STRONTIUM ISOTOPE EVOLUTION OF PORE WATER AND CALCITE IN THE TOPOPAH SPRING TUFF, YUCCA MOUNTAIN, NEVADA

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I. INTRODUCTION

Yucca Mountain, a ridge of Miocene volcanic rocks in southwest Nevada, is being characterized as a site for a potential high-level radioactive waste repository. One issue of concern for the future performance of the potential repository is the movement of water in and around the potential repository horizon. Past water movement in this unsaturated zone is indicated by fluid inclusions trapped in calcite coatings on fracture footwall surfaces and in some lithophysal cavities. Some of the fluid inclusions have homogenization temperatures above the present-day geotherm (J.F. Whelan, this volume), so determining the ages of the calcite associated with those fluid inclusions is important in understanding the thermal history of the potential repository site. Calcite ages have been constrained by uranium-lead dating of silica polymorphs (opal and chalcedony) that are present in most coatings. The opal and chalcedony ages indicate that deposition of the calcite and opal coatings in the welded part of the Topopah Spring Tuff (TSw hydrogeologic unit[1]) spanned nearly the entire history of the 12.8-million-year-old rock mass[2] at fairly uniform overall long-term rates of deposition (within a factor of five)[3].

Constraining the age of a layer of calcite associated with specific fluid inclusions is complicated. Calcite is commonly bladed with complex textural relations, and datable opal or chalcedony may be millions of years older or younger than the calcite layer or may be absent from the coating entirely. Therefore, a more direct method of dating the calcite is presented in this paper by developing a model for strontium evolution in pore water in the TSw as recorded by the strontium coprecipitated with calcium in the calcite. Although the water that precipitated the calcite in fractures and cavities may not have been in local isotopic equilibrium with the pore water, the strontium isotope composition of all water in the TSw is primarily controlled by water-rock interaction in the overlying nonwelded and essentially unfractured[4] Paintbrush Group tuffs (PTn[1]). The method of dating secondary minerals from known strontium evolution rates in rocks[5,6,7,8] cannot be used in this study because it assumes the water that deposited the minerals was in isotopic equilibrium with the rock, which is not the case for the pore water in the TSw. Therefore, the evolution of the strontium isotope composition of the water that deposited the calcite, as recorded by the strontium coprecipitated with calcium in the calcite, was used to develop a model for determining the age of the calcite.

II. STRONTIUM ISOTOPES IN PORE WATER

Strontium isotope compositions of pore water in the unsaturated zone were measured in dry-drilled core obtained from three boreholes located near the main drift of the Exploratory Studies Facility (ESF) tunnel[9]. Salts that formed only after the archived core dried out were leached and analyzed, using a method first described by Smalley and others[10]. Isotopic compositions are expressed as δ^{87}Sr, which is calculated from the measured ^{87}Sr/^{86}Sr ratio using:

$$\delta^{87}Sr = 1000 \times \left(\frac{^{87}Sr/^{86}Sr}{0.7092} - 1 \right) \quad (1)$$

where the value of 0.7092 is the approximate ^{87}Sr/^{86}Sr of modern seawater[11]. The results of pore-salt leaching experiments are presented in Figure 1 along with a histogram of δ^{87}Sr in soil carbonate samples at Yucca Mountain. Strontium isotope compositions of pore water from the Tiva Canyon welded hydrogeologic unit (TCw[1]; shallowest samples) have a similar range to those of the overlying soil. There is some variation in δ^{87}Sr with depth in the TCw, but a much larger variation is observed in the Paintbrush nonwelded hydrogeologic unit (PTn) due to the vitric character and higher strontium content of these rocks. Delta-^{87}Sr values have a much narrower range in the TSw, and it is apparent from the distributions of δ^{87}Sr in pore water (Figure 2) and in soil (Figure 1) that pore water at this depth contains

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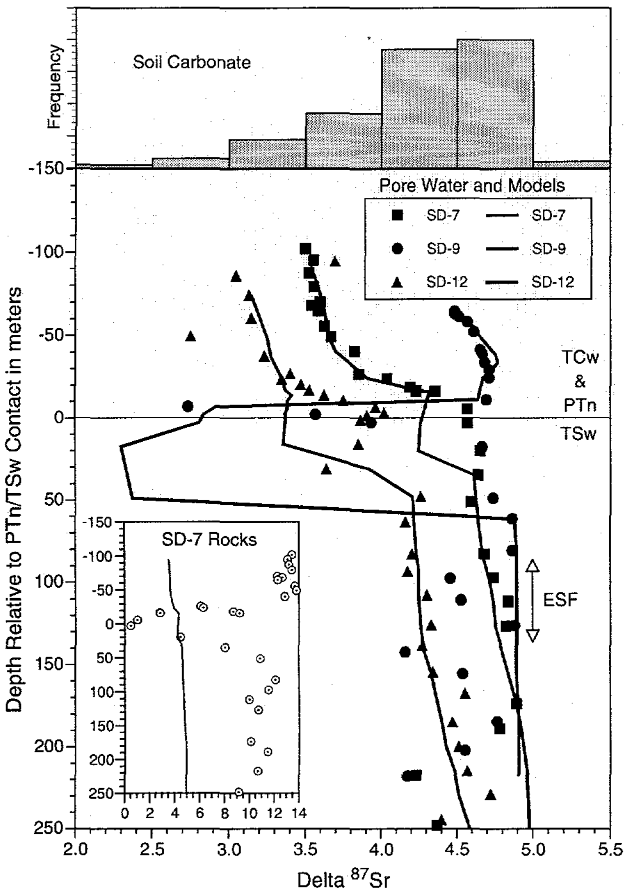

Figure 1. Delta-^{87}Sr values in soil carbonate[19] (histogram) and in pore water (measured in pore salt leaching experiments) (points) as a function of depth in three boreholes. Simulated δ^{87}Sr values in pore water using advection-reaction models shown by lines. Double-headed arrow shows approximate depth of ESF. Inset shows the δ^{87}Sr values measured in rocks (points) from USW SD-7 relative to the simulated values in pore water (line).

strontium derived almost entirely from the volcanic rocks rather than the soils. The large overlap in these two distributions is presumably due to similar water-rock interactions occurring within the soils, which are derived from similar volcanic rocks.

An advection-reaction model that describes the change in strontium isotope composition of the water as it moves downward through the volcanic rocks can be described by

$$\frac{\partial r_f}{\partial z} = (1-\phi)\cdot(r_s - r_f)\cdot\left(\frac{R}{v}\right)\cdot\left(\frac{c_s}{c_p}\right) \qquad (2)$$

where r_s and r_f are the δ^{87}Sr values in the rock and water, respectively, ϕ is the porosity of the rock[12,13,14], R (yr^{-1}) is the rate of dissolution, v (m/yr) is the pore water velocity, and c_s and c_p (mg/kg) are the concentrations of strontium in the rock and pore water, respectively[15]. This model is a steady state model and ignores dispersion. The model is fit to the data by adjusting R/v to best approximate the δ^{87}Sr value at each depth interval. Results of calculations show that δ^{87}Sr values in pore water from the TSw can be effectively explained by the model (Figure 1). However, discrepancies between the model and the data are evident near the base of the PTn, especially in borehole USW SD-9, possibly due to inadequate sampling of rocks from the intervals that are high in strontium at the base of the PTn or to oversimplification of the processes involved. The travel time for water moving through the unsaturated zone at Yucca Mountain is on the order of thousands of years[16].

III. STRONTIUM ISOTOPES IN CALCITE

Strontium isotope values in calcite coatings collected from the ESF in the TSw have a much wider range of values than the pore water (Figure 2). However, outermost calcite samples have δ^{87}Sr values that are approximately the same as the pore water, indicating that the most recently deposited calcite is consistent with precipitation from water in isotopic equilibrium with the present-day pore water. Delta-^{87}Sr values vary systematically with microstratigraphic position in calcite, and subsamples near the volcanic rock substrate always have smaller δ^{87}Sr values than subsamples closer to growth surfaces. This microstratigraphic variation is interpreted to be a result of the calcite incorporating strontium with a time-varying isotopic ratio.

IV. STRONTIUM ISOTOPE CHRONOLOGY OF CALCITE

The advection-reaction model that explains the present-day δ^{87}Sr values in pore water as well as those of the outermost calcite should also be capable of explaining the variation of δ^{87}Sr through time, provided that estimates of the time variation of the variables can be made. The model equation is presented again with the isotopic composition of the rock, r_s, the rate of rock dissolution, R, and the

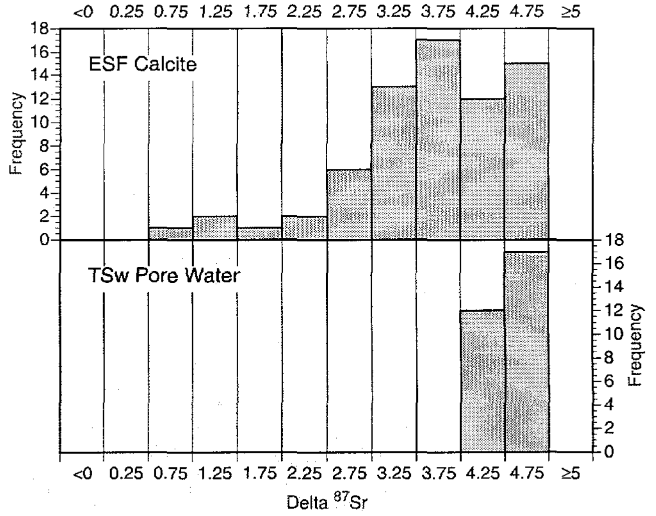

Figure 2. Histograms showing ranges of δ^{87}Sr for calcite samples from the ESF and for pore water from the TSw (ESF level and below) determined by leaching of pore-water salts from three boreholes near the ESF.

concentration of strontium in the pore water, c_p, shown as functions of time, t:

$$\frac{\partial r_f}{\partial z} = (1-\phi)\cdot\left(r_s(t)-r_f\right)\cdot\left(\frac{R(t)}{v}\right)\cdot\left(\frac{c_s}{c_p(t)}\right) \quad (3)$$

The time scale for the variation of these parameters is long (millions of years) compared to the time scale for water flow, so the model can still be considered steady-state.

Pore water and rock strontium data from USW SD-7 were used to calculate models of δ^{87}Sr in pore water over time in the TSw at the depth of the potential repository. Knowing the time variation in δ^{87}Sr of the rocks over time, which is a function of the rubidium/strontium ratio and the age, the δ^{87}Sr of the pore water over time was calculated as model 1 in Figure 3. At the earliest time calculated (12 Ma; approximately 0.8 Ma after emplacement of the TSw[2]) the δ^{87}Sr value is 3.5, much larger than the smallest values measured in calcite. It is assumed that the smallest values measured in calcite are the smallest values that are present in the calcite and that the oldest calcite is close to the age of the host rock.

The only other parameter that provides direct evidence of time variation is the concentration of strontium in the pore water. Although the variation is not as systematic as the variation of δ^{87}Sr, there is an approximate order of magnitude increase in the concentration of strontium in calcite from oldest to youngest samples. It is likely that this increase reflects a similar increase in strontium in the pore water. For model 2 (Figure 3), the ratio (c_s/c_p) is decreased linearly through time only in the PTn because these rocks have high c_s/c_p and these are the rocks that most affect the composition of the pore water in the underlying TSw. Model 2, however, still predicts δ^{87}Sr values too large for early calcite.

The final parameter that is likely to change with time is the rate of dissolution; this parameter, along with the water velocity, is used to fit the modern pore water model. Assuming an infiltration flux of 1 mm/yr, values of R range from 10^{-9} to $5\text{x}10^{-8}$ per year in the present-day model. These dissolution rates are reasonable[17], but at a rate of $5\text{x}10^{-8}$ per year or 5 percent per million years 50 percent of the rock's strontium would be dissolved in 10 million years, which is probably an overestimate. One approach to fitting the model pore water δ^{87}Sr values to the known range of δ^{87}Sr values in calcite is to decrease R in the vitric part of the Topopah Spring Tuff at the PTn-TSw contact with time while increasing R in other parts of the PTn. Because of its low rubidium/strontium ratio, the vitric part of the Topopah Spring Tuff must supply strontium with its low δ^{87}Sr value early, but must be much less reactive later. Geologically, the explanation for this apparent requirement is that the pathways through the vitric part of the Topopah Spring Tuff become armored with smectite over time[18], effectively reducing the dissolution rate. Model 3 (Figure 3) shows the predicted variation of δ^{87}Sr with time assuming linear variations in c_s/c_p and in R in some rock units. Model 4 is calculated assuming that the variations in c_s/c_p and R occur in the first 6 million years only. This model predicts more rapid changes in δ^{87}Sr in the pore water early in the rock mass history. Preliminary efforts to calibrate the model using U-Pb ages determined on opal and chalcedony indicate that model 3 may be the best model. Although precise ages cannot be determined, calibration of the model is possible in coatings containing datable silica phases.

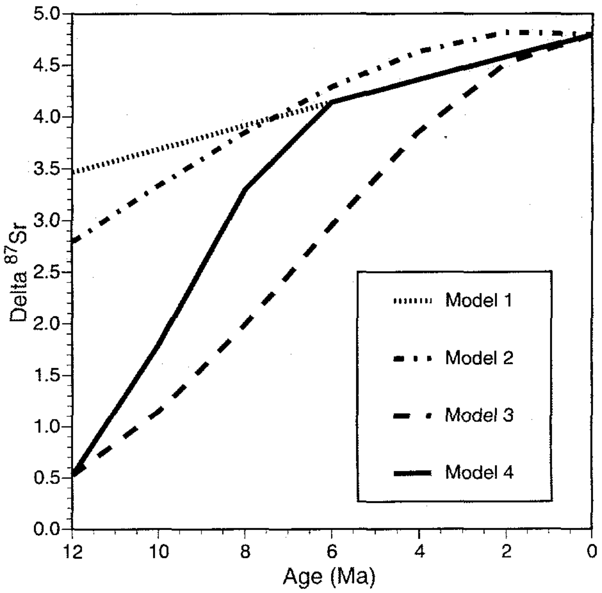

Figure 3. Calculated δ^{87}Sr in pore water as a function of age. Calculations based on USW SD-7 pore water and rock measurements of δ^{87}Sr and are for the approximate depth of the ESF.

V. CONCLUSIONS

Pore water in the Topopah Spring Tuff has a narrow range of δ^{87}Sr values that can be calculated from the δ^{87}Sr values of the rock considering advection through and reaction with the overlying nonwelded tuffs of the PTn. This model can be extended to estimate the variation of δ^{87}Sr in the pore water through time; this approximates the variation of δ^{87}Sr measured in calcite fracture coatings. In samples of calcite where no silica can be dated by other methods, strontium isotope data may be the only method to determine ages. In addition, other Sr-bearing minerals in the calcite and opal coatings, such as fluorite, may be dated using the same model.

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