Optical Microscopy
Identification of the
Phases in Fluid
Inclusions in Minerals

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Keywords: Fluid inclusions, inclusions, daughter minerals, minerals, optical crystallography, polarized light microscopy.

ABSTRACT

The identification of the gas, liquid and solid phases formed in individual fluid inclusions in minerals is essential for estimating the gross composition of the original trapped homogeneous fluid. It is, likewise, essential to all applications of fluid inclusion studies to the understanding of the geological processes during which the inclusion formed. Most ordinary inclusions consist, at room temperature, of an aqueous solution and a shrinkage bubble, possibly with a salt crystal, and hence they present few phase identification problems. But many fluid inclusions represent a trace phase in a complex geochemical system of mainly solid minerals, and hence generally contain high concentrations of many minor or rare residual components. On cooling, such multicomponent systems form a plethora of new

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phases, some of which may even be new minerals. The identification of any (or all) of these phases provides valuable data on the composition of the fluid, and on the geological processes involved.

Quantitative chemical analysis of single inclusions is possible but difficult and expensive. The new nondestructive microbeam techniques such as laser Raman, synchrotron XRF, and the proton probe are well suited but also expensive. Optical microscopy is used to provide an inexpensive, quick "identification", to various degrees of certainty, of many of the newly formed phases. The occurrence of such phases in an inclusion in a host mineral, however, places severe limitations on the number and accuracy of the optical measurements that may be made, which result, in turn, in a frustratingly high degree of ambiguity in the final "identification". This paper reviews the nature of these limitations, as well as some of the ways of avoiding them, and illustrates the strengths and weaknesses of the optical procedures that have been found to be useful.

INTRODUCTION

Almost all natural rocks, ores or gemstones have formed from, or at least have been in equilibrium with, a fluid phase. The geologist is, in effect, a detective, trying to reconstruct the geological processes of the past from the available clues. The bulk of the ancient fluids have disappeared with the cessation of the processes millions of years before, but small aliquots of these former fluids are frequently found to have been trapped in the host crystals during their growth, and hence preserved for study. Although such fluid inclusion "clues" are generally small (10^{-8} to 10^{-12} g), they can provide a vast amount of useful information.

The composition of the original trapped fluid is perhaps the most critical aspect, since it is essential in understanding many geochemical processes, such as occur during the formation of ore deposits. Ordinary fluid inclusions have trapped a homogeneous fluid at an elevated temperature. Homogenization temperature determinations, in which the inclusion is heated on a microscope heating stage until all phases merge to form a single fluid, can be made without concern for the composition of the fluid, but any attempt at converting these data to formation (i.e.,
trapping) temperatures requires, among other data, knowledge of the composition of the fluid. Similarly, all uses of fluid inclusions to determine the density or pressure of the original fluid require compositional data.

Although quantitative data on the composition of fluid inclusions can be obtained by crushing and leaching bulk samples containing millions of inclusions, most samples contain more than one generation of inclusions, that were trapped at different times, and may differ greatly in composition. To avoid this problem and hence provide more meaningful results, we must analyze single inclusions, carefully selected to have a known relationship to the process being studied. For such analyses, various modern microbeam and microchemical methods have been widely used, both nondestructive (e.g., laser Raman, proton spectroscopy, and synchrotron XRF) and destructive (e.g., SEM), but these require extensive and expensive instrumentation.

The great bulk of all compositional data obtained in fluid inclusion studies is only qualitative or, at best, semi-quantitative, and comes from simple, inexpensive optical microscopy in transmitted light, in part at low or high temperature, to identify the solid, liquid, or gaseous phases present. When combined with phase volume estimates (also from microscopy), an approximate bulk composition and density for the original fluid may be calculated. Neither of these two values are available from any source other than the study of fluid inclusions.

Ordinarily, a fluid inclusion is trapped at some elevated temperature. On cooling to surface temperature, the host crystal “bottle” shrinks, but the fluid inside shrinks much more; this difference results in formation of a vapor bubble in the liquid. In such ordinary two-phase fluid + vapor inclusions, the phase identification is generally simple, but estimates of the compositions of these two fluids almost always involve considerable uncertainty. In addition, the degree of uncertainty in the identification of any solid crystalline phases that may form in the inclusions on cooling (i.e., “daughter minerals”) ranges widely, from negligible to completely unknown, with frustratingly large ambiguity in-between. The uncertainty comes mainly from the fact that the occurrence of these phases within small inclusions in a crystalline host precludes many normal optical procedures and makes the remainder imprecise at best. It is not uncommon
to find complex multiphase inclusions containing 5-10 different solid phases in which only one or two are identifiable with moderate certainty, and the balance remain unknown.

In spite of these severe limitations, optical observations still present the simplest source of preliminary compositional data on fluid inclusions, and are the essential preliminaries to all more sophisticated analytical procedures. Figure 1 shows a hypothetical multiple phase fluid inclusion, originally trapped as a homogeneous fluid, that provides an example for the following discussion of the optical identification procedures and their limitations.

It is important to note that this discussion is limited to optical criteria; the geological occurrence of a sample provides important guidance in phase identification by suggesting logical alternatives, but is not covered here. Also not covered here is the identification of solid inclusions within host crystals. Far more details on the criteria mentioned below, and on quantification of the composition of fluid phases, can be found in several books (1-4) and in the numerous references in these books.

IDENTIFICATION CRITERIA, LIQUIDS AND VAPOR

Vapor or Gas Phase in Multiphase Inclusions

At first glance, it might seem unlikely that optical study could provide compositional information on the gas phase, and this is relatively true for observations at fixed temperature. Although seemingly of no pertinence to the bulk composition, the volume of the gas phase is of major importance in estimating the bulk density of the original fluid that was trapped. In ordinary fluid inclusions, consisting of aqueous solution and a shrinkage bubble, the pressure in the gas bubble is simply the vapor pressure...
of the fluid, and hence is nearly a vacuum; in calculating the density of the original trapped fluid, only the volume of the vapor bubble is of concern. This volume is estimated from simple optical measurements, but although these can be precise, they can be grossly inaccurate (e.g., 2, p. J)26).

Other inclusions, that may appear identical to those above, can have as much as 70 atm of CO₂ pressure in the bubble at room temperature, with no liquid CO₂ phase; such vapor bubbles may have a density of 0.3 g/cm³, and hence make a significant contribution to both the bulk density and the bulk composition of the original fluid. Still others may contain CH₄, N₂, etc., at hundreds of atmospheres.

The visual behavior of the vapor bubble on heating or cooling can provide compositional information. Over 100 years ago, Hartley (5) observed a strange behavior in some inclusions in which the “vapor bubble” became denser than the surrounding “liquid” phase on heating and actually sank in it; such density inversions of “liquid” and “vapor” later became explicable as a result of studies on the system CO₂–H₂O (6,7). Much more can be determined by the phase changes in the gas bubble on cooling. Not infrequently, a new liquid phase may form at the former interface between liquid and vapor. At first this may consist of only a thin rim that is lost in the black edge, from total reflection, at the margin of the bubble. If the bubble is distorted by the inclusion walls or other phases, this new phase may become visible only as a result of being concentrated in the regions of maximum curvature of the interface (e.g., Figure 1).

Single-Phase (i.e., “Gas”?!) Inclusions

Inclusions that are single-phase at room temperature present special problems. They may be filled with: 1) liquid aqueous solutions trapped at low temperatures; 2) low-density gas trapped at low pressures; 3) high-density gas trapped at elevated pressures; 4) Silicate melt (see below under Liquid + vapor inclusions); or 5) air (i.e., inclusions that have leaked; see below under Artifacts).

The first type, monophase liquid, is difficult to recognize with certainty; on cooling they may nucleate a vapor bubble, or may simply freeze to clear ice with no change in appearance.
The second type, low-density gas, may precipitate a rim of liquid CO$_2$ on cooling (e.g., 2, Plate 5-1). This behavior provides valuable data on the pressure at the time of trapping. Identification of this liquid as essentially CO$_2$ is obtained from determination of its triple point. The phase behavior at low temperature of gas inclusions containing mixtures of CO$_2$, CH$_4$, and N$_2$ at various pressures is complex, and estimation of the composition from optical observations alone is ambiguous (8).

The low-temperature behavior of the third type, high-density gas, is used to limit or even determine the possible composition. Thus dense pure CO$_2$ inclusions generally nucleate a vapor bubble on cooling to a temperature dependent upon their density, and show the triple point at ~56°C; this triple point is changed by the presence of other constituents such as CH$_4$, N$_2$, etc. Other inclusions that appear empty at room temperature may contain a supercritical mixture such as CH$_4$ and C$_2$H$_6$ that has a critical temperature below room temperature (e.g., Ref. 2, Plate 5-6/7).

Liquid + Vapor Inclusions

By far the most common variety of inclusion contains two phases, a more-or-less spherical bubble of "vapor" in a colorless "liquid". Generally these consist of a water solution plus a shrinkage bubble that may also contain some gas under pressure. However, many "melt" inclusions, trapped during crystallization from a molten silicate mixture, as in lavas, consist of a vapor bubble in a clear glass. This combination is frequently mistaken for, and is not always easy to distinguish from the water inclusions, even after careful microscopy. There are at least 13 criteria for making this distinction (2, p.JJ10), all based on optical microscopy and hence not including such evidence as geological occurrence.

Other than melt (i.e., glass) inclusions, the most common type of two-phase inclusion that resembles aqueous two-phase inclusions is that consisting of CO$_2$ liquid + vapor. Several simple optical procedures are adequate to distinguish these two types. Since the critical point of CO$_2$ is 31°C and most geologically expectable impurities depress this temperature, simple heating to over 31°C (e.g., by placing the slide on the warm
microscope light housing) and reexamining will suffice; if two phases are still present in the warmed inclusion, the liquid phase cannot be CO₂. The coefficient of thermal expansion of liquid CO₂ at room temperature is extremely high (about 5 vol.% per degree C, several hundred times larger than that for liquid water), resulting in visible decrease in the vapor bubble diameter with only slight temperature increase.

Liquid CO₂ also has a lower index of refraction than water solutions, and hence shows higher relief against the host, but as the appearance of relief is also greatly affected by inclusion shape (Ref. 3, Fig. 6-1), this criterion is difficult to apply. Much more significant is the difference in refractivity between the gas and the liquid phases. Since these two fluids become identical on heating to the critical point, the indices of refraction (and density) approach each other rapidly, particularly in the last few degrees. As a consequence, the relief shown by the gas bubble against the liquid—the width of the black band at the meniscus as seen in transmitted light—is smaller for CO₂ than for bubbles in liquid water, and, of course, the meniscus disappears altogether at the critical point.

Still another procedure for distinguishing CO₂ liquid from water is based on infrared absorption. Liquid CO₂ absorbs IR light with high efficiency, so unless the microscope illuminator has a very effective IR filter, the liquid CO₂ inclusions are kept at a slightly higher temperature than the surrounding host mineral plate, and the gas/liquid phase relations seen in the inclusion are appropriate for this higher local temperature. If a good IR filter is now inserted in the light path, the inclusion phase ratio responds almost instantly, as the effective distances for heat flow are minute. This phenomenon is most striking if the microscope illuminator voltage is maintained just adequate to keep the CO₂ inclusions one-phase, and the filter is inserted; the CO₂ inclusions instantly develop vapor bubbles. The same behavior is seen if the spread fingers of the hand are passed quickly through the substage light beam. An inclusion with near critical density heterogenizes and then homogenizes four times in succession, all within a fraction of a second, from the cooling of each passing shadow. (A caveat on observations of CO₂ inclusions: many ordinary microscope "heat-absorbing" or "IR" filters are not very effective, as is evident upon noting the behav-
ior of a CO₂ inclusion on placing an additional IR filter in the system.)

One last type of "normal-appearing", two-phase, liquid/vapor inclusion is relatively rare, but must be considered. This consists of "organic", hydrocarbon liquid + vapor. When the liquid is yellow or brown, oils immediately come to mind, but when the liquid is colorless, this possibility may easily be forgotten. Several procedures may suggest hydrocarbons. Many oils, even colorless ones, fluoresce brightly in UV. One does not always need an expensive UV microscope to observe and photograph this; with some oil inclusions an ordinary mineralogist's long-wave UV light held beside the stage is adequate (Ref. 3, Figure 4-2); the eyes must be dark-adapted for a few minutes first). Hydrocarbon fluids have coefficients of thermal expansion much larger than aqueous solutions, and hence if the bubble shrinks much faster than expected on heating, hydrocarbons are likely. Thus a hydrocarbon inclusion that might be expected to homogenize at 250-300°C, as a water inclusion, actually homogenizes at 124.8°C (Ref. 3, Figure 4-4). Similarly, if critical phenomena are seen at temperatures intermediate between 31°C (CO₂) and 350°C or more (most water solutions), hydrocarbons (or very rarely, H₂S) are more likely (e.g., Ref. 3, Figure 4-6). Since most hydrocarbon liquids in nature are complex mixtures for which low-temperature data are not available, their behavior on freezing is difficult to interpret.

Two other features may help to recognize hydrocarbon liquids in inclusions. First, their index of refraction is generally well above that of even highly saline water solutions; when in contact with the host fluorite (n = 1.434), some are found to match almost exactly (e.g., Ref. 3, Figure 11-24). Second, when several different fluids are present in the same inclusion, they usually assume positions of minimum surface energy. Glass, if present, is always in contact with the host mineral, and if there is no glass, aqueous solution is at that contact. Liquid CO₂, or liquid hydrocarbons, is almost always found at the contact between the bubble and the water solution. Exceptions are rare (e.g., Ref. 2, Plate 9-1).

Similarly, the aqueous fluid in some inclusions may match the index of the host mineral; in such cases the interface disappears visually, and hence the bubble and other daughter phases
may appear to be imbedded in the solid host mineral. High-calci-
mium residual fluids in some inclusions, after concentration by
 crystallization of much ice at low temperature (9), can match the
index of the host fluorite ($n = 1.434$). Similar phenomena are
seen at room temperature in other low-index minerals such as
cryolite ($n = 1.34$).

Kalyuzhnyi (10) made a detailed study of the use of total
reflection angles at flat host-crystal/fluid-inclusion interfaces to
obtain a quantitative measure of the index of refraction of the
fluid. The method is elegant in theory but difficult experimental-
ly.

One type of observation, easily made during microscopy of
aqueous inclusions, based on inclusion fluid composition, is the
direction of movement of the vapor bubble in a thermal gradi-
ent. When a minute thermal gradient is impressed on an inclu-
sion containing a vapor bubble and a liquid, e.g., by adjustment
of the microscope lighting, or by the use of a thin platinum wire
heating probe (Ref. 3, p. 92 and Figure 6-4), most bubbles fall
into two types: either they move up the gradient (most com-
mon), or they move down (less common). This movement is a
result of a negative (or positive) change in the surface tension at
the bubble/liquid interface with change in temperature, and
even provides an amazingly sensitive indicator of minute ther-
mal gradients within a microscope heating stage. Even though
the specific effects of the various possible compositional param-
eters on surface tension are not known, the empirical observa-
tion of differences in the behavior of the bubbles in a thermal
gradient, between two adjacent and otherwise similar-appearing
inclusions, show that they must differ in composition and gener-
ally cannot be coeval. An exception is possible, however, if the
inclusions were trapped from a heterogeneous system of two
immiscible fluids.

IDENTIFICATION CRITERIA, SOLIDS

Daughter minerals in inclusions—solid phases that have crystal-
lized out of the trapped fluid—indicate saturation of the fluid
with respect to these phases occurred during cooling and con-
tinued to the conditions of observation. Hence daughter miner-
als provide valuable data on the composition of the fluids.
General significance and usefulness

The problem of distinguishing between daughter minerals and accidental solid inclusions, trapped along with the liquid, is sometimes difficult. Regularity of phase ratio in several or many inclusions is by far the best criterion for a daughter-mineral origin, but recrystallization (i.e., necking down; see Figure 1 lower left) can isolate already formed daughter crystals from their parent liquid. In addition, small inclusions may not show a daughter mineral that adjacent larger ones have; this is commonly due to failure to nucleate, and hence it is important that the criterion of regularity of ratio be applied only to those inclusions in which the full complement of phases is present. Fortunately, such problems are only peripheral to identification of the phases.

Fortunately also, distances are so small in fluid inclusions that daughter phases, at least the water-soluble ones, have generally had time to reach minimum surface energy, i.e., one single crystal of each phase. Hence the number of daughter phases is generally equal to the number of daughter crystals. This relationship may not hold for very large inclusions, very slightly soluble crystals, or those that have formed during relatively fast cooling.

Every host mineral should be considered as an additional “daughter mineral” phase, as at least small amounts of it must crystallize out from almost every inclusion upon cooling. It is important to remember that each daughter phase, and the host, represent materials with which the fluid is saturated. Thus for fluids in the system NaCl–H₂O, the presence of a daughter crystal of NaCl (or if the inclusion is in an NaCl host), requires that the fluid phase at room temperature be saturated and contain ~26 wt % NaCl. This estimate is valid only if the solution contains no other solutes; if it is a strong solution of Ca and/or Mg chlorides, it might contain only ~2% NaCl at saturation.

One important aspect of fluid inclusion phase identification is the all-too-common occurrence of metastability from failure to nucleate new stable phases in these small systems. Metastability can cause serious errors in inclusion measurements. In some cases, however, it is actually useful, and can lead to some strange effects. Thus it has resulted in metastable “superheated” ice, at +6°C, under high negative pressures of perhaps 1000
atmospheres (11).

In many geological environments, particularly igneous, the fluid originally trapped in a fluid inclusion represents a minor or even a trace phase in a complex geochemical system of mainly solid minerals, and hence generally contains high concentrations of many residual components, and particularly various exotic and even rare elements and molecular species. For example, the composition of the rare-element pegmatites shows that in addition to the expectable major elements: Na, K, Ca, Mg, Si, Al, Fe, Ti, C, O, H, P, Cl, and S, various combinations of B, Be, Cs, Cu, F, Li, Mo, Nb, Rb, REE, Sr, Ta, W, Zn and Zr may also be present. On cooling to surface temperature (or below), such multicomponent systems form a plethora of new phases, some of which may even be new minerals. The identification of any (or all) of these phases provides valuable data on the composition of the fluid, and on the geological processes involved, but unfortunately, many of these phases are either poorly character-

Figure 2. Very large multiphase fluid inclusion in apatite from Cerro de Mercado, Durango, Mexico, in plain transmitted light. Liquid-l: ical properties; the identification was verified unambiguously by Raman spectroscopy. The other five daughter crystals are unknown. Scale bar in micrometers. From Rosasco et al. (18).
ized or are unknown (e.g., Figure 2), and so optical characterization is useful mainly as an empirical tool.

A good example of the concentration of rare elements into residual fluids is given by the daughter minerals in crystals of quartz from certain pegmatites in the USSR. These pegmatites are given the name “zanorysh” or “cavity” pegmatites, because they have large open central cavities, lined with very large crystals of quartz, feldspar, and fluorite, even up to a meter on an edge. These crystals exhibit multiphase fluid inclusions containing a remarkable assortment of exceedingly rare and frequently also water-soluble daughter phases, such as villiaumite (NaF), hydrous ferrous chloride (unnamed; FeCl₂•2H₂O), borax (Na₂B₄O₇•10H₂O), chiolite (Na₅Al₃F₁₄), teepleite (Na₂B₂O₄•2NaCl•4H₂O), and avogadrite (K, Cs)BF₄ (Ref. 2, Plate 12). It is fascinating to consider the parallel between these little fluid inclusions and the fluid originally filling the central cavity, which may be as much as 200 m³ in volume. These cavities were also “fluid inclusions”—the largest-of-all—but as they were enclosed by porous polycrystalline rocks, not by single crystals, they have subsequently leaked and any water-soluble daughter crystals formed from this fluid have since been flushed out by later solutions and/or groundwater. A 200 m³ “fluid inclusion” of this sort could well have originally had meter-sized crystals of rare water-soluble daughter phases! Thus if the fluid precipitated just 1% by weight of a daughter phase, there would be a one-ton crystal; precipitation of just 1 ppm would yield a 200 g crystal.

OPTICAL PHASE IDENTIFICATION CRITERIA FOR SOLIDS AT ROOM TEMPERATURE

Crystal Forms

Over 160 years ago the early mineralogists reported “squares” (i.e., cubes) in many fluid inclusions, which have since been shown to be generally NaCl, and only rarely KCl. For unknown reasons, the octahedral form, e.g., in Colombian emerald (Ref. 2, Plate 2-3/4) is exceedingly rare. One sharp cubic crystal, also in an inclusion in Colombian emerald, developed small octahedral faces (similar to those in Figure 1) on slight warming and cooling; since this is an eminently “closed” system, one would
expect this behavior to be reproducible, but even after repeated cycling, the octahedral faces have never appeared again.

More complicated crystal forms can sometimes be recognized, and even characterized as to probable crystal system, particularly when combined with optical properties, but as the microscope view one sees is effectively a two-dimensional projection of the crystal, at an arbitrary and unknown angle, the true angles between the faces seen here in profile are available only through use of a universal stage. In addition, the relationship of crystal faces and edges above and below the plane of focus is similarly obscure.

Crystal Habit

More often, only the general habit of the phase can be recognized—prismatic, platy, acicular, rounded, etc. (Figure 1)—and too frequently the "identification" of a given daughter mineral is based on too few parameters. Thus the discovery and unambiguous verification of fibrous, radial crystals of dawsonite, NaAl(CO3)(OH)2, by Coveney and Kelly (12) was followed by many other published reports of "dawsonite" or "dawsonite(?)", some of which were based on fibrous radial crystal habit, without recourse to birefringence, extinction angles, optical elongation, or even the general chemical nature of the system.

Apparent Birefringence

Although usually referred to carelessly as "birefringence", the interference color (retardation) shown by an anisotropic daughter mineral is one of the most easily seen and commonly reported optical characteristics. Determining true mineral birefringence from these interference colors is surprisingly difficult. Not only are the crystals randomly oriented, but they are of essentially unknown thickness. An apparently equant or rounded grain can be assumed to have approximately the same third dimension. Elongated grains present greater ambiguity. Unless there is independent evidence of platy shapes, perhaps the safest procedure is to assume the third dimension is about equal to the smaller of the two visible ones. The randomness of orientation introduces new problems. One must select, from a large number of examples of the same (but are they really the same?)
daughter phase, that one which shows maximum interference color for a given (assumed) thickness. Determining the interference order of small, rounded, high-index, high-birefringence grains is also difficult at times, even with careful use of the quartz wedge.

All of the above must be done with the host mineral at extinction. Even normally isotropic host minerals such as fluorite, halite, and sphalerite have so much “anomalous” birefringence in the thick plates used in fluid inclusion studies that recognition of low birefringence in a daughter crystal may require very careful use of the first-order red plate. Reflection polarization at the edge of high-index grains can also yield spurious data. Inclusions in anisotropic host minerals must be studied with the host at extinction, and rhombohedral carbonate hosts such as calcite should always be studied using the ordinary ray of the host, for several reasons (Ref. 3, p. 94).

Sometimes the host mineral plate is highly birefringent and polycrystalline and hence cannot be put at extinction. Low birefringence in a daughter phase cannot be recognized in such a case, but intermediate birefringence can usually be identified by the way the daughter mineral modifies the interference color of the immediately surrounding host. High birefringence daughter phases are also easily recognized by the large change in relief against the fluid during rotation with only the polarizer in place; this procedure is applicable even with minute daughter crystals.

Extinction Angles and Elongation

If a daughter phase is prismatic, acicular or fibrous, the extinction angle relative to the axis of elongation is a basic property that can be highly important in identification but, in far too many studies, is simply not mentioned. Equally important, and similarly neglected, is the sign of elongation in those prismatic minerals that have parallel or small extinction angles. Parallel extinction in such minerals is as easy to recognize—with the host at extinction, a glance over a field of inclusions shows no elongated birefringent daughter crystals visible in the N-S or E-W position, only those in inclined positions. Adding the first order red plate shows the optical elongation. (Note, however, that if the intermediate index parallels the crystal elongation, some of the crystals may show positive elongation, and some
negative."

Inclined extinction measurements may require a statistical approach, since only a very few of the crystals are oriented to yield the maximum value, just as in the case of measuring birefringence described above. It would seem reasonable to present here a table listing the crystal habits and optical properties of the various identified daughter minerals, but since so many obviously pertinent and readily determined facts, such as extinction angles or sign of the elongation, are not given in the literature on daughter minerals, such a table is not feasible at this time.

Index of Refraction

The simplest evidence of the index of a daughter mineral is the appearance of "relief" against the water solution. Most daughter minerals have higher indices, but it should not be forgotten that some daughter phases have extremely low indices, well below that of the water solution (Ref. 2, p. J21). If a daughter crystal is in clean contact with the host mineral, the indices can be compared by the Becke line at the interface. Thus an exact match between an isotropic daughter crystal and a certain orientation of the host quartz establishes unambiguously that the crystal is NaCl, with n = 1.5443 (Ref. 2, Plate 2-5). No other known isotropic compound has that index.

A very rough estimate of the relative index of even submicrometer crystals relative to the surrounding liquid is made by an adaptation of the Becke line procedure. If the microscope is focused up very slightly, the centers of even very minute grains appear to brighten if they are higher in index than the liquid. Very high birefringence in sub-micrometer crystals are similarly detected, using just the lower polarizer, i.e., by noting relief as the stage is rotated.

Other Observations

A variety of other optical observations have been used in special cases (see references listed in the Introduction). Included here are natural color, color induced by radiation, pleochroism, dispersion, and, for opaque phases, shape (in silhouette), reflected light color, magnetism, and Curie point.
OPTICAL PHASE IDENTIFICATION CRITERIA FOR SOLIDS AT LOW OR HIGH TEMPERATURES

Low Temperatures

Phase identification at low temperatures is based mainly on laboratory studies of synthetic systems, since many of the phases formed are not to be found among natural minerals. The most common new phase is ice; numerous criteria are used to recognize ice (Ref. 2, p. 98), but the single most important one is the low index of refraction, less than that of water. As there are other low birefringence crystal phases with indices below water, an even more definitive criterion is the volume increase on freezing, indicated by a marked reduction in the bubble size (and the reverse on melting).

The two other most commonly formed phases in inclusions at low temperature are carbon dioxide hydrate (CO₂•5.75H₂O) and hydrohalite (NaCl•2H₂O). The first is sometimes exceedingly difficult to recognize as it is isotropic and has an index of refraction very close to the water solutions in which it forms. Even when invisible, its presence can be recognized by a series of criteria (Ref. 3, p. 99). Hydrohalite has high birefringence, and is frequently seen to form during cooling by reaction of the water solution with a preexisting daughter crystal of NaCl, or with the walls of inclusions hosted in halite. The reverse process, incongruent melting of hydrohalite to halite + liquid, occurs on warming. This test is definitive (e.g., KCl forms no such hydrate), and can be made on a daughter crystal as small as 10⁻¹² g. One difficulty is that hydrohalite is slow to nucleate and grow, as well as slow to melt. Adams and Gibson (13) showed that hydrohalite crystals could persist for as long as an hour at 4°C above their melting point.

The various cations in the water solution form crystalline hydrates on freezing. These may be well known simple hydrates of a single cation, such as antarcticite (CaCl₂•6H₂O) or bischofite (MgCl₂•6H₂O), but in these complex systems, many complex “double salts” may also form. These present several problems in identification, first, because the crystals from the original freezing are generally a fine grained mixture that is impossible to work with optically, and second, because data on many of the
possible phases are simply not available. In order to obtain larger single crystals of these various phases, the fine-grained mixture is recrystallized to coarser crystals by repeated thermal cycling about an appropriate temperature, in the freezing stage.

**High Temperature**

The behavior upon heating also provides useful information for identification. The most obvious example is the differentiation of a cube of NaCl from one of KCl. As a result of the direction of the field boundary between these two fields in the NaCl-KCl-H₂O system (14), on heating an inclusion containing the two daughter crystals, the KCl dissolves rapidly, at the same time that a small amount of NaCl actually crystallizes out (i.e., it has retrograde solubility in one temperature range). At higher temperatures, large differences in solubility between different daughter phases are readily apparent and useful to distinguish, e.g., between relatively soluble chlorides and relatively insoluble silicates. Just as at low temperatures, recrystallization at high temperatures—and dissolution of many of the smaller crystals—may greatly aid in the optical problems of identification of the remainder.

**THE RECOGNITION OF ARTIFACTS**

No discussion of the optical identification of the phases present in fluid inclusions would be complete without at least some reference to this nemesis of all new inclusionists, as well as many old hands (at least on occasion). A wide variety of spurious images and apparent or real optical artifacts are commonly seen; with experience, the microscopist soon learns to ignore all the more common types, but they can cause considerable confusion and wasted time when first encountered.

The most abundant artifacts are those related to sample preparation procedures. Thus some epoxies, during curing, precipitate minute globules of an immiscible, low-viscosity liquid phase, suspended in the hardened epoxy. Each of these globules, in turn, may have a small vapor bubble, rapidly bouncing around with the same random pseudo-Brownian movement as seen in all small natural fluid inclusions (15,16). A few of these artifacts scattered through the pores and cracks in an epoxy-
impregnated sample can cause a lot of trouble! Air bubbles in
the mounting and impregnating media are seldom misidenti-
fied, but are distracting and if numerous can make it difficult to
find real inclusions. Fluid inclusions at the top or bottom sur-
faces of the plate can become filled, or worse, partly filled, with
mounting media to yield odd “inclusions” that frequently mis-
lead. Dust or dirt on these surfaces also cause problems, and the
minute globules of skin oils, as a residue from the evaporation
of fingerprints, greatly resemble true oil inclusions.

One additional type of artifact from sample preparation has
caused large and, unfortunately, unknown amounts of misun-
derstanding. This is the irreversible damage to the inclusions by
elevated temperatures or rough treatment. This can cause unrec-
ognized stretching of inclusions in soft minerals formed at low
temperature, yielding erroneously high homogenization tem-
peratures, or decrepitation, yielding empty and hence apparent
“gas” inclusions. Heating during preparation can also dissolve
daughter phases that may not renuclate on cooling.

An entirely different type of artifact is the result of purely
optical phenomena. Thus a spherical bubble in an inclusion acts
as a negative lens that can bring into apparent focus an optical
stop in the substage, giving the appearance of a bubble within a
bubble, as is actually present in many CO₂ inclusions. The offset
double images from a highly birefringent host can be similarly
misleading, particularly when one is searching for faint menisci
between CO₂ liquid and vapor at high magnification. Partial or
total reflection at nearly vertical daughter crystal interfaces
within an inclusion can yield false “Becke lines” that are not
related to the relative indices of the adjacent phases. Similarly,
total reflection at an inclined, relatively flat interface (such as a
fracture or flat inclusion) has led to misinterpretation as inclu-
sions of an opaque phase.

Postscript

Made Easy” (38), provides a fitting admonition for all inclusion-
ists involved in the many problems of phase (and artifact) iden-
tification in fluid inclusions:

“Beware of determining and declaring your
Opinion suddenly on any Object; for Imagination often gets the Start of Judgement, and makes People believe they see Things, which better Observations will convince them could not possibly be seen: therefore assert nothing till after repeated Experiments and Examinations in all Lights and in all Positions.

When you employ the Microscope, shake off all Prejudice, nor harbour any favorite Opinion; for, if you do, 'tis not unlikely Fancy will betray you into Error, and make you think you see what you would wish to see.

Remember that Truth alone is the Matter you are in search after; and if you have been mistaken, let not Vanity seduce you to persist in your Mistake."

CONCLUSIONS

Although the use of simple optical procedures to identify the phases in fluid inclusions may seem prosaic in view of the many new high-technology procedures available today, the speed and low cost of microscopy more than compensate for the obviously severe shortcomings of low accuracy and possible ambiguity of the results of microscopy. These shortcomings are inherent in the nature of the samples that must be used, but in spite of these problems, microscopy is needed before any application of the new analytical methods, to establish the relationship of the inclusion to the geological process being investigated, and to provide approximate compositional limits to guide the later work.

ACKNOWLEDGMENTS

This paper profited from thoughtful reviews by R.J. Bodnar, H.E. Belkin, and A. Kozlowski. I also want to acknowledge the great contributions to optical crystallography made by Dr. F. Donald Bloss, to whom this series of papers is dedicated. It is an unfortunate but inescapable fact that the nature of fluid inclusion samples necessitates the imprecise, inaccurate, and ambiguous optical identification procedures described here, almost the exact antithesis of the elegant and precise optical procedures Bloss has described.
References


11. Roedder, Edwin, “Metastable Superheated Ice in Liquid-


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