Limited hydrologic response to Pleistocene climate change in deep vadose zones – Yucca Mountain, Nevada

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A B S TRACT
Understanding the movement of water through thick vadose zones, especially on time scales encompassing long-term climate change, is increasingly important as societies utilize semi-arid environments for both water resources and sites viewed as favorable for long-term disposal or storage of hazardous waste. Hydrologic responses to Pleistocene climate change within a deep vadose zone in the eastern Mojave Desert at Yucca Mountain, Nevada, were evaluated by uranium-series dating of finely layered hyalitic opal using secondary ion mass spectrometry. Opal is present within cm-thick secondary hydrogenic mineral crusts coating floors of lithophysal cavities in fractured volcanic rocks at depths of 200 to 300 m below land surface. Uranium concentrations in opal fluctuate systematically between 5 and 550 μg/g. Age-calibrated profiles of uranium concentration correlate with regional climate records over the last 300,000 years and produce time-series spectral peaks that have distinct periodicities of 100- and 41-ka, consistent with planetary orbital parameters. These results indicate that the chemical compositions of percolating solutions varied in response to near-surface, climate-driven processes. However, slow (micrometers per thousand years), relatively uniform growth rates of secondary opal and calcite deposition spanning several glacial-interglacial climate cycles imply that water fluxes in the deep vadose zone remained low and generally buffered from the large fluctuations in available surface moisture during different climates.

1. Introduction

Hydrologically unsaturated zones (vadose zones) more than 100 m thick are common in arid and semi-arid regions and preserve regional climate variations as changes in rates and compositions of infiltrating pore water (Edmunds and Tyler, 2002; Glassley et al., 2002; Walvoord et al., 2004). An understanding of the long-term movement of water through thick vadose zones is increasingly important as limited water resources in these environments are evaluated in terms of both quantity and quality, and as these environments are being considered as sites for long-term isolation of toxic waste. However, the flow of small amounts of water through thick vadose zones, usually as thin films, is difficult to measure, especially at time scales required for waste isolation (thousands to hundreds of thousands of years). In particular, chronologies of pore water records are poorly constrained and may not extend beyond the last full-glacial episode (10 to 20 ka). In contrast, long and detailed histories spanning hundreds of thousands of years are common in speleothems and travertine veins formed in karst environments (Fairchild et al., 2006; Winograd et al., 1992). These types of mineral records that allow evaluation of paleohydrologic responses to climate have not been reported from non-karst settings due to the apparent absence of materials that clearly preserve the history of unsaturated flow in thick vadose zones. Secondary fracture coatings exposed in underground workings at depths of 200–300 m within Yucca Mountain, Nevada (Fig. 1), offer a unique opportunity to investigate long-term hydrologic responses of a thick vadose zone to Pleistocene climate change. Although the morphologies and growth histories are distinct from speleothems deposited in karst settings, they formed from similar depositional processes involving downward-percolating vadose water (Paces et al., 2001; Whelan et al., 2002). An understanding of the hydrologic response to climate-induced changes in moisture availability throughout the Pleistocene is critical to evaluations of sites such as Yucca Mountain, which was studied as a geologic repository for high-level radioactive waste (Department of Energy, 2008; Levich and Stuckless, 2007; Sharpe, 2007; Stuckless and Dudley, 2002, p. 2-6). Deep percolation represents the primary mechanism for release and transport of long-lived radionuclides. The Yucca Mountain site is no longer being considered as a viable option for long-term storage of spent nuclear fuel, in part, because of the perception that the fractured rock may become saturated with water during wetter climates (e.g.,
This paper focuses on determining the last 300,000 years (300 ka) of opal growth in samples of secondary mineral coatings from fracture and lithophysal cavities present in the deep vadose zone. Because of the very slow growth rates of these coatings (micrometers per thousand years, or μm/ka; Neymark et al., 2002; Paces et al., 2004), U-series disequilibrium ages were determined at spatial resolutions of ~20 μm using secondary-ion mass spectrometry (SIMS). If variations in Pleistocene climate produced large differences in infiltration and deep percolation, vadose zone minerals are likely to preserve systematic variations in growth rate caused by fluctuations in solute supply or degree of mineral saturation in percolating water. Importantly, variations in growth rates at depth should be correlated with fluctuations in surface moisture known to have affected the region (Sharpe, 2007, and references therein). Such correlations have been observed in speleothems along with chemical and isotopic data that reflect climate-induced variations in vadose hydrochemistry (Fairchild et al., 2006).

2. Hydrogeologic setting

Yucca Mountain, located on the eastern side of the Mojave Desert approximately 145 km northwest of Las Vegas, Nevada, consists of a 1–3-km-thick sequence of gently dipping, ~12.8-million-year (Ma) old tuffs with a 400–700-m-thick vadose zone (Keefe et al., 2007; Stuckless and Dudley, 2002). The repository horizon was proposed to be located in the lower of two densely welded and fractured ash-flow tuffs separated by 25 to >100 m of nonwelded ash-flow tuffs (Fig. 1C). The tuffs constituting the vadose zone have been grouped into informal hydrogeologic units, high-angle normal faults, proposed repository horizon, and static water table (Day et al., 1998).
SiO$_2$ is precipitated downward, by changes in the partial pressure of CO$_2$ within a gas-cavity, by increases in Ca concentrations in solution, and by evaporation. SiO$_2$ whereas loss of water vapor by evaporation results in opal precipitation.

Widely accepted conceptual models of infiltration in arid settings (Flint et al., 2001a,b) posit that infiltration is directly related to available surface moisture, that infiltration passing beneath the root zone (zone of evapotranspiration) recharges to the water table, and that infiltration fluxes were substantially larger than present-day values during Pleistocene pluvial climate conditions when temperatures were as much as 10–15 °C cooler and precipitation was 1.4–3 times wetter than present conditions (Forester et al., 1999; Quade et al., 2003; Sharpe, 2007; Spaulding, 1985; Thompson et al., 1999). Increased surface moisture during the last several glacial episodes supported large freshwater lakes in Death Valley and other basins in the region (Fig. 1A; Forester et al., 2005; Lowenstein et al., 1999; Smith and Bischoff, 1997) and may have produced substantially higher amounts of infiltration compared to modern estimates (300 mm/a versus 0.6–10 mm/a; Faybishenko, 2007). Despite the clear evidence for increased surface moisture in the past, the response of deep vadose percolation to Pleistocene climate fluctuations has remained difficult to quantify.

### 3. Samples and analytical methods

#### 3.1. Sample description

Secondary mineral coatings consist of 1- to 30-mm-thick irregular crusts of coarse, sparry calcite often interlayered with lesser clear hyalitic opal (Paces et al., 2001; Whelan et al., 2002). Coatings are present on a small percentage of open fracture footwalls and cavity floors exposed throughout the Exploratory Studies Facility (ESF) and East–West Cross Drift (EWCD) tunnels (Fig. 1B). Samples used here are from the upper lithophysal and middle nonlithophysal zones of the Topopah Spring Tuff in the northern part of the underground workings. This area contains some of the thicker, more delicate coatings with relatively abundant opal; however, coatings in this area are fundamentally similar to others exposed elsewhere in the ~10 km of tunnels excavated.

The sporadic distribution of mineral coatings, their restriction to sloping surfaces rather than ceilings or hanging walls of mineralized cavities, and their highly irregular and convoluted textures are interpreted as evidence that water never ponded within lithophysae. Instead, physical characteristics of the deposits are consistent with precipitation from infiltration that in some cases (Bischoff, 1997) and may have produced substantially higher amounts of infiltration compared to modern estimates (300 mm/a versus 0.6–10 mm/a; Faybishenko, 2007). Despite the clear evidence for increased surface moisture in the past, the response of deep vadose percolation to Pleistocene climate fluctuations has remained difficult to quantify.

#### 3.2. Analytical methods

Isotopes of Th and U were analyzed by secondary ion mass spectrometry (SIMS) using the Stanford-U.S. Geological Survey Sensitive High-Resolution Ion Microprobe–Reversal Geometry (SHRIMP-RG) following methods described elsewhere (Paces et al., 2004). An 18–40 nA primary beam of $^{16}$O$^+$ ions was used to sputter and ionize U and Th or their oxides from spots on polished sections of hyalitic opal.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Precision</th>
<th>Measurement Details</th>
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| $^{230}$Th | ±5% | Measured $^{230}$Th abundances in Yucca Mountain opal were normalized to the weighted mean values for the same ratio measured in a 1.9-Ma-old opal standard (M21277: Amelin and Back, 2006) to correct for systematic instrument bias and to obtain activity ratios (AR). Measured $^{230}$Th abundances in Yucca Mountain hyalitic opal are extremely small ($^{232}$Th/ $^{230}$Th$^+$ atomic ratios typically much less than 1.0) and essentially all $^{230}$Th measured in these opals is derived from in situ decay of $^{238}$U. Two-sigma uncertainties for isotope ratios are derived from counting statistics (within-run error) plus external error derived from the reproducibility of frequent analysis of the M21277 opal standard.

<table>
<thead>
<tr>
<th>Dating Equation</th>
<th>Details</th>
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| $^{230}$Th/$^{238}$U | Ages based on $^{230}$Th/$^{238}$U disequilibrium were calculated using conventional iterative $^{230}$Th/$^{234}$U, $^{230}$Th/$^{238}$U dating equations (Broecker, 1963; Ilyanovich and Harmon, 1992; Ludwig, 2003). However, $^{230}$Th/$^{238}$U ages from $<200–250$ ka have large uncertainties due to large analytical errors associated with $^{234}$U (especially $^{230}$Th). To take advantage of the longer half-life of $^{231}$U (~245 ka versus ~76 ka for $^{230}$Th), model $^{234}$U/$^{238}$U ages (Ludwig and Paces, 2002) were calculated for spots older than ~200 ka assuming that $^{234}$U/$^{238}$U in solutions at a given site remained constant through time and equal to values obtained from $^{230}$Th/$^{238}$U dating results for younger layers from the same grain. Model-age uncertainties were propagated using within-run error for the measured $^{234}$U/$^{238}$U AR combined with the 2σ range in initial $^{234}$U/$^{238}$U AR calculated for younger layers.

Concentrations of U were estimated by normalizing $^{238}$U$^{16}$O beam intensities in analyses of unknown opals to values measured for M21277 spots determined in the same analytical session and multiplying by the median value of 981.5 μg/g for M21277 U concentrations reported in Amelin and Back (2006). Errors reported for opal U concentrations are large (~30% 2σ) because of the heterogeneous U distributions in the standard. Quantification of U concentrations is not necessary for U-series dating.

Cathodoluminescence (CL) images of calcite and opal reveal alternating bright and dark bands that reflect growth (Fig. 2). This layering is important for tracing internal microstratigraphy and for recording compositional variations that reflect changes in percolation chemistry or vadose-flow conditions. Profiles of relative pixel brightness on CL images were used to analyze an image-processing add-
in Adobe Photoshop™ (The Image Processing Tool Kit™, v4.0, Reindeer Graphics, Inc.). To compensate for differences in brightness levels between images, pixel values were normalized to the maximum value present in each profile (“relative brightness”). Profile distances were converted to depths in micrometers using scale bars included on CL images and confirmed by petrographic measurements. The centers of SIMS ablation pits were projected along CL-defined growth layers until they intersected profile lines overlain on the CL image. Distances from spot centerlines to the outer surface of the mineral grain, measured in micrometers, were used as apparent microstratigraphic depths. To evaluate relations between CL brightness and U concentration, a mean value of relative brightness was calculated for pixels within a 10-μm interval on either side of each SIMS spot centerline projected to the CL profile line.

Grain mounts were oriented to minimize angular corrections for dipping layers. Verification that layering intersects the polished surface at high angles was made by petrographic examination. However, because polished surfaces are not necessarily perpendicular to growth layering, measured microstratigraphic depths represent apparent thickness that may overestimate true microstratigraphic thickness. As such, calculated growth rates represent maximum values. Corrections for layer dip angle would decrease calculated growth rates by less than 30% for layers dipping up to 45 degrees from vertical.

4. Results

4.1. Cathodoluminescence intensity and uranium concentration

Yucca Mountain hyalitic opal fluoresces bright yellow-green under short-wavelength ultraviolet light. This characteristic coloration has been attributed to activation caused by trace amounts of U that maintains a near-linear O-U-O molecular bond after inclusion in the solid phase (Hanchar, 1999). To test if UO$_2^{2+}$ also causes CL response in Yucca Mountain hyalitic opal, a traverse of 44 SIMS spots across growth layering in opal sample HD2055 (red circles in Fig. 2) yielded measured $^{238}$U$^{16}$O beam intensities of 136–13,938 counts per second and relative mean spot brightness values of 34.2–99.0% (Fig. 3; data in Table S1 of online supplementary material). CL brightness and $^{238}$U$^{16}$O beam intensity are positively correlated ($R^2$ value of 0.955). U concentrations determined for U-series age analyses also are positively correlated with CL brightness. Spot analyses of other trace elements (Mg, K, Ca, Al, Mn, Fe, Ba) were determined to evaluate potential correlations with U concentrations or CL brightness; however, no consistent trends were observed (see section on SHRIMP-RG Elemental Abundances in online supplementary material). Therefore, CL intensity in the hyalitic opal is attributed to the amount of U present. This allowed conversion of measured CL intensities to U concentrations using linear relations determined for each opal grain. Resulting U concentrations ranged from 5.4 to 550 μg/g (data in Tables S1 and S2 of online supplementary material).

4.2. Age—depth relations

An accurate age framework is essential for providing a paleohydrologic context for these samples. Both $^{230}$Th/U ages and initial $^{234}$U/$^{238}$U AR were calculated for most analyses, as well as model $^{234}$U/$^{238}$U ages for spots older than ~200 ka (Table S2 in online supplementary material). Resulting ages range from 41 to 1290 ka and pass three important geochronological tests: (i) ages increase with increasing microstratigraphic depth, (ii) coeval layers have similar ages, and (iii) secular equilibrium $^{234}$U/$^{238}$U and $^{230}$Th/$^{238}$U values are obtained for ancient opal (e.g., 1.9-Ma-old opal standard 21277 and deepest layers of Yucca Mountain opal).

Relations between age and microstratigraphic depth are remarkably linear over the last 300 ka and indicate that average opal growth rates are extremely slow, ranging between 0.42 and 1.54 μm/ka (Fig. 4). These rates are consistent with those noted previously for Pleistocene opal dated by U-series (Paces et al., 2004) and U-Pb
(Nemchin et al., 2006) methods. Given these slow rates of growth, a ~20-μm-diameter spot incorporates opal deposited over a 13–48 ka time period. Furthermore, spots that include the outermost layers of opal have 230Th/U ages ranging between 31 and 41 ka (Table S2 in online supplementary material). Regressions of age versus microstratigraphic depth yield high linear correlation coefficients ($R^2 = 0.972$ to 0.995) and low MSWD (mean square of weighted deviates, a measure of the ratio of observed scatter of points from the best-fit line to the scatter expected from assigned errors; Ludwig, 2003) values (0.46 to 0.71), both indicating that long-term average opal growth rates in individual grains remained essentially constant over the last 300 ka. The relatively large age uncertainties for spots that include layers formed over substantial time spans allow for the possibility of shorter term (less than ~10 ka) variations in growth rates. Nevertheless, deviations from linear growth are not apparent over the last 300 ka in these profiles (Fig. 4) even though layers span several climate cycles thought, on the basis of hydrologic modeling studies, to have resulted in 10- to 100-fold variations in infiltration (Faybishenko, 2007).

Unlike opal, U concentrations in Yucca Mountain calcite are too low for SIMS dating. However, opal interlayered within calcite (Fig. 5) can be dated. Results from the tips of several calcite blades yield average calcite growth rates of 0.84 and 1.21 μm/ka (Fig. 6). These rates are the same as those obtained for opal-only profiles, and with Miocene growth rates determined for cm-thick calcite-dominated coatings from the same vadose horizon (Neymark et al., 2002). Even though opal is typically present as discrete patches within calcite blades, textural relations along lateral opal/calcite contacts as well as compositional banding at the same spatial scales in both phases are interpreted as evidence of coeval growth (Paces et al., 2001; Whelan et al., 2002; Wilson et al., 2003). Therefore, growth rates determined from opal profiles are applicable to calcite deposited over the same time periods.

5. Hydrologic responses to climate change

5.1. Continuity of depositional records

The ability of the dating method to capture and resolve detailed growth histories is important for using these records to evaluate hydrologic responses to Quaternary climate. In particular, the presence of non-zero age intercepts for regressions shown in Figure 4 implies that opal was not deposited on these grains during the last 24 to 33 ka. A depositional hiatus, which includes both the wettest and driest conditions during the last 30 ka, may be an indication that water did not seep into the cavities over this time period. Therefore, it is important to understand how faithfully the secondary minerals record a history of percolation and seepage in the vadose zone.

Although the calcite-opal coatings form by general outward growth from basal layers into open cavities, detailed growth histories can be complex and difficult to deconvolute. Microstratigraphic discontinuities within opal have been observed from textural relations where opal layers separated by substantial thicknesses of calcite can be traced on CL images back to areas lacking the intervening calcite. Measured age-depth relations in these cases yield very different growth rates depending on whether the intervening calcite is included or excluded.
In the several cases where these types of profiles were dated, resulting ages indicate depositional hiatuses on the order of several hundred thousand years. Shorter hiatuses might not be readily recognized.

Non-zero age intercepts are also dependent on where the origin of a profile is located. In all three cases shown in Figure 2, outermost surfaces of opal hemispheres where chosen for zero depths. However, the opal grain in sample HD2059 (middle image) has approximately 50 μm of calcite lying on top of the outermost layer of dated opal (light gray material above spots 2 and 6). Given the 1.54 μm/ka growth rate for this opal, the youngest period of calcite deposition matches the 33 ka hiatus missing from the HD2059 depth profile shown in Figure 4. Nevertheless, calcite deposition appears to have ceased on the HD2059 grain after about 33 ka for crystallographic or chemical reasons that are not fully appreciated, although calcite deposition appears to have continued until recently.

If non-zero age intercepts from dated opal profiles truly reflected an absence of seepage into these cavities, all opal growth should have ceased. Therefore, no opal younger than about 24 ka (X-intercept in bottom plot of Fig. 2) should be present on outer surfaces of opal hemispheres from sample HD2074. However, the outermost several μm of opal from 6 other hemispheres from this same cavity have ages determined by in situ microdigestions that range from 4 ± 1.9 to 11.6 ± 0.8 ka (Table 5 of Paces et al., 2004). Furthermore, previous efforts to determine age-depth relations for two opal hemispheres from HD2074 resulted in age intercepts of 8 ± 23 ka and 8.9 ± 8.3 (determined by SIMS dating; Fig. 9 of Paces et al., 2004), and 7.7 ± 6.3 ka (determined by in situ microdigestion dating; Fig. 13 of Paces et al., 2004). Cumulatively, these results indicate that seepage into the HD2074 cavity did not stop during the current interglacial climate; however, they also indicate that not all opal grains represent a simple and continuous record of seepage history.

5.2. Numerical simulations of opal growth rates

A series of simple numerical simulations of opal growth and spot analysis were constructed to evaluate the sensitivity of the SIMS age-profiling methods used in this study (see section on Simulations of Opal Growth Rates in online supplemental material). In these simulations, opal layers were deposited in 1-μm layers at constant growth rates from seepage water with constant 234U/238U AR. U-series isotopic compositions were calculated for each layer assuming closed-system evolution since the time that each layer was formed. Ages for a hypothetical SIMS analyses were then simulated by averaging the
isotopic compositions of layers included within a 25-μm-wide “spot”. Growth rates, hiatus durations, data density, and U concentrations were varied to evaluate the effects on simulated profiles.

Simulations of a continuously growing layered opal indicate that the $^{230}$Th/$^{234}$U and $^{234}$U/$^{238}$U values obtained using a 20-μm-diameter spot yield a close approximation of the true average age for the layers analyzed. $^{230}$Th/U ages calculated using weighted average isotopic compositions (layers constituting the central part of the spot having the greatest influence) have a small, but systematic bias toward younger values due to the non-linear effects of radioactive decay (Neymark and Paces, 2000; Neymark et al., 2000). However, these effects are typically negligible relative to the 10% or larger analytical uncertainties obtained from ion microprobe counting statistics (Fig. S9 of online supplemental material). These effects are greatest for young samples deposited at slow rates (<0.5 μm/ka).

Results of simulations that included systematic depositional hiatuses (i.e., 10 to 50 ka periods of non-deposition out of every 100 ka) indicate that detailed growth histories are likely to be obscured at slow rates of growth (<1 μm/ka). Increased data density (i.e., overlapping spots) improves the chances of identifying growth hiatuses. However, for simulations using growth rates less than 1 μm/ka, it is not possible to discriminate between (1) episodic deposition at higher growth rates interspersed with hiatus of 20 ka or less, versus (2) continuous growth at slower time-averaged growth rates (Fig. S12 of online supplemental material). Deposits formed at higher growth rates between 1 and 2 μm/ka are more likely to discriminate between these two scenarios and yield accurate growth histories, especially if spots are closely spaced.

5.3. Age-calibrated uranium profiles

Regardless of the geochronological limitations and possible gaps in the depositional record, the high spatial resolution (micrometer-scale) of the distinct CL banding present in vadose zone opals captures detailed compositional information at millennial or shorter time scales. In order to evaluate whether the variations in U concentration causing this banding are dependent on cavity-specific conditions or more site-wide causes, profiles need to be calibrated using the available age information. To do this, ages were assigned to each pixel of a CL profile using the slope and intercept values derived by linear regression of age versus depth data (Fig. 4). Resulting age-calibrated profiles were checked against age-depth-intensity relations for individually dated horizons to ensure that ages for dated SIMS spots were honored. Overall uncertainties for ages estimated for CL profiles are based on uncertainties calculated for regression slopes.

Resulting age-calibrated U profiles have several distinct U-concentration peaks present between 40 and 50 ka, 120–140 ka, 230–280 ka, and 300–350 ka (Fig. 7). The timing of peaks is consistent among profiles from different cavities and generally correlate with the precisely dated δ$^{18}$O record of regional paleotemperature preserved in Devils Hole calcite (Winograd et al., 1992, 2006), located approximately 45 km south-southeast of Yucca Mountain (Fig. 1A). For each opal profile, four primary peaks (labeled 1–4) and four secondary peaks (labeled a–d) were assigned ages at either their maximum values or midpoints of peak width (Fig. 7). The calcite δ$^{18}$O profile from Devils Hole was treated similarly using peaks with higher δ$^{18}$O (warmer climate). Mean ages for high-U opal layers closely correlate with the record of warm interglacial climates, matching ages of high-δ$^{18}$O peaks from the Devils Hole profile within ~10 ka (Table 1). The close correspondence between individual opal profiles and the continuous record of calcite deposition at Devils Hole is viewed as evidence that these opal grains did not suffer depositional discontinuities long enough to compromise the climate-proxy record. Discrepancies in timing between peaks in the three opal profiles are most noticeable for the oldest, least reliably dated layers, particularly for profile HD2055, which has the poorest geochronological constraints of the three.

5.4. Time-series analyses

Astronomical forcing has been identified as a likely cause for oscillatory cycles of climate change throughout the Pleistocene (Milankovitch cycles). Paleoclimate records commonly have periodicities of 100, 41, and 24 to 19 ka corresponding to the Earth’s orbital parameters of eccentricity (departure from a circular orbit), obliquity (angle of tilt of the pole), and precession (rotation of the pole about its central axis) (Muller and MacDonald, 1997). Time-series analysis (spectral analysis) of paleoclimate signals incorporating these types of periodic features will yield spectrums with a small number of frequencies that can be related to orbital periods (Muller and MacDonald, 2000).

Time-series analyses were made of age-calibrated opal U profiles using both the multi-taper method (MTM) and maximum entropy method (MEM). Both methods evaluate total time series, but estimate spectral content in different ways. In addition, both methods assume that the SIMS-derived ages used to calibrate CL brightness profiles are true ages — no “tuning” of the age profiles was performed prior to analysis. Therefore, only the best-dated profiles were tested by spectral analysis.

Results of time-series analyses show spectra with strong internal consistency and frequencies indicating periodicities greater than 10 ka...
evaporative concentration of solutes in soil and fracture water during warmer, drier climates. Profiles of calcite abundance and δ18O in the Yucca Mountain subsurface indicate that the effects of evaporation extend into the fracture network to depths up to 100 m (Whelan et al., 2002). Studies of other thick vadose zones have recognized the importance of subsurface evaporation and upward vapor fluxes, as well as the long periods (10–100 ka) required for equilibration to near-surface conditions (Glassley et al., 2002; Walvoord et al., 2002, 2004).

Because of the strong climate signal observed in vadose zone opal formed over the last 300 ka, mineral growth rates might be expected to fluctuate along with climate-induced changes in surface moisture. Studies of speleothems from North America, Europe, and Australia have found that faster growth rates are correlated with Pleistocene periods of increased surface moisture (Ayliffe et al., 1998; Baker et al., 1993; Musgrove et al., 2001). Growth rates in modern speleothems also were shown to correlate well with rainfall and excess water (i.e.; drip rate; Banner et al., 2007; Genty and Quinif, 1996). Although growth rates of Yucca Mountain minerals are ~100,000 times slower than speleothems in karst environments (Faichild et al., 2006), calcite precipitation is likely to be controlled by similar processes in both settings. Consequently, estimates of water-to-calcite volume ratios for the deep Yucca Mountain vadose zone are similar to values reported for speleothems and laboratory experiments where both water and calcite volumes are known (Marshall et al., 2003).

Calcite and amorphous silica have remained abundant in soils at the surface of Yucca Mountain throughout at least the middle Pleistocene (Section 10.4 of Ludwig and Paces, 2002). Therefore, it is likely that water infiltrating into the vadose zone has been chemically saturated with respect to both phases over the last 300 ka. This likelihood is supported by data from modern water seeping from several fractures in shallow parts of the ESF tunnel during the wet winter of 2005 as well as water perched in the deep vadose zone with δ13C-corrected radiocarbon ages of 2 to 7 ka (p. 37 of Yang et al., 1996), all of which have compositions that were saturated with respect to calcite and silica gel (Olive and Whelan, 2006; Fig. 36 of Paces et al., 2001). Furthermore, effects of substantial variations in surface temperature during the Pleistocene are likely to be negligible within individual cavities at depths of 200 to 300 m.

Because both saturation indices and temperature likely remained constant in the deep vadose zone at Yucca Mountain, percolation flux and associated seepage into cavities is interpreted to be the dominant factor controlling rates of mineral growth. Thicker coatings have higher growth rates and are a likely consequence of greater and more continuous average seepage fluxes. Thinner coatings have lower growth rates and are interpreted to have formed in cavities that received smaller or less frequent seepage fluxes. Water-film thickness and flow velocity are likely critical factors that explain differences between thinner, opal-poor coatings lining steeply dipping fractures compared to thicker, opal-rich coatings flowing shallow dipping lithophysae. Within individual lithophysal cavities, water films supplying solutes to outer mineral surfaces may only represent a

5.5. Deep vadose zone responses to climate change

The correlation between increased U concentrations in opal and interglacial stages (along with cyclic variations of Mg concentration in similar-aged calcite; Wilson et al., 2003) are consistent with greater

Table 1

<table>
<thead>
<tr>
<th>Peak label</th>
<th>Age of profile feature (ka)</th>
<th>1</th>
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</table>

Uncertainties for individual peaks are calculated from 2σ slope uncertainties reported for regressions in Figure 4. Uncertainties for weighted means are given at the 95% confidence level and include an additional weighting factor (Student’s t times the square root of the mean square of the weighted deviates; Ludwig, 2003) if a set of peaks exhibit scatter beyond individual errors. Ages for Devils Hole are derived from the data given in Winograd et al. (1992, 2006) with uncertainties for major interglacial periods representing approximate duration of warm periods based on the widths of the dark bands shown in Figure 7.
fraction of total water flux flowing through that cavity. Nevertheless, the presence or absence of water films as well as the thicknesses of water films will remain proportional to total seepage flux. Therefore, if climate change produced fluctuations in percolation and seepage fluxes in the deep vadose zone, mineral growth rates also should have fluctuated.

Alternatively, mineral growth rates may be limited by the rates of CO2 and water vapor removal. Although gas loss is an important mechanism for deposition, a water-limiting mechanism for mineral growth is considered more likely for several reasons. Air permeability in the deep vadose zone would tend to decrease during pluvial climates if increased percolation filled fractures and reduced the overall air circulation within the deep vadose zone. As a consequence, mineral growth rates would likely be lower during wetter periods if gas flow was the driving factor for mineral precipitation. In addition, age-calibrated profiles from different cavities are strongly correlated (Fig. 7) indicating that water films were closely connected to gravity driven percolation regardless of the different geometries involved. If gas-flow was the dominant factor limiting mineral precipitation, coherency between profiles from different cavities would be less likely given the variety of fracture geometries affecting air permeability. Finally, the dependency of mineral precipitation on water rather than gas fluxes is supported by geochemical and isotopic data from the host rocks themselves. Whole-rock samples subjacent to lithophysal cavities that host 10–30-mm-thick mineral coatings show greater U losses and 234U/238U disequilibrium than rock samples subjacent to cavities hosting little or no secondary minerals (Paces et al., 2006), reflecting greater degrees of water-rock interaction associated with more-mineralized cavities.

Despite the strong evidence for a meteoric source of vadose zone water, the effects of large variations in effective surface moisture known to have occurred throughout the Pleistocene are not apparent in these deep vadose-mineral records. Although the available spatial and geochronological resolutions do not allow detailed growth histories to be defined at century or even millennial time scales, these data are consistent with more-or-less uniform percolation and seepage fluxes at depth despite the large differences in surface-moisture availability between glacial and interglacial time periods. Variations in surface moisture over the time period recorded by opal profiles is manifested by the presence or absence of pluvial lakes throughout the region, including a very wet penultimate glacial cycle (marine oxygen isotope stage 6) that resulted in pluvial Lake Manly reaching depths up to 180 m at between ~180 and 140 ka followed by a long, warm interglacial period (stage 5e, Fig. 7) from about 130 to 110 ka that allowed Lake Manly to evaporate (Forester et al., 2005; Lowenstein et al., 1999). These records of climate change form the basis for large fluctuations in model infiltration simulated between glacial and interglacial climates (Faybishenko, 2007).

The uniform rates of mineral growth within the deep vadose zone at Yucca Mountain are interpreted as strong evidence that the amount of water flowing through the deep vadose zone was buffered from variations in surface moisture and shallow infiltration. Hydrogeologic processes contributing to this buffering may include: down-slope diversion of water at the contacts between colluvium and welded Tiva Canyon Tuff and between the Paintbrush nonwelded tuff and the underlying welded Topopah Spring Formation (Fig. 1C) as first proposed by Montazer and Wilson (1984); increased evapotranspiration by plant communities that adapt to cooler, wetter climates;
reduction of water fluxes in shallow fractured tuffs by evaporation and upward water flux; uniform release of percolation stored in nonwelded tuffs overlaying fractured repository units; and reduction of deep fracture flux by evaporation and/or imbibition into the welded tuff matrix of the deep vadose zone. These processes, most likely working in combination, may be effective at limiting the amount of water that infiltrates into the subsurface, reducing the percolation flux as it migrates downward, and buffering the percolation flux that enters into the deep vadose zone.

5.6. Meteoric versus upwelling water sources

Age-calibrated profiles of U concentration in opal that correlate with Pleistocene regional climate variations demonstrate that water flowing through the deep vadose zone was derived from a meteoric water source. This conclusion strongly contrasts with recently reported interpretations of measured hydrogen and calculated oxygen isotope data for fluid inclusions in calcite coatings from similar depths within Yucca Mountain (Dublyansky and Spötl, 2010). Those authors concluded that an apparent enrichment of δ18O in water from calcite-hosted fluid inclusions (calculated using measured δD values, fluid inclusion homogenization temperatures, and the assumption of O isotopic equilibrium between calcite and water) required water/rock exchange and a deep-seated hydrothermal water source. However, elevated temperatures are only applicable to the oldest parts of the mineral coatings (Whelan et al., 2008; Wilson et al., 2003): secondary minerals formed in the last 2 to 4 million years were deposited under modern thermal conditions. If the isotope measurements reported by Dublyansky and Spötl were from inclusions formed during this younger time frame, then temperature corrections are inappropriate. Without temperature corrections, measured δD and δ18O values (Table 1 of Dublyansky and Spötl, 2010) scatter on either side of the global meteoric water line.

Other than the well-documented hydrothermal alteration of tuffs well below the water table at Yucca Mountain that are associated with Timber Mountain caldera eruptions at ~10.5 Ma (e.g., Bish and Aronson, 1993; Whelan et al., 2008), there is no credible evidence requiring hydrothermal activity. Preservation of fragile fumarolic O isotopic signatures in vadose zone nonwelded tuffs precludes post-depositional hydrothermal modification (Holt, 2002). Furthermore, seismic pumping, the mechanism that Dublyansky and Spötl (2010) invoke to inject calcite- and opal-depositing hydrothermal fluids hundreds of meters up into the vadose zone is not widely accepted (Bredhoef, 1992; Carrigan et al., 1991; Rojstaczer, 1999). In contrast, the opal climate-proxy records presented here are consistent with a simple mechanism of gravity-driven, vadose zone flow, and a large body of other evidence from both surface and subsurface hydrogeochemical deposits (Marshall et al., 2005; National Research Council, 1992; Neymark et al., 2005; Paces et al., 2001; Sonnenthal et al., 2005; Stuckless et al., 1991, 1998; Vaniman and Whelan, 1994; Vaniman et al., 1994, 2001; Whelan and Stuckless, 1992; Whelan et al., 1994, 2002, 2005, 2008; Wilson and Cline, 2005; Wilson et al., 2003) that overwhelmingly supports a meteoric source.

6. Conclusions

The hydrologic response of deep vadose zones to changes in climate-induced surface moisture is an important aspect of understanding travel times, recharge rates, and potential water fluxes in arid environments, especially at sites chosen for isolating toxic wastes over long periods of time. The accepted paradigm of a direct correlation between effective surface moisture and deep fracture flow is shown to be questionable at Yucca Mountain within the arid Mojave Desert of southern Nevada. Instead, data from secondary hydrogenic minerals indicate that water fluxes through the deep vadose zone are at least partly decoupled from surface moisture and shallow infiltration, both of which have experienced large fluctuations over the past million years.

Data supporting this conclusion were obtained from detailed geochronological studies of U-rich opal formed in natural cavities at depths of 200 to 300 m below land surface. Profiles across individual hemispherical grains were dated by U-series methods using secondary ion mass spectrometry with spatial resolutions of approximately 20 μm. Ages obtained for 1-mm-thick grains range from 41 to 1290 ka. Opal grains also exhibit intricate growth banding that is manifested most notably in cathodoluminescence images. Oscillatory CL intensity is shown to be a function of U concentration which varies from 5.4 to 550 μg/g. Opal growth rates calculated over the past 300 ka are extremely slow, ranging from 0.42 to 1.54 μm/ka for different grains. Growth rates of associated calcite are shown to be similar. In spite of the variations in growth rates between different opal grains, rates remained more-or-less constant within individual profiles over time given the current degree of spatial and geochronological resolution. Ages are used to calibrate the more detailed U concentration profiles which show a remarkable correspondence with climate-proxy records and with frequencies indicative of planetary orbital forcing factors. Major peaks in U concentration correspond closely with interglacial episodes and are interpreted to be the result of increased amounts of evaporative concentration in soil water and shallow infiltration.

The uniform, linear rates of opal growth indicate that hydrologic conditions in the deep vadose zone remained stable throughout the Pleistocene despite multiple climate cycles, including the particularly cold and wet penultimate glacial episode (Sharpe, 2007). Long-term hydrologic stability also is implied by similar growth rates for older parts of the same coatings (Neymark et al., 2002; Whelan et al., 2008) despite Miocene and Pliocene climates that were warmer and wetter relative to Pleistocene conditions (Thompson, 1991; Winograd et al., 1985). These results imply that seepage fluxes in the deep vadose zone are decoupled from effective surface moisture and buffered from large variations in shallow infiltration. A number of hydrogeologic processes likely contribute to this long-term hydrologic stability including runoff and down-slope diversion at contacts between soil and bedrock and between nonwelded and welded tuffs, changes in evapotranspiration rates, evaporation and upward flux of shallow fracture water, storage and uniform releases of percolation from nonwelded tuffs, and reduction of deep fracture flux by evaporation and imbibition. Other deep vadose settings likely contain similar mineral records that could be used to evaluate hydrologic response to climate change.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.epsl.2010.10.006.


