be based on pure random chance or on various degrees of knowledge of the likelihood of success in the area. Although some deposits have been found by pure chance, selection based on knowledge is obviously more effective, and its effectiveness
is more or less directly dependent upon the amount, nature, and particularly the validity of the available knowledge. Success comes more often to those who, from the voluminous lore of gems, can recognize and use those specific facts that are actually valid and helpful in prospecting. Many of these facts are purely empirical and are based on the observations of generations of keen miners, completely free of any scientific interpretation. Thoughtful miners have frequently found useful signs—commonly associated minerals in stream gravels, color or texture differences of the host rock, variations in the nature of the soil, etc. These signs should never be ignored simply because a scientific raison d'être has not been established. Obviously, however, the more that is known about the nature of the process involved in the formation of any given type of deposit, the more intelligent can be the selection of places to prospect or of ways to search for extensions of a given deposit.

Fluid inclusions do not provide a panacea, but do provide some insights into the nature of the processes involved which can, in theory if not in practice, put the mining of known deposits and the exploration for new deposits on a more rational basis.

Identification of Gemstones and Recognition of Their Sources

Gübelin (1953) has shown that the shape and nature of the inclusions, both the liquid, and more particularly, the solid types, can be helpful in the identification of unknown stones and are an exceedingly important factor (along with color, etc.) in deciding upon the source of a given gem. Thus, the presence of cubes of halite along with liquid and vapor in the inclusions in an emerald has long been considered definitive of a Colombian source for the stone. Although this is generally true, recent work has shown that emeralds from some other localities, e.g., Poona, Western Australia (Grändorff 1974), and an unspecified new field in India (Oughton 1968) also have such cubic (presumably halite) daughter crystals. This is not surprising, as halite is by far the most common daughter crystal and is present in inclusions from minerals from many types of geological occurrence (Roedder 1972).

Because fluid inclusions contain an assortment of ions other than just those of the host mineral, the ratios of these various trace elements in the fluids probably will vary widely from locality to locality. Such variations might well be much larger than those shown by the trace elements in the gems themselves, because these latter elements are limited by the crystal chemistry of the host structure. Sometime in the future, when analytical procedures are improved, I predict that nondestructive analysis of the soluble constituents in fluid inclusions will provide a "fingerprint" method to characterize the locality of origin for a given gem.

Identification of a Given Stone

The fluid inclusions within a given gemstone can be recorded photographically and are obviously just as useful in verification and recognition of stolen stones as any other internal characteristic that cannot be easily eliminated by slight recutting.

Guidance in Attempts at Synthesis

Unfortunately, in growing gemstones, Nature does not normally use procedures that yield the rapid growth necessary for economic synthesis by man. However, some of the all-too-frequent problems in the control of cracking and other imperfections, and particularly in control of color, might be helped by study of the fluids used by Nature. Thus, in the 1950's I tried (unsuccessfully) to use the composition of the fluids from which natural radio-grade quartz crystals had grown, as determined from the analysis of fluid inclusions, in an attempt to understand why the synthetic crystals had significantly different (and poorer) electrical properties in frequency-control devices.

Recognition of Natural vs. Synthetic Stones

Because the fluids that have been used in synthesis of most gems in the laboratory are usually
quite unlike those used by Nature, a study of the nature of the fluid inclusions can provide the critical evidence to distinguish between natural and synthetic stones. Thus, there is a large difference between the low-pressure gas-bubble inclusions in boule-grown sapphire and the dense, high-pressure CO₂ inclusions in some natural sapphires (e.g., plate 1, photos 14–15). A similarly large difference exists between the fused tungstate-melt inclusions in a flux-grown emerald and the NaCl-H₂O-CO₂ inclusions found in some natural ones. Caution is necessary here, however, since such knowledge can be self-defeating. As long as a large price differential exists between the synthetic and the natural, knowledge of the characteristic inclusions in the latter may well be used to set up synthesis conditions which, although perhaps not yielding high growth rates, may yield synthetic gemstones containing fluid inclusions that label them “natural”.

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Edwin Roedder has been with the U.S. Geological Survey since 1955. Both educator and research scientist, Roedder's research interests include terrestrial, lunar and meteoritic fluid inclusions (both liquid and melt), silicate liquid immiscibility and the problems of nuclear waste disposal. Roedder initiated and has been editor of "Fluid Inclusions Research—Proceedings of COFF," since 1968, and has served terms as associate editor of "G.S.A. Bulletin," "American Mineralogy" and "Economic Geology."

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Patterson began his involvement in the colored stone industry in 1957 when he became a lapidary and began dealing in colored stones in 1960. He is a registered engineer with degrees in both mechanical and metallurgical engineering.