

## Synthetic fluid inclusions: Part XI. Notes on the application of synthetic fluid inclusions to high *P-T* experimental aqueous geochemistry

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### ABSTRACT

A new modification to the procedure for trapping synthetic fluid inclusions effectively allows the experimenter to control the timing of the onset of inclusion formation. The main advantage of the new procedure is that inclusion trapping may be postponed until the experimental pressure and temperature are stabilized and the fluid has equilibrated at *P* and *T* to a constant and uniform composition and density throughout the capsule. Thus, *PVTX* studies may be extended to higher temperatures in cases where premature fracture healing previously resulted in volumetric and compositional heterogeneity among inclusions from a single sample.

The new method has been found to improve significantly the precision of volumetric determinations in the CO<sub>2</sub>-H<sub>2</sub>O system at temperatures above 600 °C. Additionally, the technique shows promise in the investigation of high-salinity brines and for mixed-gas aqueous systems where fluid compositions may evolve through time. The ability to sample the fluid phase at *P* and *T* after equilibration at *P* and *T* may prove invaluable in speciation studies at high pressures and temperatures involving kinetically slow buffers or diffusional processes and in the experimental study of H<sub>2</sub>O-rock interactions.

### INTRODUCTION

In early studies of synthetic fluid inclusions, Roedder and Kopp (1975) and Shelton and Orville (1980) demonstrated that the density of H<sub>2</sub>O trapped in synthetic inclusions was the same as the density of H<sub>2</sub>O at the experimental conditions. Shaposhnikov and Ermakov (1978) reported the presence of daughter crystals of NaCl and KCl in inclusions trapped from concentrated brines and were able to detect CO<sub>2</sub> and HF in inclusions formed from solutions containing dissolved gases. Thus, it became apparent that synthetic inclusions represented a microscopic sample of the fluid phase present at the time of their formation—at least to a first approximation. The results of these early studies were welcomed by geoscientists because they validated the fundamental assumptions in fluid inclusion geothermobarometry: that natural inclusions contained fluids that were compositionally and volumetrically representative of the fluid phase(s) present at the time of their formation. Thus, pressure, temperature, and the composition of fluids present during a geologic event can be constrained using microthermometric measurements of natural fluid inclusions together with appropriate phase diagrams.

These early studies had another important implication: with prior knowledge of fluid composition and pressure and temperature conditions of inclusion growth, it should be possible to derive phase diagrams from appropriate microthermometric data. This was demonstrated by Sterner and Bodnar (1984), who presented a detailed pro-

cedure for routine synthesis of fluid inclusions and demonstrated the plausibility of deriving phase equilibria and volumetric properties for a number of geologically relevant fluid systems. Investigations by these and other workers have provided a wealth of information both about fluids at high pressures and temperatures (cf. Bethke et al., 1990; Bodnar and Sterner, 1985; Bodnar et al., 1985; Knight and Bodnar, 1989; Kotelnikova and Kotelnikov, 1988; Kotelnikov and Kotelnikova, 1990; Popp and Frantz, 1990; Sterner and Bodnar, 1986, 1991; Sterner et al., 1984, 1988; van den Kerkhof, 1988; Vanko et al., 1988; Zhang and Frantz, 1987, 1989) and about the properties of fluid inclusions themselves (cf. Bodnar et al., 1989; Boullier et al., 1989; Davis et al., 1990; Haynes et al., 1988; Pecher and Boullier, 1984; Pecher, 1981; Smith and Evans, 1984; Sterner and Bodnar, 1989).

An important advantage of the synthetic fluid inclusion technique over more conventional methods is the ability to obtain a sample of the fluid(s) present at equilibrium at *P* and *T* using relatively simple (and inexpensive) equipment. Major drawbacks of the technique have included somewhat reduced accuracy and difficulties in obtaining homogeneous samples of certain fluid compositions. The latter point arises, in part, because all fluid components, including gases, must normally be loaded into the experimental capsules as condensed phases. (Expandable gases require the use of solid or liquid compounds that decompose upon heating to yield the desired species.) Furthermore, in multicomponent fluids there is a tendency to begin to form inclusions before the components mix completely (Bodnar and Sterner, 1987).

Important modifications to the “synthetic fluid inclu-

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sion method" have evolved since the publication of the first paper in this series in 1984 and have significantly extended the applicability of the method. The primary objective of this communication is to discuss these advances in light of future applications of synthetic inclusions to geologic problems.

### BACKGROUND

Quartz has been used in the majority of fluid inclusion synthesis studies to date. The choice of quartz as the host material is logical for several reasons. First, quartz provides a direct analogue to natural systems; it is the most commonly studied mineral for fluid inclusions because of its widespread natural occurrence. Quartz has relatively low solubility in most aqueous fluid systems over much of geologically important *P-T* space so that its presence can usually be expected to have an insignificant effect on the fluid property being investigated; at the same time, the solubility of quartz in aqueous systems is high enough to allow the formation of fluid inclusions using a dissolution-precipitation mechanism. Quartz is stable over a wide range of pressures, temperatures, and fluid compositions. Finally, quartz is a relatively "strong" mineral in that inclusions in quartz will withstand substantial amounts of internal over- or under-pressure without stretching or shrinking (Bodnar et al., 1989; Sterner and Bodnar, 1989). Therefore, aside from the effects of thermal expansion and compressibility, which are easily taken into account, inclusions in quartz represent isochoric systems under normal experimental conditions.

While quartz remains the best candidate for general inclusion synthesis, other minerals may be better suited to some specific applications. Hydrocarbon-bearing fluid inclusions for microanalytical calibration have been synthesized in sylvite at low temperature by precipitating the salt from saturated solutions (Pironon, 1990); the anomalously high strength of olivine may provide an alternative to quartz in high-pressure *PVT* and *PTX* determinations, whereas the stretching and decrepitation behavior of inclusions in softer minerals like calcite and barite could be best characterized using synthetic inclusions of known fluid composition so that internal pressures could be accurately calculated. The list of host minerals that have been used in synthetic fluid inclusion studies is extensive: forsterite, enstatite and diopside (Johnson 1990; Johnson and Jenkins 1991); calcite, sphalerite, and pyrite (Parilov et al., 1990; Lefauchaux et al., 1972); sodium barium plagioclase (Kotelnikov et al., 1990); fluorite (Loredoperez and Garcia-Iglesias, 1984); halite (Davis et al., 1990); and scapolite and wollastonite (Kotelnikova and Kotelnikov, 1988; Kotelnikov and Kotelnikova, 1989).

Initial efforts in inclusion synthesis in quartz were directed toward the formation of primary inclusions in newly precipitated overgrowths on seed crystals. It soon became apparent that although it was indeed possible to form inclusions in overgrowths, from a practical standpoint it was preferable to form them as secondary inclusions along preexisting fractures as was done by Shelton

and Orville (1980). A single fracture plane parallel to the microscope stage could contain dozens of pancake-shaped secondary fluid inclusions, each with its shortest axis perpendicular to the stage—the orientation resulting in the best possible optical resolution. Primary fluid inclusions on the other hand were sparse, randomly distributed, and usually did not occur in such advantageous geometries.

With the above considerations in mind, attempts were made to minimize the effort involved in producing inclusions so that the emphasis could be placed on the goals of the particular study. The procedure given in Sterner and Bodnar (1984) was found to satisfy this requirement by consistently producing large numbers of easily measurable fluid inclusions over a broad range of experimental conditions. The significant feature of this procedure is that it involves the use of prefractured quartz cores produced by heating the quartz in an oven to 310 °C (not 350 °C as previously reported) and then rapidly quenching in cold distilled H<sub>2</sub>O. Fractures produced by this thermal fracturing technique (Fig. 1a) are superior in orientation and number to those resulting from mechanical fracturing (Shelton and Orville, 1980), and the procedure is considerably simpler.

The fractured quartz cores are sealed with an arc welder into noble-metal capsules along with fluid of the desired composition. The capsules are then placed in a hydrothermal pressure vessel at the desired *P-T* conditions for several days, allowing fluid inclusions to form along the fracture planes.

The above procedure is completely satisfactory for many synthetic fluid inclusion applications such as the preparation of low-salinity brine inclusions for use as calibration standards (Haynes et al., 1988; Mernagh and Wilde, 1989; Frantz et al., 1988) or in studies of properties of the inclusions themselves (Bodnar et al., 1989; Sterner and Bodnar, 1989). However, for the application of synthetic inclusions in phase equilibria or *PVT* studies, the most accurate control possible of fluid composition, density, temperature, and pressure is required. Toward this end, several modifications to the 1984 procedure have been devised and are reviewed in the following discussions.

### Compositional and volumetric heterogeneity

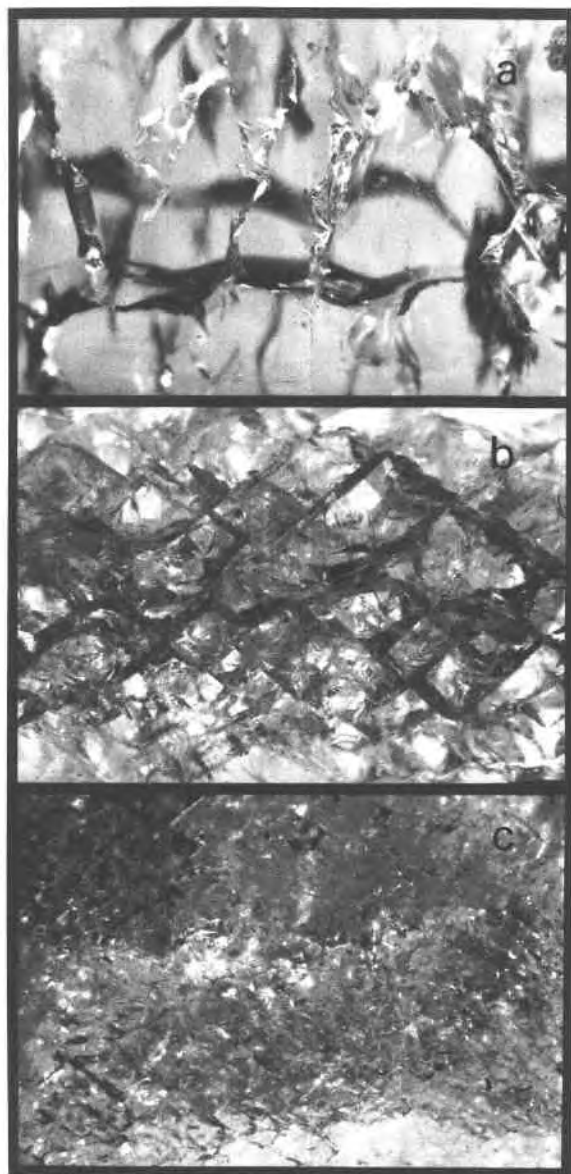
Under some circumstances, the procedure described by Sterner and Bodnar (1984) produces inclusions with variable compositions or densities within a single sample, even though the experimental *P-T* conditions are in the one-fluid phase field for the particular bulk composition. This situation arises when the inclusions begin to form (1) before the fluid components mix thoroughly in the capsule or (2) before the experimental pressure and temperature have been stabilized or (3) both. The first scenario occurs with bulk compositions that are immiscible at low temperatures (e.g., CO<sub>2</sub>-H<sub>2</sub>O mixtures and high-salinity brines). These compositions will remain unmixed in the capsule until heating has begun at the start of an experiment. Although mixing occurs as temperature in-

creases, inclusions may begin to form before the fluids completely homogenize, resulting in a compositionally heterogeneous sample.

A clear statement of this problem is presented in Bodnar and Sterner (1987). Compositionally homogeneous populations of inclusions may be prepared from undersaturated or moderately oversaturated brine solutions using the 1984 procedure. However, the components fail to mix uniformly before the inclusions begin to form if the bulk salinity is above approximately 40 wt%. Consequently, large ranges in composition result in inclusions within a single sample. This does not occur with undersaturated brines because they can be loaded as a single phase or will mix in the capsule prior to heating. The problem can be minimized by using a low synthesis temperature, but this is often impractical because of the fluid

phase relations or because high-temperature fluid properties are being sought.

A potential solution to the problem of premature fracture healing, presented by Bodnar and Sterner (1987), involves the use of unfractured quartz cores. Capsules are loaded as described above except that unfractured quartz is used; the capsules are allowed to stand in the cold seal vessel at the experimental  $P$  and  $T$  for sufficient time (days) to allow the fluid to homogenize. At some point, the experimental vessel is removed from the furnace and air quenched a few hundred degrees. The quartz is fractured as it passes rapidly through the  $\alpha$ - $\beta$  transition, which occurs at 573 °C at 1 bar and 25 °C higher with each successive kilobar of pressure. The vessel is then immediately reinserted into the furnace, and the temperature and pressure restablize in about 25 min. Inclusions are trapped along the newly formed fractures from the homogeneous fluid. This procedure effectively reduces the compositional heterogeneity of the resulting inclusions to a point at which other experimental uncertainties become more important (i.e., thermal gradients in the heating-freezing stage and thermocouple calibration). Unfortunately, the technique has several drawbacks. First, it applies only to experimental conditions within the  $\beta$  quartz field (the high-temperature side of the transition). Second, the fractures occur at 45° angles to the long axis of the quartz core (Fig. 1b), which makes them less than ideal for later microscopy using ordinary sample preparation procedures. Also, the large fractures penetrate most of the way through the quartz, often resulting in disintegration of the core during later sample preparation. Lastly, inclusions formed by this procedure are few and far between—one encounters lots of poorly healed fractures. Still, in some cases this approach may provide a viable solution to problems of inclusion heterogeneity.



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Fig. 1. Photomicrographs of typical fracture patterns produced in quartz by the different procedures described in the text. Each photograph is a side view of a 5-mm diameter quartz core with its axis oriented horizontally (i.e., the short dimension of each photo is  $\approx$  5 mm). The fracture orientations are apparently controlled only by the physical geometry of the quartz and are unrelated to its crystallographic orientation. (a) A typical fracture pattern resulting from thermal shock according to the 1984 procedure. The numerous fracture planes oriented perpendicular to the long axis of the core (vertical in the photo) provide ideal localities for inclusion synthesis and later microscopic observation following sample preparation. The pattern of fractures shown in (b) is typical of those formed as the core passes rapidly through the  $\alpha$ - $\beta$  phase transition of quartz. Inclusions occurring along fractures produced by this procedure are ill suited to routine microthermometric study owing to incomplete crack healing and problems in sample preparation. Typical fractures resulting from the IFS procedure are shown in (c). Note the much greater fracture density, smaller individual fractures, and apparent random orientation compared with a and b. Such fractures rarely penetrate the core deeper than 1.0–1.5 mm and therefore present no difficulties during later sample preparation.

Sterner et al. (1988), using prefractured quartz cores, found that by cycling the pressure several kilobars during the first few hours of an experiment the fractures could be held opened long enough for very high salinity fluids (ca. 90 wt% NaCl) to homogenize. This approach reduces compositional heterogeneity to a level comparable with other uncertainties while still yielding large numbers of measurable inclusions. However, the procedure frequently causes substantial volumetric heterogeneity; in experiments with high-salinity salt solutions, vapor bubble disappearance temperatures sometimes vary by as much as 100 °C within a single sample.

Volumetric heterogeneity can also arise in the absence of pressure cycling if, at sufficiently high temperatures (above  $\approx 600$  °C), inclusions start to form before the final  $P$ - $T$  conditions are reached and, therefore, before the density is stabilized. Under these circumstances, a substantial range in homogenization temperatures (from which inclusion densities are calculated) is also recorded. One possible solution is to attain the desired experimental conditions as rapidly as possible. This can be partially implemented by preheating furnaces and using small od pressure vessels (smaller thermal mass), but these procedures will not totally solve the problem. Also, the faster the desired experimental conditions are achieved, the less apt initially heterogeneous fluids are to mix completely before inclusion formation.

Zhang and Frantz (1987) overcame the problem of volumetric heterogeneity by using a rapid-quench design pressure vessel (Wellman, 1970; Frantz and Popp, 1979). In this approach, the pressure vessel is sufficiently long so that the hot end can be placed in the furnace and preheated to the desired temperature while the capsule resides at the cold end outside the furnace at a temperature near 25 °C. After the temperature stabilizes, the vessel is rapidly pressurized with Ar, simultaneously forcing the capsule into the hot zone. The capsule reaches the desired temperature "in just several minutes" according to Zhang and Frantz.

The Zhang and Frantz (1987) procedure results in volumetrically homogeneous generations of inclusions from fluids that are compositionally homogeneous at low temperature. However, the extremely rapid heating from low temperature would probably not allow sufficient time to homogenize an initially heterogeneous bulk composition such as a high-salinity brine. Adjustments could undoubtedly be made to this procedure to enhance its applicability to compositional heterogeneity problems. Specifically, the capsule could be maintained at an intermediate temperature at high pressure for some time and then the vessel tilted, allowing the capsule to slide into the hot end.

The  $\alpha$ - $\beta$  transition fracturing procedure described previously is applicable to problems of both compositional and volumetric heterogeneity. However, because approximately 25 min are required to return to the experimental conditions, the possibility of variable densities still exists along with the poor quality of the inclusions.

It is apparent from the above discussions that although it is frequently possible to address either the problem of compositional or volumetric heterogeneity, the solution to one problem can be the cause of another. The ultimate aim of the synthetic inclusion approach or any experimental procedure designed to study fluid properties at high pressures and temperatures is to stabilize the system at  $P$  and  $T$ , obtain a representative sample of the fluid, and then analyze the sample or preserve it for later analysis. If the system is unstable or if the sample decays before analysis, the procedure is unsatisfactory for that application. During a recent synthetic fluid inclusion study of the  $\text{CO}_2$ - $\text{H}_2\text{O}$  system (Sterner and Bodnar, 1991), a method was devised whereby both compositional and volumetric homogeneity could be routinely achieved in high-temperature ( $\geq 600$  °C) experiments from fluids that are immiscible at low temperature (Sterner, 1990). This new procedure involves fracturing the quartz inside the pressure vessel during the experiment and, therefore, will be referred to as the *in situ* fracturing method (ISF). The new modifications to the inclusion synthesis procedure are outlined in the discussions that follow along with some potential applications brought about by the improved experimental design.

#### IN SITU FRACTURING PROCEDURE (ISF)

The general procedure follows that described in Sterner and Bodnar (1984) and elaborated on in Bodnar and Sterner (1987). Cylindrical cores 4.5 mm in diameter and about 1 cm long are cut from inclusion-free Brazilian quartz. The unfractured cores are loaded into 5-mm diameter, 18-mm long noble-metal capsules along with suitable starting materials to generate the desired fluid composition at the experimental conditions. The capsules are sealed at each end by welding metal end caps in place as described by Bodnar and Sterner (1987). A maximum of two such capsules is loaded into a cold-seal pressure vessel followed by a 7-cm length of filler rod (Fig. 2). (The overall length of the pressure vessel, excluding the closure nut, is 30 cm.)

The loaded pressure vessel is then installed on a specially designed rack that includes a sliding furnace, high-pressure plumbing, and thermocouple assemblies for controlling and monitoring temperature. A schematic diagram of the apparatus is presented in Figure 3. The important feature of the design of this cold-seal rack is that it allows complete rotation of the pressure vessel-furnace assembly through nearly 180° (from vertical through horizontal to vertical) while the system is at pressure.

The pressure vessel is held in place by a rigid connection to the high-pressure coupling, as shown in Figure 3, and supported initially by a removable metal strap. At the beginning of the experiment, the furnace is slid into place and locked, and the entire assembly is rotated to a vertical position with the closure nut at the top (Fig. 2A). A few sharp raps on the closure nut with a metal rod insure that the capsules and filler rod slide all the way to the opposite end. While still in this vertical orientation,

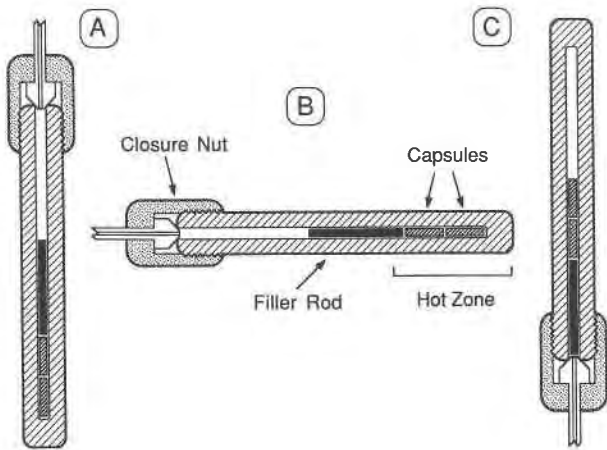


Fig. 2. Schematic illustration of the pressure-vessel, capsule, and filler-rod geometries used in the in situ fracturing procedure for fluid inclusion synthesis.

the vessel is pressurized to approximately 500 bars and the furnace is turned on. In experiments involving the generation of  $\text{CO}_2$  from silver oxalate, the vertical orientation is maintained until the gas is liberated to insure that the capsules are not forced toward the closure nut by the explosive decomposition reaction.

Following the completion of any decomposition reactions required to generate desired fluid components, the pressure vessel–furnace assembly is rotated to the horizontal position and locked (Fig. 2B). During continued heating, sufficient pressure is maintained in the vessel to prevent the capsule(s) from rupturing. Once the desired temperature is achieved, the pressure is set and the system is allowed to stabilize. There is no urgency at this point because inclusions have not yet begun to form. After the experiment has stood long enough to ensure complete thermal stability and fluid homogeneity, the quartz cores are fractured as described below, and inclusion synthesis ensues.

Regardless of the desired synthesis pressure, the experimental vessel is brought to a temporary pressure of 2 kbar with the common line opened. The pressure vessel–furnace assembly is then unlocked and rotated to the vertical position—this time with the closure nut pointed down (Fig. 2C). The filler rod and capsules slide into the cold end of the vessel, and contact with the colder pressure medium forced up around the filler rod fractures the quartz within the capsules (Fig. 1c). Again, a few sharp raps on the closure nut will jar loose a bound capsule. Immediately after hearing the filler rod and capsules collide with the closure nut, the pressure vessel–furnace assembly is rotated through horizontal to the vertical position with the closure nut on top (Fig. 2A). The capsules can be heard to drop back into the hot end of the pressure vessel, and the entire apparatus is then returned to the horizontal position (Fig. 2B) and locked for the duration of the experiment. Finally, the pressure is returned to the desired

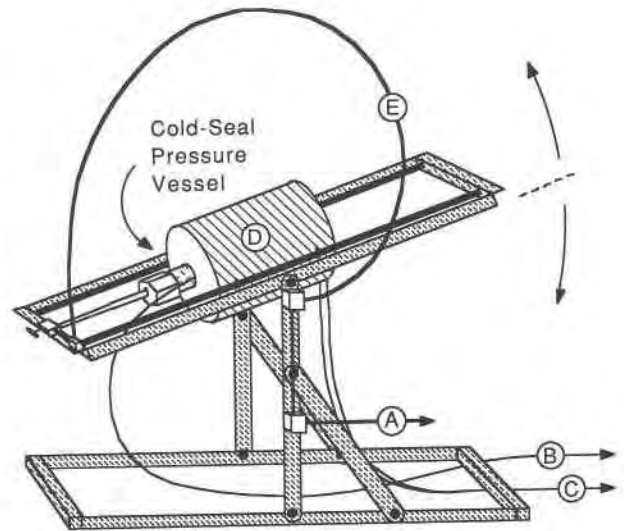


Fig. 3. Schematic illustration of the pressure vessel–furnace assembly used in the in situ fracturing procedure for fluid inclusion synthesis. A, B, and C are the high-pressure, thermocouple, and furnace power leads, respectively. D is the sliding furnace, and E is the flexible (5-mm, high- $P$ ) pressure line. The rectangular-shaped rack supporting the furnace is capable of rotation through  $180^\circ$  as indicated.

experimental value and the common line kept opened until the temperature again stabilizes (approximately 4 min). The temperature should return to its exact prefracture value with no further adjustment.

The experimental conditions are maintained for several days following the fracturing procedure during which time fluid inclusions form as imperfections along fracture planes. At the end of the experiment, the furnace is switched off and the vessel is allowed to cool slowly through the  $\alpha$ - $\beta$  transition until the pressure-temperature conditions are within the  $\alpha$  quartz field. The furnace may then be slid off and the vessel cooled with room air, or a forced-air quench may be implemented. Rapid cooling through the  $\alpha$ - $\beta$  transition will cause further fracturing of the quartz core, and though this generally does not result in the formation of new fluid inclusions, the unhealed  $\alpha$ - $\beta$  fractures will cause the core to disintegrate during later sample preparation. Following the quench, the capsules are removed from the pressure vessel and opened, and thin sections are prepared according to the procedure described in Bodnar and Sterner (1987).

In the original procedure described by Sterner and Bodnar (1984) a full-length filler rod was used (see Kerrick and Boettcher, 1971). The purpose of the filler rod is to minimize thermal gradients within the hot zone of the pressure vessel. Although satisfactory results have been obtained using a 7-cm filler rod in the procedure described above, it is possible that somewhat longer filler rods (and commensurately longer pressure vessels) would more effectively reduce the gradient. A further check on the temperature control would be afforded by testing the chosen system geometry using an internal thermocouple.



### Density determinations using the ISF method

The effectiveness of the above procedure in producing homogeneous populations of inclusions under extreme experimental conditions has been demonstrated in the *PVTX* study of the  $\text{CO}_2\text{-H}_2\text{O}$  system by Sterner and Bodnar (1991). Extensive fluid immiscibility exists in the  $\text{CO}_2\text{-H}_2\text{O}$  binary at temperatures below 200–300 °C. Thus, for a broad range of bulk compositions the fluid cannot homogenize in a hydrothermal experiment until substantial heating has occurred. This posed no problem at moderate experimental temperatures; densities of  $\text{CO}_2\text{-H}_2\text{O}$  fluids were successfully determined up to 600 °C using the 1984 procedure. However, above 600 °C premature fracture healing significantly reduced the accuracy of density measurements made using this approach.

Molar volumes ( $MV$ s; 1/molar density) of  $\text{CO}_2\text{-H}_2\text{O}$  fluids calculated from fluid inclusions formed at 700 °C and 3 kbar using the synthesis procedures of Sterner and Bodnar (1984) are shown as open circles in Figure 4. Details of the molar volume calculation are given in Sterner and Bodnar (1991). Each datum represents the average of calculated  $MV$ s from several inclusions in a given sample. The solid line corresponds to  $MV$ s derived assuming ideal mixing of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at 700 °C and 3 kbar. The relatively large uncertainties associated with each measurement and the erratic magnitudes of the  $MV$ s themselves result from inclusions formation prior to equilibration at the final  $P\text{-}T$  conditions. The large range in  $MV$ s calculated from inclusions within a single sample (reflected in the uncertainties for these data shown on Fig. 4) is indicative of inclusion trapping through time during changing  $P\text{-}T$  conditions, whereas the consistently low values of the calculated volumes result from trapping while approaching the final  $P\text{-}T$  conditions from the low- $MV$  (high-density) direction.

Uncertainties in  $MV$ s calculated from this set of experiments have been solely attributed to variation in fluid density resulting from trapping prior to attainment of the final  $P\text{-}T$  conditions and, thus, are represented by vertical error bars. However, the final errors could be due, in part, to compositional variation among individual inclusions resulting from trapping prior to the attainment of capsule-wide fluid homogeneity and, as such, may be more properly represented by both vertical and horizontal error bars. The extent of contribution from each of these factors is unknown—only that the combined effect results in substantial errors in the final calculated molar volumes.

Molar volumes of  $\text{CO}_2\text{-H}_2\text{O}$  mixtures were redetermined at 3 kbar and 700 °C using the ISF procedure described above. The resulting volumes are shown as filled circles in Figure 4. Note that both the overall scatter and the individual uncertainty in calculated volumes for individual samples are greatly improved. The new volumes are both internally consistent and of reasonable magnitude (Sterner and Bodnar, 1991), implying both compositional and volumetric homogeneity among the inclu-

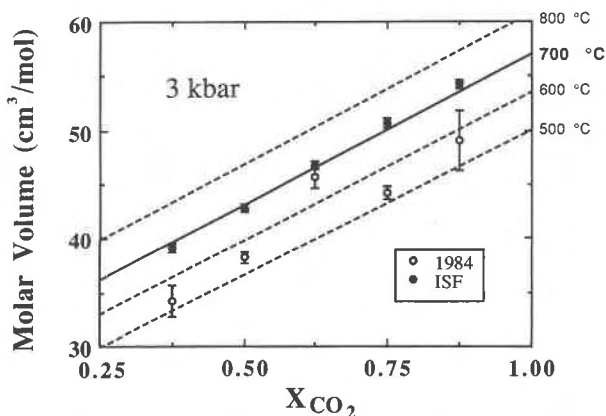


Fig. 4. Comparison of molar volumes of  $\text{CO}_2\text{-H}_2\text{O}$  mixtures at 700 °C and 3 kbar determined using the ISF method (filled circles) and the 1984, prefractured quartz approach (open circles).  $X_{\text{CO}_2}$  equals the mole fraction  $\text{CO}_2$  relative to  $\text{CO}_2 + \text{H}_2\text{O}$ . The solid line represents ideal mixing of the binary fluids at the same pressure and temperature based on volumes of the pure end-members predicted by Haar et al. (1984) and Shmonov and Shmulovich (1974). Dashed lines are ideal mixing volumes at 500, 600, and 800 °C.

sions within each sample and attesting to the effectiveness of the new procedure.

A detailed error analysis of the volumetric study is presented by Sterner and Bodnar (1991). The average uncertainty in experimentally derived molar volumes of  $\text{CO}_2\text{-H}_2\text{O}$  mixtures is 0.80 vol%. The average uncertainty in  $MV$  determinations at 400, 500, and 600 °C (1984 method) is 0.82 vol%, yet the average at 700 °C (ISF method) is only 0.74 vol%. Although statistics for data at 700 °C represent only a modest improvement over those of the lower temperature data, they are significantly better than the results obtained by using the 1984 synthesis approach at 700 °C (see Fig. 4).

Although the accuracy of *PVTX* data derived from synthetic fluid inclusions varies from one system to another, it is instructive to identify the principal sources of error in a given study with the hope of improvement in future applications. The leading causes of error in volumetric determinations of  $\text{CO}_2\text{-H}_2\text{O}$  mixtures, using either the 1984 approach or the ISF procedure, are uncertainties in experimental  $P$  and  $T$  and ensuing variation in  $\text{Th}(\text{CO}_2)$  within a given sample. Assuming that the inclusions are indeed trapped from homogeneous, one-phase fluids, the variation in  $\text{CO}_2$  homogenization temperature between inclusions in a given sample probably reflects true bulk density variations and arises from fluctuations in temperature and pressure during the experiments. These are difficult problems to eliminate, but with proper electronic isolation and (ambient) temperature stability in the laboratory they can be further reduced.

### Discussion

The ISF method has been found to produce large numbers of compositionally and volumetrically homogeneous

fluid inclusions within a single sample. While the optical clarity and abundance of inclusions produced in this way are somewhat less ideal than those synthesized using the 1984 method, a sufficient number of large inclusions will invariably be found in each sample. The new procedure has been found to work well at experimental temperatures of 600, 700, and 800 °C, although resulting fracture density and, thus, the number of inclusions formed is rather low at 600 °C. At temperatures below 600 °C, the formation rate of inclusions appears to be slow enough that the ISF procedure has been unnecessary thus far. At experimental temperatures above 700 °C, the fracture density can become so large that inclusions are literally stacked on top of each other. Under such circumstances, the inclusion density can be reduced by increasing the pressure above 2 kbar during the fracturing procedure. A 1- or 2-kbar increase can significantly reduce the fracture density, although it will increase the risk of vessel failure so that additional safety precautions are advised.

In microthermometric studies of synthetic fluid inclusions, it is frequently observed that most inclusions along a single fracture plane are of nearly identical composition and bulk density. Early in the synthesis process, entire fracture planes are initially sealed off along their outside edges, thereby isolating their contents from the bulk capsule fluid. Subsequent dissolution and reprecipitation of quartz within this large cavity causes necking and results in the formation of numerous smaller inclusions. The composition of the smaller inclusions will reflect that of the fluid in the original fracture and may be different than the bulk fluid composition if large-scale heterogeneity existed within the capsule at the time of initial isolation. The density of the smaller inclusions will depend on both the fluid composition in the original fracture and the *P-T* conditions of the system at the exact moment the fracture was sealed off. Thus, the number of measurements from independent fracture planes is more important than the total number of inclusions measured for obtaining a representative set of microthermometric data. Use of the ISF method results in a relatively large number of small, randomly oriented, intersecting fractures (Fig. 1c) along which a small number of inclusions have formed. Although the total number of measurable inclusions present in a given chip will generally be less than that produced using the 1984 method, the number of measurable inclusions occurring on independent fractures is frequently greater.

During the ISF procedure, a rapid temperature deflection of about 30 °C will be recorded on an externally mounted thermocouple. Obviously, the actual temperature drop experienced by the samples is much larger than 30 °C—enough to result in thermal shock of the quartz—yet the temperature will return to within one degree of set point within approximately 4 min. This recovery time is apparently instantaneous with respect to the time required to begin to trap fluid inclusions. In our laboratory, the experimental temperature is monitored using an Inconel-sheathed, K-type thermocouple positioned in a well drilled in the end of the pressure vessel. However, our

electrical configuration allows temperature controlling from either a pressure vessel-mounted thermocouple or a thermocouple located within the furnace. Although the procedure appears to work equally well when controlling from either thermocouple, the temperature stabilizes at the desired value somewhat sooner when the furnace thermocouple is used for temperature control.

The greater frequency of capsule failure using the ISF method compared with the 1984 approach is undoubtedly due to the additional deformation experienced by the metal during the fracturing procedure. Therefore, it is recommended that the capsule weights be recorded before and after each experiment to detect any fluid leakage.

The ISF method has been found to work equally well using H<sub>2</sub>O, CH<sub>4</sub>, or Ar as the pressure medium. Thus, the procedure may be easily implemented on either gas- or H<sub>2</sub>O-pressure cold-seal stations. Because of the unlimited time available to reach chemical equilibrium prior to inclusion formation, interesting possibilities present themselves regarding the use of mixed-gas buffering systems.

A precursor to the experimental apparatus shown in Figure 3 was developed by S. M. Sterner and C. S. Oakes. A length of 5-mm diameter, high-pressure tubing was formed into a flexible coil approximately 18 cm in diameter containing four complete revolutions. The coil linked the pressure vessel to the high-pressure coupling on a standard cold-seal rack. In situ fracturing of the quartz cores was accomplished by sliding the furnace off and rotating the pressure vessel through the necessary orientations (Fig. 2) then replacing the furnace. Results similar to the ISF method described above were obtained using this technique except that the removal of the furnace resulted in considerable heat loss so that the experimental temperature required much longer to restabilize. If experimental pressures are low ( $\leq 2$  kbar), 2-mm diameter pressure line can be used to facilitate this procedure; however, the ISF method described above is considerably safer, and the present (coil) method presents no apparent advantages aside from simplicity.

A fundamentally different cold-seal apparatus, in principle, also capable of in situ fracturing, was designed by Phil Ihinger at the California Institute of Technology. The pressure vessel–furnace assembly in this configuration remains stationary in the vertical position with the closure nut toward the bottom. The capsules are supported by a thin rod that extends downward through the seal into another inverted, cold-seal vessel. A small magnet is affixed to the lower end of the thin rod inside the lower pressure vessel. The capsule–thin rod–inner magnet assembly is capable of several centimeters of vertical motion while the entire apparatus is at pressure and the upper vessel is at temperature. During operation, the lower vessel stays at room temperature and the capsule(s) are moved in or out of the hot zone by adjusting the position of the inner magnet using a larger circular magnet located external to the lower vessel.

### ADDITIONAL CONSIDERATIONS

#### Correction for the nonisochoric behavior of quartz

Fluid inclusions are not strictly isochoric systems. At high temperatures the solubility of the host mineral can become appreciable and the volumes of individual inclusions as well as the properties of the fluids can be affected by dissolution of the inclusion wall. Silicate melt inclusions (Roedder, 1984) formed at temperatures near the silicate liquidus are an extreme case where the proportion of dissolved silicate is greater than the amount of aqueous phase. Although host dissolution can often be neglected for quartz and other silicate host phases because of their low solubilities even at relatively high temperatures, the validity of this assumption should always be assessed with regard to the particular system under investigation.

It is frequently necessary to account for the change in the volume of an inclusion cavity between two sets of  $P$ - $T$  conditions because of thermal expansion and compressibility of the host. For quartz, the maximum correction is on the order of a few percent and can be accomplished using information given in Figure 5 constructed from equations presented in Hosieni et al. (1985). The volume change factor is used to relate the volume of an inclusion at a new set of  $P$ - $T$  conditions to its volume at an initial pressure and temperature as follows:

$$V^{P_2, T_2} = V^{P_1, T_1} \left( \frac{V_{\Delta}^{P_2, T_2}}{V_{\Delta}^{P_1, T_1}} \right) \quad (1)$$

where  $V^{P_1, T_1}$  and  $V^{P_2, T_2}$  are the inclusion volumes (or specific volumes) at the initial and final  $P$ - $T$  conditions, respectively, and  $V_{\Delta}^{P_1, T_1}$  and  $V_{\Delta}^{P_2, T_2}$  are the volume change factors corresponding to each set of conditions. The computation is facilitated by a Fortran program available from the author that calculates  $V^{P_2, T_2}$  using  $V^{P_1, T_1}$ ,  $P_1$ ,  $P_2$ ,  $T_1$ , and  $T_2$  as initial input. The program uses the equations of Hosieni et al. (1985) with corrections described in Sterner and Bodnar (1991). Both the Fortran program and Figure 5 are amenable to use with natural samples, although it should be recalled that the specific equations from which they are derived are applicable only to inclusions in quartz. Also, uncertainties in compositions of natural samples usually yield much larger errors than those resulting from the nonisochoric behavior of the host.

#### Liquid-vapor equilibria determinations

Synthetic fluid inclusions have been applied to liquid-vapor equilibrium determinations in several fluid systems: NaCl-H<sub>2</sub>O (Bodnar et al., 1985; NaCl-KCl-H<sub>2</sub>O (Sterner and Bodnar, 1986); CO<sub>2</sub>-H<sub>2</sub>O (Sterner and Bodnar, 1991); CO<sub>2</sub>-H<sub>2</sub>O-NaCl (Sterner et al., 1984; Kotelnikov and Kotelnikova, 1990; Popp and Frantz, 1990); CO<sub>2</sub>-H<sub>2</sub>O-CaCl<sub>2</sub> (Zhang and Frantz, 1989). Most of these determinations employed the 1984 synthesis approach.

In studies of salt H<sub>2</sub>O systems (e.g., Bodnar et al., 1985), initial fluid compositions at or below room-temperature saturation are used to insure fluid homogeneity at the

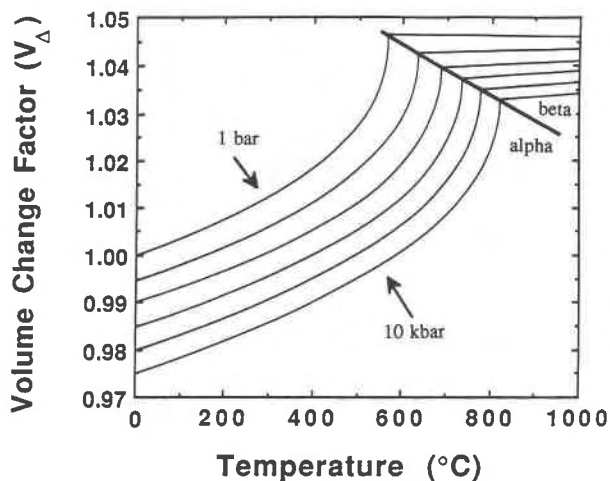


Fig. 5. Volume change factor ( $V_{\Delta}$ ) relating the volume of a fluid inclusion at 20 °C and 1 bar to its volume at high  $P$  and  $T$  (see Eq. 1). The light solid lines correspond to the 1 bar and 2, 4, 6, 8, and 10 kbar isobars of  $V_{\Delta}$ . Alpha and  $\beta$  quartz regions are separated by the heavy solid line. The diagram was constructed using equations from Hosieni et al. (1985).

start of the experiment. The desired experimental temperature ( $T^{exp}$ ) is achieved and stabilized before the fluid is allowed to unmix. The topologies of salt-H<sub>2</sub>O systems lend themselves to this approach because experiments can be initially heated at high pressures well within the one-fluid phase field. The two phase field is then entered by rapidly decreasing the pressure, and unmixing ensues at  $P$  and  $T$ . The sudden pressure drop appears to cause the nucleation of a large number of small vapor bubbles that become trapped more or less randomly throughout the fracture system, frequently resulting in the intimate coexistence of both vapor- and liquid-rich inclusions along the same fractures. Available solubility and freezing-point depression data for the geologically common salts allow the determination of compositions of the resultant inclusions using microthermometric measurement.

In addition to forming inclusions representing end-member (or near end-member) fluid compositions, the above procedure also results in the formation of numerous inclusions that have trapped mixtures of the liquid and vapor phases present at equilibrium. Liquid-rich inclusions from a given sample generally display a very narrow range in composition, whereas a much broader compositional range is frequently recorded for vapor-rich inclusions. This is likely the result of trapping only the liquid in the liquid-rich inclusions and the concurrent trapping of small but variable amounts of liquid in the vapor-rich inclusions. Thus, the determination of the equilibrium liquid composition is straightforward, whereas that for the composition of the coexisting vapor phase is somewhat arbitrary—generally taken to equal the lowest salinity measured. This phenomenon necessitates the salinity determination of a large number of vapor-rich inclusions. Since there is no guarantee of finding an



inclusion that has trapped only the vapor, the procedure yields only a maximum salinity estimate for the composition of the vapor end-member.

The observed range in composition of the vapor-rich inclusions can be significantly reduced by entering the two-phase field slowly during isobaric heating at the final experimental pressure. The result is to segregate physically the vapor and liquid, thereby reducing the opportunity to form mixed inclusions. The separation can be further enhanced by maintaining the capsules in a vertical position during the experiment. However, problems may arise using this approach if, at some point after initial phase separation, continued heating to  $T^{\text{vap}}$  results in increasing salinity of the equilibrium vapor or decreasing salinity of the equilibrium liquid. Under such circumstances, the physical separation of the two fluids may prevent spontaneous remixing before inclusion begin to form (see Bodnar et al., 1985). For all pressures above 500 bars in the system NaCl-H<sub>2</sub>O, neither branch of the solvus begins to close below 1000 °C (see Fig. 10 in Bodnar et al., 1985). Whether this is true of other geologically relevant brine systems is not known, so the consequences of premature fracture healing must be considered.

Using an isobaric heating approach at high temperatures will undoubtedly result in the trapping of some inclusions at  $T < T^{\text{vap}}$ . Provided the system is characterized by divergence of both branches of the solvus with increasing temperature, the appropriate extreme compositions measured for each type of inclusion should represent the best experimental values.

In studies of gas-bearing systems, a bracketing procedure is followed in the determination of liquid-vapor equilibria because the exact composition of such inclusions cannot be determined microthermometrically (Stern et al., 1984; Kotelnikov and Kotelnikova, 1990; Zhang and Frantz, 1989). There is little choice of  $P$ - $T$  paths in these systems because immiscibility occurs at low temperatures at most pressures; thus, it is virtually impossible to avoid the two-phase field. Fortunately, much geologically relevant information may be gleaned from these systems at low to moderate temperatures ( $\leq 600$  °C), where experience has shown that fluid equilibrium will be closely approached prior to the onset of inclusion formation (Stern and Bodnar, 1991).

It is not clear whether the ISF method would represent any improvement over its precursor in the direct determination of liquid-vapor equilibria. Advantages resulting from the relatively instantaneous stabilization of pressure and temperature would likely be offset by the formation of large numbers of mixed inclusions. However, the ISF method has been successfully employed in the indirect determination of liquid-vapor equilibria in the CO<sub>2</sub>-H<sub>2</sub>O system (Stern and Bodnar, 1991). In this procedure, inclusions are synthesized in the one-fluid phase field from a fluid of known composition. The  $T$  coordinate of a point on the solvus is determined from the measured inclusion total homogenization temperature ( $Th_{\text{tot}}$ ), and the  $P$  coordinate is determined from an appropriate equa-

tion of state or a complete set of volumetric data. A serious drawback to this procedure compared with the bracketing approach is the inability to measure accurately  $Th_{\text{tot}}$  when homogenization occurs in the vapor phase (see discussion in Stern and Bodnar, 1991).

#### Generation of multicomponent fluids at $P$ and $T$

Another important aspect of inclusion synthesis is obtaining fluid(s) of desired composition at the experimental  $P$  and  $T$ . This is an important consideration—not only in  $PVTX$  studies but also in the preparation of synthetic fluid inclusions to be used as microanalytical standards. The chemical reagents and procedures listed below have been successfully employed by a number of investigators to generate multicomponent fluids of known compositions in hydrothermal experiments.

Low-salinity brines (undersaturated at room temperature) are the most straightforward and are generally loaded into the capsule as premixed solutions using a syringe. More concentrated salt-H<sub>2</sub>O solutions are prepared by loading the anhydrous salts and independently weighing the amount of each component. Salts that hydrate readily, like CaCl<sub>2</sub> and NaOH, require special treatment to achieve known concentrations. Undersaturated CaCl<sub>2</sub>-H<sub>2</sub>O solutions may be accurately prepared by gravimetric titration of CaCO<sub>3</sub> with concentrated HCl until a neutral solution is obtained, whereas the preparation of high-salinity CaCl<sub>2</sub>-H<sub>2</sub>O brines may require the direct loading of the anhydrous salt in an inert atmosphere (i.e., using a glove box). Alkali-hydroxide solutions are best determined by titration with a standard acid after preparation.

Expandable gases have been loaded in hydrothermal experiments using solid compounds that break down at high temperatures to yield stoichiometric amounts of the desired components. Holloway and Reese (1974) recommended several organic and inorganic reagents for generation of fluids in the C-O-H-N system. Additional compounds are discussed by Frantz et al. (1989), and to the list one may also add silver azide (AgN<sub>3</sub>), native sulfur, and HCL<sub>aq</sub>. Two recent innovations in capsule loading protocol have been proposed for the direct introduction of volatile components. The first, by Frantz et al. (1989), involves the cryogenic adsorption of known quantities of gases onto a solid substrate (gel) placed in the bottom of the capsule. The substrate significantly reduces the vapor pressure of the gas such that even N<sub>2</sub> can be condensed at liquid N<sub>2</sub> temperatures. The second procedure, by Boettcher et al. (1989), employs a special fixture that allows room-temperature loading of gases and gas mixtures at high pressures (up to 100 bars). Both procedures show promise for generating geologically relevant fluids in synthetic fluid inclusion experiments.

Another technique for obtaining desired fluid compositions at elevated  $P$  and  $T$  involves the use of buffers and semipermeable membranes to control fluid speciation once the experimental conditions have been realized (Chou, 1987; Gunter et al., 1987). Using this approach, some components are added directly to the capsule (e.g.,

some form of C, H<sub>2</sub>O, etc.); others are provided (or removed) by solid-fluid interaction (e.g., O, S, etc.) while H is allowed to diffuse in and out through the capsule walls. The problem with these procedures in the context of conventional fluid inclusion synthesis (i.e., the 1984 method) is that the fluid phase requires time to equilibrate. The length of time is a complex function of diffusion rates, temperature, chemical potential gradients, bulk composition, system mass, reaction kinetics, and a multitude of other considerations. At almost all temperatures there is the imminent possibility (probability) that inclusions will begin to form before speciation in complex systems has reached equilibrium. This includes virtually all cases where species directly loaded into the capsule, or those that are the result of initial decomposition reactions are out of chemical equilibrium at the prevailing experimental conditions. The new ISF method of inclusion synthesis could have significant impact in investigations of such systems under these conditions by allowing better control of the timing of fluid sampling relative to the rate of fluid evolution.

#### FUTURE APPLICATIONS OF SYNTHETIC FLUID INCLUSIONS

The ISF procedure is not a panacea for synthetic fluid inclusion research. However, having eliminated the complication of premature inclusion trapping in many applications, the problems that remain (e.g., adequate control of experimental pressure and temperature, difficulties in generating desired fluid compositions, etc.) appear much more manageable. Perhaps the most important contributions of the new procedure will be in the preparation of homogeneous populations of inclusions from chemically complex fluids for the purposes of *PVT* investigations, studies of low-*P-T* phase equilibria, and standardization of microanalytical techniques. A number of geologically important fluid components that have thus far eluded study because of problems associated with their slow production or dispersion throughout the capsule should be accessible using the new procedure.

Because the ISF method allows the bulk fluid to equilibrate at *P* and *T* prior to inclusion formation, there is considerable potential for high-*P-T* fluid speciation studies using buffers and H<sub>2</sub> membranes to control  $f_{O_2}$ ,  $f_{H_2}$ ,  $f_{S_2}$ , pH, etc. Kinetically sluggish equilibria could first be established at the desired experimental conditions, followed by trapping representative fluid samples as homogeneous populations of inclusions. Chemical speciation, volumetric properties, and phase equilibria could then be investigated using microthermometric measurement of phase transitions coupled with chemical analysis by various methods such as laser Raman microprobe analysis, bulk leaching, or crushing into a gas chromatograph or mass spectrometer. The presence of large numbers of inclusions having identical compositions within an individual sample will insure ample quantities of material for most bulk analytical techniques. Additionally, the residual capsule fluid may be analyzed using chro-

matographic techniques like those described by Frantz et al. (1989).

The new procedure will aid in solubility studies of both sparingly and highly soluble species. In both cases in situ fracturing should allow homogeneous distribution of dissolved species throughout the capsule prior to inclusion trapping. For those species that dissolve and precipitate rapidly, any precipitation during the fracturing procedure would likely occur in the form of numerous small nuclei that would immediately redissolve during reheating. The rapid reestablishment of the original experimental *P-T* conditions after fracturing should preclude any large-scale diffusion of dissolved species that would result once again in bulk fluid heterogeneity. It is unlikely that kinetically sluggish species would precipitate in the short time available between fracturing and return to the original pressure and temperature.

Finally, volumetric determinations of high-salinity brines have presented difficulties in the past because techniques required to insure compositional homogeneity of the bulk fluid have often resulted in the production of volumetrically heterogeneous inclusion populations within a given sample (Sterner et al., 1988). Use of the new synthesis procedure should provide both compositional and volumetric homogeneity resulting in more accurate determinations of *PVT* properties at high concentration.

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