EVIDENCE FOR AN UNSATURATED-ZONE ORIGIN OF SECONDARY MINERALS IN YUCCA MOUNTAIN, NEVADA

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INTRODUCTION

The unsaturated zone (UZ) in Miocene-age welded tuffs at Yucca Mountain, Nevada, is under consideration as a potential site for the construction of a high-level radioactive waste repository. Secondary calcite and silica minerals deposited on fractures and in cavities in the UZ tuffs are texturally, isotopically, and geochemically consistent with UZ deposition from meteoric water infiltrating at the surface and percolating through the UZ along fractures[1]. Nonetheless, two-phase fluid inclusions with small and consistent vapor to liquid (V:L) ratios that yield consistent temperatures within samples and which range from about 35 to about 80°C between samples have led some to attribute these deposits to formation from upwelling hydrothermal waters[2,3]. Geochronologic studies have shown that calcite and silica minerals began forming at least 10 Ma and continued to form into the Holocene[1,4]. If their deposition were really from upwelling water flooding the UZ, it would draw into question the suitability of the site as a waste repository.

Past studies of calcite fluid inclusion petrography and temperature were based on samples from drill cores that extended well into the saturated zone (SZ)[5,6]. Secondary calcite in the SZ is part of a mineral assemblage formed by hydrothermal activity[7] about 10.4 Ma[5] from heated fluids likely originating in the Paleozoic marine sedimentary rock aquifer[1] that underlies the Miocene volcanic sequence. Potassium-argon ages of illite and smectite formed during this event[5] have a weighted average of 10.5±0.4 Ma (95% confidence level) using ISOPLOT[8]. Fluid inclusions in the SZ alteration minerals indicate temperatures ranging from about 100°C up to about 250°C in the deepest samples[5,6]. Both studies, however, reported that calcite-hosted fluid inclusions in the UZ that might provide reliable indications of depositional temperature were rare and concluded that the fluid inclusion assemblages (FIAs) in the UZ calcite were consistent with formation at low temperature under unsaturated zone conditions as described by Goldstein[9].

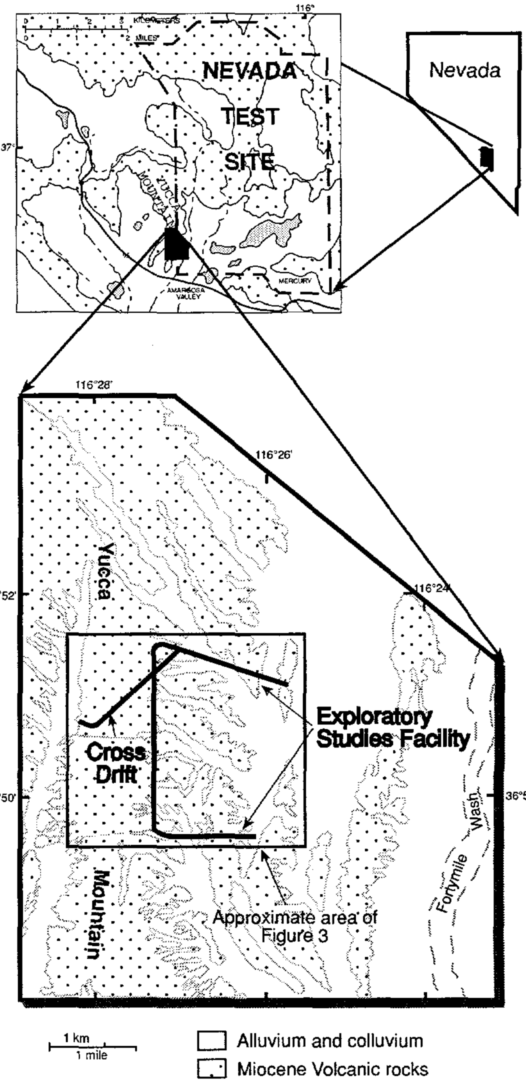

Figure 1. Maps showing the location of Yucca Mountain, the potential repository site, the Exploratory Studies Facility, and the east-west cross drift. The area shown in figure 3 is outlined in black.

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At the request of the Department of Energy in 1999, the U.S. Geological Survey (USGS) and the University of Nevada at Las Vegas agreed to conduct comprehensive, but independent, fluid inclusion studies of UZ calcite to determine the distribution, petrography, temperature, and timing of calcite-hosted fluid inclusions. Data were to be collected by the participants from splits of 155 samples jointly collected from the Exploratory Studies Facility (ESF) and east-west cross drift (EWCD) underground workings at Yucca Mountain (Fig. 1). This paper reports preliminary USGS results from these samples. Although about one-half of the calcite coatings contain fluid inclusions indicating elevated formation temperatures (35 to 85°C), such inclusions are restricted to the basal and, locally, middle portions of the coatings. Outer portions of the coatings do not contain such inclusions indicating that such temperatures apparently did not persist into the last several million years. The calcite fluid inclusion assemblages, including those indicating elevated temperature (<100°C), are more consistent with a UZ setting than with a flooding scenario requiring upwelling of water from depth.

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GEOLOGIC SETTING

The UZ at Yucca Mountain is composed of the Miocene-age Tiva Canyon and Topopah Spring Tuffs, both thick and mostly welded units, separated by the thin and bedded, non-welded, Yucca Mountain and Pah Canyon Tuffs. The welded tuffs are highly fractured, creating many percolation pathways. Coatings of calcite and silica minerals (quartz, chalcedony, and opal) with minor fluorite and zeolites have been deposited on the footwalls of some of these fractures and on the floors of some lithophysal cavities intersected by fractures. Deposits of these minerals on the hanging walls of fractures or the walls or ceilings of cavities are uncommon. On steeply dipping fractures, the deposits form thin, regular to patchy, coatings of more or less even thickness; in the Tiva Canyon Tuff, these fractures generally contain silica minerals interlayered with the calcite, whereas in the Topopah Spring Tuff they commonly contain only calcite. On shallowly dipping fractures and on cavity floors the deposits form uneven, but generally thicker, crusts commonly consisting largely of discrete, freestanding calcite blades. This calcite is commonly intergrown with local and discontinuous layers of botryoidal to colloform chalcedony or drusy quartz, in the early stages, or opal, in the later stages.

Coatings and crusts are heterogeneously distributed. Mineralized and unmineralized fractures are commonly found within 1 m or less of each other and in many exposures intersect, and mineral coatings are commonly local with barren zones both up and down dip along the fractures. Underground mapping of 30-m sections at 100-m intervals over the entire ESF (7800 m) shows that <6% of fractures over 1 m long contain mineral coatings. Mapping of lithophysae in five 30-m sections indicated only 1 to 42% were mineralized[10]. Most potential mineralization sites on fractures and in cavities are barren.

METHODS

Paragenetic (mineral deposition) sequences and the distribution and description of FIAs were determined by examination of doubly-polished thick (about 150 micrometer) sections with a petrographic microscope. Mineralogic distinctions between the silica minerals are based on visual assessments of crystallinity that are less precise than other means, such as X-ray diffractometry. Homogenization temperatures (T_h) of two-phase fluid inclusions were measured with a Linkam[a] heating/freezing chamber at a precision of about ± 1.0°C.

Phase relations in low-temperature fluid inclusions are easily disturbed, particularly in calcite[11]. Samples of calcite used in this work were, therefore, carefully protected from temperatures <0 or >30°C during collection, transport, and preparation of sections for microscope study.

Fluid inclusions found in minerals can reflect the physical and chemical conditions during mineral growth. If trapping occurs at above ambient temperature, the liquid will shrink as the host mineral cools and, if the stress from shrinkage exceeds the surface tension of the liquid, a vapor bubble will nucleate, resulting in a two-phase V+L fluid inclusion. Accepted assumptions and procedures were used to reconstruct depositional temperatures from two-phase fluid inclusions[11,12]. The T_h of two-phase fluid inclusions is measured by slow heating until the shrinkage bubble disappears. This temperature, corrected for the external pressure on the depositional system at the time of

[a] Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

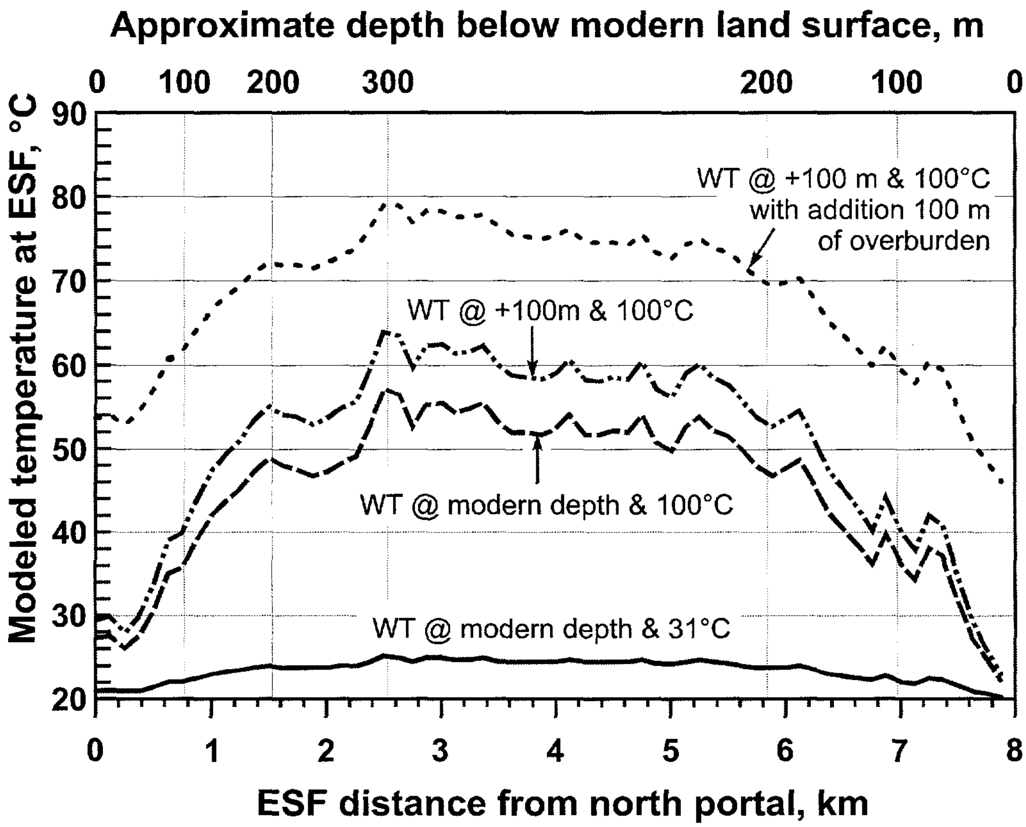

Figure 5. Model ESF temperatures assuming linear thermal gradients from the water table (WT), fixed at either 31° or 100°C, to the land surface with an assumed mean annual temperature of 20°C. ESF temperatures are also calculated for conditions of an elevated water table (100 m higher than modern) and the modern land surface as well as with 100 m of overburden added uniformly to the modern land surface.

deposits in the north and south ramps of the ESF has $\delta^{18}O$ <10‰, some as low as 3.4‰[16] (Fig. 4). Assuming a $\delta^{18}O_{H2O}$ of about –13‰, comparable to that presently found in the UZ[17], the calcite $\delta^{18}O$ values <10‰ of the early stage are generally consistent with temperatures of 50 to 100°C and, in fact, show excellent agreement with fluid inclusion T_h for those samples where both values are available. The

Comparison of fluid inclusion T_h with temperatures calculated from calcite $\delta^{18}O$ values

Location	$\delta^{18}O$cc	$\delta^{18}O$cc Temperature	Fluid Inclusion T_h
ESF 1+62.3	3.2 to 6.3	77-100	64, 85
ESF 12+15.58	6.7	74	54 to 66
ESF 14+06	7.6, 9.8	53, 68	55, 64
ESF 72+94.5	8.6	60	57, 62
ESF 75+74.7	8.9	58	<60

gradual increase of calcite $\delta^{18}O$ during the early and intermediate stages, from values of 10-11‰ to 17-18‰, is consistent with temperatures decreasing from about 50°C to 25 to 30°C, comparable to present-day ambient conditions.

Fluid inclusion T_h and $\delta^{18}O_{cc}$ variations both indicate that 1) the highest depositional temperatures occurred during the early stage and in the north and south ramp sections; 2) depositional temperatures decreased with time during the early and intermediate stages; and 3) no evidence has been found for elevated temperatures during deposition of the late-stage calcite.

YUCCA MOUNTAIN THERMAL HISTORY

Tuffs below the water table at Yucca Mountain were altered by 100 to 200°C hydrothermal fluids associated with magmatic activity within the Timber Mountain caldera as late as about 10 Ma[5], one of a number of regional hydrothermal events in this time frame[18]. Heat input into the UZ rock mass during this period would be largely by conduction. As a means of evaluating possible UZ conditions at this time, a simple model assuming a linear thermal gradient between the water table and the surface has been used to estimate temperatures within the ESF (Fig. 5). For modern conditions (water-table temperature of 31°C[19], water-table elevation at 730 m above sea level[20], average surface temperature of 20°C, and measured elevations of the land surface and ESF from G.S. Mongano [Bureau of Reclamation, written commun., 2000]), maximum temperatures of about 25°C are calculated for areas of the ESF having the thickest overburden (solid line, Fig. 5). This value is similar to fluid trapping, is assumed to be the depositional temperature. In a near surface setting, the pressure correction is 0°C for minerals formed above the water table and only a few degrees for settings up to several hundred meters below the water table.

RESULTS

The mineralogy, paragenesis, and fluid inclusion petrography have been described for about two-thirds of the secondary mineral samples. A generalized depositional sequence for these minerals is shown in figure 2.

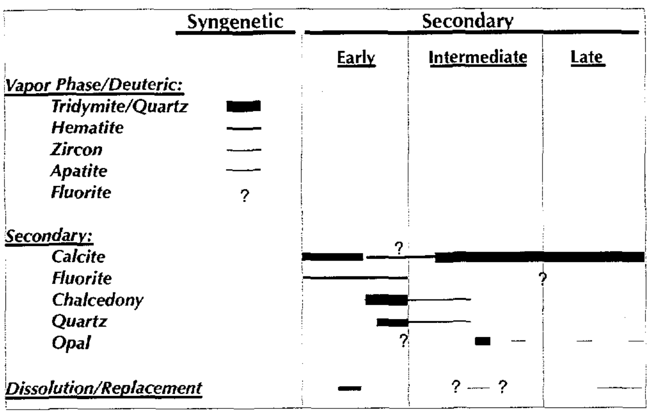

Figure 2. Generalized paragenetic sequence of syngenetic, high-temperature vapor phase and later low-temperature secondary minerals in the unsaturated zone of Yucca Mountain, Nevada.

Paragenetic sequence. High-temperature fluids deposited vapor-phase minerals during post-eruptive cooling of the tuffs. This depositional stage, which consists primarily of tridymite with minor hematite and other silicates (Fig. 2), is not relevant to the depositional temperatures of calcite-hosted fluid inclusions.

Calcite is the earliest mineral in the secondary mineral paragenesis. In many samples, chalcedony, locally intergrown with or coated by drusy quartz and growing on or replacing the early calcite, marks the end of early-stage deposition. Fluorite and zeolites are found in or with early-stage calcite and chalcedony. Intermediate-stage deposits consist of calcite, bladed in the cavity settings, locally with scattered patches or intercalated masses of botryoidal or spheroidal opal. Chalcedony and quartz are rare in the intermediate stage. Late-stage calcite is clear and euhedral and commonly intergrown or interlayered with patchy to spheroidal opal. Silica minerals are common in lithophysal cavities of both the Tiva Canyon and Topopah Spring Tuffs, and in Tiva Canyon Tuff fractures, but rare in steeply dipping fractures of the Topopah Spring Tuff. Also, the different calcite stages may not be easily distinguished in deposits coating steeply dipping fractures but have characteristic textures in shallowly dipping fracture and lithophysal cavity settings. In those settings: early-stage calcite forms intergrowths or mosaics of semi-equant grains with local growth zoning; intermediate-stage calcite is commonly bladed with buried growth faces marked by planes of solid and fluid inclusions; and, late-stage calcite forms clear, inclusion-poor, euhedral overgrowths on intermediate-stage blades and may contain prominent growth zones defined by etched crystal faces and (or) periods of opal deposition.

Corrosion of calcite includes dissolution and possible replacement by early-stage chalcedony, minor etching of existing or buried crystal growth faces, or development of large-scale secondary porosity in the basal portions of cavity crusts (Fig. 2). The source(s) of calcite-undersaturated fluids in the UZ are not obvious but evaporation and recondensation of water vapor within a UZ setting would provide one means of locally lowering fluid salinities or pH and dissolving calcite.

Not all deposits contain the entire paragenetic sequence. It is commonly complete in the larger cavity deposits, but smaller cavities and fractures typically display only portions of the sequence. Furthermore, silica mineral abundances appear to decrease with depth. Notwithstanding the incomplete paragenetic sequences of many deposits, the mineralogic differences between fracture and cavity deposits and between near-surface and deeper deposits, and the long (≥10 m.y.) record of mineral deposition[4], isotopic and geochronological studies indicate concurrent deposits in the ESF had common fluid sources. The observed mineralogic and paragenetic variability may reflect local depositional controls, such as ease of evaporative concentration of fluids, rather than chemical or temporal differences in fluid input.

Fluid inclusion petrography. Petrographic examination of almost 100 thick sections indicates that the FIAs in UZ calcite contain numerous all-liquid inclusions with lesser numbers of two-phase inclusions characterized by large and variable V:L ratios. These findings corroborate earlier results[6,13]. In this study, however, about 42% of the samples also contain two-phase inclusions with small and consistent V:L ratios (TPVL) suitable for measurement of T_h. Where found, TPVL inclusions may compose <10 to nearly 100% of the inclusions in those FIAs that contain them. Nonetheless, TPVL inclusions are still a very small portion of the total because most FIAs do not contain them. The absence of TPVL inclusions in earlier studies[6,13], including, possibly, Bish and Aronson[5], probably reflects inadvertent heating during sawing, mounting, or polishing of those samples. Once-heated, low-temperature two-phase fluid inclusions are indistinguishable from all-liquid inclusions because they rarely renucleate a shrinkage bubble. The location of samples examined to date and the distribution of those containing TPVL fluid inclusions are shown on figure 3.

Preliminary fluid inclusion T_h measurements show spatial variations in temperature. Figure 3 shows the distribution of these temperatures in Yucca Mountain on the basis of more than 2000 determinations of T_h. The temperatures listed reflect peaks from T_h histograms; data from individual samples or FIAs have standard deviations ranging from 1.5 to 7.1°C. Homogenization temperatures ≥85°C, about 20°C higher than any other location, are found in samples from a fracture near the north portal. Elsewhere, T_h ranges from about 55 to 65°C in the north and south ramp to about 40 to 60°C in the north bend area. TPVL inclusions have not been observed in calcite samples from the EWCD beyond about station 10.

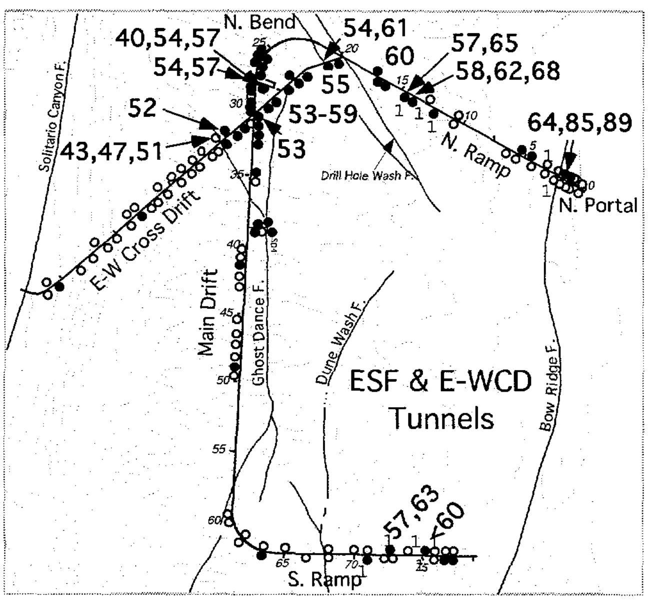

Figure 3. Map of the Exploratory Studies Facility and east-west cross drift showing the sample locations as circles, filled if TPVL fluid inclusions were found. Sites with calcite having $\delta^{18}O$ values <10.0 ‰ are labeled with an "1". Modes of fluid inclusion homogenization temperature distributions (°C) are shown; multiple values indicate multiple T_h peaks in the histograms.

Most of the FIAs containing TPVL inclusions are in early-stage calcite. Some samples from the north bend area, however, contain FIAs with TPVL inclusions in intermediate-stage calcite as well. Some of these display a range of T_h 50 to 60°C to as low as 35°C that correlates with deposition beginning in the early stage and extending into the early part of the intermediate stage (Fig. 3). Fluid inclusion assemblages containing TPVL inclusions have not been found in the late-stage calcite.

OXYGEN ISOTOPE TEMPERATURES

Calcite $\delta^{18}O$ values can provide an estimate of formation temperature, because the oxygen isotopic fractionation between calcite and water (approximated by $\delta^{18}O_{cc}$ - $\delta^{18}O_{H2O}$) decreases as depositional temperature increases[14]. In the ESF, $\delta^{18}O$ values of early-stage calcite generally range from 10 to 15‰, increase gradually through the intermediate stage, and range from 16 to 21‰ in the late stage (Fig. 4). The $\delta^{18}O$ values of the late-stage calcite are consistent with deposition at present-day rock mass temperatures from meteoric water infiltrating at the surface, interacting with the overlying soils, and percolating down through the UZ rock mass along fracture pathways[1]. Variations of $\delta^{18}O$ in late-stage calcite probably reflect climate-driven changes in the $\delta^{18}O$ of meteoric water. The general increase of $\delta^{18}O$ through the early and intermediate stages (Fig. 4) could also reflect climate, but there is no independent evidence for such a long-term climate shift. Furthermore, this would imply improbably light meteoric waters (-20 to 25‰) during the early stage; such water is presently found in Canada and Alaska. Gradual cooling of the rock mass during the early and intermediate stages can account for the $\delta^{18}O$ increase and is also consistent with the fluid inclusion temperatures. Assuming that the percolating water $\delta^{18}O$ values remained within the same 4 to 5‰ range indicated by the $\delta^{18}O$ of late-stage calcite, rock mass temperatures during the early and intermediate stages can be estimated, with lower $\delta^{18}O$ values indicating warmer rock mass temperatures.

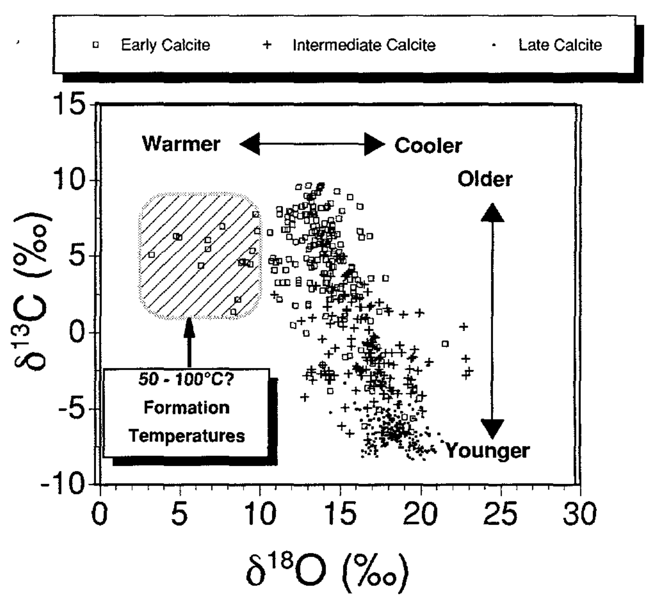

Figure 4. The $\delta^{18}O$ and $\delta^{13}C$ values of ESF calcite sampled from the different paragenetic stages[17]. Variations of $\delta^{18}O$ are discussed in the text.

Calcite with low $\delta^{18}O$ values indicating warmer temperatures was reported from drill core samples[15] and from early-stage calcite in the ESF[16]. Calcite from some rock temperatures of 23.5°C measured in nearby boreholes (Mark Kurzmack, U.S. Geological Survey, written commun., 2000) and 27°C measured on rock surfaces in the East-West Cross Drift (Alan Flint, U.S. Geological Survey, personal commun., 2000). Increasing the water-table temperature to 100°C, an upper bound for the period of shallow hydrothermal activity, increases the maximum ESF temperatures to about 55°C (dashed line, Fig. 5). Steepening the geothermal gradient by raising the water table an additional 100 m[21] increases the maximum ESF temperature to about 65°C (dash-dot line, Fig. 5). If an additional 100 m of overburden was present (representing an erosion rate of 0.01 mm/year over the last 10 m.y.), maximum ESF temperatures may reach nearly 80°C (dotted line, Fig. 5). One-dimensional thermal modeling of conduction[22] indicates that thermal perturbations from a long-lived magma body beneath the Timber Mountain caldera (from about 13 to 10 Ma) require million-year time scales for the upper crust (including the Yucca Mountain UZ) to return to pre-magmatic thermal gradients[23]. These calculations demonstrate that meteoric water percolating downward through the UZ is likely to have been at temperatures consistent with those measured in TPVL fluid inclusions during the early stages of mineral deposition.

Most secondary calcite, including that formed at an elevated temperature, is restricted to fracture footwalls or cavity floors, indicating formation from a liquid in an unsaturated zone setting, and therefore at <100°C. Initial cooling of the 300-m-thick tuffs was probably brief, on the order of tens-to-hundreds of thousands of years. Nonetheless, water could have circulated through the tuffs during the waning stages of cooling and deposited some of the early-stage minerals. Fumarolic activity altered the tuffs near Station 10[24], for instance, and might account for the calcite on a fracture at ESF Station 1+62.3, which has the highest T_h and lowest $\delta^{18}O$ yet measured (Fig. 3).

Ages measured on opal or chalcedony that microstratigraphically overlie calcite containing low $\delta^{18}O$ values or TPVL fluid inclusions support a protracted episode of UZ cooling (Leonid Neymark, U.S. Geological Survey, written commun., 2000). Most of these $^{207}Pb/^{235}U$ ages indicate that the calcite with signatures of elevated temperature formed prior to 5 to 10 million years ago. No TPVL fluid inclusions have been found in calcite younger than 1.9 Ma. These data indicate that ambient UZ temperatures remained elevated during the earlier stages of mineral formation, and required millions of years to cool to the temperatures found in the rocks at present.

ORIGIN OF SECONDARY MINERALS

The sporadic distribution of secondary mineral deposits on no more than 6% of fractures (on footwalls) and only 1 to 42% of lithophysal cavities (on floors) is consistent with simulations of fracture flow processes in a UZ setting, as modeled by Pruess[25]. The distribution and restriction of deposits to footwalls and floors is inconsistent with a rise in the water table, or even localized hydraulic saturation, which would indiscriminately and universally mineralize all fractures and cavities in the regions of flooding.

Early-stage calcite commonly contains FIAs consisting of all-liquid FIs, some two-phase FIs with large and variable V:L ratios, and two-phase FIs with small and consistent V:L ratios[26,27] and with T_h ranging from 35 to 85°C[2,3,26,27]. In a few locations, they appear to extend into the intermediate stage of mineralization. The calcite T_h, as well as calcite $\delta^{18}O$ values that are locally <10‰, indicate an early period of elevated depositional temperatures. Warmer temperatures do not, however, require flooding of the UZ, and the FIAs do not support flooding of the host rocks then or at any other time. The vapor-rich inclusions, with large and variable V:L ratios and internal pressures consistent with trapping of atmospheric gases[6], are consistent with FI trapping in the UZ[12] at temperatures above 30 to 35°C, but <100°C. Elevated temperatures during the early stage followed by a gradual decrease to ambient conditions during the intermediate stage are indicated by both the fluid inclusion T_h and $\delta^{18}O$ values of calcite during those stages. The data indicate that the rock mass has probably been unsaturated during secondary mineral deposition and at near-ambient temperatures for at least the last 2 million years, and possibly as much as 4 million years[4,16].

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