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Fluid Inclusion Studies of Calcite Veins from Yucca Mountain, Nevada, Tuffs: Environment of Formation

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ABSTRACT

Calcite vein and vug fillings at four depths (130-314m), all above the present water table in USW G-1 bore hole at Yucca Mountain, Nevada, contain primary fluid inclusions with variable vapor/liquid raitos: most of these inclusions are either full of liquid or full of vapor.

The liquid-filled inclusions show that most of the host calcite crystallized from fluids at <100°C. The vapor-filled inclusions provide evidence that a separate vapor phase was present in the fluid during crystallization. Studies of these vapor-filled inclusions on the microscope crushing stage were interpreted in an earlier paper as indicating trapping of an air-water-CO_2 vapor phase at "<100°C"[1]. Our new studies reveal the additional presence of major methane in the vapor-filled inclusion, indicating even lower temperatures of trapping, perhaps at near-surface temperatures. They also show that the host calcite crystals grew from a flowing film of water on the walls of fractures open to the atmosphere, the vapor-filled inclusions representing bubbles that exsolved from this film onto the crystal surface.

I. INTRODUCTION

The origin of secondary calcite within Yucca Mountain has been addressed by stable isotope[2], trace element[3], and radiogenic isotope studies[4]. Within the thick (500 to 700 m) unsaturated zone above water table, fractures and other open spaces often contain calcite. Near the surface, this calcite is texturally and mineralogically similar to the pedogenic calcite found in the overlying soils; below ~15 m, the calcite is sparry and locally coats fractures and forms drusy masses within lithophysal cavities. The unsaturated zone calcite appears to have precipitated from rainwaters that have descended along interconnected fractures carrying dissolved carbonate from the overlying soil environment; CO_2 escape from the fluid is a likely mechanism for the precipitation of this calcite within the unsaturated zone tuffs[2]. Below the present water table, calcite occurs as veins, often with chlorite and quartz or chalcedony, and as a replacement cement of altered tuffs. This calcite is part of an alteration mineralogy formed during a low-temperature hydrothermal event that occurred ~10.4 ma at temperatures up to ~250°C, based on earlier fluid inclusion studies[5]. Calcite $\delta^{13}C$ values indicate that the fluids responsible for this alteration came from the underlying Paleozoic marine carbonate aquifer[2].

Vein and vug fillings of secondary calcite at four depths (130, 204, 292, and 314 meters), all above the present water table in drill core USW G-1 from Yucca Mountain, Nevada (Figs. 1 and 2), show two principal types of primary fluid inclusions: either full of liquid or full of vapor. These range in size from about 100 to less than 2 micrometers. Each of the two types provides different, useful data on the preexisting environments under which they were formed, i.e., trapped:

- Liquid-filled inclusions provide, by their very existence, semi-quantitative bounds on the temperature of trapping. Those few liquid inclusions with vapor bubbles also provide an impression of trapping temperature through visual estimates of their vapor/liqiud ratio (high vapor/liqiud ratios reflect high temperatures of trapping; low ratios indicate low temperatures of trapping).
- Vapor-filled inclusions provide, by their very existence, evidence of the presence of a vapor phase along with the liquid phase from which the host crystal grew. Studies of such vapor-filled inclusions on a microscope crushing stage can provide semi-quantitative bounds on the pressure at the time of trapping, as well as some rough qualitative information on the chemical composition of the vapor

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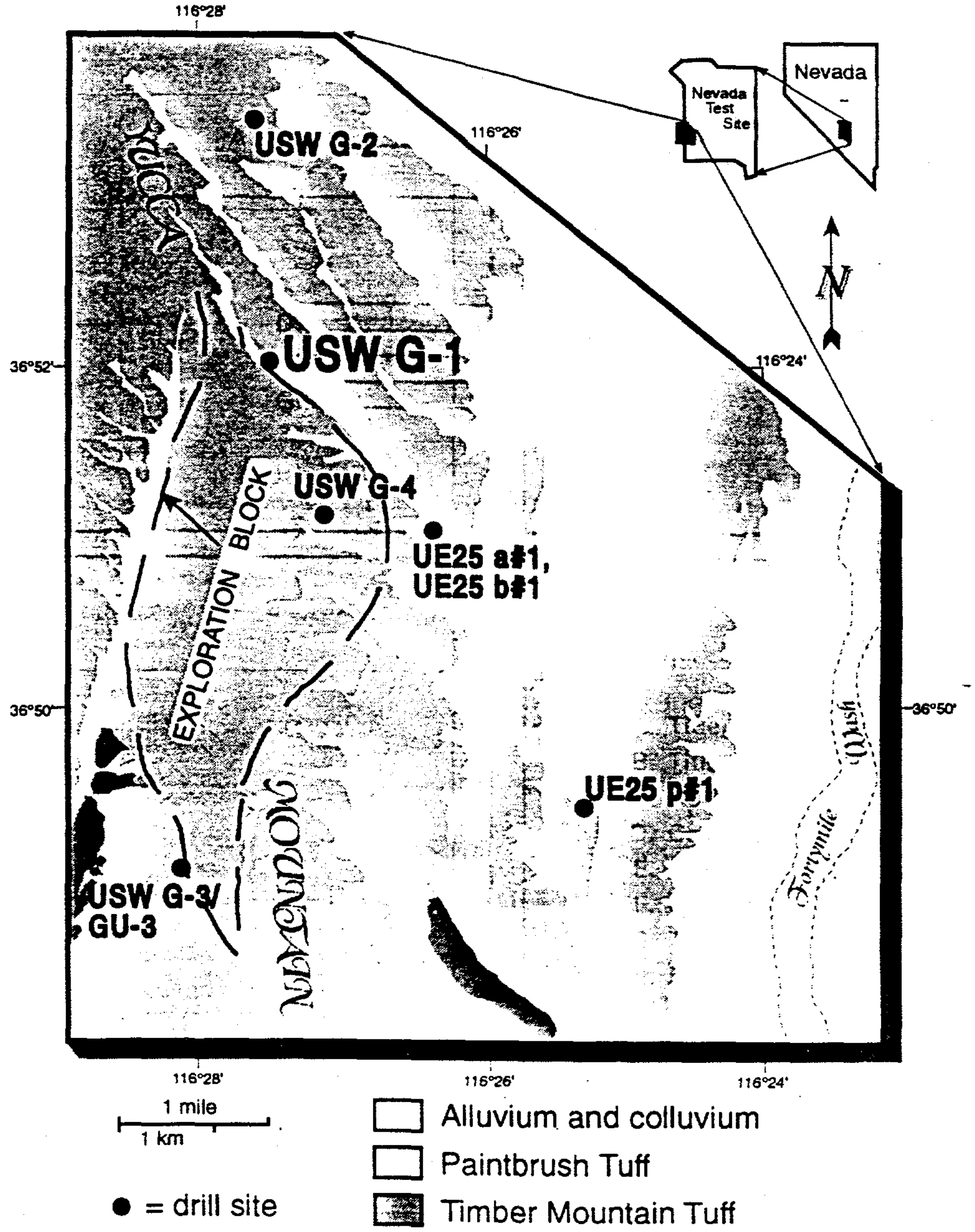

Figure 1: Location of bore hole USW G-1 at Yucca Mountain

itself. This latter can be used, in turn, to place some constraints on the environment in the vein at the time of crystallization of the host calcite.

The crushing test[6] provides a qualitative estimate of the gas pressure within a vapor inclusion at the time of crushing. It involves immersing the host grain in oil at 1 atmosphere under the microscope and stressing it until a crack reaches the inclusion. An inclusion filled with air at one atmosphere would not change when the crack reaches it, and on complete crushing, the original host grain would yield a bubble of the same volume as the original inclusion. An inclusion originally formed by the trapping of water vapor as a steam bubble would instantly fill with oil, once a crack reaches it, as the entrance of the oil at 1 atmosphere would collapse the very low-pressure water vapor completely. The present inclusions filled only partly (Fig. 3), suggesting that they contained, at room temperature, less than one atmosphere gas pressure; as a result of trapping a mixture of water vapor plus non-condensable gases such as air and/or CO_2.

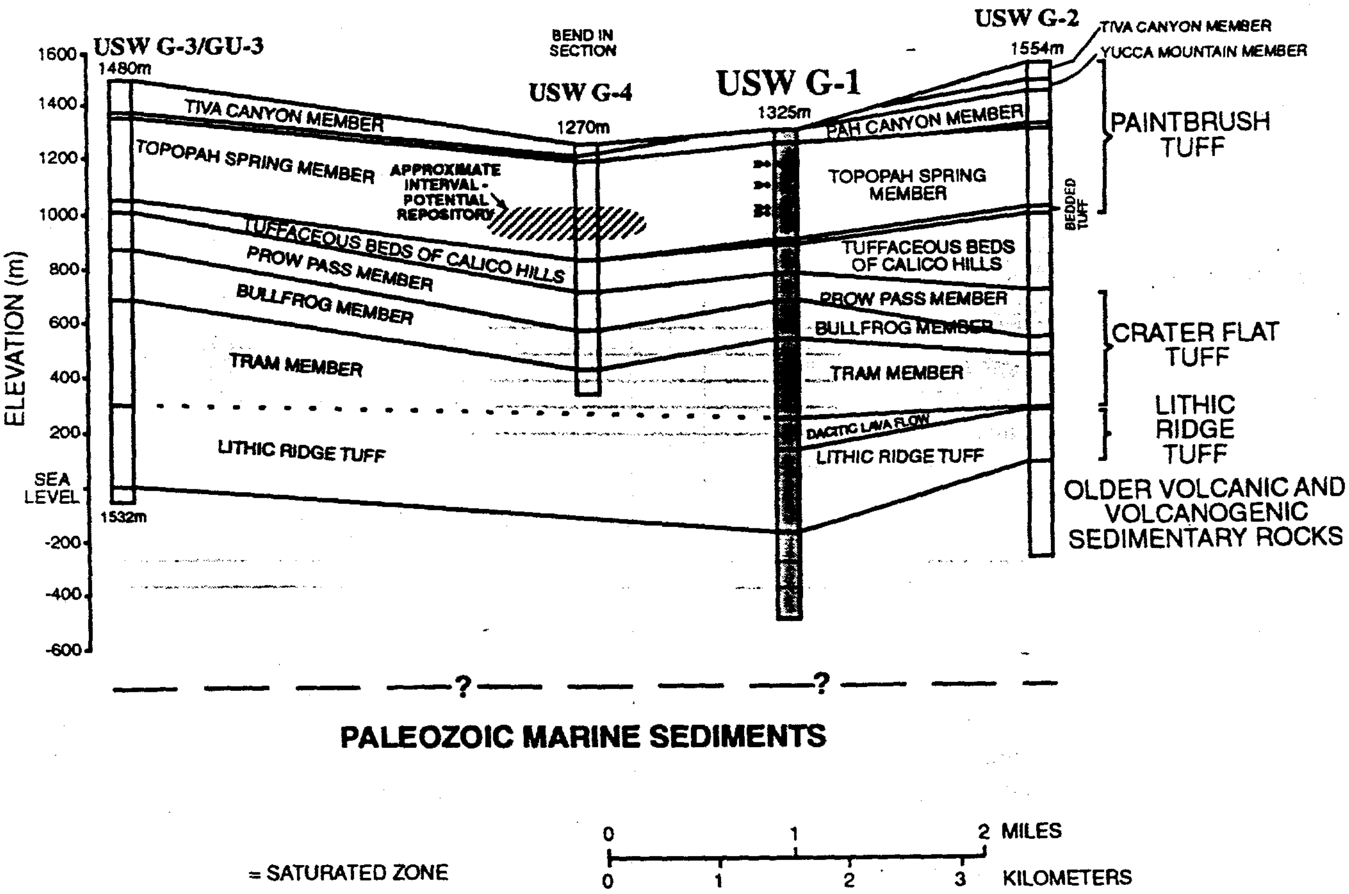

Figure 2: Roughly north-south cross-section of Yucca Mountain tuffs showing approximate locations of USW G-1 samples referred to in text (➻) and water table elevations.

II. PROCEDURES

A. Determination of the Th of Two-Phase Inclusions

Doubly-polished thin sections of calcite, mounted with acetone-soluble "superglue" resin, are made with a minimum of stressing of the sample and without any use of heat, and the entire slide is photographed at low magnification to provide a record and relocating guide. One or more suitable primary fluid inclusions, preferably >20 micrometers in diameter, are found by petrographic study and photographed. Primary refers to those inclusions trapped at the same time as the surrounding host mineral, using the criteria given by Roedder[7] [a]. The location of the group is marked on the record photograph and on the upper polished surface of the doubly-polished plate. Marking on the slide is best done with a fine-tipped pen, using acetone-insoluble ink. After the ink has dried, the slide is turned over onto a firm but non-scratching white surface (permitting the ink marks to be seen) and a diamond pencil is used to score the slide on two (or three) sides of the marked area. The glass slide and its attached doubly-polished plate are then carefully broken along the scribed lines to yield a sample small enough and shaped appropriately for use in the microscope heating stage, where the temperatures of homogenization (Th) of the vapor bubbles are determined by standard procedures[7,b]. The low Th in most of these samples permit leaving the polished plate on the glass; if the homogenization temperatures are high, the plate may have to be removed from the glass slide with acetone solvent before inserting in the microscope heating stage.

B. Determination of Behavior in the Microscop Crushing Stage;

After a suitable single vapor-filled inclusion, preferabl >20 micrometers in diameter, has been located and marke as above, the doubly-polished thin section is freed from th glass slide and then remounted in a high-viscosity index oi Via a series of steps involving a needle and some manu

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[a] Chapter 2, pp. 43-45.

[b] Chapter 7

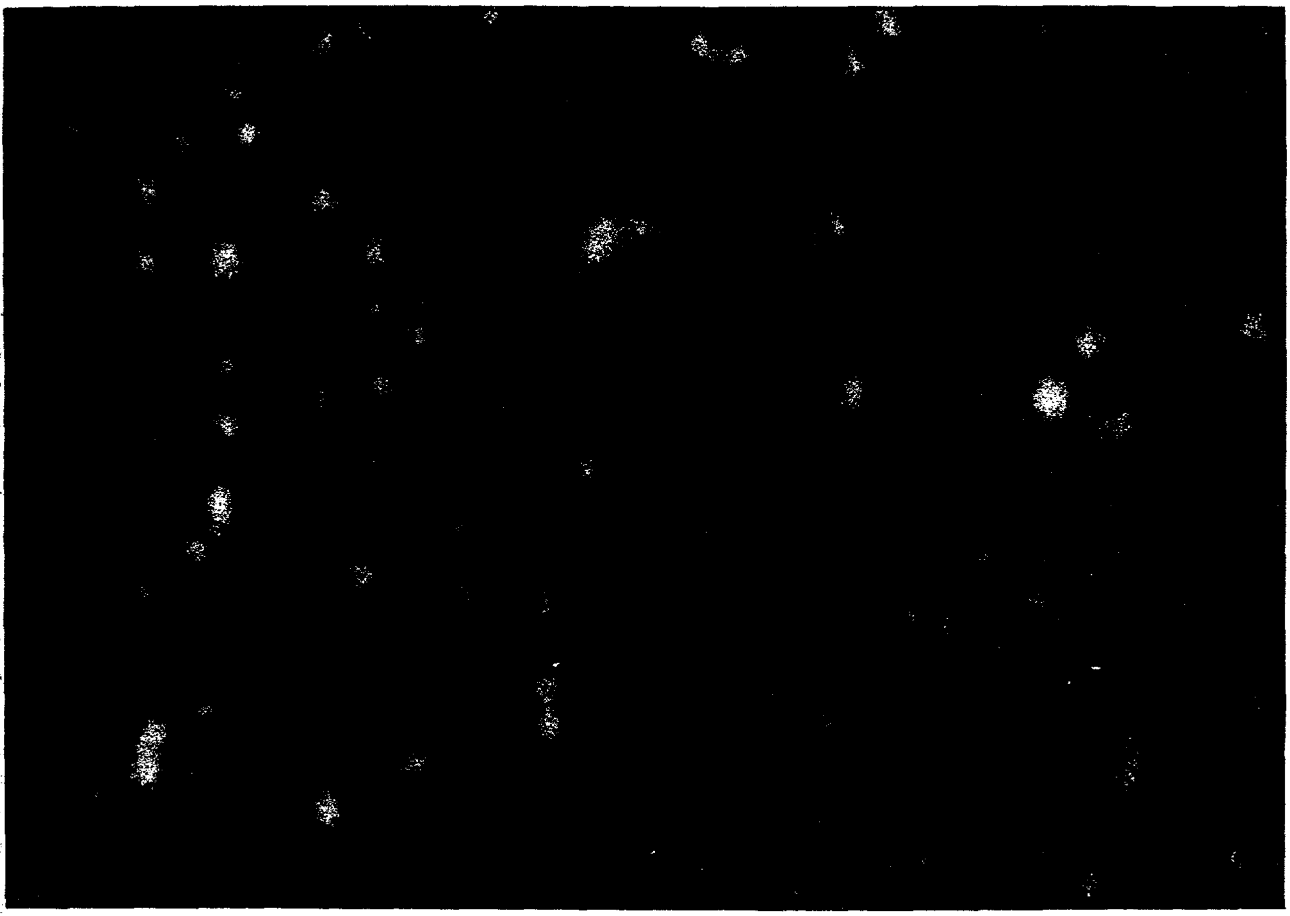

Figure 3: Series of photographs of a typical crushing experiment showing the initial vapor-rich inclusion, the inclusion after rupture along a cleavage fracture, and partial filling of the inclusion by the immersion oil.

dexterity, a fragment of calcite about 0.5 mm in size, containing the inclusion, is broken free and transferred to the microscope crushing stage where it is crushed in oil, following the procedures given by Roedder[6]. Optical measurements are made to establish the approximate volume of the inclusion before crushing, and the volume of gas remaining after crushing, as volume percent of the original volume.

III. RESULTS

A. Homogenization Runs

Suitable primary liquid-filled inclusions, containing a shrinkage vapor bubble, were found in only a few samples. As in all fluid inclusion studies, the most important step is that of sample selection[7]. Such selection of "suitable" inclusions must be done with considerable care or the data obtained will be invalid and misleading. In these samples, two-phase, vapor-liquid (V/L) inclusions were not rare, but most were "unsuitable" on the basis of petrographic evidence that they fell in one or another of the following categories:

1. Inclusions of non-primary (i.e., secondary) origin, using the criteria given by Roedder[7].
2. Inclusions with highly variable V/L ratios (on a visual basis) from the trapping of small amounts of liquid along with the vapor bubble.
3. Inclusions with highly variable V/L ratios (on a visual basis) that were intersected by a visible fracture, natural or from sample preparation, and thus were presumed to have lost some liquid by leakage.
4. Inclusions whose V/L ratio increased visibly during, or after, the homogenization run, indicating leakage of liquid.
5. Inclusions whose Th during a rerun were more than 2°C above the original values, indicating stretching or leakage.

6. Inclusions that decrepitated before homogenization occurred.

Most of the suitable inclusions occurred in groups, with an apparently uniform and small V/L ratio, which visually indicated that the inclusions had formed at low temperatures, probably ≤-100°C.

B. Crushing Runs

The very small number of suitable inclusions in the slides, and the numerous losses along the way from the vagaries of the various steps involved resulted in only ten inclusions being successfully crushed; i.e., conditions were such that optical observation of the behavior of the inclusion could be made at the moment of crushing. In each of these, oil entered the inclusion, suggesting at first that the gas pressure within the inclusion at room temperature was less than atmospheric (Fig. 3). Later experiments using glycerol instead of oil showed that the vapor inclusions were at essentially atmospheric internal pressure (see section IV.B.2).

IV. SIGNIFICANCE OF THE DATA

A. Homogenization Data

The meager Th data indicate that at the time of growth of the host calcite the ambient temperature was equal to the measured Th (as shown in section V, no "pressure correction" is needed).

Most of the samples contain all-liquid inclusions, i.e., without vapor bubbles, ranging in size from approximately 100 micrometers down to less than 2 micrometers. These tell us that there was a liquid phase at the growing surface of the calcite crystal, but as they have no vapor bubble, no quantitative temperature data can be obtained from them. However, they do permit some qualitative bounds to be placed on the temperature at the time of trapping, based on well-known limitations on the nucleation of a vapor phase[7,8,c]. The smaller the inclusion, the less likely is the nucleation of any new phase, for two reasons: 1) The smaller the system, the less likely that a suitable nucleation site, a "mote", will be present, either as some appropriate irregularity of the inclusion cavity walls, or as a minute grain of a foreign substance, that will aid heterogeneous nucleation. 2) Fluid inclusions are small systems, so small that the probability statistics involved in the process of homogeneous nucleation by random molecular movement become significantly influenced by size and, hence, actual numbers of molecules involved.

On cooling from the temperature of trapping of a liquid inclusion, the point representing the system follows down an isochore in pressure-temperature space until it reaches the V/L two-phase line, where a bubble of vapor should nucleate. (This is the same point at which the bubble will disappear on heating during an homogenization run.) In practically all cases, however, nucleation does not occur at this point on cooling. Further cooling merely moves the all-liquid inclusion along the metastable extension of the isochore, into the field for vapor. Under these conditions, the liquid is an undercooled, "stretched" liquid, with a metastably lower density than it should have. When the first minute bubble of vapor nucleates, it instantly expands, the liquid shrinks to its correct density, and the system — now stable, not metastable— returns to the two-phase V/L line.

High temperatures at the time of trapping and large inclusion size both tend to minimize the amount of undercooling needed to induce nucleation of vapor. Extensive studies of samples from many environments show that inclusions >100 micrometers, trapped at temperatures >100°C, usually nucleate a bubble with only a few degrees of supercooling. Inclusions <100 micrometers in size, particularly if trapped at <100°C, frequently will not nucleate a bubble. Inclusions in the 10-20 micrometer range, trapped at <100°C, almost never nucleate a bubble, even after millions of years of metastability at near-surface temperature. As the samples studied here have many primary all-liquid inclusions as much as 100 micrometers in size, we can presume that they were trapped at temperatures well under 100°C.

B. Crushing Data

1. Formation of vapor-filled inclusions. The vapor-filled inclusions can have formed in various ways:

a. The host crystals may have grown from a vapor phase. For several reasons, this is very unlikely for these samples: the solubility of $CaCO_3$ would probably be very low unless the temperatures were high, yet the all-liquid inclusions indicate that the temperatures were very low.

b. They may have been liquid-filled inclusions that leaked and lost all their liquid through cracks (e.g., cracks formed during the borehole drilling). Such cracks can be below the limit of optical visibility. The inclusions would now be filled with air at one atmosphere.

c. They may have trapped a bubble of a vapor phase present in a heterogeneous, two-phase system of vapor plus liquid, as is known to have

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[c] Chapter 10

occurred in many other geological systems. This vapor phase may have consisted of:

(1) Steam, i.e., from boiling of a liquid water phase. On cooling, such inclusions would precipitate an invisibly thin layer of liquid on the walls, and leave the inclusion filled with a low pressure water vapor phase, almost a vacuum.

(2) Air. Air could have been trapped at 1-atmosphere pressure, if the system were open to the surface, or at >1-atmosphere pressure, if trapping occurred from air bubbles under some hydrostatic head.

(3) CO_2. Carbon dioxide gas bubbles could exsolve from water solutions and become trapped as inclusions. Unlike boiling of the water, which requires temperatures of at least 100°C, such effervescence of a CO_2 vapor phase can occur at any temperature. This CO_2 phase would be in equilibrium with liquid water, so it would also contain water vapor at the partial pressure appropriate for the temperature of trapping.

2. Crushing test rationale. The crushing test[6] provides a qualitative estimate of the gas pressure within an inclusion at the time of crushing, unless a gas is present that is soluble in the crushing oil. It involves breaking an inclusion open under the microscope while the host mineral grain is immersed in oil at 1-atmosphere pressure. An inclusion filled with a gas having a pressure greater than atmospheric, or one filled with a fluid having a vapor pressure greater than atmospheric (e.g., light hydrocarbons) would instantly expand, or "boil", into the oil. If filled with liquid water containing CO_2 at >1-atmosphere pressure, a vapor bubble would form, just as in opening a bottle of beer. An inclusion filled with air at 1-atmosphere wouldn't change, i.e., would yield a bubble of the same volume as the original inclusion. An inclusion formed by trapping of a steam bubble, since it would have a pressure of only about 30 mm after cooling to room temperature (above possibility c-1), would instantly fill with oil. Inclusions containing CO_2 (above possibility c-3) would have a more complex behavior; the vapor would expand or collapse by an amount controlled by the pressure, temperature and composition of the system at the time of trapping.

If the gas phase trapped in the vapor inclusion consisted of a bubble of non-condensable gases such as air and/or CO_2 in equilibrium with the aqueous fluid from which the calcite crystallized, there would also be an amount of water vapor in the trapped gas corresponding to the partial pressure of water at the temperature of trapping. On cooling to room temperature, condensation of this water vapor would create a partial vacuum in the inclusion. On crushing, the surrounding immersion oil would enter such an inclusion in an amount corresponding to the partial pressure of water vapor during trapping. This logic was used to estimate the temperature of trapping of some inclusions from these samples; these temperatures were estimated be "<100°C"[1].

The temperature values obtained by this method are actually only maximum values, as a result of a caveat not mentioned in the previous study[1] — if a gas in the vapor inclusion is highly soluble in the oil used in the crushing procedure, oil will dissolve this gas and enter the inclusion just as though it was a partial vacuum at the time of crushing. Since the previous report[1] we have obtained preliminary qualitative Quadrupole^{TM} mass spectrometer analyses of the gases in the inclusions in these samples, through the courtesy of Dr. Gary P. Landis of the USGS. These analyses show that the gases are mixtures of nitrogen and oxygen (at near "air" ratios), CO_2, and methane. Methane is highly soluble in the immersion oil used, and we now believe that most or even all of the collapse of the gas inclusions that was found on crushing stems from dissolution of the methane. As such, the temperatures calculated for trapping are well under the "<100°C" reported earlier, and could have been near surface temperatures. Some corroboration of this interpretation was obtained by crushing additional vapor inclusions in glycerol, a fluid that is not a good solvent for methane. Neither collapse nor expansion occurred in glycerol, suggesting that the contribution of water vapor to the collapse in oil was minimal and that trapping occurred at near-surface temperatures.

V. ENVIRONMENT OF FORMATION OF THE CALCITE VEINS

The presence of all-liquid inclusions, and the absence of two-phase, liquid + vapor, inclusions in the upper thousand feet of the USW G-1 borehole together establish that these calcites have formed at low temperatures, <100°C, possibly comparable to modern ambient temperatures. The higher temperatures found on homogenization of the few two-phase inclusions present in deeper parts of the core corroborate published research documenting a deep hydrothermal system at 10.4ka, coincident with the formation of the Timber Mountain caldera just to the north of Yucca Mountain[5].

The phase relations at the point and time of trapping can be deduced, with relatively little ambiguity, from the inclusion evidence. The all-liquid inclusions tell us only that a liquid phase was present. It could have been merely a film of water flowing down the walls of the fracture, or the entire vein could have been filled. However, a vapor phase was also present. Such mixture of all-liquid and all-vapor inclusions might be expected from a thin, flowing film of water in which small vapor bubbles occasionally form on the crystal faces and are trapped, or in calcite growing into a vein filled with liquid, out of which small amounts of gas was exsolving as bubbles. The inclusion evidence favors the water film environment, as the vapor inclusions show essentially atmospheric internal pressure (when crushed in glycerol), even in samples as deep as 314 m. If the vein were filled with water to this depth, these vapor inclusions would have been trapped at pressures ≤30 atmospheres. Thus, these inclusions were formed in the unsaturated zone. (If crushing experiments show similar low pressures for the samples for which Th were determined, there would be no need for a "pressure correction" to be added to the homogenization temperatures to obtain trapping temperatures.)

Although the above arguments seem to establish that the calcite crystallized from a descending film of water on the walls of a vein that was open to the atmosphere, the origin of the gases in the inclusions is not as clear. The gases could simply be "air", pumped in and out of the vein by barometric pressure changes. The CO_2 and methane could be of bacterial origin, carried down with the water and exsolved as temperatures rise slightly. Alternatively, all gases ("air", CO_2, and methane) could have been exsolved into the vein system from deeper circulating ground waters. We have not as yet found any inclusion evidence for the age of formation of the host calcite.

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