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**PORE-WATER ISOTOPIC COMPOSITIONS AND UNSATURATED-ZONE FLOW,
YUCCA MOUNTAIN, NEVADA**

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I. INTRODUCTION

Site characterization at Yucca Mountain, Nevada, the site of a potential high-level radioactive waste repository, has included studies of recharge, flow paths, percolation flux, perched water bodies, and chemical compositions of the water in the thick unsaturated zone (UZ). Samples of pore water from cores of two recently drilled boreholes, USW SD-6 near the ridge top of Yucca Mountain and USW WT-24 north of Yucca Mountain (fig. 1), were analyzed for isotopic compositions as part of a study by the U.S. Geological Survey (USGS), in cooperation with the U.S. Department of Energy, under Interagency Agreement DE-AI08-97NV12033. The purpose of this report is to interpret ^{14}C , $\delta^{13}\text{C}$, ^3H , δD and $\delta^{18}\text{O}$ isotopic compositions of pore water from the core of boreholes USW SD-6 and USW WT-24 in relation to sources of recharge and flow paths in the UZ at Yucca Mountain. Borehole designation USW SD-6 and USW WT-24 subsequently will be referred to as SD-6 and WT-24. The sources of recharge and flow paths are important parameters that can be used in a UZ flow model, total system performance assessment (TSPA), and the license application (LA) for the potential repository at Yucca Mountain.

Yucca Mountain, located near the western boundary of the Nevada Test Site about 160 kilometers (km) northwest of Las Vegas, consists of a rugged series of north-trending fault-block ridges that generally have an eastward tilt of 5 to 10 degrees¹. A thick section of volcanic rocks of Miocene age overlies sedimentary strata of Paleozoic age in the Yucca Mountain region², with tuffs of the 12.8 to 12.7 million-year-old (Ma) Paintbrush Group (Tertiary age)³ forming most

exposures^{4,11}. Two thick densely welded ash-flow tuffs, the Tiva Canyon and the Topopah Spring Tuffs, form the major bedrock of Yucca Mountain. These two welded tuffs are separated by a much thinner interval of mostly nonwelded pyroclastic rocks. Differences in the hydrologic character of the welded and nonwelded tuff sequences led Montazer and Wilson⁵ and Ortiz et al.⁶ to develop thermo-mechanical or hydrogeologic designations for these units (fig. 2). Because the hydrogeologic units are based on similarity of properties⁷, they do not correspond exactly with the stratigraphic units⁸, in which physical properties (such as welding, degree of alteration, fracturing, and permeability) vary significantly both laterally and vertically within single flow units. Both nomenclatures will be used in this report, but they are not interchangeable. The Tiva Canyon welded hydrogeologic unit (TCw) consists of the welded part of the Tiva Canyon Tuff. The Paintbrush Tuff nonwelded hydrogeologic unit (PTn) consists of the nonwelded basal part of the Tiva Canyon Tuff; the entire Yucca Mountain and Pah Canyon Tuffs, and bedded tuffs; and the nonwelded upper part of the Topopah Spring Tuff. The Topopah Spring welded hydrogeologic unit (TSw) consists of the welded part of the Topopah Spring Tuff. The underlying Calico Hills nonwelded hydrogeologic unit (CHn) consists of the nonwelded basal part of the Topopah Spring Tuff (TS), the entire Calico Hills Formation (CHF) and the Prow Pass Tuff (PP), and the nonwelded upper part of the Bullfrog Tuff (BF).

II. WORK DESCRIPTION

A. Extraction of Pore Water

Three different techniques were used to extract pore water.

- Pore water from cores of nonwelded tuff (PTn and CHF) was extracted by using a high-pressure one-dimensional (uniaxial) compression method^{8,9,10, 11,12}. The extracted water was

filtered through 0.45-micrometer (μm) filters into glass bottles for carbon (^{14}C and $\delta^{13}\text{C}$), oxygen ($\delta^{18}\text{O}$), and deuterium (δD) isotope analyses.

- Pore water from cores of TCw, TSw, TS, PP, and BF was extracted by using a Beckman model L8M/P* high-speed centrifuge. About 150 grams (g) of core were broken up by hammer and chisel into pieces of 1 to 3 centimeters (cm) in diameter to fill 3 titanium centrifuge cups. A perforated plate located near the lower end of each cup separated the rock samples from the extracted water draining into the attached glass water-receiving cup. Each cap was screwed tightly to the body of the titanium cup and all three cups were placed inside the aluminum bucket. Each joint of the cup assembly was sealed with an O-ring so that all 3 cups were airtight. The process of sample preparation was accomplished within 10 minutes to minimize evaporative loss of moisture. Core samples were spun for a total of 12 hours at a rate of 16,000 revolutions per minute (27,800G). After centrifugation, the bottom glass cup containing water was disconnected from its upper titanium cup, and the extracted water was collected in a clean and dry syringe. The water in the syringe was filtered through 0.45- μm filters into glass bottles. The amount of pore water extracted from 150 g of core sample was about 3 to 4 milliliters (mL) at most, only enough for analysis of oxygen and deuterium isotope compositions.
- After pore water was extracted from cores by uniaxial compression or high-speed ultra-centrifugation, the cores were distilled in a vacuum to extract the remaining water. The water was distilled by heat in a vacuum system and captured in a cold trap at -78°C . A temperature of 150°C was maintained at the heating mantle, resulting in a core temperature of about 110°C . Vacuum-distilled water samples were stored in glass bottles for analysis of tritium, $\delta^{18}\text{O}$, and δD . The distilled water from welded cores of the TCw, the TSw, the PP, the BF and the nonwelded TS Tuff

* The use of brand name in this paper is for identification purpose only and does not imply endorsement by the U. S. Geological Survey

cores was analyzed for tritium, $\delta^{18}\text{O}$, and δD . Water distilled from PTn and CHF cores containing clay and zeolite minerals was analyzed for tritium only, because the ground water fractionated when it flowed into pore space of zeolite or clay minerals and became more depleted in the heavy ^{18}O and D isotopes¹².

B. Isotope Analyses of Pore Water

Tritium concentrations in pore water were analyzed at the USGS Yucca Mountain Project Branch (YMPB) hydrochemistry laboratory in Denver, Colorado according to procedures published by Thatcher et al.¹³. Tritium values were calculated by regressing to the date of sample collection so that tritium decay was considered between sample collection and dates of analysis. Analytical precision of about ± 12 TU (2σ) was determined based on 76 replicate analyses of pore-water samples. Estimates for the precision based on the counting statistics alone are about 1.5 to 2 times smaller than these based on the reproducibility. This was due to the presence of other sources of error such as variability of the counting efficiency and changing chemical stability of the fluorescent cocktails. Tritium detection limit as estimated at 95 percent confidence level was about 14 to 20 TU. The large detection limit is the result of the stability of the background and reproducibility of 76 replicate analyses. Therefore, for these data, tritium concentrations above 20 TU were considered to be positive indication of the post-bomb (or recent) water.

Carbon isotopes were analyzed by Beta Analytic, Inc., in Miami, Florida, using a Tandem Accelerator Mass Spectrometer (TAMS) for ^{14}C , and conventional mass spectrometer for $\delta^{13}\text{C}$. Uncertainty in ^{14}C was ± 0.7 percent modern carbon (pMC) and in $\delta^{13}\text{C}$ was ± 0.2 per mil.

$\delta^{18}\text{O}$ and δD were analyzed using a mass spectrometer at the U.S. Geological Survey YMPB laboratory in Denver, Colorado. Values of $\delta^{18}\text{O}$ were determined by equilibrating the

sample water with a small amount of pure carbon dioxide (CO_2) in a constant-temperature bath. The $^{18}\text{O}/^{16}\text{O}$ ratio of the equilibrated CO_2 gas was measured using the mass spectrometer, and the $\delta^{18}\text{O}$ value of the water was calculated from the ratio. Values of δD were determined by reducing the sample water to hydrogen gas and measuring the D/H ratio of the hydrogen in the mass spectrometer. Uncertainty in $\delta^{18}\text{O}$ values was ± 0.1 per mil and in δD was ± 0.5 per mil at 1σ . The reference standard for these stable isotope values was V-SMOW (Vienna Standard Mean Ocean Water).

III. RESULTS AND DISCUSSION

A. Tritium Profiles

Tritium concentrations of pore-water samples from the parts of boreholes SD-6 and WT-24 that were cored mostly ranged from 0 to 15 TU (figs. 3 and 4).

Two large peaks of tritium concentration values, where larger tritium concentrations are located below a smaller tritium concentration in a vertical profile, were observed in borehole SD-6 (fig. 3), one about 20 to 32 TU at a depth between 437.7 m and 439.2 m, and the other about 30 to 43 TU at a depth between 534.0 m and 535.8 m. Also two large tritium peaks were observed in WT-24 (fig. 4), one about 30 to 50 TU at a depth between 514.8 m and 518.2 m, and the other about 18 to 35 TU at a depth between 764.1 m and 769.9 m. In both boreholes, these large tritium concentration peaks were near the basal vitrophyre zone of the Topopah Spring Tuff and near the upper part of the PP.

Tritium-concentration peaks indicate non-vertical preferential flow through fractures. The lower part of the TSW and the upper part of the PP are welded tuff and are more likely to create a fast-flow path through connected fractures than the nonwelded tuff units. The source of the recent water at borehole WT-24 probably was recharge from The Prow to the north, which then flowed

laterally southward through the dipping, highly fractured TSw. The source of the young water at borehole SD-6 probably was water flow from the Solitario Canyon fault to the west, which then flowed laterally through the TSw and CHF.

Yang et al.^{11,12} reported that the tritium-concentration peaks observed in many UZ and SD boreholes at Yucca Mountain mainly occurred in the matrix pore water of the PTn and the upper part of the TSw. In contrast, the tritium-concentration peaks in SD-6 and WT-24 occurred in the lower part of the Topopah Spring Tuff and in the PP unit.

B. ^{14}C Profiles

The ^{14}C activity of pore water from borehole SD-6 could only be determined in one sample, near the bottom of the CHF, with a ^{14}C activity of about 58 pMC (fig. 3). This is because the TSw and the upper (vitric) part of the CHF cores had too low a moisture content to yield enough pore water for ^{14}C determination.

The ^{14}C activities of pore water in the CHF of borehole WT-24 (fig. 4) ranged from 50 to 65 pMC except in two samples: ^{14}C activities increased abruptly to 80 and 85 pMC in two samples at the bottom of the CHF. Yang et al.¹² (p. 23) stated that the apparently young ^{14}C ages in the CHF in many boreholes were caused by atmospheric $^{14}\text{CO}_2$ contamination during drilling. However, the extent of contamination by the drilling air should be comparable through each segment of core. The fact that the two large ^{14}C activities in figure 4 deviate from the ^{14}C vertical trend implies that the large ^{14}C activities were caused by the infiltration of post-bomb young water and not by the drilling-air contamination. This conclusion was supported by the $\delta^{13}\text{C}$ data. If large ^{14}C activities are caused by atmospheric contamination from the drilling air, $\delta^{13}\text{C}$ values for these two samples should be significantly heavier than other samples because the atmospheric $\delta^{13}\text{C}$ value of CO_2 is about -7 per mil. The $\delta^{13}\text{C}$ values of these two samples were not significantly heavier than the others.

The large ^{14}C activities at this depth coincide with the large tritium values observed, providing further evidence of a lateral fast-flow path. The pore water ^{14}C activities are less than 100 pMC, indicating that younger post-bomb water was probably mixed with the older water.

C. Stable-Isotope Profiles

The stable-isotope data ($\delta^{18}\text{O}$ and δD) for SD-6 and WT-24 were analyzed from pore-water samples extracted by vacuum distillation, compression, and ultra-centrifugation. For previous data, samples extracted by vacuum distillation had reliable results for $\delta^{18}\text{O}$ and δD values from tuffs free of clay and zeolite minerals but not for tuffs with large hydrated mineral contents. This is because the ground water likely interacts with clay or zeolite minerals and fractionates to more depleted oxygen and deuterium isotopes in small pore spaces (Yang et al.¹², p. 44). For the bedded tuff, PTn, and CHF cores containing clay and zeolite minerals, compression and centrifugation extraction of pore water produced isotopically unfractionated water. One sample from the upper part of the CHF in SD-6 was extracted using vacuum distillation because this core sample was from the vitric CH welded tuff.

Most of the values of $\delta^{18}\text{O}$ and δD for pore-water samples from borehole SD-6 plot on a decreasing trend line from the lower part of the Topopah Spring Tuff to the upper part of the BF, except for one sample at the bottom of the CHF and δD values for samples at the bottom of the Topopah Spring Tuff (fig. 5). The δD values at the bottom of the Topopah Spring Tuff shift abruptly to extremely negative values. This shift is not because of the presence of clay or zeolite minerals in the basal vitrophyre zone of the Topopah Spring Tuff, but is probably due to the presence of residual pore water from the last ice age. This shift also was observed in pore-water δD from boreholes USW SD-9, USW SD-12, and USW-14¹⁴.

The sample of compressed water at the bottom of the CHF in SD-6 that plots off from the $\delta^{18}\text{O}$ and δD vertical trends is less than a foot deeper than another sample that plots on the

vertical trend. The shallower sample at 526.7m plots on the trend line for both $\delta^{18}\text{O}$ and δD data and the deeper sample at 526.9 m had a more positive value off the trend line in both graphs. The more positive $\delta^{18}\text{O}$ and δD values indicate younger water¹⁴, so these isotopic data (near the depth where large tritium values were measured) also support the fast-flow path suggested in the previous sections.

Values of $\delta^{18}\text{O}$ and δD in samples of pore water versus depth for borehole WT-24 are plotted in figure 6. Values of $\delta^{18}\text{O}$ near the bottom of the TSw in borehole WT-24 are more negative than the values of the other samples from the borehole. The very negative δD values near the bottom of the TSw unit in the vitrophyre zone are consistent with the very negative δD values previously reported for boreholes USW SD-9, USW SD-12, and USW UZ-14¹⁴. In the thick CHF both $\delta^{18}\text{O}$ and δD values vary little except at the bottom where the trends may increase slightly toward more positive values, similar to the more positive $\delta^{18}\text{O}$ and δD values at the bottom of the CHF in borehole SD-6. This is the same depth where the large tritium peak and large ^{14}C is observed in borehole WT-24.

CONCLUSIONS

Isotopic compositions of core-water samples from boreholes USW SD-6 and USW WT-24 indicate that recent water has been introduced at depth. Tritium, carbon, oxygen, and deuterium isotopic compositions all support younger water at depth in the two boreholes, although this evidence had not been seen previously in other borehole data at Yucca Mountain. Peaks in tritium concentrations in pore-water samples, indicating younger water than the other samples, observed near the basal vitrophyre of the Topopah Spring Tuff and at the bottom of the CHF and the top of the PP in both boreholes SD-6 and WT-24. Larger ^{14}C activities in two pore-water samples from WT-24 at the bottom of the CHF and the top of the PP indicate younger

water than in other samples from WT-24. More positive $\delta^{18}\text{O}$ and δD values indicate younger water¹⁴ in samples of pore water at the bottom of the CHF in boreholes SD-6 and WT-24.

The isotopic compositions indicating younger water at depth in boreholes SD-6 and WT-24 occur at the basal vitrophyre zone of the Topopah Spring Tuff and the bottom of the CHF/upper part of the PP, probably from lateral preferential flow through connected fractures (fast-flow paths). The source of the young water at borehole WT-24 probably was recharge from The Prow to the north, which then flowed laterally southward through the highly fractured TSw. The source of the young water at borehole SD-6 probably was water flow from the Solitario Canyon fault to the west, which then flowed laterally through the TSw and CHF.

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Figure 1. Map showing locations of unsaturated-zone boreholes at Yucca Mountain, Nevada

Stratigraphic unit	Tuff lithology	Hydrogeologic unit
Alluvium	—	Alluvium
Tiva Canyon Tuff	MD	Tiva Canyon welded unit (TCw)
Yucca Mtn Tuff	NP,B	Paintbrush nonwelded unit (PTn)
Bedded Tuff		
Pah Canyon Tuff		
Bedded Tuff	MD	Topopah Spring welded unit (TSw)
Topopah Spring Tuff		
Calico Hills Formation	(V) NP,B (D)	Calico Hills nonwelded unit (CHn)
Prow Pass Tuff	(in part zeolitic)	
Bullfrog Tuff	MD,NP,B (undifferentiated)	Crater Flat Tuff (CFu)

Figure 2. Hydrogeologic units at Yucca Mountain, Nevada [modified from Montazer and Wilson (1984), table 1]. MD, moderately to densely welded; NP, nonwelded to partially welded; B, bedded; (V), vitric; (D), devitrified. Stratigraphic names are taken from Sawyer and others (1994).

Figure 3. Tritium (H-3) and carbon-14 (C-14) concentrations of pore water in borehole USW SD-6

Figure 4. Tritium (H-3) and carbon-14 (C-14) concentrations of pore water from borehole USW WT-24

Figure 5. Delta O-18 and Delta D values of pore water from borehole SD-6. Symbol sizes are larger than 2 sigma deviations.

Figure 6. Delta O-18 and Delta D values of pore water from borehole WT-24. Symbol sizes are larger than 2 sigma deviations.