Application of an improved crushing microscope stage to studies of the gases in fluid inclusions

Application of an Improved Crushing Microscope Stage to Studies of the Gases in Fluid Inclusions[1])

By *Edwin Roedder* (Washington, D.C.)*)

With 3 figures in the text

Abstract

Ever since DEICHA (1950) described the use of his crushing stage to detect the presence of gases under pressure in fluid inclusions, this technique (crushing a sample in oil between glass plates) has been applied in a variety of inclusion studies. Several new versions of Deicha's stage have been constructed; they are inexpensive, easy to use, and adaptable to a variety of situations. The devices consist, in essence, of a pair of metal plates, joined by a horizontal hinge pin at one end and a vertical screw at the other. The lower plate is heavy, to provide stability without clamping when placed on the stage of the microscope. The glass plates with sample are placed between the metal plates, and centered on a vertical viewing hole. Crushing force is applied by the screw. Automatic aligning and correction from simple rotary to partially translational movement of the glass plates is achieved by mounting the support for the lower plate on a round, segmented horizontal pivot pin, whose axis is parallel with the hinge axis. The axis of the pivot pin is interrupted where it crosses the optical axis. Ordinary glass microscope slides are used for most operations, so that loss from scratching or breaking will be of no concern.

The crushing technique permits the recognition of the presence of as little as 10^{-14} grams of noncondensable gases (less than a billion molecules). In this low range its use has placed some exceedingly low limits on the maximum rate of leakage of certain fluid inclusions, based on the complete absence of noncondensable gases. Its use has also placed extremely low limits on the maximum rate of diffusion of air through obsidian glass, both anhydrous and hydrated, at surface temperatures.

When the embedding oil is replaced with appropriate solvents or nonsolvents for specific expected gases (methane, CO_2, etc.), the technique permits some qualitative "analysis" of the gases evolved, and even the recognition of some mixtures of several gases. Its greatest usefulness lies in providing estimates of gas pressure at room temperature (permitting better extrapolations to that at the time of trapping), and in the ease with which useful data may be obtained on the many samples that are too small for quantitative analysis by more elegant methods such as mass spectrometry.

INTRODUCTION

The behavior of fluid inclusions when they are opened to the atmosphere has provided much geologically useful data on the gas pressures in them. DAVY (1822) drilled into inclusions in some quartz samples that were immersed in water, oil, or mercury, and reported that upon breaking in, the bubble collapsed very markedly, and the external fluid was drawn in. Other samples contained gas at pressures greater than one atmosphere, as it expanded into the surrounding liquid when the drill broke in. Similar experiments have been reported frequently in the literature on fluid inclusions, because they are very useful in placing some limits on the possible composition of the inclusion contents. Thus a normal "two-phase" inclusion contains a gas bubble in a liquid at room temperature, and generally consists of liquid water and a bubble of water vapor (a very low density gas, almost a vacuum, at 20 mm pressure). However, it could also consist of liquified gas such as ethane or CO_2 under high pressure, plus a bubble of gas under that pressure (70 atmospheres for CO_2). These two types can appear identical unless they are crushed, or a series of non-destructive tests is applied (ROEDDER, 1970).

Drilling or crushing has been widely used in the Soviet Union to extract the gases for microchemical analysis (for example, KALYUZHNYI, 1960; MASLOVA, 1958, 1961) but only on large inclusions or samples. DEICHA (1950) showed that by crushing a mineral grain in oil between glass plates on the stage of the microscope, the presence of gas under pressure in even minute inclusions could be detected by the sudden expansion of the gas to form bubbles in the viscous oil surrounding the grain[2]. The present report describes several new versions of Deicha's crushing stage, and their applications to a variety of geological problems.

CONSTRUCTION

The crushing stage is simply a device to press two glass plates together while observing a mineral grain in oil between them. As the mineral is commonly harder than glass (quartz, olivine, etc.), deep pits and cracks form which interfere with later viewing. For this reason the stage was designed to make use of expendable microscope slides.

The essential details of design are shown in Fig. 1[3]. The device consists of

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[2] A crushing stage based on DEICHA's design is manufactured by Microscopes Nachet, 17, Rue Saint Séverin, Paris Ve, France.

[3] While this paper was in preparation, a paper describing a somewhat similar device was found in the Russian ceramic literature (SLAVYANSKII and KRESTNIKOVA, 1953). The device uses two mated curved glass surfaces for crushing, the lower one concave upward, but has no horizontal pivot pin. MASLOVA (1958) and SHUGUROVA (1968) used versions of this device for opening large inclusions in small pieces of flat mineral plates, for microanalysis of the contents.

a pair of metal plates, hinged together at one end and forced together at the other by a knurled nut on a screw. The screw is pivoted on the base plate and fits into a notch in the end of the upper plate for ease in cleaning and assembly. A nylon washer (N) under the nut makes the action smooth. Before hardening, the upper plate (steel) is machined into a dish shape (D) about the vertical viewing hole to permit quick rotation of the microscope turret head from one objective to another as necessary. The two glass slides with the sample (S) are placed between the metal plates and centered over the viewing hole. The crushing stage is then placed on the stage of the microscope and the screw tightened slowly, applying increasing pressure on the mineral grains.

To avoid the necessity of clamping, the entire device is made heavy enough to stay in place by weight alone. If simple radial motion about the hinge pin were used to push the glass plates together, there would be a tendency for the plates to tip, particularly if several grains of different size were mounted. For this reason the support for the lower plate on the stage is equipped with a segmented, horizontal pivot pin. The axis of this pin parallels the hinge axis and crosses the optical axis of the microscope near the level of the sample. Movement about this axis automatically aligns the plates, correcting for various grain sizes in the sample, and in effect converts the simple rotary motion of the metal plates to partially translational movement. This pin actually consists of two co-linear segments, one on either side of the viewing hole, each with a locating pin for horizontal positioning. A small piece of rubber placed between the plates near the hinge prevents premature crushing of delicate grains.
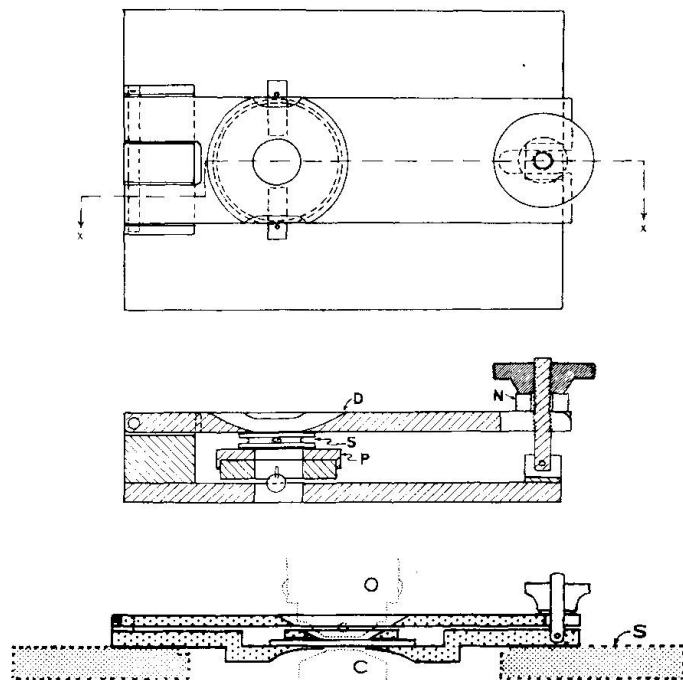

Fig. 1. Plan and section of crushing microscope stage (upper two diagrams) and section of modified version for crushing tiny grains at high magnifications (lower diagram).

For crushing very tiny grains a modified version of the crushing stage is needed to permit the use of condensers and objectives of very short working distance and high magnification. In principle it is very similar to the preceding version, but can be much lighter in construction (bottom diagram in fig. 1). Adequate illumination is very important, and as the high power condenser is generally designed to illuminate objects at a level just 1 mm (the thickness of a normal glass microscope slide) above the microscope stage surface (S), the lower plate of this "microcrusher" is stepped down in the center to place the slide at this level. (The central plate on the microscope stage is removed before placing the instrument.) The lower side of the viewing hole must be beveled strongly to permit the approach of the condenser (C). The pivot pin assembly for automatic aligning is inverted to above the sample, and made very thin and beveled strongly to permit the use of a short focus objective (0). Ordinary coverglases are adequate.

Another modification, designed for crushing larger crystals up to about 1 cm, perhaps should be called a "macrocrusher". It consists of an open steel cup with a small central viewing hole in the flat bottom which sits on the stage of the microscope. Surrounding this hole is an annular groove in the inside bottom surface, into which is placed a flexible plastic O-ring for sealing. A heavy glass disk (≈ 7 mm thick) is placed over the O-ring and viewing hole and the cup filled with an oil such as silicone or even motor oil. The sample is placed on this disk and another thick disk, mounted in a horizontal metal plate, is placed on top. The oil level is made barely high enough to contact the lower surface of the upper disk. The metal plate slips down over two vertical threaded rods welded to the bottom of the cup, one on either side of the viewing hole. Pressure is applied by thumb screws on these rods. Light compression springs on the rods keep the plate from falling. The space between the nearest approach of the wings on the thumb screws must be adequate for the microscope objective. This version has been particularly useful where only a very few inclusions were available in small crystals with relatively clear faces (for example, ROEDDER, 1963, p. 190). It is limited, of course, to inclusions large enough to be viewed with the rather long optical path through the thick plates. As the plates are only roughly circular, and are cut from scrap pieces of broken plate glass, they are inexpensive and may be discarded as soon as scratched or cracked.

USE

To use the crushing microscope stage, the sample grain or grains are placed on an ordinary glass microscope slide (about 1 mm thick) with an appropriate mounting fluid (discussed below), and generally covered with a half of another microscope slide as a substitute for a coverglass. Care must be used to avoid trapping air bubbles in the mount. The slide is then placed over the viewing

hole with the grain centered and pressure applied gradually with the screw. Some grains break with a series of subparallel fractures, forming in sequence from the outside inward. This behavior is particularly suitable for inclusion studies, as it permits accurate observations of the phenomena at the instant that the first crack reaches the inclusion.

Other grains may build up stress and yield with what appears (through the microscope) to be considerable violence[4]). Even though a part of the grain may fly out of the field of view (for example, see first two frames of sequential photograph series, fig. 24, in ROEDDER, 1965), the main part of the grain usually stays in place. Care must be used in the interpretation of bubbles left in the liquid whenever such violent movement has occurred, as the velocities may be high enough to cause cavitation of the liquid, and as this liquid is generally air saturated, the resulting exsolved air bubbles have a finite lifetime and may seem to come from the inclusions. Also, if the grain is near to the edge of the mount, so that an air-oil meniscus is close, air bubbles may be sucked in, causing ambiguity.

As a result of the relatively large unsupported glass area of the viewing hole, the glass slides do occasionally break. Inconvenience from this breaking can be avoided if the spacer plate (P) is removed and an extra plate of glass used beneath the slide. This prevents breaking downward and contamination of the substage with broken glass and oil. If the upper glass breaks, oil may be splattered on the objective lens. To avoid this a thin circular glass plate (coverglass) is placed over the viewing hole, on top of the upper plate. Breakage can be minimized if the viewing hole is made as small as convenient for the particular purpose, and the glass plates are as thick as the optics and grain size permit. Scraps of various thicknesses of window and plate glass give considerable leeway. As the breaking of grains may cause sudden movements of the glass plates toward each other, droplets of the mounting oil may be splattered sideways. These are caught by a loop of soft foam plastic or tissue placed around the glass plates after the first contact with a grain is made.

If very tiny inclusions are to be studied, high magnification is needed, precluding the use of a 1 mm thick "coverglass". When this is the case, only a single very tiny grain is used, and a coverglass of 0.3 mm thickness (usually sold as poor quality, "grade 3") suffices for crushing. A very small upper viewing hole is necessary; it can be achieved by an auxiliary disk, clipped onto the upper plate. Better still, the modified "microcrusher" version (Fig. 1, bottom) may be used.

When there are a number of grains in the same mount, they usually break

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4) After an hour or so of use of the crushing stage, the operator may notice a peculiar soreness of the jaw muscles. This is a perfectly normal symptom from the almost involuntary clenching of the teeth in anticipation while slowly tightening the screw.

in sequence and rarely simultaneously, as the largest one supports practically all of the pressure until it breaks. It is obviously desirable for the observer's eyes to be focused on the one that is going to break next, and it is frustrating to guess wrong time after time. Two procedures help in eliminating this guess-work. First, as the plates gradually move together, the viscous oil, as it is squeezed out, carries with it any grains not actually being squeezed, so these moving grains may be ignored. Second, if hard minerals such as olivine or quartz are being crushed, and the optics permit it, it is convenient to remove the spacing plate and mount the grains on a stack of two slides rather than one. Faint transmission interference color fringes will then appear around the next grain to crack, as the distortion of the glass locally reduces the air gap between the two plates.

When very soft or small grains are to be crushed, a much simpler procedure is adequate and very much more rapid. A needle point gently placed at the correct point on the coverglass will crush the grain and yet not interfere with the viewing. Low quality, thick coverglasses are adequate. Even hard minerals such as olivine may be crushed by using a piece of microscope slide as a cover and a dentist's steel probe to apply pressure.

In the crushing of tiny grains of pumice, detailed in the next section, it was necessary to watch the behavior of many grains. Even the needle technique was tiresome and time-consuming. To avoid the problems of the ineptness of the fingers at this scale of operation, as well as the trouble and expense of a micro-manipulator, I found that the needle procedure could be streamlined further. A uniform sample mount was made with a fairly dense distribution of grains, and a large but very thin, flexible ("grade 0", or better, "grade 00", at 0.090 mm) coverglass was used. This thin coverglass bends readily under the needle and hence crushes only the grains in the immediate vicinity of the needle point. The needle is braced against the objective, and tipped down until it just starts to crush grains in the center of the field, and is held in that position while the other hand is used to move the mechanical stage slowly. The viscous drag of the mount carries the coverglass along with the slide under the needle. By this simple expedient one can watch hundreds of grains marching dutifully by the point near the needle where they are crushed in sequence, right at the point of focus of the observer's eyes.

The use of the "macrocrusher" is similar in general to that of the other microscope crushing stage. The oil must be poured slowly to avoid bubbles. An oil nearly matching the index of refraction of the crystal is best, in an amount such that the crystal will be just covered. The crystal is then placed on the lower glass disk. Care should be used here also to avoid bubbles, but some may form anyway around irregularities in the crystal. These cause no trouble if the crystal is first inserted into the liquid off to the side of the cup, and adhering bubbles brushed away there, before moving it laterally to the glass plate.

In both modifications, when a single relatively large grain is to be crushed, there is an annoying tendency for the upper glass (either thin coverglass or plate glass) to tip and pull all the mounting fluid away from the grain, forming bubbles. This can be avoided by placing three tiny lumps of plasticine (a clay-oil paste) in a triangle to support the plate temporarily. Bubbles can also be avoided by mounting the grain in a very small drop of oil on the lower plate, and wetting the center of the upper plate with another small drop before lowering it. After contact and the application of slight pressure, a plastic squeeze bottle with a very thin outlet tip is used to add more oil beside the grain. Care must be used to squeeze to fill the tip before inserting it, or bubbles will be injected beside the crystal where they are very difficult to remove. Similarly the whole device can be placed vertically and the oil with its bubbles, unclamped fragments, and loose debris from partial crushing flushed out and replaced with clean oil for further crushing of a given grain.

GEOLOGICAL APPLICATIONS

1. Leakage of ground water or air into inclusions

Most fluid inclusions contain a water solution of various relatively non-volatile salts, and essentially no gases. As a result the pressures in them at surface temperatures are very much less than atmospheric, and if partial leakage occurs, it should be inward. The rocks containing such fluid inclusions have been immersed in ground water for geologic time, at pressures of approximately 100 atmospheres per kilometer of depth (and in air at one atmosphere since they were brought to the surface), yet when the inclusions are examined on the crushing stage, each now contains a vapor bubble that is nearly a vacuum, and contains no noncondesable gases, proving that inward leakage under these conditions has been minor or nonexistent.

2. Diffusion of gas through rhyolitic glass into pumice vesicles

Pumice provides us with a special type of "fluid inclusion" – minute vesicles in glass, each of which contained at the time of eruption a gas at about one atmosphere pressure. On cooling to surface temperature, the bulk of this gas (mainly steam) condenses to form a very small amount of liquid water which then diffuses into the glass walls. When grains of relatively recent pumice (10,000 years or less) are crushed in oil, the tiny, apparently empty vesicles are found to fall into two categories: 1. Some release a gas bubble of the same volume as the original vesicle when the embedding oil enters the vesicle; 2. others fill up completely with oil almost instantaneously (Fig. 2). It is thus apparent that those containing gas at atmospheric pressure have simply leaked, and hence

are full of air, but the others have maintained their original vacuum. This maintenance of a vacuum for geologic time is rather surprising when it is realized that the average wall thickness involved, between the vesicle and atmospheric pressure, is only a few to a few tens of micrometers. This is caused by the fact that many long tubular vesicles and cracks in pumice act as channels to bring atmospheric pressure throughout the grains. It should be remembered also that floating pumice eventually becomes waterlogged and sinks. Only the isolated vesicle, completely surrounded by unfractured glass walls, maintains a vacuum. Although no actual diffusion rates for atmospheric gases through volcanic glass have been determined, it is obvious that these rates must be very low.

In order to place some limits on these rates, we must know the sensitivity of the crushing procedure. If noncondensable gases such as air are present in an inclusion, the smallest amount that can be detected by the crushing procedure is that which will form a visible bubble in the mounting medium that enters on crushing. With the light microscope it is easy to resolve bubbles of one half micrometer diameter in small fluid inclusions. However, bubbles this size are never seen in free liquids. The difference is caused by the increase in solubility of gases in liquids with increase in pressure, and the increase in internal pressure in a bubble with decrease in bubble size, due to surface tension. The internal pressure from surface tension alone in a bubble two micrometers in diameter is about one atmosphere. Below a diameter of about two micrometers, this (geometrical) increase in pressure with decreasing size becomes so great that once a bubble is reduced to that size, further reduction, and complete solution in the liquid, takes place suddenly. This can be observed easily under the microscope by watching a gas bubble dissolve in a liquid. The size reduces gradually to about two micrometers, after which the bubble "blinks out" so suddenly that the process appears to be instantaneous. Thus the limit on the sensitivity of

Fig. 2. Crushing of relatively large vacuum vesicles in a pumice known to be about 3 million years old.

Frames 1 and 2 show fragments of pumice mounted in a nearly matching index liquid, on the crushing stage. The dark elongated areas are vacuum vesicles containing only water vapor and a trace of liquid water (in the pointed ends). Frames 3 and 4 show these same grains after crushing. The mounting oil has filled the cavities completely and instantly, leaving just the tiny fillets of water visible (arrows). The larger dark areas in 3 and 4 are other, unopened vesicles. Other, smaller vesicles in this sample contained a higher ratio of liquid water to vapor. Sample ER 64–49, Jemez Mountains, New Mexico.

Fig. 3. Crushing of small vacuum vesicles in a pumice known to be about 10 million years old.

A series of tubular vesicles, each containing a centrally located water vapor bubble (dark) in liquid water. Several cracks have transected a part of these inclusions, and permitted the mounting index liquid, which matches the glass, to replace the water vapor bubbles, yielding a series of odd crescent-shaped menisci of water against oil (arrows). Sample ER 62–64, Nevada Test Site, Nevada.
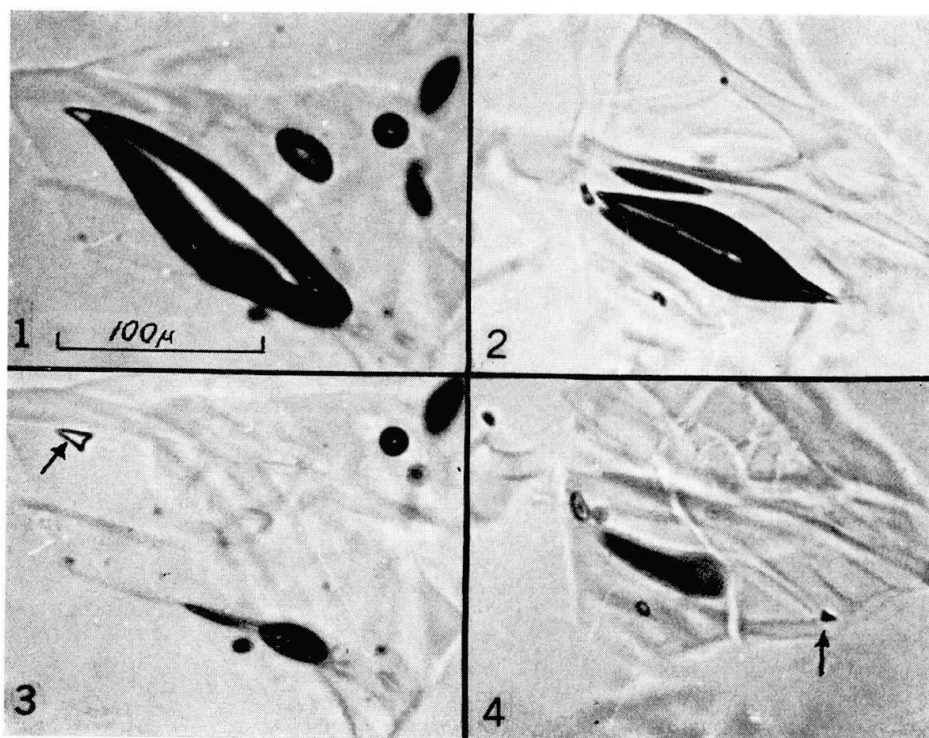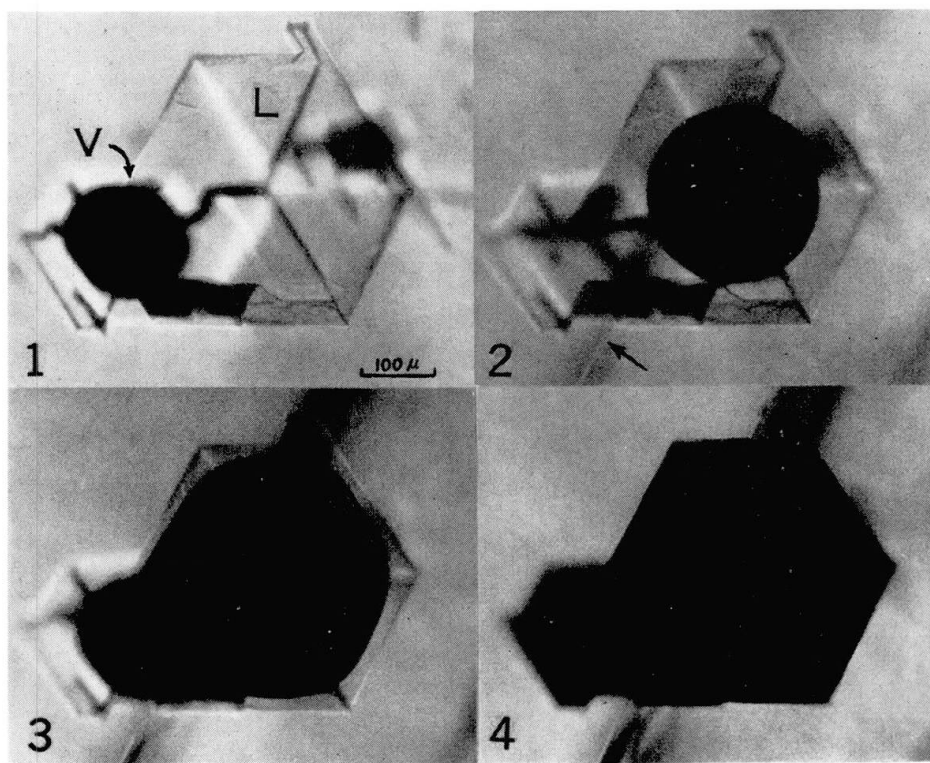
Plain transmitted light

Fig. 2.
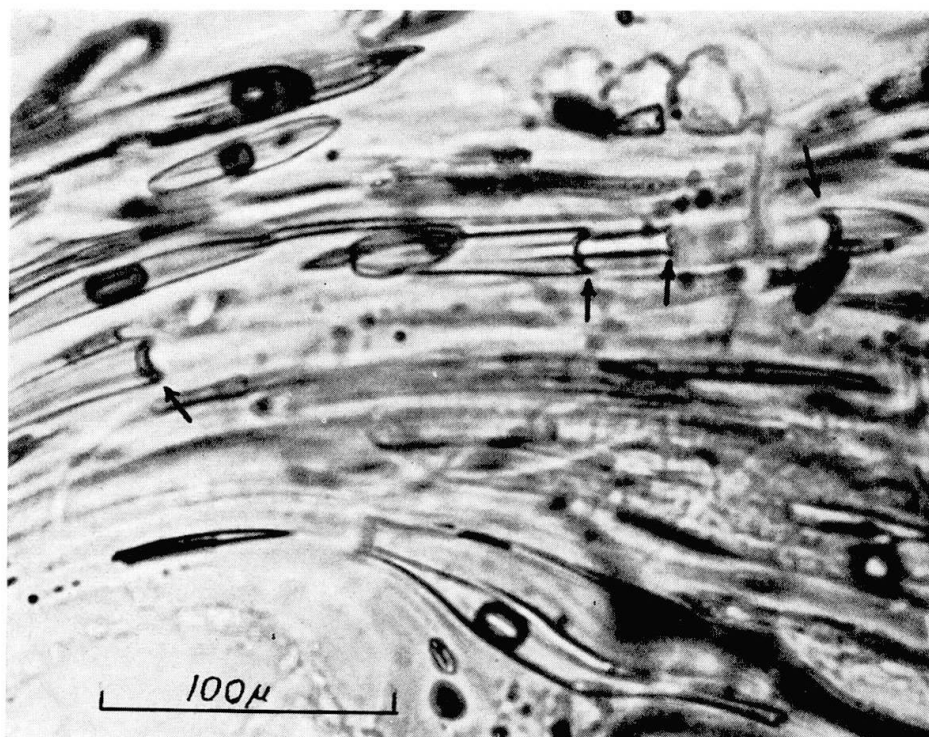
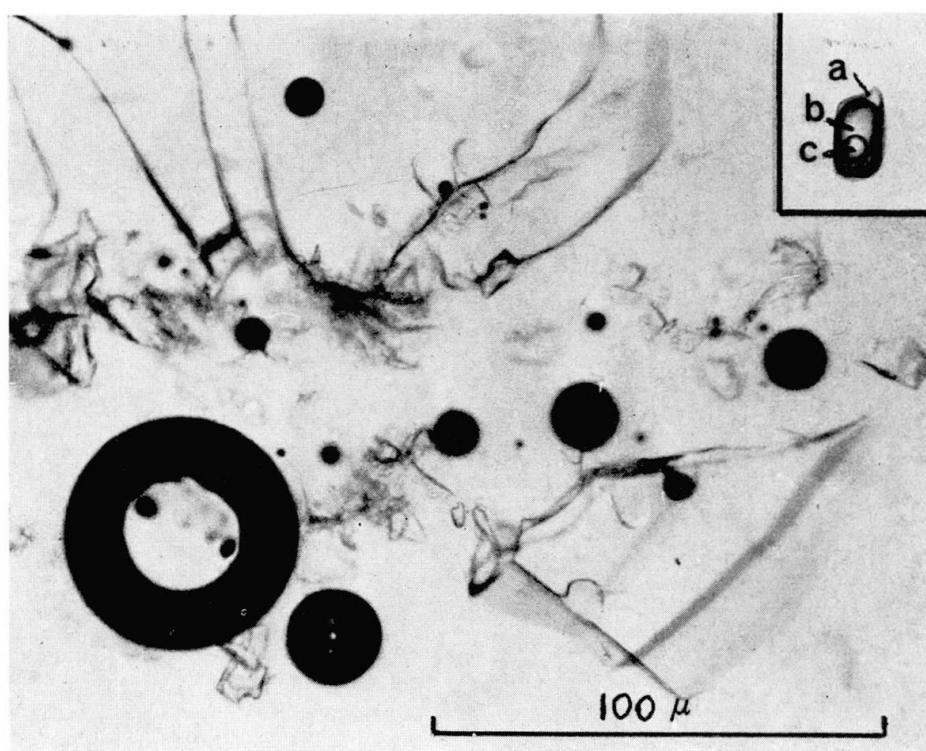Plain transmitted light

Fig. 3.

Plain transmitted light

Fig. 4.

Plain transmitted light

Fig. 5.

Plain transmitted light

Fig. 6.

Fig. 4. Crushing of primary negative crystal inclusion in fluorite, containing brine saturated with methane under pressure.

Frame 1 shows the inclusion before crushing. The brine (L) contains approximately 28 weight percent salts. The dark vapor bubble (V) is slightly below the plane of focus. In frame 2, a crack (arrow) has intersected the inclusion and the bubble is enlarging rapidly. Frames 3 and 4, taken just seconds after 2, show the expulsion of the last of the brine. Shortly after frame 4 was taken, the gas in the inclusion contacted the mounting medium (kerosene), and kerosene was sucked in to fill the inclusion cavity quickly and completely as the gas dissolved in it. The whole sequence of events usually occurs in less than a second; in this example the crack was apparently very tight. Sample ER 59–6, Hill mine, Cave-in-Rock, Illinois (southern Illinois zinc-fluorite district).

Fig. 5. Crushing of primary oil inclusions in fluorite.

The three oil inclusions in frame 1 (A, B, and C) each contains a dark vapor bubble, and a birefringent crystal. In A this crystal projects into the wall to the right. In 2, crushing in water has opened inclusions A and B and yielded the large bubbles. Frame 3 shows the remains of the largest of these bubbles and unopened inclusion C, just before a new crack released the gas pressure in it, shown in frame 4. Each such oil inclusion shows an expansion of approximately 15- to 30-fold. Same sample as in Fig. 4.

Fig. 6. Crushing of pseudosecondary inclusion from pegmatitic smoky quartz, containing liquid CO_2.

The inclusion before crushing is shown in the inset. It consists of aqueous solution of moderate salinity (a), liquid CO_2 (b), and a bubble of CO_2 gas (c). The main photograph shows the broken fragments and gas bubbles after crushing in a mounting medium of chlorinated hydrocarbon oil somewhat higher in index of refraction than quartz. Both photographs are at same magnification. The volume expansion, if assumed to be only from the liquid CO_2, is 150–200 fold. The difference between this and the predicted 300-fold expansion may well be due to solution in the mounting oil in the time before the photograph was taken (15 seconds). Sample ER 61–28a, Volta Bala, Teófilo Otoni, Minas Gerais, Brazil.
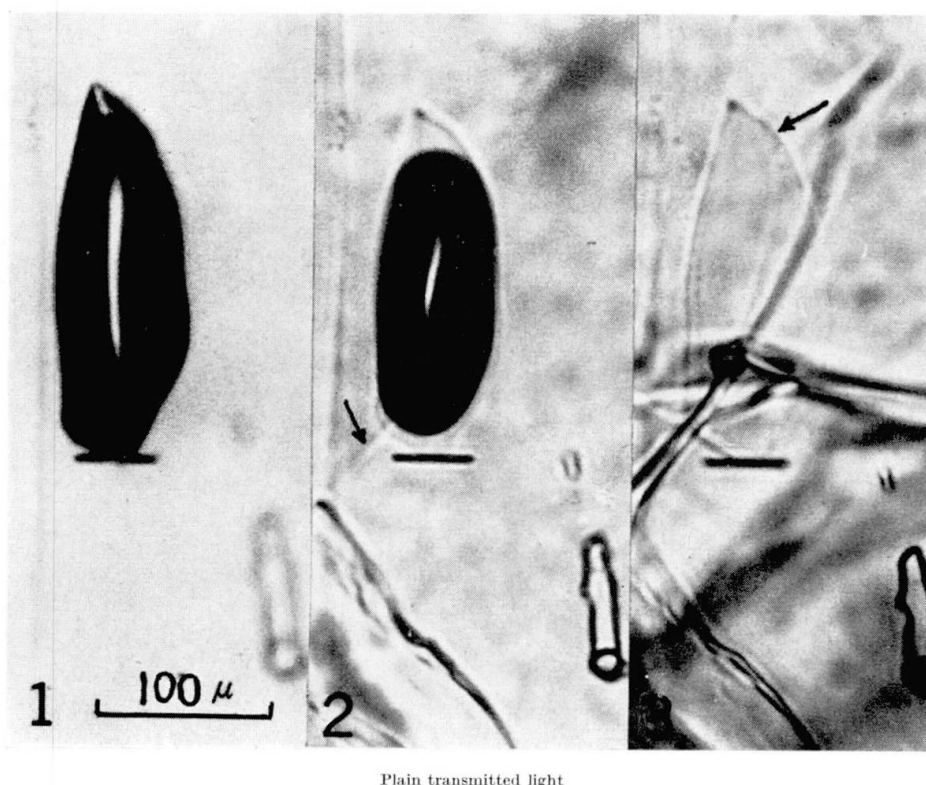
Plain transmitted light

Fig. 7. Crushing of "empty" (steam) inclusion in quartz.

This sample, from the Amethyst 5 level, OH vein, Creede, Colorado, apparently grew in a boiling solution, as it contains many large apparently empty inclusions (trapped steam bubbles), as well as normal two-phase inclusions homogenizing at about 200°C (one of these is visible at lower right). Frame 1, before crushing. Frame 2, just after a very tiny fracture (arrow) let in a little of the mounting medium (1.55 index liquid). Frame 3, after a slight additional crushing, which opened several larger cracks and filled the inclusion almost instantly, leaving a small bubble (much less than 1 volume percent), which then dissolved in a few seconds, before frame 3 was taken. Only a faint trace of the inclusion outline is visible (arrow). The small dark spot at the intersection of the two cracks is crushed mineral and not a bubble. Sample ER 57-25.

the crushing procedure is the amount of gas in a two-micrometer bubble at one atmosphere. This amount of gas ($4 \mu m^3$), if it consists of nitrogen at one atmosphere, weighs 5×10^{-15} g and contains only about 100 million gas molecules. As the surface of the vesicles being considered is of the order of $10^3 \mu m^2$, these data would indicate that the rate of diffusion of atmospheric nitrogen through the glass walls was less than 300,000 molecules/cm²/sec.

Several unknowns seriously limit the precision of this estimate. As the mounting medium flows in, some part of the gas present in the inclusion may dissolve in it. However, the mounting medium is generally saturated with air at one atmosphere, and might even be expected to *exsolve* some gas as it flows into the vacuum environment of the vesicle. If the mounting medium flows in suddenly (as generally occurs), there are two additional effects. The sudden compression of the gas in the vesicle causes transient but high temperatures. Working in the opposite direction, however, is the similarly transient but high pressures

existing at the center of a collapsing bubble. Both of these effects have been studied extensively in connection with the problem of negative pressures and cavitation in liquids (HICKLING, 1965), but the unknowns involved in fluid inclusion studies are too large to permit quantification. In any case, it is evident that the thin volcanic glass walls of pumice vesicles do hold a vacuum well.

An additional, useful facet of this study of pumice vesicles is the discovery that they may be used to determine the age of the pumice. The method is crude and only semiquantitative at best, but, as it yields a "dating" at the cost of only a few minutes of time, it is useful (ROEDDER and SMITH, 1964). It is mentioned here briefly only because the crushing technique is an integral part.

On eruption, most rhyolitic glass is almost completely anhydrous. At surface temperatures, however, water from the atmosphere or ground diffuses into the glass to form a hydrated glass with about 3 percent water. The network of interconnecting channels and fractures through pumice results in its complete hydration after about 10,000 years. The unopened vesicles, however, still contain only water vapor. So liquid water gradually accumulates in them, diffusing through from one atmosphere pressure outside toward 20 mm pressure inside. Stages in this slow process are visible under the microscope. First only the very tiny pointed ends of large vesicles show a fillet of liquid water (Fig. 2). This generally occurs at about 10^4 years. Within the interval 10^4–10^6 years the smallest vesicles develop about 10 percent liquid water, and beyond 10^6 years the smallest vesicles become more nearly filled with water (Fig. 3), and are frequently full, with no vapor bubble.

The crushing procedure is necessary to prove that any given partially filled vesicle is actually sealed and that it is not merely filled with ground water and air at one atmosphere from leakage. Crushing also permits recognition of the difference between sealed vesicles and air-filled vesicles that have become partially filled with mounting oil by capillarity.

It is interesting to note also that vesicles in pumices known to be 10^6–10^7 years old still have held their vacuum, as the vapor bubbles in the liquid water within the vesicles collapse instantly and completely on crushing in oil (Fig. 3). Neglecting the solubility of air in water, this fact reduces the maximum diffusion rate for atmospheric gases calculated above by another two or three orders of magnitude.

3. Presence and significance of noncondensable gases in inclusions of ore fluids

There are numerous reasons why it is desirable to know whether any given ore fluids contained noncondensable gases. The pressure in an inclusion in an ore mineral at the temperature of homogenization is the minimum pressure for formation of the ore deposti. YPMA (1965) has described a pressure balance and

pressurized crushing stage with which this minimum pressure may be experimentally measured. In the absence of such apparatus, it is necessary to calculate the pressure from the salinity and homogenization temperature of the inclusions using data on the vapor pressure of known solutions. This estimate must be increased, however, if gases are present, and the pressure of such gases in an inclusion at surface temperature is generally a minimum pressure of ore formation. If gases are present at high pressure even at room temperature, they can add very significantly to the pressure at the conditions of ore formation.

The presence of noncondensable gases in inclusions in ore minerals increases the likelihood that the ore-forming fluids might have boiled at higher levels during their ascent, and hence suggests the possibility of bonanza-type ore bodies at those levels from the drastic chemical changes implicit in boiling of most multicomponent solutions.

Gases under pressure have been reported in fluid inclusions from numerous ore deposits (ROEDDER, 1970). Thus crushing studies show that in many of the Mississippi Valley ore deposits, gases under very appreciable pressure are present in both the oil and the brine inclusions. When a crack reaches a brine inclusion, the bubble, which normally occupies only about five volume percent, almost instantly expands to approximately fill the inclusions, driving the liquid out the crack. In Fig. 4 the expansion was slow, presumably because the crack was tiny, and thus permitted serial photomicrographs[5]). The liquid brine wets the walls of the inclusion and crack, and so even if the crack only touches one corner, all but a film of liquid is forced out. If this expansion represents strictly the expansion of the original vapor bubble itself, the 20-fold volume change would correspond to approximately 20 atmospheres pressure. The true pressure in the bubble was undoubtedly lower than this, as the presence of additional gas in solution in the brine provides a reservoir for further expansion. If we assume the gas to be methane (see below) the solubility in these brines at geologically reasonable pressures is probably about one volume of gas per volume of liquid, and because distances for diffusion are small, only 10-100 micrometers, degassing of the brine could occur rapidly. Thus the entire apparent expansion of the gas bubble could be accomplished solely from this liquid reservoir. In addition to the implicit pressures at the time of formation, this methane also may be of some chemical significance. BARTON (1967) has proposed that the metals in these ore deposits were transported in a fluid in which most of the sulfur was present as sulfate; slow reduction of the sulfate by methane or other reductants in the nonequilibrium solution would avoid

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[5]) It must be mentioned that the photomicrographs are also atypical in another sense. In crushing, the operator must be prepared for a fairly high percentage of disappointments, in that many grains develop fractures that obscure the inclusion before it is opened, and even more frequently, the grains merely withstand the pressure build-up until they suddenly collapse into a useless pile of rubble and bubbles of unknown source.

the problem of simultaneous transport of sulfide and metal in the same fluid. The known solubility of methane alone in such brines under geologically reasonable conditions is adequate to provide a reducing capacity to form about two grams of $S^=$ per liter of solution (DUFFY and others, 1961).

Along with the brine inclusions, the Mississippi Valley-type deposits frequently contain primary inclusions of oil, representing the trapping of immiscible globules of oil floating in the ore fluids. When these are crushed in kerosene, the absorption of the evolved gas bubbles is so rapid that their former presence is only registered on the retina as a latent image – a circular black image that is gone before the eye can really see it. Crushing in water, however, shows evolution of a gas volume of 10 to 100 times the volume of the oil (Fig. 5). The amount of expansion is apparently influenced strongly by the degree of degradation of the original homogeneous yellow oil to dark bitumens (?) and a colorless, highly volatile liquid (ROEDDER, 1962, p. 40). The high solubility in kerosene, the low solubility in water, the general predominance of methane in natural gases, the thermodynamic calculations of BARTON (1967), and the evidence obtained during vacuum analyses of the presence of small amounts of a gas not condensable at $- 194°$ C, all indicate this gas is probably methane, in both the brine and the oil inclusions.

Many ore deposits form from fluids so rich in gases that they form a separate liquid phase on cooling. This liquid is most commonly found to be CO_2, particularly in skarn and other high temperature assemblages, but also in some gold quartz veins (ROEDDER, 1970). Liquid CO_2 is very common in the inclusions in the quasi-pegmatitic quartz crystal deposits from many areas of the world (Fig. 6). The crushing procedure provides a verification of the identification of liquid CO_2. If inclusions of regular shape are found, it is possible to estimate the approximate volume of liquified gas present. If the sample is then crushed in a fluid that is not a solvent for the gas, the diameter of the bubble or bubbles may be measured and the volume expansion calculated. As all gases are soluble to some extent in every liquid, it is best to photograph the view immediately after crushing. This is particularly important if the expansion has been violent, yielding many tiny bubbles with much surface.

As the various processes of origin of ore-forming fluids generally tend to concentrate gases in these fluids, their known *absence* in fluid inclusions from some ore deposits may also have geological significance. One of the most likely possibilities is that those particular ore fluids have boiled, and hence have been effectively purged of such gases.

Thus when inclusions are crushed from those environments where boiling seems to have occurred, very little or no noncondensable gases are found. At Creede, Colorado, an epithermal lead-zinc-silver vein shows some field relations that suggest the fluids may have boiled. When normal two-phase liquid plus vapor inclusions are crushed, the bubble collapses completely, or almost com-

pletely, indicating very little noncondensable gas. Similarly, large apparently
empty primary inclusions (Fig. 7) from the top level in the mine (presumably
formed by the trapping of steam bubbles) fill completely or almost completely
on opening. The noncondensable gas in them totals well under one volume
percent.

4. Composition of the gases in fluid inclusions

Although the crushing procedure can only give crude information on the
quantity and nature of the gases evolved from any inclusion, it is possible to
obtain qualitative information by this procedure that would otherwise be very
difficult to obtain. Evidence on the composition of the evolved gases comes
mainly through the use of specific solvents, or nonsolvents, for expected gases.
The choice of a suitable mounting medium is difficult at best and must always
be a compromise. In preliminary work, optical visibility is most important,
and hence the use of a matching index liquid is the best choice. The ideal fluid
for simple detection of compressed gases should match the mineral in index of
refraction, be able to wet it, be easy to free of bubbles during mounting, be
transparent, and not absorb even very minute quantities of the expected gases.
The mass of the emitted gas bubble is usually so small (10^{-11} grams or less)
relative to the mass of the surrounding liquid that even a very low solubility
will permit the bubble to dissolve in a relatively few seconds. Thus the liquid
within a zone only one bubble radius in width from this nominal bubble weighs
4000 times as much as the gas, so a solubility of only 250 ppm would cause it to
dissolve completely, yet the average diffusion distance into this fluid would be
only 5 micrometers. Similarly, a solubility of only 1 ppm will permit a gas
bubble 4 μm in diameter to dissolve in the fluid within a radius of only 20 μm.

If CO_2 is expected, a water solution of barium chloride can be used. When
acidified, this is a rather poor solvent for CO_2; when alkaline, it dissolves CO_2
almost instantly. As mentioned above, kerosene is an excellent solvent for
methane and other organic gases. Other solvents are discussed by SHUGUROVA
(1968). Sphalerite is particularly difficult to work with, due to its very high
index. High index liquids are almost required here, even though the solubilities
of various gases in them are completely unknown[6]).

The process of solution of the bubble in the various fluids should be watched
carefully. If the diameter of the bubble is measured accurately at various times,

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[6]) In 1952, DEICHA published an ingenious technique for detecting the presence of
water in inclusions by decrepitation in a hot viscous silicone liquid in a transparent vessel,
permitting microscopy. This could be adapted to crushing as well, by first crushing in
room temperature silicone to observe the noncondensable gases, and then crushing
further at a temperature above the boiling point for the expected fluid salinity to observe
the steam bubbles.

and plotted against time since release, breaks in the slope of the plot may indicate the presence of several different gases. Bubbles from brine inclusions in Illinois fluorite similar to Fig. 4 show several such breaks, although the bulk of the absorption of the bubble follows a smooth curve, presumably indicating that one constituent dominates. The actual mechanism of solution (and hence shape of the plotted curve) of such a composite bubble is complicated, for as the concentration gradients are changing from diffusion, the radius of the bubble is also changing, and with it the width of the zone of liquid reached by diffusion, as well as the ratio of bubble surface to volume.

Most of the bubbles of CO_2 from crushing olivine crystals from the olivine nodules that are found in alkali basalts throughout the world (ROEDDER, 1965) are moderately soluble in 1.64 index oil (alpha monobromonaphthalene) down to a radius corresponding to about one percent of their original volume, after which the rate is much slower. Potassium-argon determinations on some of these nodules (FUNKHOUSER and NAUGHTON, 1968) yield high ages, so possibly this second gas is the "excess" argon.

All of the qualitative data obtained by crushing on the microscope stage can, in theory, be obtained in quantitative form by the more elegant method of opening the inclusions in a mass spectrometer. There are several factors in favor of crushing under the microscope, however. First, the quantity of gas released is generally orders of magnitude less than the amounts required by any but a very special gas mass spectrometer. The alternative of crushing larger samples in the mass spectrometer to get larger quantities of gas requires a homogeneity of sample that is rarely found. Second, the quantitative values obtained by a mass spectrometer are frequently subject to large uncertainties due to problems of calibration, loss by adsorption, and contamination from many sources, all problems that become larger as the sample size decreases. Third, the crushing procedure requires little or no expenditure for special equipment (microscopic study would be required in either procedure), and can be performed in a few minutes.

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