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HYDROCHEMICAL INVESTIGATIONS IN CHARACTERIZING THE UNSATURATED ZONE AT YUCCA MOUNTAIN, NEVADA

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 98–4132

Prepared in cooperation with the
NEVADA OPERATIONS OFFICE,
U.S. DEPARTMENT OF ENERGY, under
Interagency Agreement DE–AI08–97NV12033

Hydrochemical Investigations in Characterizing the Unsaturated Zone at Yucca Mountain, Nevada

By In C. Yang,[1] Pei Yu,[2] Gordon W. Rattray,[1] Janine S. Ferarese,[1] and Joseph N. Ryan[3]

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Denver, Colorado
1998

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary

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CONVERSION FACTORS AND VERTICAL DATUM

Multiply	By	To obtain
nanometer (nm)	3.937×10^{-8}	inch
centimeter (cm)	3.937×10^{-1}	inch
kilometer (km)	6.214×10^{-1}	mile
meter (m)	3.281	foot
meter per day (m/d)	3.281	foot per day
micrometer (µm)	3.937×10^{-5}	inch
millimeter (mm)	3.937×10^{-2}	inch
square centimeter per second (cm^2/s)	0.1550	square inch per second
square meter (m^2)	10.76	square foot
cubic centimeter (cm^3)	6.102×10^{-2}	cubic inch
cubic meter (m^3)	6.102×10^{4}	cubic inch
liter (L)	0.2642	gallon
milliliter (mL)	6.102×10^{-2}	cubic inch
gram (g)	2.2×10^{-3}	pound, mass
gram per cubic centimeter (g/cm^3)	3.6×1^{-2}	pound per cubic inch
megapascal (MPa)	144.7	pound per square inch
microgram per liter (µg/L)	1	part per billion
milligram per liter (mg/L)	1	part per million

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

°F = 9/5 (°C) + 32

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Hydrochemical Investigations in Characterizing the Unsaturated Zone at Yucca Mountain, Nevada

By In C. Yang, Pei Yu, Gordon W. Rattray, Janine S. Ferarese, *and* Joseph N. Ryan

ABSTRACT

Hydrochemical and isotopic investigations of ground water at Yucca Mountain, Nevada, site of a potential permanent national nuclear-waste repository, demonstrate that younger rocks are dominated by calcium-sulfate or calcium-chloride water and that older rocks contain sodium-carbonate or sodium-bicarbonate water. Furthermore, unsaturated-zone pore water has significantly larger concentrations of major ions and dissolved solids than does the saturated-zone water. Recharge of perched or saturated-zone water, therefore, requires rapid flow through fractures or permeable regions in the unsaturated zone to avoid mixing with the chemically concentrated water in the unsaturated zone. This conceptual model is consistent with observations of rapidly moved post-bomb (post-1954) tritium and chlorine-36 in the deep unsaturated zone at Yucca Mountain. Presence of post-bomb tritium in matrix water away from fracture zones further indicates that parts of the fast-flow water that moves through fractures have been diverted laterally into nonwelded units.

Discrepancy in carbon-14 activities between gas and water phases from various boreholes within individual and from different lithologic units may be due to atmospheric contamination during drilling. Larger carbon-14 activities (indicating younger ages) are seen in water from some parts of a nonwelded unit of Miocene age than in samples elsewhere in the same unit, and gaseous-phase carbon-14 activities in one unit are smaller (older ages) than pore-water activities of the underlying unit. The gaseous-phase carbon-14 age profiles across the entire unsaturated zone in one borehole increase in age with depth, confirming previous results from another borehole and demonstrating that gas transport in the Yucca Mountain unsaturated zone occurs through a diffusion mechanism.

Experimental data show that different lithologic units require specific water-extraction methods for stable-isotope analyses of hydrogen and oxygen to ensure accurate characterization. Vacuum-distillation and compression-extraction methods both can yield accurate data but must be used with specific lithologies. Column experiments demonstrate that percolating water can exchange with pore water of the core as well as water held in zeolite minerals in the core. Exchange rates range from days to months. Pore-water samples from core, therefore, reflect the most recently infiltrated water but do not reflect percolating water of the distant past.

Stable-isotopic compositions of perched water generally plot close to the Yucca Mountain precipitation line, which indicates little evaporative loss before recharge, although exceptions do exist. Estimated evaporation under conditions of largest possible loss produced 6-percent volumetric loss. Winter precipitation is the likely source of recharge to the unsaturated zone.

INTRODUCTION

A thorough understanding of hydrochemical processes in the unsaturated zone (UZ) is essential to the site-characterization program for the potential permanent repository for nuclear waste at Yucca Mountain, Nevada. Chemical composition of pore water reflects the extent of water-rock interaction between the recharge water and the rock matrix. Tritium (^3H) and carbon-14 (^{14}C) ages provide insight as to the nature of flow mechanisms and residence times of the unsaturated-zone water. Carbon (^{14}C) concentrations measured in the gaseous phase can provide information relevant to the residence time of carbon dioxide (CO_2) in this unusually thick unsaturated zone, and carbon isotopic data ($\delta^{13}C$) can help to identify carbon sources, a necessary step in ^{14}C age estimation. Carbon isotopic data of CO_2 as a function of depth provide information on gas-flow mechanisms through the unsaturated zone as well as interactions with water and secondary calcite. Stable-isotopic compositions of hydrogen and oxygen in fracture and matrix waters can help to identify fracture/matrix interactions and sources of water. From the present chemical and isotopic data, along with previously published data collected at Yucca Mountain (for example, Yang and others, 1993 and 1996), conceptual hydrologic flow at Yucca Mountain can be described. Such investigations are important because ground water is the most likely transport medium for radionuclides from a repository to the accessible environment.

The purpose of this study is to obtain hydrochemical data, such as chemical compositions of pore and perched waters, and to determine flow mechanisms and residence times of gas and water and extent of fracture/matrix interactions for water. All of these can be used to calibrate flow and transport models, which can be used to estimate repository performance and safety.

A method of pore-water extraction for chemical-composition analysis developed by Yang and others (1988) and later modified by Mower and others (1991, 1994) was used in this study. Methods of pore-water extraction for stable-isotope analysis were investigated in this study. Lithologic units that contain different minerals require different methods of pore-water extraction for stable-isotope analyses of hydrogen and oxygen, such as compression extraction or vacuum distillation. Validations of the methods that were applicable to each lithologic unit are presented in the section on the stable-isotope compositions of pore water.

Yucca Mountain, located near the western boundary of the Nevada Test Site in southern Nye County about 160 km northwest of Las Vegas, consists of a rugged series of north-trending fault-block ridges that are composed of volcanic rocks that generally have an eastward tilt of 5° to 10° (Scott and Bonk, 1984). A thick section of volcanic rocks of Tertiary age overlies sedimentary strata of Paleozoic age in the Yucca Mountain region (Byers and others, 1976), with units of the 12.8 to 12.7 million-year-old (Ma) Paintbrush Group (Tertiary age) (Sawyer and others, 1994) forming most exposures (Christiansen and Lipman, 1965; Scott and Bonk, 1984). Two voluminous, densely welded ash-flow tuffs underlie Yucca Mountain (the Tiva Canyon and Topopah Spring Tuffs), separated by a much thinner interval of mostly nonwelded pyroclastic rocks. Stratigraphic nomenclature was recently revised and improved with many new isotopic ages (Sawyer and others, 1994) and that stratigraphic nomenclature is used here (fig. 1). Numerous washes, generally underlain by alluvium, dissect the eastern side of the mountain. Nearly three-fourths of the annual precipitation falls from October through April (Quiring, 1983). No perennial streams exist in the Yucca Mountain area. Surface runoff is infrequent and of short duration, occurring only as a direct result of intense precipitation or rapid snowmelt.

Numerous geologic and hydrologic investigations conducted in the extensive characterization effort at Yucca Mountain have resulted in overlapping nomenclature to describe aspects of the geologic setting. Obvious differences in the hydrologic character of the welded and nonwelded sequences led Montazer and Wilson (1984) and Ortiz and others (1985) to develop thermo-mechanical (or hydrogeologic) designations for these units (fig. 1). Because the hydrogeologic units are based on similarity of properties (see Luckey and others, 1996, p. 17–20 for discussion), they do not correspond exactly with the stratigraphic units, in which physical properties (welding, degree of alteration, fracturing, permeability) vary significantly both laterally and vertically within single flow units. Note that both nomenclatures will be used in this report, but they are not interchangeable. For example, the Calico Hills nonwelded hydrogeologic unit (CHn) contains basal parts of the Topopah Spring Tuff, the entire Calico Hills Formation and the Prow Pass Tuff, and upper parts of the Bullfrog Tuff. Stratigraphic and hydrogeologic correlations are shown graphically in figure 1.

This report describes ongoing investigations of unsaturated-zone water chemistry and isotope hydrology at Yucca Mountain. New data collected in 1996 include CO_2 concentrations and carbon isotopic compositions (^{13}C and ^{14}C) of rock gas from several

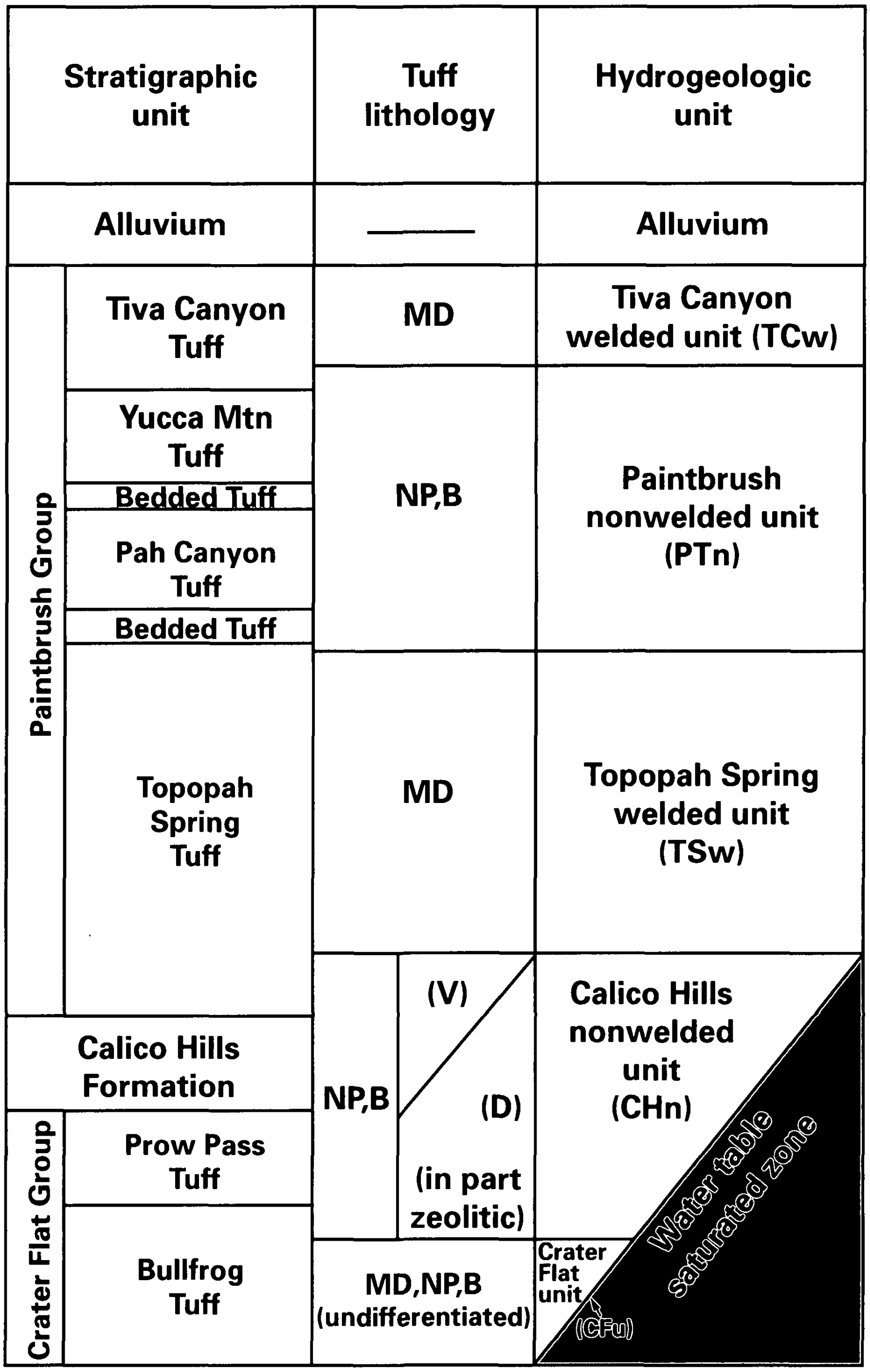


Figure 1. Hydrogeologic units at Yucca Mountain, Nevada [modified from Montazer and Wilson (1984), table 1]. MD, moderately to densely welded; NP, nonwelded to partially welded; B, bedded; (V), vitric; (D), devitrified.

boreholes and major-ion concentrations and isotopic compositions of water from those and additional boreholes. Pore-water chemical compositions and ^{14}C data are from bedded tuff and the Calico Hills nonwelded unit (fig. 1). Limited ^{3}H data were obtained from intervals of each of the boreholes.

This investigation was conducted by the U.S. Geological Survey (USGS) in cooperation with the U.S. Department of Energy under Interagency Agreement DE-AI08-97NV12033.

CHEMICAL AND RADIOACTIVE-ISOTOPE COMPOSITIONS (^{3}H AND ^{14}C) OF GAS AND PORE WATER FROM THE UNSATURATED ZONE

A vacuum-reverse air-circulation drilling method (Whitfield, 1985) was used to drill all boreholes in the UZ drilling program. This method is intended to prevent contamination of the unsaturated rocks with drilling fluids and thus allow collection of native pore water and gas from the UZ for hydrochemical analysis. Locations of boreholes where gas and pore-water samples were collected are shown in figure 2. Borehole designation, drilling date, depth, and perched-water detections are given in table 1. Abbreviated borehole names will be used throughout the text.

Boreholes From Which Data Were Collected

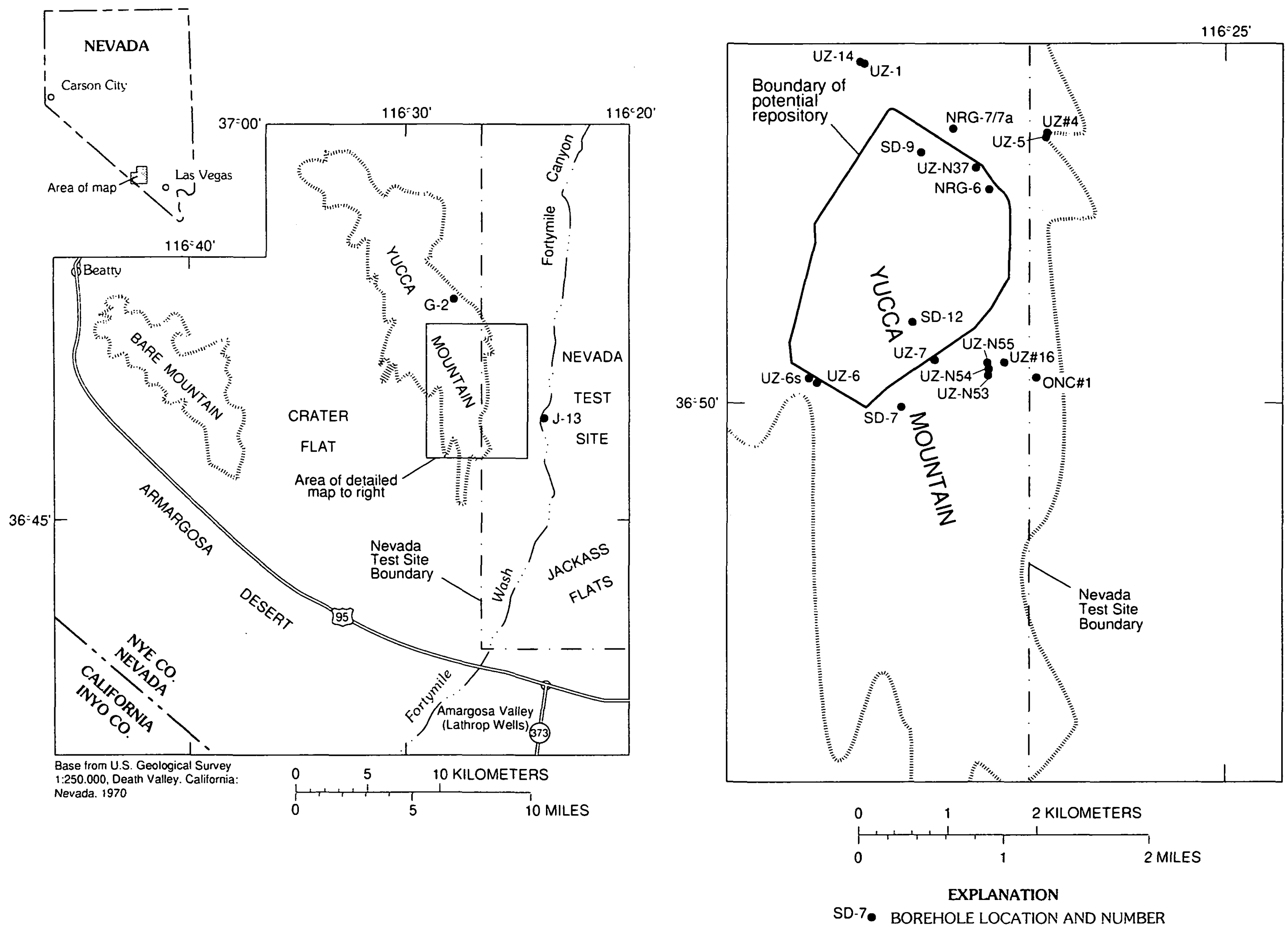
Drilling of geologic borehole NRG-6 was started on November 23, 1992, and the borehole was cored to a depth of 335.3 m, terminating in the Topopah Spring Tuff by March 3, 1993. NRG-7a was drilled beginning October 21, 1993, and cored to a depth of 461.3 m in the upper Calico Hills Formation by May 6, 1994. Cores above the Topopah Spring Tuff from these two boreholes were used for water extraction. Drilling of borehole SD-7 in the systematic drilling program was started on October 3, 1994; SD-7 was cored to 615.8 m with a 10-cm bit by September 14, 1995, and completed to a depth of 815.3 m in the Tram Tuff on November 9, 1995. The water-table level in this borehole was at 633.3 m on November 13, 1995. Perched water was reached in this borehole between 479.7 m and 488.3 m. SD-9 was started on May 10, 1994, and completed to a depth of 677.6 m, terminating in the Prow Pass Tuff on September 26, 1994. Perched water also was reached in this borehole at 453.8 m. Borehole SD-12 drilling was started on January 23, 1994, and was completed to a depth of 660.3 m, terminating in the Prow Pass Tuff on September 14, 1994. The static water table in SD-12 was located between 610.8 m and 612.9 m. These SD holes yielded cores from both the Paintbrush nonwelded (PTn) and the Calico Hills nonwelded (CHn) hydrogeologic units for water extraction.

The UZ-14 borehole is located in Drill Hole Wash, 26.2 m from UZ-1. Drilling of the borehole was started on April 15, 1993, and it was cored to a depth of 672.6 m by April 29, 1994, and completed to a total depth of 677.8 m on May 6, 1994. Chemical and radioactive-isotope data from UZ-14 have been previously reported from the interval from the surface to 528.8 m (Yang and others, 1996). This report includes data from the depth interval of 528.8 to 640.1 m.

Gas samples were collected from the full depth range of SD-12 from 16 sampling ports. Boreholes SD-7 and SD-9 were not instrumented. Only one sample was collected from the Calico Hills nonwelded unit in SD-7, and two samples were obtained from SD-9 (one above and one below the Topopah Spring Tuff). For gas sampling from these open boreholes, an inflatable borehole liner was used.

Sample Collection and Analysis

Details of drilling were designed to enhance analysis. After a borehole was drilled, the atmospheric air that entered during the drilling process was removed by evacuation from the surface with a large-capacity pump. All drilling air was tagged with a tracer: sulfur hexafluoride (SF_6). The tracer concentration in the evacuated air was continuously monitored, and disappearance of the SF_6 [concentration less than 0.1 part per million (ppm)] assured essentially complete removal of the drilling air. Packers were installed inside the open boreholes in SD-7 and SD-9 for gas-sample collections. The diameter of the rotary core was 6 cm. Cores from the rock formation were obtained using a 1.5-m core barrel with a split inner tube. Core recovery typically was greater than 90 percent. Three pieces of continuous, unfragmented solid core, each approximately 15 cm long, are needed to obtain enough water for age and chemical determinations.



Base from U.S. Geological Survey 1:250,000, Death Valley, California; Nevada, 1970

Figure 2. Locations of boreholes completed in the unsaturated zone, Yucca Mountain area, Nevada.

Table 1. Borehole designation, drilling date, depth, and perched-water occurrence of selected boreholes at Yucca Mountain area

[m, meter; ---, not found (source of information: Yang and others, 1996; Rautman and Engstrom, 1996)]

Borehole designation	Borehole abbreviation	Drilling date		Depth of borehole (m)	Perched water detected at depth (m)
		Start	Finish		
USW NRG-6	NRG-6	11-23-92	03-03-93	335.3	---
USW NRG-7a	NRG-7a	10-21-93	05-06-94	461.3	460.2
USW SD-7	SD-7	10-03-94	11-09-95	815.3	479.7
USW SD-9	SD-9	05-10-94	09-26-94	677.6	453.8
USW SD-12	SD-12	01-23-94	09-14-94	660.3	---
USW UZ-14	UZ-14	04-15-93	05-06-94	677.8	384.6

Sample-handling procedures affect the success of extracting uncontaminated water from cores of tuff. Evaporation of pore water increases with sample exposure time in a dry climate, and strict precautions were taken to avoid loss of moisture or contamination of pore water in the cores (Striffler and Peters, 1993). Each core was wrapped in a thin plastic sheet, placed inside a Lexan liner, and capped on both ends of the Lexan liner. The Lexan-contained core was then placed inside a thick aluminum-foil bag and heat-sealed for moisture protection. The sealed cores were packed carefully into plastic coolers and transported from the drill site to the Sample Management Facility (SMF) at Jackass Flats, Nevada, for log-in and storage. The storage temperature was kept at 6° to 9°C until the cores were removed for pore-water extraction.

Analyses were contracted out by the USGS except for tritium, gas composition, and CO_2 concentration, which were analyzed by the USGS in Denver, Colorado.

Collection of Gas Samples from Boreholes SD-7, SD-9, and SD-12

The whole-gas (WG) method or batch sampling was used to collect samples for $\delta^{13}C$ analysis. A gas stream was allowed to flow into a Mylar-balloon sample container to purge the balloon several times before sampling. When the gas had filled up the balloon, the sample container was removed from the flow line. The collection time was less than 5 minutes.

The molecular-sieve (MS) method was used to collect gas samples for ^{14}C and $\delta^{13}C$ analyses. The gas stream was initially passed continuously through a silica-gel tower to remove moisture, then through a 300-mL stainless-steel cylinder containing a 50-nanometer (50-nm), anhydrous (dehydrated under a vacuum at 350°C) MS to trap the CO_2 gas. The CO_2 gas trapped in the MS was degassed in the laboratory to release the trapped CO_2. Released CO_2 was collected in a cold trap, the volume of CO_2 was measured, and the CO_2 was transferred to storage cylinders.

Boreholes SD-7 and SD-9 were open boreholes. For gas sampling from these boreholes, an inflatable borehole liner was used. Gas samples were collected from individual tubes connected to open ports located along the length of an impermeable membrane liner. The liner is inflated to seal the formation wallrock from direct contact with the atmosphere. Two intervals were packed in SD-9: one from the surface to 453.5 m (lithologic units of Tiva Canyon and Topopah Spring Tuff), and the other from 453.7 to 560 m (Calico Hills nonwelded hydrogeologic unit). Only one interval was packed in SD-7, from 508 to 633 m (Calico Hills nonwelded unit). Gas data from SD-12 were obtained from the entire borehole, in contrast to the SD-7 and SD-9 data obtained from selected intervals.

Collection of Pore-Water Samples from SD-7, SD-9, SD-12, NRG-6, and NRG-7a

Pore water was extracted from the cores by using a high-pressure, one-dimensional (uniaxial) compression procedure (Mower and others, 1991, 1994). The compression operations were described in a previous report (Yang and others, 1996). A pressure of 103.4 megapascals (MPa) was initially applied and gradually increased to a final pressure of 827 MPa. Additional pore water was extracted by injecting dry nitrogen gas (greater than 99.99 percent pure) into the pore space and by forcing out pore water at the end of compression. The extracted water was filtered through 0.45-micrometer (0.45-µm) Nuclepore filters into suitable bottles. Samples for major ions were stored in polyethylene bottles, and samples for stable isotopes and ^{14}C were stored in glass bottles.

Analyses of Gas and Water Samples

Gas samples for ^{14}C and $\delta^{13}C$ analyses were sent to the Desert Research Institute (DRI) in Las Vegas, Nevada, for conventional liquid scintillation counting for ^{14}C and mass spectrometry for $\delta^{13}C$. The precision of $\delta^{13}C$ analysis was about 0.2 per mil [one standard deviation (1σ)]. Uncertainty in the ^{14}C measurement was 0.7 percent modern carbon (pmc) (1σ).

Cation concentrations were measured using inductively coupled plasma emission spectroscopy, and anion concentrations were measured using ion chromatography at Huffman Laboratories, Inc., in Golden, Colorado. The analytical error is ±5 percent for all major ions except sulfate, for which the error is ±10 percent. Charge balance is calculated by subtracting total milliequivalent anions from total milliequivalent cations divided by the total milliequivalents of cation and anion multiplied by 100. However, silica concentration is not considered in the charge balance because of difficulty in assessing charge on silicate species. The tritium was analyzed at the USGS Yucca Mountain Project Branch (YMPB) UZ Hydrochemistry Laboratory using procedures published by Thatcher and others (1977). Tritium values were calculated by regressing to the date of sample collection so that tritium decay is considered between sample collection and date of analysis. Tritium errors were approximately 4 tritium units (1σ) [1 tritium unit (1 TU) = 1 ^{3}H atom per 10^{18} ^{1}H atoms]. Carbon-14 and $\delta^{13}C$ samples were sent to Beta Analytic, Inc., in Miami, Florida, for analysis by Tandem Accelerator Mass Spectrometer (TAMS). Uncertainty in $\delta^{13}C$ values was 0.2 per mil and for ^{14}C was 0.7 pmc. All uncertainties quoted are one standard deviation (1σ).

The aluminum (Al) concentration in pore water is mainly controlled by aluminum silicates. Except for extreme pH conditions, dissolved Al is usually below the detection limit (less than 1 milligram per liter (mg/L). Very fine filters (0.1 µm) must be used to remove particulate Al to obtain trustworthy measured concentrations for dissolved Al. Because 0.45-µm filter paper was used for pore-water filtration in this study, reported Al values for pore waters are total Al concentration, including dissolved and particulate components.

Data and Interpretations of Chemical and Radioactive-Isotope Analyses

This section presents hydrochemical data obtained to date and interpretations of those data related to possible flow mechanisms and residence times in the UZ. Data are chemical compositions (major cations and anions) and isotopic concentrations, which include ^{3}H, ^{14}C, and $\delta^{13}C$ of pore water in cores obtained from boreholes in the UZ. Preliminary conceptual hydrologic flow models are derived from the present chemical and isotopic data, along with previously published data collected at Yucca Mountain (Yang and others, 1996).

Spatial Variabilities in Chemical Compositions

Recent analyses augment previously published data from major-ion chemical investigations. Major-ion chemical compositions of pore water from UZ-14, from the surface to 528.7 m were published previously by Yang and others (1996). Additional data from waters obtained mostly below 528.7 m are presented in table 2 and plotted in figure 3. NRG-6 and NRG-7a major-ion chemical compositions are presented in table 3 and plotted in figure 4. Major-ion chemical compositions of samples from boreholes SD-7, SD-9, and SD-12 are presented in table 4 and plotted in figure 5. Several samples from the Topopah Spring Tuff were analyzed because not many samples of pore water could be extracted for chemical analysis. In the previous report by Yang and others (1996), only a few samples from the caprock unit (usage after Scott and Bonk, 1984) of the Topopah Spring Tuff from UZ-4 and UZ-5 were analyzed.

Table 2. Chemical composition of pore-water samples from borehole USW UZ-14, Yucca Mountain area

[- - -, data not available; 0, values below detection limit; m, meter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; charge balance, (meq cation - meq anion)/(meq cation + meq anion) × 100; PTn, Paintbrush nonwelded; CHn, Calico Hills nonwelded; PP, Prow Pass Tuff; YM, Yucca Mountain Tuff; CFu, Crater Flat unit]

Sample identification	Symbol in Piper diagram (fig. 3)	Average depth (m)	Date	pH	Specific conductance (µS/cm)	Calcium Ca (mg/L)	Magnesium Mg (mg/L)	Sodium Na (mg/L)	Silica SiO_2 (mg/L)	Aluminum Al (mg/L)	Bicarbonate HCO_3 (mg/L)	Carbonate CO_3 (mg/L)	Chlorine Cl (mg/L)	Bromine Br (mg/L)	Nitrate NO_3 (mg/L)	Sulfate SO_4 (mg/L)	Charge balance
UZ-14/45.0-45.4/PTn/YM	1	13.78	09-19-94	8.6	1,320	19.6	6.1	249.3	59.5	1	245	18	245	0	35	33	-1.8
UZ-14/1735.3-1735.53/CHn	a	528.95	05-04-95	9.0	700	1.7	0.0	158	46.9	0.0	288	18	37.4	0.0	3.4	15.4	1.5
UZ-14/1804.5-1804.7CHn/PP	b	550.04	05-10-95	8.7	480	0.5	0.2	111	43.0	1.0	181	12	25.1	0.0	15.3	14.9	2.5
UZ-14/1825.8-1826.0/CHn/PP	c	556.53	06-22-95	9.4	590	0.6	0.1	138	47.9	0.9	42	112	23.5	0.0	11.8	12.9	4.3
UZ-14/1854.89-1855.1/CHn/PP	d	565.40	07-07-95	9.2	460	0.5	0.2	107	34.5	1.6	181	23	18.8	0.0	13.7	15.9	-1.4
UZ-14/1865.7-1865.9/CHn/PP	e	568.70	07-20-95	9.1	480	0.3	0.0	115	30.4	0.8	204	18	17.3	0.0	11.7	12.6	1.4
UZ-14/2014,7-2014.9/CHn/PP	f	614.11	07-27-95	9.3	1,520	3.2	0.2	392	37.7	0.2	409	219	32.1	0.0	1.8	22.2	5.6
UZ-14/2015.2-2025.7CHn/PP	g	615.85	08-02-95	9.2	1,450	0.9	0.0	312.7	68.6	- - -	339	176	23.2	0.1	0.5	21.7	4.2
UZ-14/2025.1-2025.3/CHn/PP	h	617.28	08-02-95	9.3	1,550	4.0	0.2	414	54.8	0.2	493	189	36.5	0.0	6.9	26.3	6.3
UZ-14/2095.6-2095.8/CFu	n	638.71	08-18-95	9.0	530	0.0	0.0	112.8	63.0	- - -	143	29	30.0	0.1	0.3	29.0	1.3
UZ-14/2104.05/bottom/CFu	*	641.33	04-22-94	9.4	- - -	2.1	0.7	143	352	38	229	19	10	0	4	23	10.1

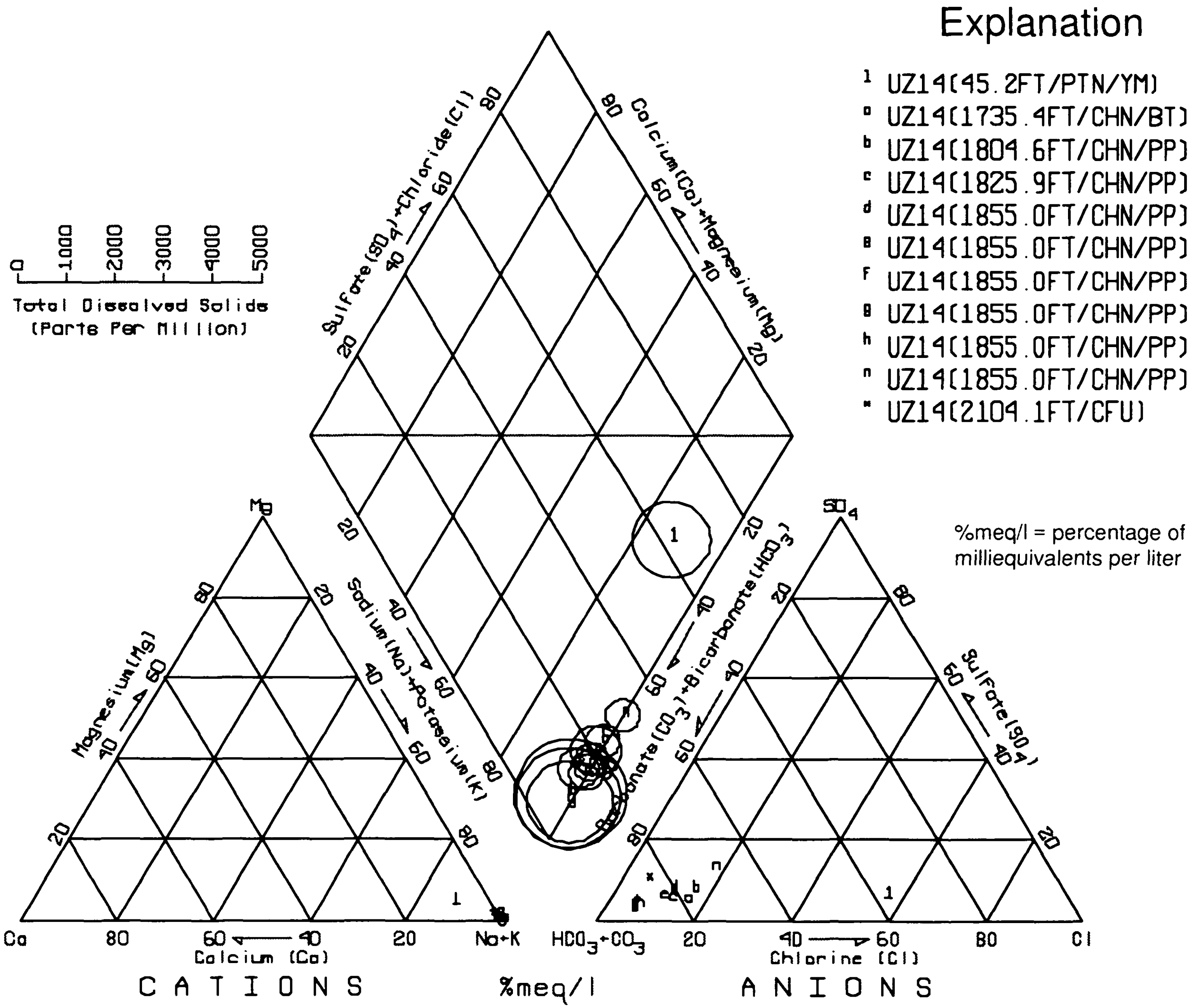


Figure 3. USW UZ-14 pore-water compositions.

Table 3. Chemical composition of pore-water samples from boreholes USW NRG-6 and NRG-7a, Yucca Mountain area

[m, meter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; 0, values below detection limit; charge balance, (meq cation - meq anion)/(meq cation + meq anion); PTn, Paintbrush nonwelded; BT, bedded tuff; PC, Pah Canyon; CHn, Calico Hills nonwelded]

Sample identification	Symbol in Piper diagram (fig. 4)	Average depth (m)	Date	pH	Specific conductance (µS/cm)	Calcium Ca (mg/L)	Magnesium Mg (mg/L)	Sodium Na (mg/L)	Silica SiO_2 (mg/L)	Aluminum Al[1] (mg/L)	Bicarbonate HCO_3 (mg/L)	Carbonate CO_3 (mg/L)	Chlorine Cl (mg/L)	Bromine Br (mg/L)	Nitrate NO_3 (mg/L)	Sulfate SO_4 (mg/L)	Charge balance
NRG-6/158.2 158.6/PTn/BT	A	48.28	07-06-94	6.8	1,070	122	23.3	35.6	97.4	0	34	0	185	1	32	159	-0.2
NRG-6/160.8-161.2/PTn/BT	B	49.07	01-17-95	8.0	860	104	18	35.0	84.0	1.6	55	0	148	0.9	35	139	-2.0
NRG-6/171.0-171.3/PTn/BT	C	52.18	07-21-94	7.4	620	70.5	11.5	29.2	79.4	0	48	13	58	0	43	94	2.0
NRG-6/175.6-176.0/PTn/PC	D	53.58	08-01-94	7.3	520	49.2	8.6	29.4	78.1	0	60	0	47	0	42	64	1.5
NRG-6/219.9-220.2/PTn/PC	E	67.09	11-30-94	7.4	660	24.3	4.2	99.3	61.4	1	92	0	77	0	47	77	-1.3
NRG-6/244.6-245.0/PTn	F	74.62	01-10-95	7.2	630	33	4.9	72.0	51.0	0.6	61	0	49	0.1	40	115	-2.3
NRG-6/255.9-256.1/PTn	G	78.03	01-12-95	6.7	1,920	176	19	215.0	68.0	0.9	61	0	115	0.0	35	840	-6.2
NRG-7A/165.8-166.0/PTn/BT	H	50.57	09-08-95	7.3	500	55.3	5.6	31.7	68.3	0	89.0	0	38.9	1.3	45.5	63.4	0
NRG-7A/258.0-258.4/PTn/BT	I	78.70	10-17-95	8.3	595	43	3.7	82	68.9	1.0	128	0	53.6	0.3	43.7	65.5	2.9
NRG-7A/1483.5-1483.8/CHn/BT	J	452.22	10-25-95	8.0	580	61	0.6	94	48.6	0.3	323	0	33.1	0.1	16.7	24.4	1.3
NRG-7A/1492.7-1493.1/CHn/BT	K	455.04	05-26-94	8.6	510	30.6	0.3	74.7	71.5	0.0	104	34	39	0	18	23	0.9
NRG-7A/1498.6-1498.9/CHn/BT	L	456.83	06-28-94	8.3	500	28.7	0.5	73.2	83.0	1	156	0	50	0	17	18	0.4

[1] 0.45-µm filter paper was used; hence, particulate aluminum is likely included in these values.

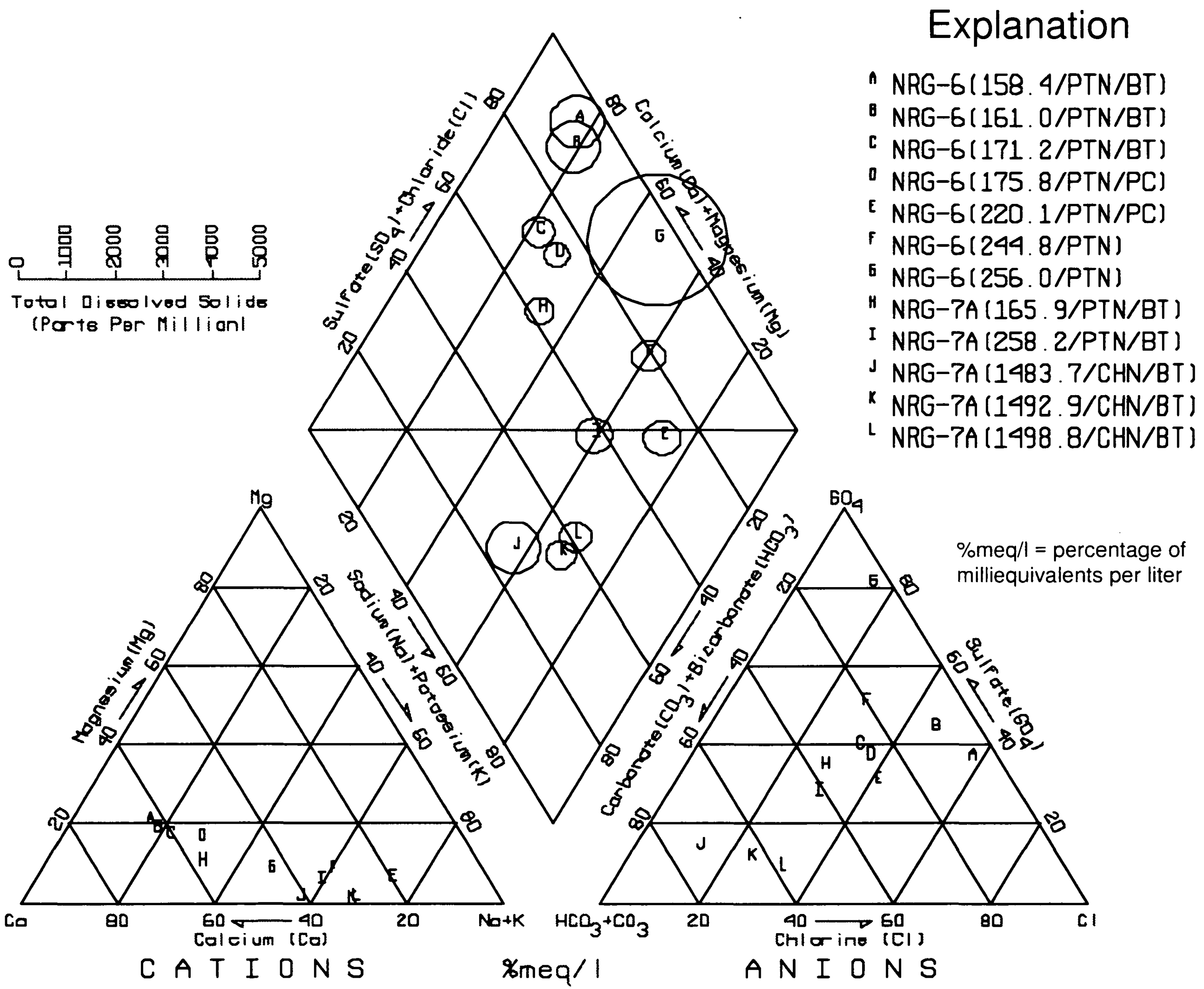


Figure 4. USW NRG-6 and NRG-7a pore-water compositions.

Table 4. Chemical composition of pore-water samples from boreholes USW SD-7, SD-9, and SD-12, Yucca Mountain area

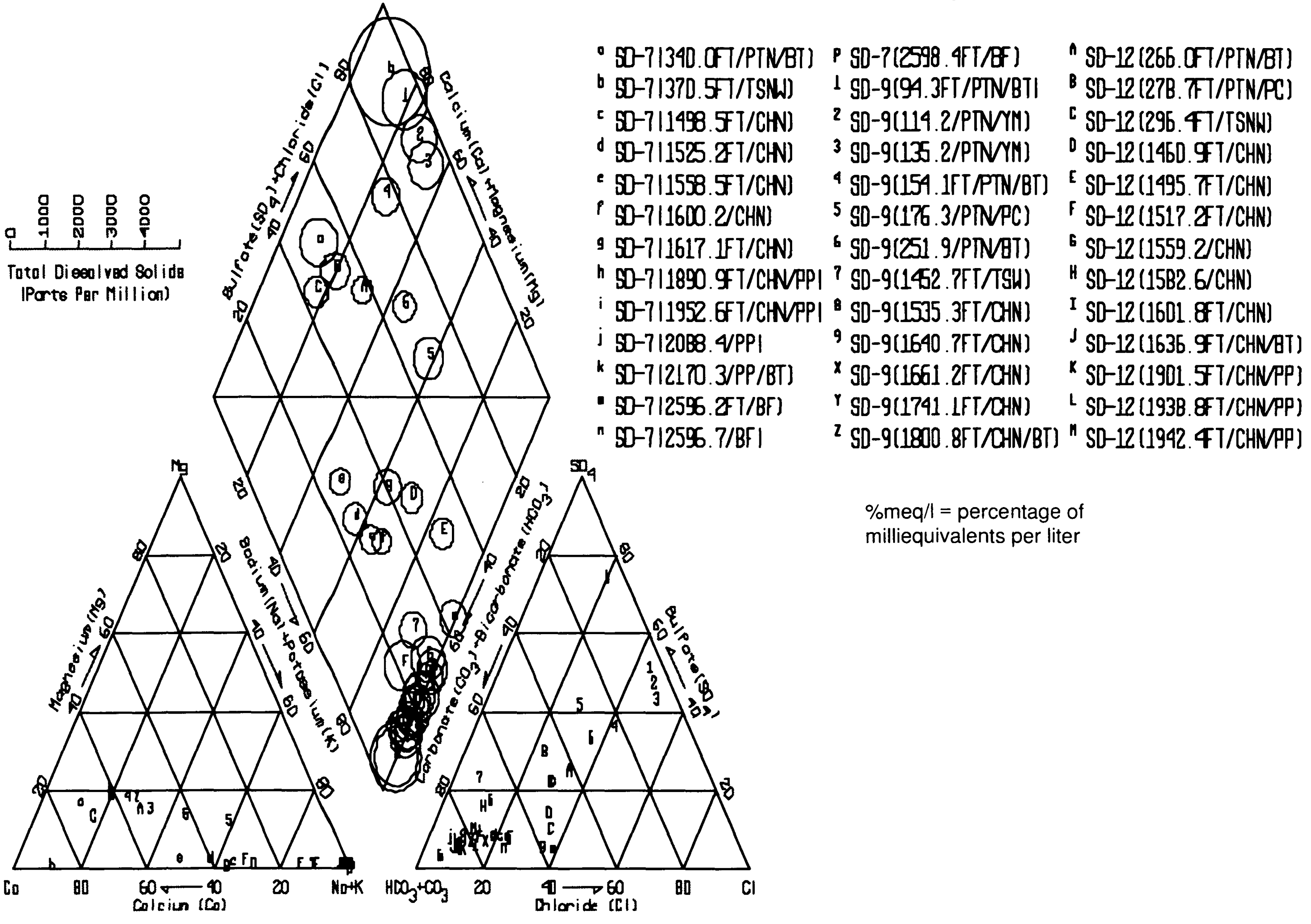
[m, meter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; ---, data not available; 0, values below detection limit; -, less than; N/S, not sampled; charge balance, (meq cation - meq anion)/(meq cation + meq anion) × 100; PTn, Paintbrush nonwelded; CHn, Calico Hills nonwelded; PP, Prow Pass Tuff; BT, bedded tuff; TSw, Topopah Spring Tuff; YM, Yucca Mountain Tuff]

Sample identification	Symbol in Piper diagram fig. 5	Average depth (m)	Date	pH	Specific conductance (µS/cm)	Calcium Ca (mg/L)	Magnesium Mg (mg/L)	Sodium Na (mg/L)	Silica SiO_2 (mg/L)	Potassium K (mg/L)	Bicarbonate HCO_3 (mg/L)	Carbonate CO_3 (mg/L)	Chlorine Cl (mg/L)	Bromine Br (mg/L)	Nitrate NO_3 (mg/L)	Sulfate SO_4 (mg/L)	Charge balance
SD-7/339.7-340.2/PTn/BT	a	103.63	04-25-96	7.2	720	110	15	20	82.8	---	220	0	77.2	0.5	1.5	76.7	1.3
SD-7/370.3-370.6/TSnw	b	112.93	05-14-97	6.7	1,420	289	0.2	39	25.9	---	73	0	133	0.4	0.6	650	-6.7
SD-7/1498.4-1498.6/CHn	c	456.74	04-05-96	7.4	405	31	0.6	67	63.5	---	171	0	28.9	0.4	13.6	14.1	4.4
SD-7/1524.6-1525.7/CHn	d	464.85	01-12-96	7.7	490	38.7	0.9	57.6	68.6	7	203	0	30.1	0.1	12.4	15.9	-0.2
SD-7/1558.4-1558.6/CHn	e	475.03	03-13-96	7.4	370	39	0.9	43	69.3	---	171	0	25.1	0.1	9.0	14.9	-1.0
SD-7/1600.1-1600.3/CHn	f	487.74	07-14-97	7.6	380	23	0.6	59	66.7	---	150	0	31	0.0	5.7	12	1.2
SD-7/1617.0-1617.2/CHn	g	492.87	10-25-96	7.2	570	40.2	0.4	79	62.2	---	194	0	65	0.1	11.0	14	0.0
SD-7/1890.9/CHn/PP	h	576.35	05-09-97	8.7	850	0	0.2	206	67	---	334	78	18	0.0	4.8	10	0.6
SD-7/1952.6/CHn/PP	i	595.15	05-16-97	8.8	980	0	0.3	251	67.4	---	353	120	22	0.0	6.7	11	0.9
SD-7/2088.2-2088.5/PP	j	636.54	03-25-97	9.3	720	0	0	173	54.3	---	157	101	15	0.1	4.0	25	3.9
SD-7/2170.1-2170.5/PP/BT	k	661.51	03-27-97	9.2	670	0	0	164	55.3	---	100	103	18	0.0	3.8	18	8.4
SD-7/2596.1-2596.3/BF	m	791.28	08-23-96	9.1	670	0.6	0.2	158	64.3	---	79	65	83	0.1	3.2	12	6.4
SD-7/2596.5-2596.9/BF	n	791.47	08-21-96	9.0	660	0	0	148	53.2	---	95	71	46	0.0	2.2	12	7.7
SD-7/2598.3-2598.5/BF	p	791.95	08-15-96	8.8	630	0.9	0.0	152	94.8	---	231	59	22	0.1	4.0	18	-1.2
SD-9/94.2-94.4/PTn/BT	1	28.7	07-08-96	6.2	1,050	125	24	43	74	---	37	0	170	0.9	11	260	-4.3
SD-9/114.1-114.3/PTn/YM	2	34.81	03-13-97	6.7	950	95	18	55	62.2	---	31	0	138	0.3	10.9	181	1.6
SD-9/135.1-135.3/PTn/YM	3	41.21	03-11-97	7.5	890	91	15	66	60.0	--	37	0	144	0.3	12.0	162	2.5
SD-9/154.0-154.2/PTn/BT	4	46.97	07-26-96	6.9	650	72	13	36	55	---	90	0	93	0.9	4.7	106	-1.1
SD-9/176.2-176.4/PTn/PV	5	53.74	03-07-97	7.5	720	43	9.5	95	58.5	---	122	0	64	0.1	1.9	124	4.7
SD-9/251.8-252.0/PTn/BT	6	76.78	02-10-97	7.2	510	44	8.0	53	55.0	---	92	0	60	0.0	14.2	73	8.2

Table 4. Chemical composition of pore-water samples from boreholes USW SD-7, SD-9, and SD-12, Yucca Mountain area—Continued

[m, meter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; ---, data not available; 0, values below detection limit; -, less than; N/S, not sampled; charge balance, (meq cation - meq anion)/(meq cation + meq anion) × 100; PTn, Paintbrush nonwelded; CHn, Calico Hills nonwelded; PP, Prow Pass Tuff; BT, bedded tuff; TSw, Topopah Spring Tuff; YM, Yucca Mountain Tuff]

Sample identification	Symbol in Piper diagram fig. 5	Average depth (m)	Date	pH	Specific conductance (µS/cm)	Calcium Ca (mg/L)	Magnesium Mg (mg/L)	Sodium Na (mg/L)	Silica SiO_2 (mg/L)	Potassium K (mg/L)	Bicarbonate HCO_3 (mg/L)	Carbonate CO_3 (mg/L)	Chlorine Cl (mg/L)	Bromine Br (mg/L)	Nitrate NO_3 (mg/L)	Sulfate SO_4 (mg/L)	Charge balance
SD-9/1452.6-1452.8/TSw	7	442.78	08-30-95	7.5	520	6.9	0	112	62.5	---	256	0	15.7	0.1	10.6	62.5	1.4
SD-9/1535.2-1535.4/CHn	8	467.96	09-07-95	7.4	530	0.8	0.1	112	54.9	7	226	0	15.6	0.9	10.6	15.5	4.7
SD-9/1619.9-1661.4/CHn	9	500.09	01-26-96	8.9	610	0.4	0	136.6	55.6	4	232	12	50.2	0.1	9	18.3	-0.7
SD-9/1661.1-1661.3/CHn	X	506.33	01-22-96	9.1	670	0.7	0.0	164	48.8	---	317	0	42.0	0.1	8.2	18.9	1.9
SD-9/1741.0-1741.2/CHn	Y	530.69	07-18-96	9.1	520	0.2	0	125	52	---	185	41	19	1.1	4.4	10	2.2
SD-9/1741.7-1741.9/CHn	–	530.90	07-12-96	8.8	310	0.2	0	74	53	---	113	12	15	0.2	3.8	8.7	5.0
SD-9/1800.8/CHn/BT	Z	548.88	01-30-96	9.3	790	0.8	0	180.7	59.6	6	137	106	32.3	0.4	4.6	20.9	5.6
SD-12/265.8-266.1/PTn/BT	A	81.08	10-27-95	7.2	470	48.9	7.6	28.6	62.7	3	107	0	49.6	0.9	15.9	47.5	-0.1
SD-12/278.6-278.8/PTn/pc	B	84.95	06-20-97	7.3	580	74	12.7	27	71.2	---	159	0	46	0.2	16.0	75	1.7
SD-12/296.1-296.6/TSnw	C	90.34	09-10-96	7.1	490	75	8.0	21	72.2	---	163	0	60	0.2	18.0	21	2.2
SD-12/1460.7-1461.0/CHn	D	445.28	04-17-96	8.5	490	31	0	89	65.5	---	98	30	55.9	0.1	7.3	30.1	4.7
SD-12/1495.5-1495.8/CHn	E	455.89	06-24-97	8.5	550	16	0.2	108	87.3	---	49	57	57	0.3	8.1	55	-0.7
SD-12/1517.0-1517.4/CHn	F	462.44	02-21-96	8.3	660	14	0	150	56.9	---	323	0	35.6	0.1	6.4	22.5	2.5
SD-12/1558.9-1559.5/CHn	G	475.24	08-01-97	8.5	640	4.4	0.1	155	76.1	---	210	41	33	0.2	0.4	54	0.7
SD-12/1582.5-1582.7/CHn	H	482.38	08-05-97	8.5	420	1.2	0.1	97	71.0	---	113	29	17	0.1	4.5	27	4.4
SD-12/1600.6-1603.0/CHn	I	488.23	05-08-96	9.1	540	2.6	0	129	65.7	---	79	90	27.8	0.1	2.6	12.6	3.2
SD-12/1636.9/CHn/BT	J	498.93	03-22-96	9.0	535	3.8	0	129	64.6	---	67	102	15.2	0	1.7	11.2	5.6
SD-12/1901.5/CHn/PP	K	579.55	09-16-96	9.1	470	1.3	0	122	90.7	---	151	59	22	0.1	5.7	9.3	0.2
SD-12/1938.8/CHn/PP	L	590.93	02-28-96	8.8	625	1.4	0	165	55.0	---	171	66	34.0	0.1	1.0	26.1	5.2
SD-12/1942.4/CHn/PP	M	592.04	03-11-96	9.1	520	1.3	0	140	60.1	---	134	66	24.0	0.1	3.5	24.4	4.3



%meq/l = percentage of milliequivalents per liter

Figure 5. USW SD-7, SD-9, and SD-12 pore-water compositions.

In all tables in this paper, core samples are identified as "UZX-YYYY-ZZZZ/UPN/" or "UZX-YYYY-ZZZZ /T/UPN/D". The first three letters "UZX" are used to identify the unsaturated-zone borehole number; for example UZ-14. The next group of letters YYYY-ZZZZ indicates the depth interval (in feet unless noted otherwise) where core was obtained; UPN stands for uniaxial compression first stage (UP1) or second pressure stage (UP2), and so on; "D" stands for distillation; and "T" stands for imbibed test water (not the original pore water). For example, a sample identification of "......../UP1/D" indicates a vacuum-distilled water sample from core that has undergone first-stage uniaxial compression. If there is no "UPN" in front of "D" (such as "UZ14-YYYY-ZZZZ/D"), the water was extracted by vacuum distillation without compression.

Chemical compositions of water samples show clear variations. Locations of UZ-14, SD-9, and the NRG boreholes are in the northern part of Yucca Mountain, while boreholes SD-12 and SD-7 are in the southern part of the mountain. The pore waters extracted from bedded tuff are calcium-chloride- or calcium-sulfate-type waters which plot near the top part of the diamond in a Piper-type diagram (see figure 3, for example). Three samples from Topopah Spring Tuff, one from each borehole, are shown in figure 5. Two of them, "b" (SD-7) and "C" (SD-12), are from the upper nonwelded unit and one, "7" (SD-9), is from the lower welded unit of the Topopah Spring Tuff. Chemical composition of upper and lower units also are different, with the upper unit closer to calcium-chloride and calcium-sulfate type, and the lower unit closer to sodium-bicarbonate type. Chloride concentration in the lower unit is less concentrated than the upper unit, indicating dilution by the fracture water. The pore waters extracted from the Calico Hills nonwelded hydrogeologic unit are sodium-carbonate- or sodium-bicarbonate-type waters which plot near the lower part of the diamond. Samples represented by "c", "d", "e", "f", "g", "D" and "E" in figure 5 are pore waters from borehole SD-7 and SD-12 in the Calico Hills nonwelded unit. These waters tend toward calcium-chloride- and calcium-sulfate-type waters instead of the sodium-bicarbonate- or sodium-carbonate-type waters typical of the Calico Hills nonwelded unit in the other boreholes. This could be due to less Ca/Na cation exchange, with less sodium ion released into water in the SD-7 and SD-12 boreholes. Therefore, in spite of large distances separating these boreholes, chemical compositions are, with few exceptions which will be described below, in general similar and vary according to the lithologic units in which they were obtained.

The dissolved solids concentrations of the pore-water samples from the Yucca Mountain Tuff at 13.78 m and from the Prow Pass Tuff at 614.11 m (table 2), at 615.85 m, and at 617.28 m in UZ-14 (shown by points 1, f, g and h in figure 3) have very high concentrations of dissolved solids (about 1,200 mg/L for the 13.78-m sample and 2,000 mg/L for samples in the Prow Pass Tuff). Also, pore-water sample G in figure 4 from the NRG-6 borehole at 78.03 m has a total dissolved solids concentration of 3,500 mg/L. Evaporative concentration and/or extended water-rock interactions can result in such a large concentration. If the waters were concentrated by evaporation, one possible mechanism could involve evaporation by vapor transport in the unsaturated zone.

The sample from UZ-14 at a depth of 13.78 m (UZ14/45.0-45.4/PTn/YM in table 2) has Na and Cl concentrations of 249.3 mg/L and 245 mg/L, respectively. Samples at slightly greater depth, such as UZ14/85.2-85.6/up 1UZ14/91.0-91.3/up1, and UZ14/95.5-95.9/up1 (table 3, Yang and others, 1996), have an average Na concentration of 39 mg/L and Cl concentration of 60 mg/L. Sample UZ14/45.0-45.4/PTn/YM is more concentrated in Na by a factor of 6 and in Cl by a factor of 4 than the latter. If evaporative concentration is the cause, both Na and Cl should be elevated by the same factor, a relation that is not observed. Further, the stable-isotope composition of this pore water (δD and $\delta^{18}O$ values) plots close to the Yucca Mountain Precipitation Line (YMPL) in the δD versus $\delta^{18}O$ diagram (see fig. 19) indicating little moisture loss by evaporation. (A detailed explanation is given later in the section on the interpretation of stable-isotope data.) These two lines of evidence indicate that high total dissolved solids in this sample are the result of water-rock interactions with only a minor contribution from evaporative concentration. Similarly, for samples from the Prow Pass Tuff from UZ-14 and the NRG-6 sample from a 78.0-m depth, the concentration factors for Na and Cl are different, again indicating extensive water-rock interaction. The δD and $\delta^{18}O$ values of these pore waters, when plotted on the δD versus $\delta^{18}O$ diagram, also show deviation from the YMPL, indicating loss of water by evaporation. Evaporative concentration does occur to some extent (less than 10 percent) but cannot account for the observed doubled concentration factor. (See detailed explanation later in the interpretations of stable-isotope data.) Water-rock interactions thus appear to be the major cause of high dissolved-solid concentrations, and there is no evidence from these samples for major unsaturated-zone vapor transport.

The concentrations of major ions in the pore water are three to ten times larger than those in the perched or saturated-zone waters. These pore waters are from bedded/nonwelded tuffs of the Paintbrush nonwelded (PTn) and Calico Hills nonwelded (CHn) hydrogeologic units only, not from the large block of the welded Topopah Spring Tuff (TSw) hydrogeologic unit at Yucca Mountain. If the more dilute infiltrating waters provide recharge to the perched or saturated-zone waters, they must flow rapidly through fractures or permeable zones in the intervening PTn or CHn units to avoid mixing with the chemically concentrated pore waters in those units. The water flux through such a flow regime is small based on the narrow shape of the tritium peaks. This conceptual model is also supported by the detection of post-bomb ^3H in the deep unsaturated zone of the mountain, indicating a fast flow path (Yang and others, 1996).

Tritium Profiles in Boreholes

Pre-1952 tritium concentrations in precipitation were around 10 TU (Davis and Bentley, 1982). In 1954, atmospheric nuclear tests artificially increased the average annual tritium concentration in precipitation near Yucca Mountain to about 200 TU, with a monthly maximum of about 700 TU. By 1963, further nuclear tests in the atmosphere increased the average annual tritium concentration in precipitation to about 2,000 TU, with a monthly maximum of about 4,000 TU (International Atomic Energy Agency reports, 1969–86). After three half-lives of tritium decay from 1954 to 1990, the average annual tritium concentration in precipitation for 1954 input still remained at 25 TU, with a monthly maximum of about 87 TU. For 1963 input, average annual tritium concentration in precipitation after two half-lives from 1963 to 1987 still remained at 500 TU with a monthly maximum of 1,000 TU. Therefore, water samples extracted from rock core with tritium concentrations greater than 25 TU in 1990 would indicate mixtures derived from pre- and post-1954 precipitation. Tritium concentrations greater than 500 TU in 1987 would indicate mixtures derived from pre- and post-1963 precipitation. Assuming piston flow is dominant in the unsaturated zone of Yucca Mountain, an assumption described by Yang and others (1996), the high tritium concentrations of pore-water samples such as these can be attributed mainly to post-1954 or post-1963 precipitation.

The purpose of the following interpretations of tritium concentrations is not to determine the age of pore water in the unsaturated zone but to isolate any pore-water samples that could have been derived mainly from post-1954 precipitation. Tritium profiles for pore waters in borehole UZ-14 are shown in figure 6. Tritium concentrations between 20 to 40 TU are observed in the intervals between 30 to 45 m in the Pah Canyon Tuff and at 385 m depth in the Topopah Spring Tuff. Only small intervals of the NRG-6 and NRG-7a cores were analyzed for pore-water tritium and ^{14}C. The data are shown in figures 7A and 7B. High tritium concentrations of about 30 to 150 TU in a broad peak are observed in NRG-6 boreholes (fig. 7A) from 53.3 m to 74.7 m in the Pah Canyon Tuff and near the top of the Topopah Spring Tuff. One large tritium concentration of about 47 TU is observed at a depth of 108.7 m in NRG-7a. Tritium data for pore waters extracted from SD-7, SD-9, and SD-12 borehole cores are shown in figures 8, 9A, and 9B. The tritium concentrations are less than 10 TU in SD-7 samples and as large as 14.3 TU in the CHn unit of SD-12; SD-9 core samples have tritium concentrations as high as 21 TU at 50-m depth. As mentioned previously, only limited samples were analyzed from each borehole. Therefore, some fast flow paths may not have been detected.

Residence Times of $^{14}CO_2$ and Pore Water

Gaseous-phase ^{14}C and $\delta^{13}C$ data from SD-7, SD-9 and SD-12 are shown in table 5. The $\delta^{13}C$ samples collected by the WG balloon method varied from -10 to -25 per mil in $\delta^{13}C$ values for the replicate samples. Therefore, these data are not listed here. Problems likely were in the balloon nozzle. Values of $\delta^{13}C$ values obtained by Desert Research Institute (DRI) are less variable, although they tend to be systematically more negative by a few units per mil when collected with the molecular sieve. The other possible explanation of $\delta^{13}C$ values less than -20 per mil could be due to Exploratory Study Facility (ESF) ventilation, which causes degassing of pore-water-dissolved CO_2 that was collected during gas sampling

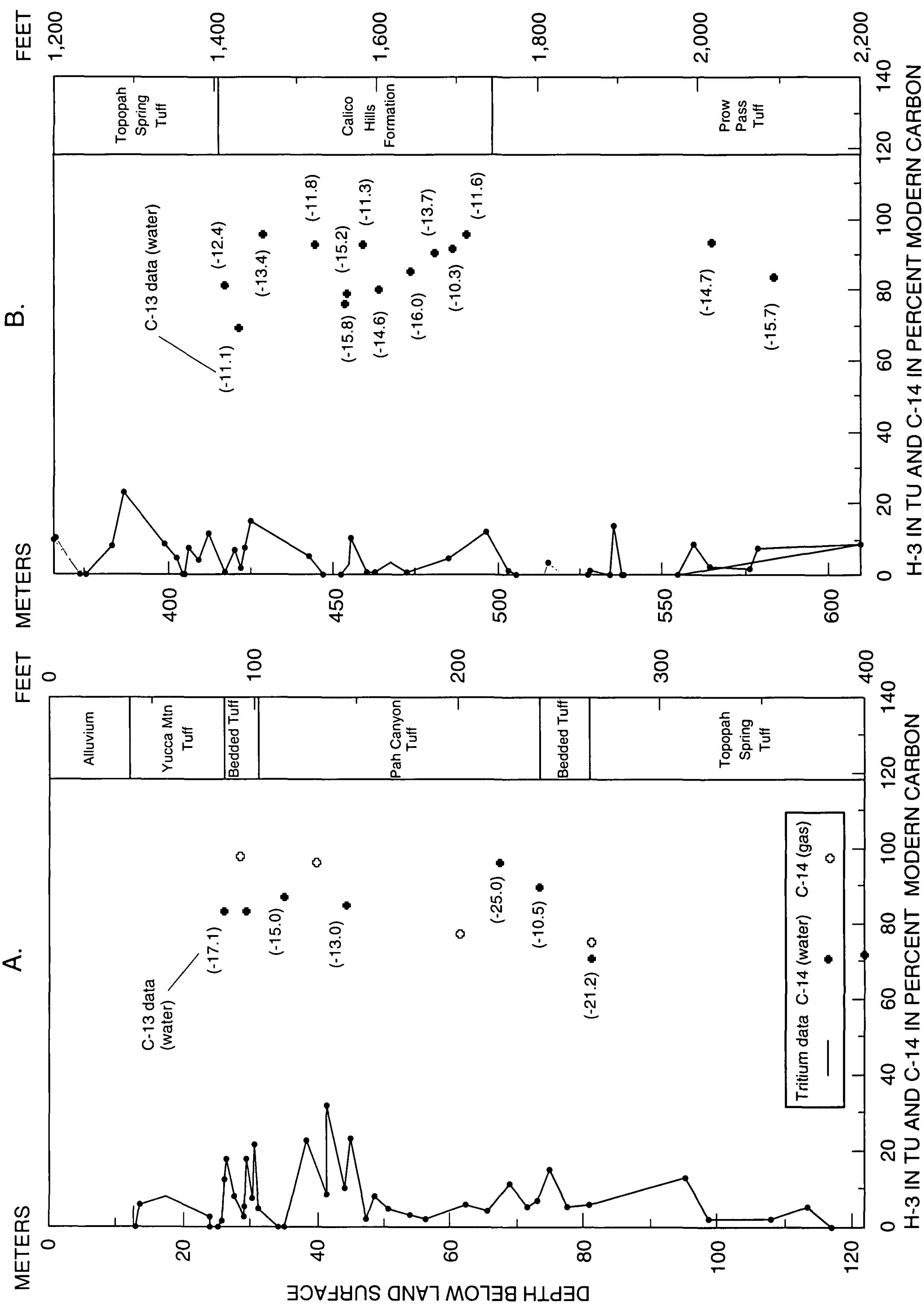


Figure 6. Lithologic units, tritium, and ^{14}C (water) concentrations of borehole USW UZ-14, (A) top 121.9 m, (B) bottom 274.3 m in Calico Hills Formation and Prow Pass Tuff.

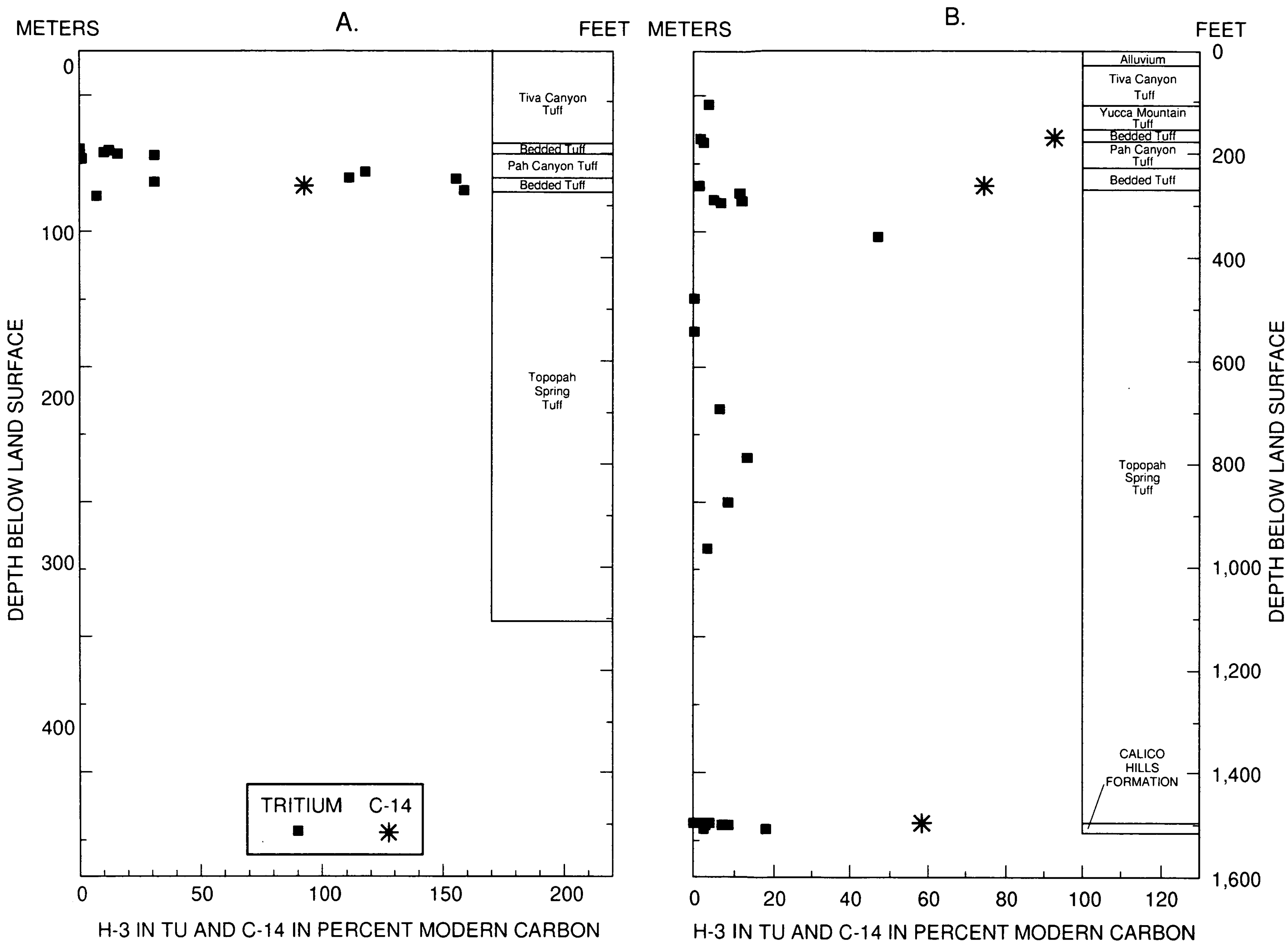


Figure 7. Lithologic units, tritium, and ^{14}C (water) concentrations of boreholes, (A) USW NRG-6 and (B) USW NRG-7a, Yucca Mountain area.

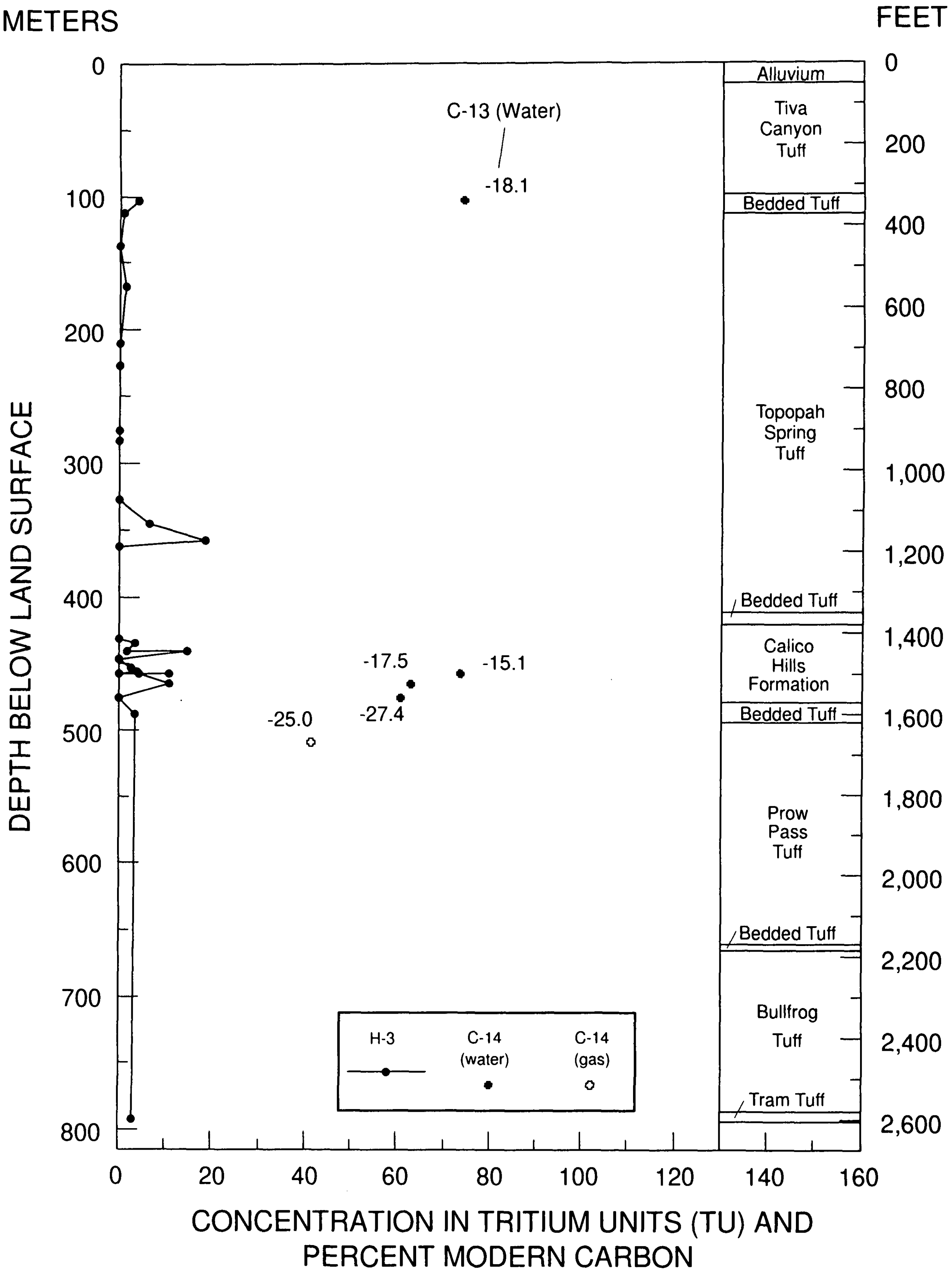


Figure 8. Lithologic units, tritium, and ^{14}C (gas and water) concentrations of borehole USW SD-7, Yucca Mountain area.

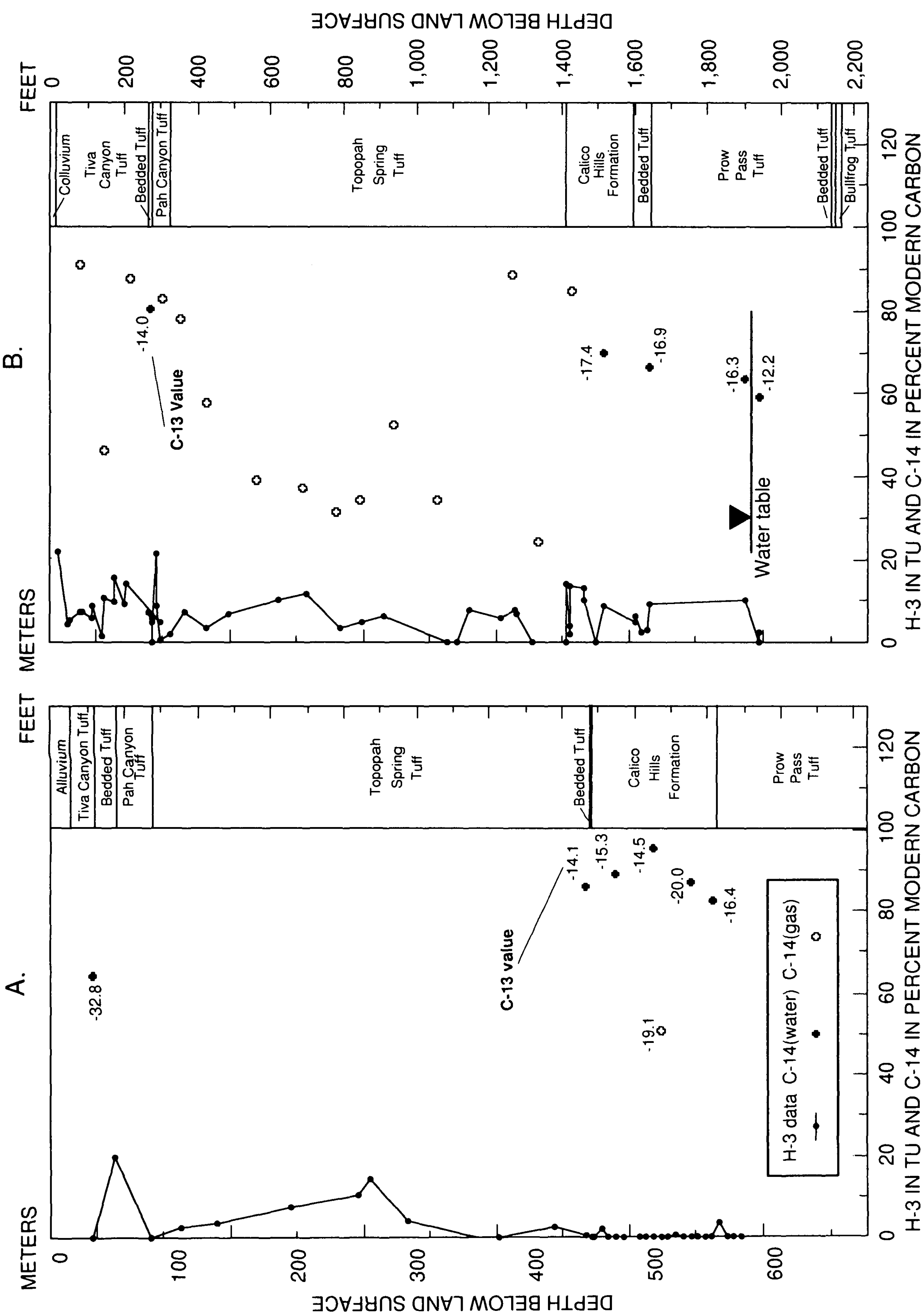


Figure 9. Lithologic units, tritium, and ^{14}C (gas and water) concentrations of boreholes (A) USW SD-9 and (B) SD-12, Yucca Mountain area.

Table 5. Gaseous-phase carbon-14 (^{14}C), δ^{13}C (gas), and fracture-frequency data from boreholes USW SD-7, SD-9, and SD-12, Yucca Mountain area

[m, meter; pmc, percent modern carbon; ---, data not analyzed]

Borehole	Depth (m)	Station with instrument	Lithologic unit[1]	^{14}C (pmc) DRI[2]	δ^{13}C (per mil) DRI[2]	Published 3.05-m composite
SD-7	508-633	---	Prow Pass Tuff	41.5	-25.0	---
SD-9	0-450.5	---	Tiva-Topopah Spring Tuff	96.7	-16.1	---
SD-9	450.5-537.7	---	Calico Hills nonwelded unit	51.0	-19.1	---
SD-12	24.7	P	Tiva Canyon Tuff	91.0	-22.6	8
SD-12	43.9	O	Tiva Canyon Tuff	49.2	-20.2	4
SD-12	65.2	N	Tiva Canyon Tuff	87.4	-22.0	15
SD-12	91.7	L	Topopah Spring Tuff	82.7	-16.4	---
SD-12	107.0	K	Topopah Spring Tuff	77.8	-21.6	5
SD-12	128.9	J	Topopah Spring Tuff	58.0	-22.1	6
SD-12	171.0	I	Topopah Spring Tuff	39.0	-23.6	5
SD-12	208.2	H	Topopah Spring Tuff	36.9	-24.7	18
SD-12	236.8	G	Topopah Spring Tuff	31.6	-25.6	62
SD-12	256.6	F	Topopah Spring Tuff	34.1	-24.4	6
SD-12	285.0	E	Topopah Spring Tuff	52.4	-21.9	13
SD-12	322.5	D	Topopah Spring Tuff	34.3	-23.8	35
SD-12	385.6	C	Topopah Spring Tuff	88.7	-22.9	48
SD-12	407.2	B	Topopah Spring Tuff	24.4	-24.6	7
SD-12	435.9	A	Calico Hills nonwelded unit	84.5	-17.3	---

[1] Lithologic unit from Sandia National Laboratory Reports: SD-7, Rautman and Engstrom, September 1996; SD-9, Engstrom and Rautman, September 1996; and SD-12, Rautman and Engstrom, November 1996.

[2] Desert Research Institute (DRI), δ^{13}C values are measured from subsample of ^{14}C collected in molecular sieve. Delta^{13}C is defined as relative ^{13}C/^{12}C values of sample, expressed in part per mil (‰) relative to Pee Dee belemnite (PDB) standard.

(a kinetic fractionation effect). Carbon dioxide concentrations are not reported here due to variable data, with values ranging from 1,000 to 7,000 ppm.

The excess CO_2 could come from dissolved CO_2 in pore water of the Topopah Spring Tuff. The ^{14}C activities of CO_2 gas from boreholes SD-9 and SD-12 are plotted in figures 9A and B, and δ^{13}C values from SD-12 are plotted in figure 10. One ^{14}C activity of gaseous-phase CO_2 was derived from the interval between the top of the Calico Hills nonwelded unit and the water table of SD-9. The ^{14}C activity of this sample is 51 pmc, significantly smaller than the ^{14}C activities of pore waters (between 82.3 and 95.3 pmc) in the same zone. If the CO_2 in the gaseous phase were in isotopic equilibrium with CO_2 in the aqueous phase of the pore water, the ^{14}C activities in the two phases should be comparable. The fact that they are different possibly could be due to atmospheric $^{14}CO_2$ contamination to the pore water during drilling.

The ^{14}C activities of gaseous-phase CO_2 in instrumented borehole SD-12 (table 5) decreased from surface to depth with some irregularly large ^{14}C activities in stations E, C, and A and small ^{14}C activity in station O. Anomalously large ^{14}C activities in station C and A may indicate contamination of the samples. Samples from station C may have been affected by leakage through the borehole instrumentation support pipe (J.P. Rousseau, U.S. Geological Survey, oral commun., 1997). Station A lies in a region of strongly low pressure at depth (identified from monitoring sensors) with complete attenuation of the surface (synoptic) barometric-pressure signal. Gas-monitoring evidence indicates that station A likely was contaminated with atmospheric air drawn in due to the low pressure, prior to the instrumentation and sealing of the borehole (J.P. Rousseau, U.S. Geological Survey, oral commun., 1997). Moderately large ^{14}C activity at station E may be related to the relatively high fracture frequency noted at that station (table 5). The majority of ^{14}C activities in gas-phase CO_2 from SD-12, however, are consistent with the data obtained from borehole UZ-1 and further are consistent with gas

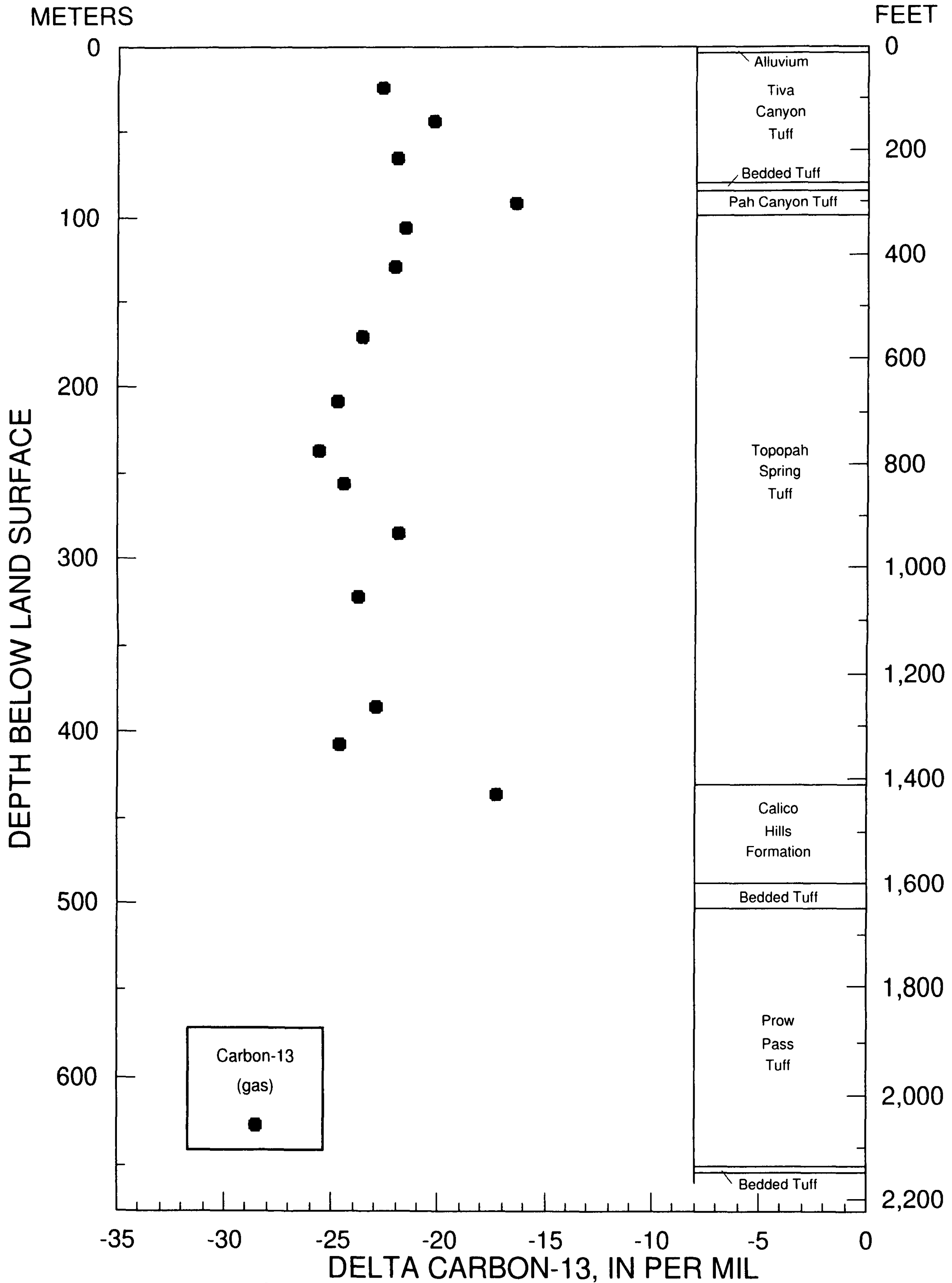


Figure 10. Lithologic units and $\delta^{13}C$ (gas) values, borehole USW SD-12, Yucca Mountain area.

transport by a postulated diffusion mechanism as previously concluded (Yang and others, 1996).

Yang and others (1996) stated that the high pore-water ^{14}C pmc values in the CHn from borehole UZ-14 could be related to (1) $^{14}CO_2$ in the gaseous phase possibly exchanging with the bicarbonate species in the pore water; and/or (2) the large amounts of cement used below a perched-water zone at 383.1 m to seal off the borehole wall and prevent perched-water leakage (Portland cement contains $Ca(OH)_2$ which will absorb atmospheric CO_2 during mixing with water and release the CO_2 during exothermic curing). In more recent pore-water data obtained from the Calico Hills nonwelded unit in SD-9, ^{14}C values ranged from 82.3 pmc to 95.3 pmc between depths of 467.9 m and 548.6 m. Those data are in the same range of ^{14}C values obtained in the Calico Hills Formation from UZ-14. Both boreholes are located in the northern part of Yucca Mountain; SD-9 was drilled without using cement. Therefore, it is unlikely that the ^{14}C data in the Calico Hills nonwelded unit from UZ-14 were contaminated by cement.

With regard to exchange of young ^{14}C in gaseous-phase CO_2 with the bicarbonate species in the pore water in the Calico Hills nonwelded unit of UZ-14 and SD-9, the sparse data obtained so far are inconclusive. Gaseous-phase ^{14}C data (table 5) from one analysis from the Calico Hills nonwelded unit in SD-9 show 51.0 pmc (calculated age about 5,800 years), but one analysis from the Calico Hills nonwelded unit in SD-12 shows 84.5 pmc (about 1,340 years). From the ^{14}C data of gaseous-phase CO_2 obtained in the UZ-1 and SD-12 boreholes, true gaseous-phase ^{14}C activities likely are about 50 pmc in the Calico Hills nonwelded unit (Yang and others, 1998). A possible explanation for the discrepancy between large ^{14}C activities in the Calico Hills nonwelded unit in UZ-14 and SD-9 is that pore waters were contaminated with atmospheric $^{14}CO_2$ during drilling or mixing of young water with old water. However, the fact that ^{14}C activities in the Calico Hills nonwelded unit in SD-7 and SD-12 are about 40 to 85 pmc would exclude large contamination of cores by the drilling air (with ^{14}C about 120 pmc) because all these boreholes were drilled with air. The $\delta^{13}C$ values of bicarbonate carbon in pore water from the Calico Hills nonwelded unit in SD-9, UZ-14, SD-7, and SD-12 also do not show large contamination from atmospheric $^{14}CO_2$ ($\delta^{13}C$ of -7 to -8 per mil in atmospheric CO_2). For confirmation of positive ^{14}C values in pore water, ^{14}C analyses should be made on cores that are drilled with compressed nitrogen gas (which contains no carbon dioxide as a coolant) instead of atmospheric air. In contrast, perched water encountered in boreholes likely is uncontaminated by the $^{14}CO_2$ in the drilling air because the mass of carbon in these water reservoirs is orders of magnitude larger than in the drilling air.

STABLE-ISOTOPE COMPOSITIONS (δD AND $\delta^{18}O$) OF PORE WATER FROM USW UZ-14

Oxygen, deuterium (^2H), and hydrogen isotopic ratios of water have great value in hydrologic studies because they are intimately dependent upon the nature of physical processes that govern water transport (Craig, 1961b; Gat, 1980). Stable-isotope ratios ($^{18}O/^{16}O$ and $^2H/^1H$) expressed as $\delta^{18}O$ and δD can be used to indicate the origins of water, climatic and evaporative history of water, and flow paths through the unsaturated zone. They can also be used as indicators of transport properties or water interactions with other minerals. The lack of long-term direct measurements of infiltration requires proxy indicators of water movement through the unsaturated zone to extend the record into the past. The isotopes most commonly used in hydrology are those that are constituents of water molecules (^{18}O, ^2H, and ^3H). Other environmental isotopes (^{14}C, ^{13}C, and ^{36}Cl) that occur in dissolved compounds are also valuable for studying ground-water cycles (Fontes, 1980) and have been applied in the previous section.

Hydrogen has two stable isotopes (^2H and ^1H), and oxygen has three stable isotopes (^{16}O, ^{17}O, and ^{18}O). Because hydrogen and oxygen are components of the water molecule, isotopic fractionation of both is usually co-variant. Consequently, the isotope ratios of these two elements generally are discussed together. Natural variations of the abundance of these stable isotopes can be related to the history of the water molecules (Gat and Gonfiantini, 1981). Rather than express these variations as the absolute abundance of the isotopes, Vienna standard mean ocean water (VSMOW) is used as the standard against which the natural variations are measured.

Thus:

$$\delta^{18}O(\text{per mil}) = [(R_o - R_{std,o})/R_{std,o}] \times 10^3$$

$$\delta D(\text{per mil}) = [(R_h - R_{std,h})/R_{std,h}] \times 10^3$$

where $\delta^{18}O$ (per mil) and δD (per mil) are the deviation in ^{18}O and D of the sample from the reference standard in units of per mil respectively, $R_o = {}^{18}O/{}^{16}O$ and $R_h = D/{}^1H$ of the sample being studied, and $R_{std,o} = {}^{18}O/{}^{16}O$ and $R_{std,h} = D/{}^1H$ of the VSMOW.

After surface water enters the ground-water system, its original isotopic composition is typically conserved. Some factors, however, can cause the $\delta^{18}O$ and δD concentrations of unsaturated-zone water and ground water to differ from local meteoric water. These factors include:

1. Recharge from a water body of partially evaporated surface water. Evaporation from surface water bodies is a nonequilibrium process that enriches $\delta^{18}O$ and δD in the water such that the $\delta D/\delta^{18}O$ slope is less than 8 and usually between 3 and 6.
2. Recharge to an aquifer from an area of different altitude or latitude.
3. Mixing of two or more sources of water.
4. Recharge of either the ground water or UZ water from a different climatic regime in the past.
5. Interaction with aquifer carbonate or silicate rocks at high temperature. Exchange of oxygen in water and rock at high temperatures increases the $\delta^{18}O$ of the water (the $\delta^{18}O$ shift).
6. Fractionation between the ground or pore water and mineral-hydration water.

Methods of Pore-Water Extraction for δD and $\delta^{18}O$ and Analysis

It is important that a pore-water extraction method extract only the hydrologically active water (percolating mobile water), or the stable-isotope data of the extracted water will be misinterpreted. Extraction methods using vacuum distillation and toluene azeotropic distillation to remove water from soil and clay-rich soil have been reported by Revesz and Woods (1990), Walker and others (1994), and Ingraham and Shadel (1992). However, none had been applied to tuffaceous volcanic rocks. The distribution of minerals at Yucca Mountain differs from borehole to borehole, but certain commonalities are apparent. The major mineral groups of Yucca Mountain are zeolites, clays, alkali feldspar, silica polymorphs, and glass. The zeolites are primarily clinoptilolite, mordenite, and analcime. The clays are principally smectites and illite with lesser kaolinite (Broxton and others, 1986; Bish and Vaniman, 1985; Bish and Chipera, 1989). Zeolite and clay contain water of crystallization that can be released during the heat-distillation process. Three extraction methods—toluene distillation, vacuum distillation, and compression—were used on core samples of volcanic rocks from Yucca Mountain in order to establish a standard extraction procedure.

Toluene Distillation

Toluene distillation of water from soil for isotopic analysis was first used by Allison and Hughes (1983). The principle of the toluene distillation method is that the toluene forms an azeotropic mixture with water at 84.1°C but separates from water at room temperature. The boiling point of the toluene-water azeotrope is 84.1°C, significantly lower than the boiling point of water (100°C) and toluene (110°C). Ingraham and Shadel (1992) found that the isotopic compositions of water extracted during toluene distillation will fractionate when the distillation process is not completed. This result is predicted by the Rayleigh distillation model. The results indicate that the toluene is simply a carrier of water. Thus, fractionation will occur during the toluene distillation if the extraction is not complete.

The toluene distillation method used in this study is similar in design to that of Revesz and Woods (1990). The Dean-Staark apparatus used for toluene distillation (fig. 11) consists of a laboratory heating element, a flask, a specially designed receiving trap, and a straight condenser. The funnel has a wide area above the joint to prevent loss of water by uneven, explosive boiling (Revesz and Woods, 1990). Enough water-free toluene is added so that the sample remains covered throughout the entire distillation process. During distillation, the temperature is maintained at the boiling point (84.1°C). The temperature of the solution is then raised to 110°C. At the beginning of the distillation, water and toluene are distilled together, forming a cloudy liquid. The distillation continues until the condensate turns clear and no water

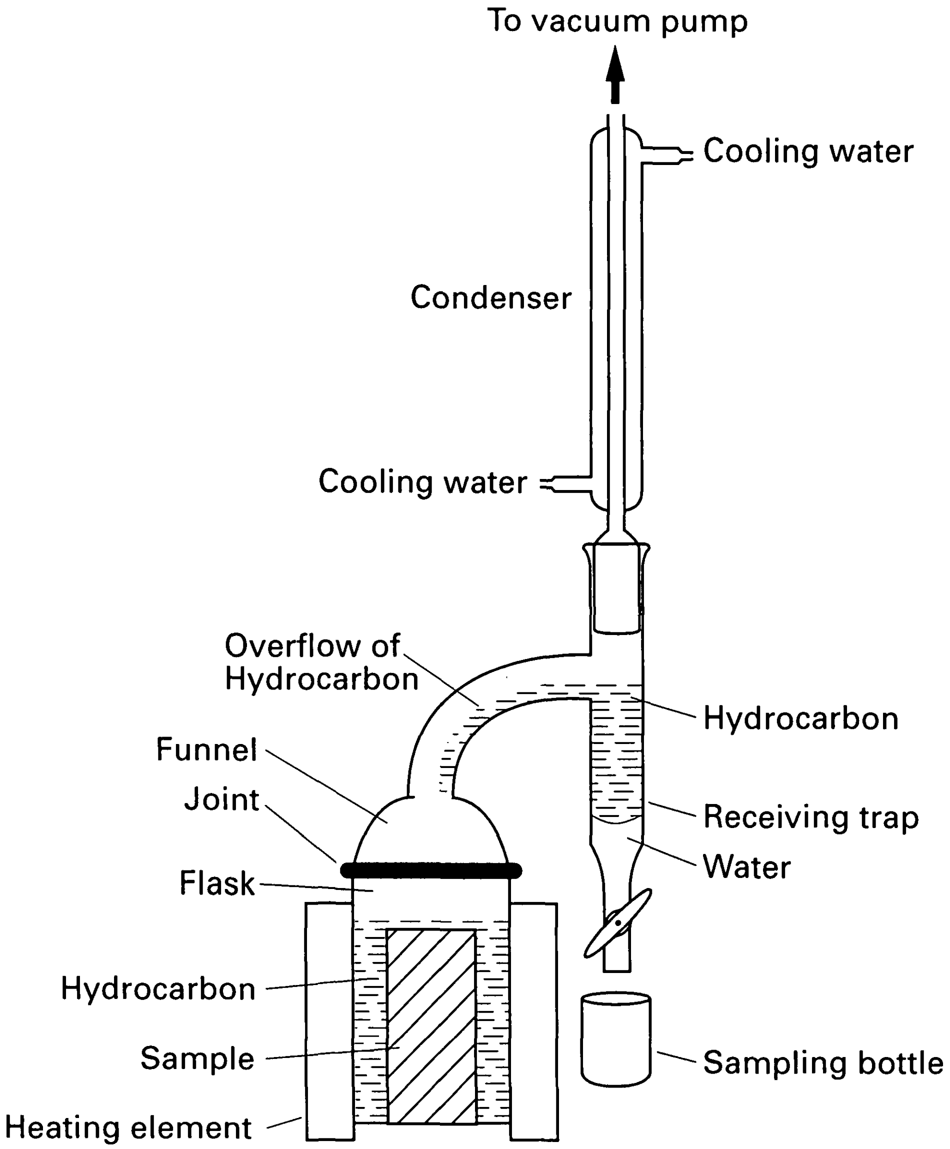


Figure 11. Toluene distillation apparatus for pore-water extraction.

drops remain on the glass wall of the entire apparatus. After collecting the water in a glass bottle with Teflon cap, any trace of toluene is removed by adding paraffin wax (enough to solidify after dissolving the toluene) to the water and warming it in the closed sample bottle to the melting point of the wax (60–70°C). The bottle is shaken and allowed to cool, and the wax solidifies. The water is decanted easily. The wax procedure can be repeated to ensure complete removal of the toluene. The wax procedure was repeated three to four times in this study.

Vacuum Distillation

The vacuum distillation technique uses a distillation apparatus consisting of vacuum glassware, nitrogen gas, dry ice, a set of heating elements, and a vacuum pump (fig. 12). The procedure consists of four steps: (1) the core segment is weighed and placed inside the distillation apparatus; (2) a vacuum is applied to the distillation apparatus for a couple of hours and heated to 150°C (as measured at the heating mantle) resulting in a core temperature of about 110°C (the reason for choosing this temperature is explained below); (3) the core water is expelled into a flask cooled with a dry ice/alcohol mixture at a temperature of about -80°C; and (4) the total volume of water recovered is measured under nitrogen gas. The distilled core was placed inside an oven at 104°C for three days to check for any further loss of water. The third step may take around 24 hours to ensure complete extraction of core water. If the core water yield is less than 99.75 percent of the total measured water in the subsample (a small piece of core chipped

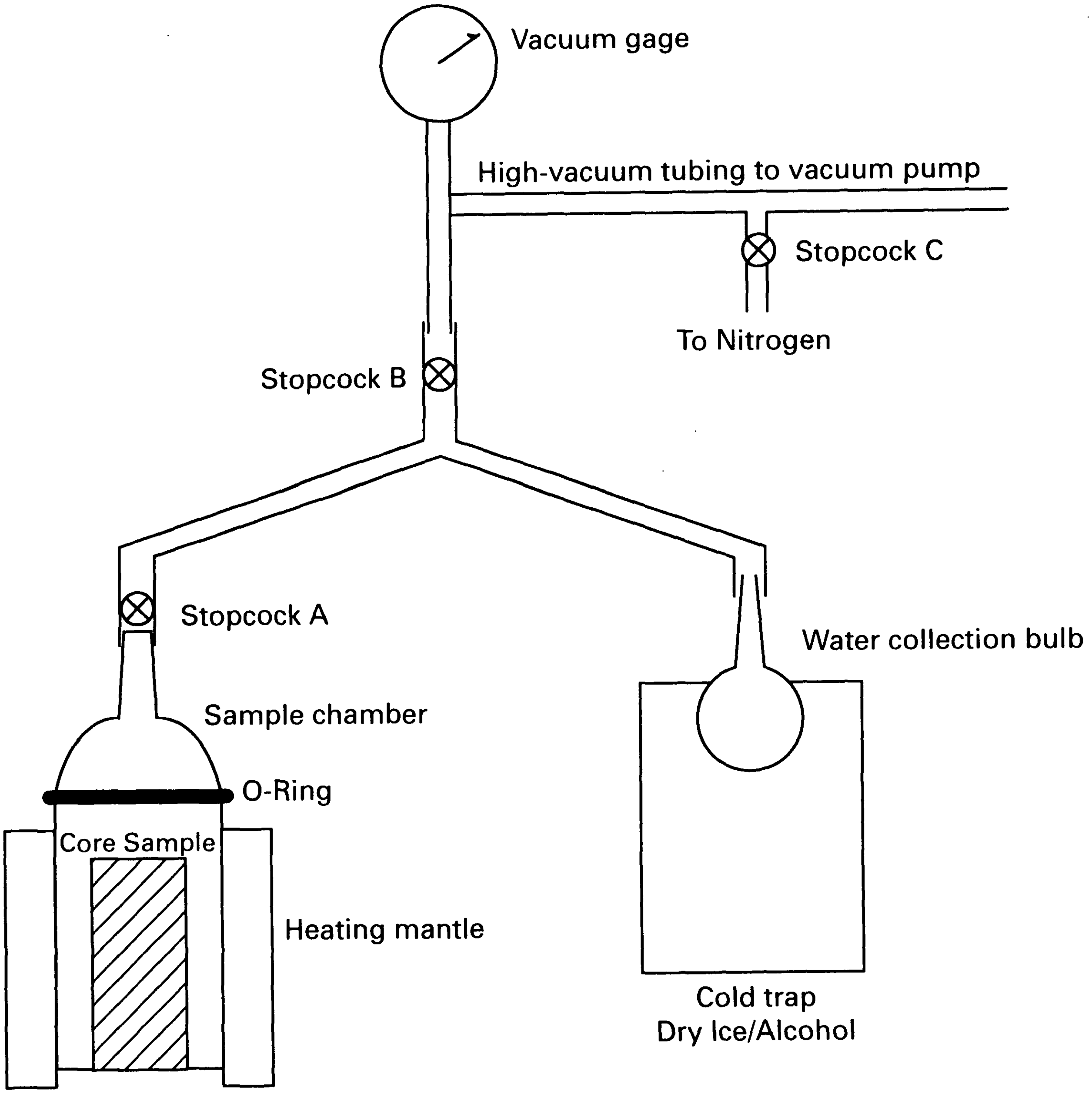


Figure 12. Vacuum distillation apparatus for pore-water extraction.

off and dried in the oven at 105°C to measure water content), there can be an appreciable amount of fractionation (Knowlton and others, 1989). If incomplete extraction was suspected, an additional core was vacuum-distilled for a longer time to make sure the water yield was greater than 99.75 percent.

The distillation temperature of the core sample will affect (1) the release of hydrated water, (2) the water-rock interaction at high temperature, and (3) the efficiency of extraction. Hydration water may mix with the pore water, thus masking the values of stable isotopes of pore water. The exchange of ^{18}O between water and rock at high temperature (greater than 150°C) will enrich the ^{18}O of water (Panichi and Gonfiantini, 1981). Extraction efficiency increases with distillation temperature, but high temperature will cause problems from release of hydrated water and/or water-rock interaction. For clay-bearing soil, the temperature at which hydrated water is released is about 110°C, as reported by Ingraham and Shadel (1992). They postulated that the hydration water of clay soils may not be released at temperatures below

110°C; thus, an extraction method with a low temperature may be advantageous. Araguàs-Araguàs and others (1995) concluded that if the isotopic compositions of mobile water are of interest, the distillation temperature should be kept as low as possible to minimize the impact of removing the weakly bound hydration water. Feng and Savin (1993) found that some zeolite species (clinoptilolite, heulandite, and stilbite) will lose about 50 percent of hydrated (channel) water during overnight evacuation. Hydrated water is held in the structural channels of those minerals. However, the exchange of framework oxygen with bulk-water oxygen in zeolite was less than 5 percent at temperatures below 110°C. For low-temperature distillation, Wood (1990) used vacuum distillation at room temperature, but the extraction was very poor because of incomplete recovery of water.

The distillation temperature for this study therefore was chosen at 150°C at the heating mantle, resulting in a core temperature of about 110°C. From time-series measurements of mantle temperature and core temperature for different lithologic cores, the temperature distribution indicates that the temperature of the core increased with the temperature of mantle and equilibrated to core temperature of about 110°C when the heating-mantle temperature was at 150°C (Yu, 1996).

The time required for complete distillation of soil samples was reported by Ingraham and Shadel (1992) and Araguàs-Araguàs and others (1995) to be about 7 hours. However, other factors affect the time required for complete extraction, such as sample size, moisture, distillation temperature, and distillation system design. The optimum length of time for distillation was determined experimentally by comparing the stable-isotopic compositions of water distilled from a piece of selected Yucca Mountain core cut into five sections that were distilled for different time periods (4, 8, 12, 24, and 36 hours). Five different lithologic cores were selected for the test—one core from the Pah Canyon Tuff, three cores from the Topopah Spring Tuff, and one core from the Calico Hills nonwelded hydrogeologic unit (table 6). The minimum distillation times are different, depending on the lithology. For Pah Canyon and Topopah Spring Tuff cores, at least 24 hours are required for complete extraction, but for Calico Hills nonwelded unit cores, more than 36 hours are required.

Compression Extraction

One-dimensional compression extraction (Higgins and others, 1997) was also tested. Compression operations were similar to the procedures described previously for pore-water extraction for chemical compositions and ^{14}C analyses. Water samples were collected in glass syringes attached to the compression cell when an adequate volume was extracted. The extracted water was filtered through a 0.45-μm filter into glass bottles for stable-isotope analysis. The effect of the compression process on the alteration of original stable-isotope compositions of pore water can be investigated by two methods: (1) water samples are collected at each pressure level during the compression procedure, and stable-isotope compositions at each pressure level are then compared; and (2) a water of known stable-isotope composition is imbibed into dry cores (from each tuff) after the core was oven-dried overnight. The isotopic values of known water can be compared with those of the water extracted then from the imbibed cores by the compression method. If there is no change in composition as a function of pressure in the first test, this would indicate that the compression method did not cause pore-water fractionation. The results of the second test may indicate which pool of water inside the core is extracted by the compression method. If there is no difference in isotopic composition between known water and compression-extracted water, this would also indicate that compression processes did not alter the original pore-water isotopic compositions. On the other hand, if the stable-isotope composition of compression-extracted water is different from the imbibed water, and the extracted water does not change with pressure, the possible explanation is that the water imbibed into the dried core has been fractionated. That can be investigated by comparing the stable-isotope compositions of residual water with those of compression-extracted water.

Water Analyses for $\delta^{18}O$ and δD

Stable-isotope ratios $\delta^{18}O$ and δD were analyzed using mass spectrometers at the University of Colorado, Institute of Arctic and Alpine Research Stable Isotope Laboratory and at the U.S. Geological Survey Research Laboratory in Reston, Virginia. The $\delta^{18}O$ values were determined by isotopically equilibrating water with a small amount of pure CO_2 in a constant-temperature bath. The equilibrated CO_2 gas

Table 6. Stable-isotopic compositions and water yield of water distilled from Yucca Mountain cores by use of different distillation times

[$\delta^{18}O$, delta oxygen-18; δD, delta deuterium; VSMOW, Vienna Standard Mean Ocean Water; NA, not analyzed. There was not enough sample to perform oxygen-18 analyses]

Step number	Collection time (hours)	Water yield (percent)	$\delta^{18}O$ relative to VSMOW (per mil)	δD relative to VSMOW (per mil)
Run A. Core ID: UZ14-156.2 from Pah Canyon Tuff				
1	4	10.12	-15.1	-115
2	8	15.12	-13.2	-104
3	12	18.33	-12.9	-99
4	24	19.78	-12.2	-96
5	36	19.82	-12.1	-96
Run B. Core ID: UZ14-1020 from Topopah Spring Tuff				
1	4	3.42	-14.9	-110
2	8	4.51	-14.2	-104
3	12	5.20	-13.3	-99
4	24	5.21	-13.6	-99
5	36	6.03	-13.4	-99
6	48	6.03	-13.2	-98
Run C. Core ID: UZ14-1187.8 from Topopah Spring Tuff				
1	4	2.16	NA	-106
2	8	3.71	-16.3	-103
3	12	3.96	-16.5	-103
4	24	4.08	-15.0	-102
5	36	4.08	-15.1	-102
Run D. Core ID: UZ14-1391.2 from Topopah Spring Tuff				
1	4	11.13	-16.2	-112
2	8	17.55	-16.7	-109
3	12	18.43	-16.5	-108
4	24	21.90	-16.7	-109
5	36	21.90	-16.7	-109
Run E. Core ID: UZ14-1430.2 from Calico Hills nonwelded hydrogeologic unit				
1	4	4.28	-19.1	-140
2	8	16.67	-16.3	-112
3	12	17.35	-16.2	-108
4	24	18.53	-16.0	-109
5	36	18.50	-15.9	-106
6	48	18.51	-15.8	-107

was measured in the mass spectrometer, and the $\delta^{18}O$ of the water was calculated from this value. Typically 4 mL of water are used, although smaller samples (down to 2 mL) can be measured in this way. The equilibration system is automated and controlled by a computer that also controls the operation of the mass spectrometer. All critical parameters of the system (pressures and temperatures) are monitored by the computer, and any sample that experiences conditions outside of acceptable ranges is rejected. The $\delta^{18}O$ equilibration system is capable of measuring 20 samples and 4 standards overnight.

The δD values were determined by reducing water to hydrogen gas and by measuring the δD of the hydrogen in the mass spectrometer. Water was injected into a hot evacuated cell. The water vapor thus formed was passed through a capillary tube and over uranium metal at 600°C. The uranium metal reduced water vapor to hydrogen gas. The injection of water, reduction to hydrogen, and measurement of δD values in the mass spectrometer are all controlled by computer. The volume of water required is 2 mL. This system is capable of measuring 20 samples and 6 standards in about 20 hours. Samples prepared for this method should have a conductivity of 2,000 μS/cm or less to avoid salt buildup in the evacuated cell. Uncertainty in $\delta^{18}O$ values was 0.2 per mil and in δD was 1.0 per mil. These uncertainties are one standard deviation (1σ). Relative $^{18}O/^{16}O$ ($\delta^{18}O$) and D/H (δD) values of water expressed in ‰ relative to VSMOW water (0 ‰) on a scale normalized so that the $\delta^{18}O$ and δD of Standard Light Antarctic Precipitation (SLAP) water are -55.5 ‰ and -428 ‰, respectively.

Inconsistency in δD and $\delta^{18}O$ Data with Different Extraction Methods

The extraction of isotopically representative water from porous media for stable-isotope analysis has been sometimes difficult, particularly in the case of unsaturated core, in which not all pore spaces are filled with water. It is mandatory that no fractionation (change in isotopic composition) occurs during the extraction processes. Pore water extracted from samples from the same piece of core by different methods ideally should yield the same isotopic composition.

Review of Water-Extraction Methods Published in the Literature

Walker and others (1992, 1994) compared the stable-isotope data from 14 different laboratories on four continents for soil water derived by various extraction methods. They distributed soils rehydrated with water of known stable-isotope composition to the 14 laboratories where the soil water was extracted and returned for analysis. Extraction methods included toluene-azeotropic distillation (six laboratories), vacuum distillation (seven laboratories), microdistillation (three laboratories), and centrifugation (one laboratory). The comparison showed large variation among laboratories in isotopic compositions of the extracted water (up to 30 per mil for δD and 4.4 per mil for $\delta^{18}O$). The measured compositions from extracted waters were commonly lighter than those of the introduced water by more than 10 per mil in δD and 2 per mil in $\delta^{18}O$. The variation increased as the water content of the soil decreased and was greater for clays than for sand at a comparable matrix suction force. The variation was caused by incomplete extraction of soil water from the soil samples. Centrifugation followed by toluene-azeotropic distillation gave the results closest to the known value.

Because few studies have examined extraction methods for stable-isotope analyses of hydrated mineral soil (soil containing certain clays or gypsum), Walker and others (1992, 1994) suggested that toluene-azeotropic distillation and vacuum distillation are unsuitable for gypsum media because gypsum is unstable above about 45°C. At temperatures above 45°C, gypsum releases its hydrated water to form bassanite, which results in the fractionation. Centrifugation and compression at room temperature may be useful but are generally restricted to samples of high water content only.

Other studies examined these problems. Ingraham and Shadel (1992) did a comparative study of the toluene and vacuum distillation methods using Hanford loam soil. The stable-isotope compositions of water extracted by these two methods were significantly different from those of the added water when the water content of the soil was low (3.6 to 5.2 percent). They postulated that some of the added water bound with minerals in the soil with an associated fractionation and was not released at extraction temperatures below 110°C. At low soil-moisture content, the volume of fractionated bound water is enough to affect the remaining extracted soil water. Leaney and others (1993) used the azeotropic distillation method with kerosene as a solvent for soils with high clay content (20 to 60 percent). They found a large discrepancy in the δD composition between added water and extracted water. The extracted water was 3 to 10.8 per mil more depleted in deuterium than the added water, depending on the temperature of distillation and the content of clay. Only deuterium was measured in that experiment. When extrapolated to zero percent clay content, the extracted water was 3 per mil more depleted than added water. They concluded that fractionation likely occurred during solvent extraction of soil and that the extracted water would be depleted by more than 3 to 4 per mil in δD compared with the true value of soil water. Araguàs-Araguàs and others (1995) performed the vacuum-distillation method on clay-bearing soil. The data indicated that the extracted water was depleted in deuterium by about 5 to 10 per mil and 0.36 per mil in oxygen, when compared with mobile water.

Analytical Data from Methods Used in This Study

Eleven sections of cores, three from nonwelded bedded tuff, one from the Pah Canyon Tuff, four from the Calico Hills nonwelded unit, and three from the Prow Pass Tuff, were chosen to determine if there is any alteration of the stable-isotope compositions of pore water extracted by toluene-azeotropic distillation, vacuum distillation, and compression extraction. Clay or zeolite minerals occur in the nonwelded bedded tuff and the Calico Hills nonwelded unit but not in the Pah Canyon Tuff. Cores from the Prow Pass Tuff, from depths of 550.0 m and 625.1 m, contain zeolite, but core from a depth of 564.2 m does not. A comparison of data from the Topopah Spring Tuff was not possible because the water content of this formation is too low to provide enough water for analysis by the compression method.

Isotopic Data from Toluene-Azeotropic Distillation

Five sections of cores from Yucca Mountain Tuff, Pah Canyon Tuff, Topopah Spring Tuff, Calico Hills Formation, and Prow Pass Tuff were imbibed with water of known isotopic composition. The source water was Boulder, Colorado, tap water with an isotopic composition of -17.7 per mil for $\delta^{18}O$ and -129 per mil for δD. The imbibed cores were then subjected to toluene distillation to extract water for stable-isotope analyses. Table 7 shows the stable-isotope compositions of distilled water, water recovery, and major mineralogy of cores. The data indicate that the isotopic compositions of recovered water were more depleted than the source water by 1.9 to 3.7 per mil for $\delta^{18}O$ and 9 to 23 per mil for δD. The water recoveries are much less than 100 percent, indicating incomplete recovery of core water by toluene distillation. Small water yields may be due to the use of intact core instead of crushed core, which would yield more surface area for water distillation. Based on the observation of Ingraham and Shadel (1992), the variation of the stable isotopes may be caused by incomplete extraction. From the results of the imbibition tests, the toluene distillation method is evidently unsuitable for extracting water from the Yucca Mountain cores and is not considered further in this report.

Comparison of Vacuum-Distillation and Compression-Extraction Methods

In a comparison test, eleven sections of dried core were chosen to test effects of the vacuum-distillation and compression-extraction methods on the measured stable-isotope compositions of in-situ pore water. Different samples were used than for the toluene extraction (table 7), but samples covered a similar lithologic range (three from bedded tuff, one from the Pah Canyon Tuff, four from the Calico Hills nonwelded hydrogeologic unit, and three from the Prow Pass Tuff). Table 8 shows mineralogic data from the samples chosen for the vacuum-distillation and compression-extraction tests.

In the bedded tuff (table 9), three cores from depths of about 26 to 29 m indicate that the stable-isotope compositions of the water collected by the compression method are heavier than the remaining water (water extracted by vacuum distillation after compression) in the range of 5 to 14 per mil for δD and 0.2 to 1.9 per mil for $\delta^{18}O$. The compressed water also is more enriched than water extracted from samples from nearby core by vacuum distillation in the range of 6 to 9 per mil for δD and 0.1 to 1.1 per mil for $\delta^{18}O$. The stable-isotope compositions of compressed water collected at different pressure steps during the compression process changed little with pressure changes. Mineralogic data indicate that all of the bedded tuff cores contain clay minerals.

The tested cores of Pah Canyon Tuff from a depth of 49 m (table 10) indicate that the stable-isotope compositions of water collected by different methods are not substantially different. The stable-isotope compositions of the water collected at different pressure steps during the compression process are similar, with little variation as a function of pressure. These data imply that both distillation and compression methods have no effect on the stable-isotope compositions of pore water for cores from Pah Canyon Tuff, which contain few hydrated minerals and which especially lack zeolites (table 8).

Three cores were sampled from the depth interval of 446.7 m to 476.9 m from the Calico Hills nonwelded hydrogeologic unit (table 11). Mineralogic data (table 8) indicate that these cores contain abundant zeolitic minerals. The stable-isotope compositions of the water collected by the compression method are heavier relative to the remaining water extracted by vacuum distillation in the range of 2.6 to

Table 7. Results of the toluene-distillation method in extracted water from imbibed cores, Yucca Mountain area

[VSMOW, Vienna Standard Mean Ocean Water; source water, water with known isotopic composition used for imbibing test; %, percent]

Sample identification, lithology, and mineralogy Lithology (Mineralogy)	$\delta^{18}O$ relative to VSMOW (per mil)	δD relative to VSMOW (per mil)	Water recovery (percent)
UZ14-77.4/T16/To	-21.3	-152	60.5
Yucca Mountain Tuff: Amorphous 30-35%, montmorillonite 14%, plagioclase 20%			
UZ14-215/T16/To	-19.6	-138	80.2
Pah Canyon Tuff: Mineralogic data not available			
UZ14-1271.7/T16/To	-21.4	-149	52.1
Topopah Spring Tuff: Plagioclase 34%, K-spar 20%, Amorphous material 10-15%			
UZ14-1514.2/T16/To	-20.5	-141	67.8
Calico Hills Formation: Amorphous 15-20%, Zeolite 67%			
UZ14-1943.6/T16/To	-19.7	-140	60.7
Prow Pass Tuff: Zeolite 28%, Plagioclase 11%, Amorphous material 25-30%)			
Source water	-17.7	-129	

Table 8. Mineralogic data from Yucca Mountain core samples used for comparing the vacuum-distillation and compression-extraction methods for stable-isotope analysis

Sample identification	Zeolite (percent)	Clay (percent)	Plagioclase (percent)	Amorphous material (percent)	Other (percent)	Lithology
UZ14-85.2	0	56	5	30-35	4-9	Bedded tuff
UZ14-91.0	0	30	20	20-30	20-30	Bedded tuff
UZ14-95.5	0	30	20	20-30	20-30	Bedded tuff
UZ14-155.7	0	0	30	30-35	35-40	Pah Canyon Tuff
UZ14-1465.5	35	0	10	30-35	20-25	CHn Calico Hills nonwelded unit
UZ14-1542.3	35	0	10	30-35	20-25	CHn Calico Hills nonwelded unit
UZ14-1564.3	35	0	10	30-35	20-25	CHn Calico Hills nonwelded unit
UZ14-1734.5	32	0	15	20-30	33-43	CHn Calico Hills nonwelded unit
UZ14-1804.8	0	56	5	30-35	4-9	Prow Pass Tuff
UZ14-1854.8	0	0	30	5-10	60-85	Prow Pass Tuff
UZ14-2015.2	28	0	11	25-30	21-26	Prow Pass Tuff

Table 9. Stable-isotope compositions of compressed water (/UP), remaining water extracted by vacuum distillation (/UP/D), and water distilled (/D) from bedded tuff cores

[Remaining water, water remaining in the core after compression; distilled water; the whole-core water extracted only by vacuum distillation; VSMOW, Vienna Standard Mean Ocean Water]

Sample identification	$\delta^{18}O$ relative to VSMOW (per mil)	δD relative to VSMOW (per mil)
UZ14-85.2-85.6/UP1	-12.7	-90
UZ14-85.2-85.6/UP2	-12.4	-89
UZ14-85.2-85.6/UP5	-12.6	-91
UZ14-85.2-885.6/UP6	-12.7	-91
UZ14-85.2-85.6/UP/D	-13.2	-103
UZ14-84.3-65.6/D	-12.8	-97
UZ14-91.0-91.4/UP	-12.4	-90
UZ14-91.0-91.4/UP/D1	-13.9	-103
UZ14-91.0-91.4/UP/D2	-14.3	-104
UZ14-89.6-91.4/D	-13.5	-97
UZ14-95.5-95.9/UP1	-12.4	-90
UZ14-95.5-95.9/UP2	-12.3	-90
UZ14-95.5-95.9/UP3	-12.3	-89
UZ14-95.5-95.9/UP4	-12.7	-91
UZ14-95.5-95.9/UP/D	-13.6	-103
UZ14-94.8-95.9/D	-13.4	-98

Table 10. Stable-isotopic compositions of compressed water (/UP) and water distilled (/D) from the Pah Canyon Tuff cores

[VSMOW, Vienna Standard Mean Ocean Water]

Sample identification	$\delta^{18}O$ (per mil) relative to VSMOW	δD (per mil) relative to VSMOW
	Core ID: UZ14-155.7-156.2	
UZ14-155.7-156.2/UP1	-12.5	-88
UZ14-155.7-156.2/UP2	-11.7	-88
UZ14-155.7-156.2/UP3	-11.8	-88
UZ14-155.7-156.2/UP4	-11.6	-88
UZ14-155.7-156.2/D	-12.2	-88

Table 11. Stable-isotope compositions of compressed water (/UP), remaining water extracted by vacuum distillation (/UP/D), and water distilled (/D) from the Calico Hills Formation cores

[VSMOW; Vienna Standard Mean Ocean Water]

Sample identification	$\delta^{18}O$ (per mil relative to VSMOW	δD (per mil) relative to VSMOW
Core ID: UZ14-1455.5-1466.1		
UZ14-1465.5-1466.1/UP2	-13.6	-102
UZ14-1465.5-1466.1/UP3	-13.6	-102
UZ14-1465.5-1466.1/UP4	-13.5	-102
UZ14-1465.5-1466.1/UP5	-13.6	-102
UZ14-1465.5-1466.1/UP6	-13.6	-102
UZ14-1465.5-1466.1/UP7	-13.6	-102
UZ14-1465.5-1466.1/UP/D	-16.1	-121
UZ14-1465.5-1466.1/D	-15.9	-111
Core ID: UZ14-1542.3-1542.7		
UZ14-1542.3-1452.4/UP	-13.4	-100
UZ14-1542.3-1452.4/UP/D	-16.1	-117
Core ID: UZ14-1564.3-1564.7		
UZ14-1564.3-1564.7/UP	-13.7	-103
UZ14-1564.3-1564.7/UP/D	-20.0	-125
UZ14-1564.3-1564.7/D	-18.0	-114

6.3 per mil for $\delta^{18}O$ and 17 to 22 per mil for δD. The compressed waters also are heavier than the water extracted from the adjacent core by vacuum distillation in the range of 2.3 to 4.3 per mil for $\delta^{18}O$ and 9 to 11 per mil for δD. The stable-isotope compositions of the compressed water collected at different pressure steps during the compression process are similar. As with the bedded tuff samples (table 9), the differences in stable-isotope compositions may be attributed to extraction of isotopically depleted water from hydrated minerals during the distillation process.

Three cores also were sampled from the Prow Pass Tuff from depths of 550.0 m to 614.3 m (table 12). One core contains zeolitic minerals (UZ14-2015.2), and one does not (UZ14-1854.8). For the clay-bearing core, the stable-isotope composition of compressed water is heavier than the remaining water by 20 per mil for δD and 4.1 per mil for $\delta^{18}O$ and also is heavier than water extracted by whole-core vacuum distillation by 13 to 16 per mil for δD and 3.2 to 5.8 per mil for $\delta^{18}O$. For the non-zeolite and nonclay-bearing core (UZ14-1854.8), the stable-isotope compositions of compressed water are similar to the distilled water. These data indicate that if core samples contain zeolites, distilled water and compressed water will have different δD and $\delta^{18}O$ values.

Table 12. Stable-isotope compositions of compressed water (/UP), remaining water extracted by vacuum distillation (/UP/D), and water distilled (/D) from the Prow Pass Tuff cores

[VSMOW, Vienna Standard Mean Ocean Water]

Sample identification	$\delta^{18}O$ (per mil) relative to VSMOW	δD (per mil) relative to VSMOW
Core ID: UZ14-1804.8-1805.3		
UZ14-1804.8-1805.3/UP	-13.1	-98
UZ14-1804.8-1805.3/UP/D	-17.2	-118
UZ14-1804.8-1805.3/D	-16.3	-111
Core ID: UZ14-1854.8-1855.3		
UZ14-1854.8-1855.3/UP	-13.3	-100
UZ14-1854.4-1854.8/D	-13.4	-101
Core ID: UZ14-2015.2-2015.6		
UZ14-2015.2-2015.6/UP	-12.5	-99
UZ14-2014.0-2014.4/D	-18.3	-115

Laboratory Tests

From these data, it is clear that the stable-isotope compositions of compressed water, the remaining water collected after compression by vacuum distillation, and the whole-core distillation of adjacent core are different for bedded tuff, the Calico Hills nonwelded hydrogeologic unit, and Prow Pass Tuff, which contain hydrated minerals (the δD and $\delta^{18}O$ of compressed water were heavier than those of distilled water). A laboratory test was designed to investigate why different results are obtained with different extraction procedures. The plan for this laboratory test was to imbibe the dried Yucca Mountain cores with known isotopic-composition water followed by extractions using different methods. This provided information on the types of pore water (hydrated water or channel water and pore water) extracted with each procedure. It also provided information on how the original infiltrating water was fractionated when it permeated pore spaces.

A column experiment also was conducted to evaluate whether the channel water of zeolite is exchangeable with bulk water. If it is exchangeable, what is the exchange rate? The details of this test provide information on the source of zeolite channel water. Does channel water represent the most recent percolation water or fluid percolated in the distant past at Yucca Mountain? Araguàs-Araguàs and others (1995) used a column experiment with clay soil to reveal that weakly bound water in clay is easily exchangeable with isotopically different mobile water.

Imbibing Dry Core with Known Isotope-Composition Water: Imbibing Test

The purpose of this test was to determine (1) whether the pore-water stable-isotope compositions are altered during the core-water extraction from different tuff lithologies, (2) if the compressed water represents percolating water, (3) if the distillation method removes hydration water, and (4) if the stable-isotope compositions of hydrated water fractionates from bulk water (which includes pore water, residual water for the core sample, and intergranular water for the zeolite powder sample).

The sample cores for imbibition were dried in an oven at 250°C for approximately 2 days. Dried samples were then evacuated and cooled in a sealed jar. While still under vacuum, water with a known stable-isotopic composition (source water) was imbibed into sample cores (shown in fig. 13). Various amounts of water were used to provide cores representing saturated and unsaturated conditions. The imbibed cores were kept under vacuum at room temperature for 10 days to allow the sample and water to equilibrate. After equilibration, the core water was extracted by various methods, and the stable-isotope compositions of extracted water and the source water were measured for $\delta^{18}O$ and δD.

Extracting Imbibed Water by Vacuum Distillation

Five cores of Yucca Mountain Tuff, Pah Canyon Tuff, Topopah Spring Tuff, the Calico Hills nonwelded unit, and Prow Pass Tuff were selected for this imbibing test. Each test was performed in duplicate. Each core was imbibed with water of known isotopic composition (source water). Two sources of water (two samples of Boulder, Colorado, tap water) with isotopic compositions of -16.7 and -16.1 per mil for $\delta^{18}O$ and -123 and -121 per mil for δD were used. The imbibed core was then placed in the vacuum distillation line to extract water for stable-isotope analyses. The stable-isotope compositions of distilled water, water recovery, and lithology are shown in table 13.

The data indicate that the stable-isotope compositions of distilled water were more depleted than corresponding source waters by 0 to 11 per mil for δD and 0 to 2.2 per mil for $\delta^{18}O$, and that the extent of depletion is strongly dependent on the lithology. The water recoveries were close to 100 percent except for the Calico Hills nonwelded unit core. The core of Topopah Spring Tuff does not contain hydrated minerals, and the $\delta^{18}O$ and δD values of extracted water were close to those of the source water. The cores from Yucca Mountain and Pah Canyon Tuffs contain clay minerals, and the $\delta^{18}O$ and δD compositions were more depleted than source water by approximately 0.6 per mil and 5 per mil, respectively. These results agree with those of Araguàs-Araguàs and others (1995) who reported depletions of 5.2 to 9.6 per mil in δD and 0.36 to 0.47 per mil in $\delta^{18}O$ for clay-rich soil water extracted using vacuum distillation. For the core from the Calico Hills hydrogeologic unit, which is rich in zeolite, water recovery was less than for other cores, and the stable-isotope compositions also were more depleted than others (averaging about 10 per mil in δD and 2.0 per mil in $\delta^{18}O$). These data indicate that it is difficult to extract all water from the

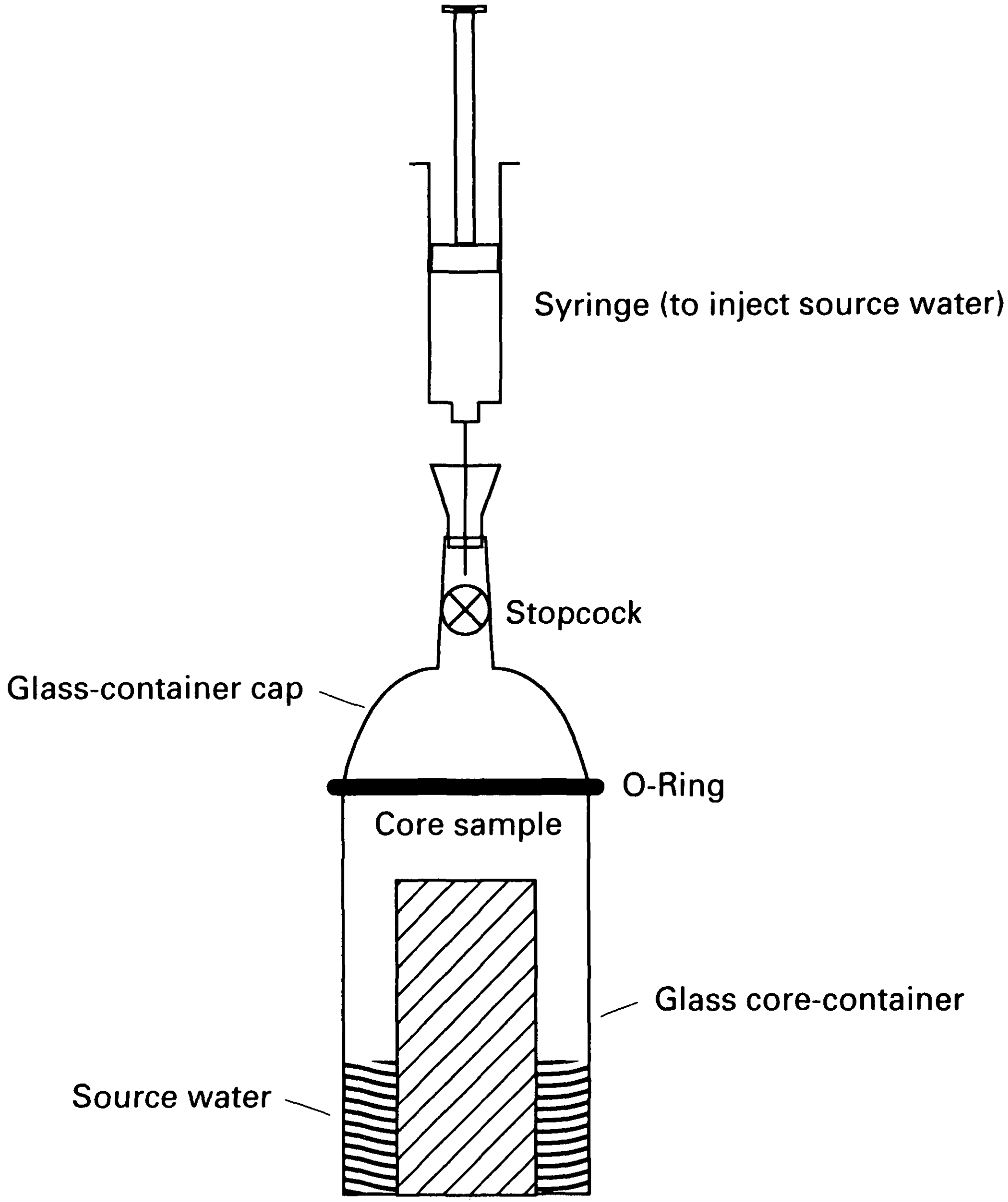


Figure 13. Apparatus for imbibing test.

Table 13. Stable-isotope compositions of the vacuum-distilled water from the imbibed cores

[VSMOW, Vienna Standard Mean Ocean Water]

Sample identification	$\delta^{18}O$ (per mil) relative to VSMOW	δD (per mil) relative to VSMOW	Water recovery (percent)	Lithologic unit
UZ14-77.4/T1/D	-16.8	-127	98.6	Yucca Mountain Tuff
UZ14-77.4/T2/D	-17.0	-127	99.0	Yucca Mountain Tuff
UZ14-215/T1/D	-17.6	-128	99.0	Pah Canyon Tuff
UZ14-215/T2/D	-16.4	-128	99.3	Pah Canyon Tuff
UZ14-1271.7/T1/D	-16.8	-127	99.3	Topopah Spring Tuff
UZ14-1271.7/T2/D	-17.0	-124	99.6	Topopah Spring Tuff
UZ14-1514.2/T1/D	-17.7	-133	98.2	Calico Hills nonwelded unit
UZ14-1514.2/T2/D	-18.3	-132	96.4	Calico Hills nonwelded unit
UZ14-1864.8/T1/D	-16.7	-123	99.2	Prow Pass Tuff
UZ14-1864.8/T2/D	-16.4	-124	99.6	Prow Pass Tuff
Source water (T1)	-16.7	-123		
Source water (T2)	-16.1	-121		

zeolite-rich cores using vacuum distillation. The Prow Pass samples (table 13) showed no depletion. A zeolite-free Prow Pass sample (UZ 14-1854.8) also showed no depletion effects (table 12).

The stable-isotope compositions of distilled water are generally more depleted than the source water or compressed water. For the nonhydrated mineral cores, such as the Topopah Spring Tuff, the δD and $\delta^{18}O$ of distilled water are typically close to those of the source water. Therefore, the vacuum-distillation technique can be applied to extract core water for stable-isotope analyses on nonhydrated mineral cores. The δD and $\delta^{18}O$ values of water extracted by the vacuum-distillation method from zeolite- or clay-bearing cores, however, are more depleted than those of source water by about 10 per mil in δD and 1.0 to 2.2 per mil in $\delta^{18}O$ for zeolite, and by about 5 per mil in δD and 0.8 per mil in $\delta^{18}O$ for clay. This may be caused by incomplete removal of hydrated water by the distillation method.

Extracting Imbibed Water by Compression

Six cores from the Yucca Mountain Tuff, bedded tuff, the Pah Canyon Tuff, the Topopah Spring Tuff, the Calico Hills nonwelded unit, and the Prow Pass Tuff were selected for this imbibing test. Mineralogic data are shown in table 14. Hydrated minerals (clay or zeolite) occur in Yucca Mountain Tuff, bedded tuff, Calico Hills nonwelded unit, and the Prow Pass Tuff but do not occur in the Pah Canyon Tuff and the Topopah Spring Tuff. Each core was imbibed with

Table 14. Mineralogic data of the imbibed cores used in the compression method

Sample identification	Zeolite (percent)	Clay (percent)	Plagioclase (percent)	Amorphous (percent)	Other (percent)	Lithology
UZ14-77.4	0	56	5	30-35	28-38	Yucca Mountain
UZ14-78.6	0	22	13	45-50	15-20	Bedded tuff
UZ14-144.7	0	0	30	30-35	35-40	Pah Canyon
UZ14-869.1	0	0	38	10-15	47-52	Topopah Spring
UZ16-1431.3	46	1	5	20-25	23-28	Calico Hills nonwelded unit
UZ14-1764.2	32	0	15	20-25	28-33	Prow Pass

water of known isotopic composition. Boulder, Colorado, tap water with isotopic composition ranging from -16.1 to -16.7 per mil for $\delta^{18}O$ and -121 to -125 per mil for δD was used as a source water. The stable-isotopic composition of Boulder, Colorado, tap water changed little as a function of time. The imbibed cores were compressed, and extracted core water was collected at different pressure steps for stable-isotope analyses. The conditions and results of the stable-isotope compositions of extracted core waters are listed in tables 15 through 17.

These Pah Canyon Tuff and Topopah Spring Tuff cores do not contain hydrated minerals. The stable-isotope compositions of compressed water from these cores change little with pressures and are very close to those of the source water (table 15). The variation is typically near the precision of measurement (1 per mil for δD and 0.2 per mil for $\delta^{18}O$). The results indicate that fractionation did not occur when the source water was imbibed into these dried cores.

The data from high clay-content cores from Yucca Mountain Tuff and bedded tuff are shown in table 16. The stable-isotope compositions of the compressed water do not change with pressure, as also was true of Pah Canyon and Topopah Spring Tuffs. The δD of compressed water is heavier than the source water by 1 to 3 per mil, but the $\delta^{18}O$ of compressed water is not significantly different from that of the source water. These observations agree with those reported by Stewart (1972) that little, if any, isotopic fractionation occurs between hydrated water and bulk water in $\delta^{18}O$ and that the hydrated water is depleted in deuterium relative to the bulk water for clay-rich soils.

For the high zeolite-content cores from the Calico Hills Formation and the Prow Pass Tuff, the data show that the stable-isotope compositions of compressed water do not change as a function of pressure (table 17). The δD and $\delta^{18}O$ of compressed water are about the same as those of residual water (source water remaining in the container after the core was imbibed) but lighter than those of the source water by 6 to 12 per mil for δD and 2 to 3 per mil for $\delta^{18}O$. The most likely reason for the difference between source

Table 15. Stable-isotope compositions of water extracted by the compression method from Pah Canyon Tuff and Topopah Spring Tuff cores (nonhydrated water-bearing cores)

[VSMOW, Vienna Standard Mean Ocean Water; Ksi, thousand pounds per square inch; *, not enough water for analysis]

Sample identification	$\delta^{18}O$ (per mil) relative to VSMOW	δD (per mil) relative to VSMOW	Pressure (Ksi, 10^3 pounds per square inch)
TEST A: Core From Pah Canyon ID: UZ14-144.0-144.7			
T/source water	-16.5	-123	
UZ14-144-144.7/T/up/1	-16.4	-123	0-6
UZ14-144-144.7/T/up/2	-16.4	-122	0-15
UZ14-144-144.7/T/up/3	-16.2	-123	6-15
UZ14-144-144.7/T/up/4	-16.4	-122	15-45
UZ14-144-144.7/T/up/5	-16.2	-122	15-30
UZ14-144-144.7/T/up/6	-16.4	-123	30-45
UZ14-144-144.7/T/up/7	-16.2	-123	45-75
UZ14-144-144.7/T/up/8	-16.3	-123	75-120
TEST B: Core From Topopah Spring ID: UZ14-869.1-869.7			
TEST10/source	-16.3	-124	
UZ14-144-144.7/T10/residue[1]	-17.0	-126	
UZ14-144-144.7/T10/up1	-16.8	-125	30-75
UZ14-144-144.7/T10/up2	*	-125	0-120
UZ14-144-144.7/T10/up3	*	-123	75-120

[1] Water remaining in the container after core was imbibed.

Table 16. Stable-isotope compositions of water extracted by the compression method from the Yucca Mountain Tuff and bedded tuff (clay-bearing) cores

[VSMOW, Vienna Standard Mean Ocean Water; Ksi, thousand pounds per square inch; NA, not applicable; *, not enough water for analysis]

Sample identification	$\delta^{18}O$ (per mil) relative to VSMOW	δD (per mil) relative to VSMOW	Pressure (Ksi, 10^3 pounds per square inch)
TEST C: Core From Yucca Mountain ID: UZ14-77.4-78.0			
TEST 6/source	-16.2	-122	N/A
UZ14-77.4-78.0/T6/up/1	-16.1	*	3-6
UZ14-77.4-78.0/T6/up/2	-16.2	-121	6-10
UZ14-77.4-78.0/T6/up/3	-16.4	-121	6-10
UZ14-77.4-78.0/T6/up/4	-16.3	-120	10-30
UZ14-77.4-78.0/T6/up/5	-16.3	-120	10-30
UZ14-77.4-78.0/T6/up/6	-16.2	-121	30-40
UZ14-77.4-78.0/T6/up/7	-16.2	-121	40-75
UZ14-77.4-78.0/T6/up/8	-16.2	-121	75-120
UZ14-77.4-78.0/T6/up/9	-16.1	-121	75-120
TEST D: Core From Bedded Tuff ID: UZ14-94.8-95.4			
TEST 10/Source	-16.3	-124	NA
UZ14-94.8-95.4/T10/UP1	-16.1	-121	4-6
UZ14-94.8-95.4/T10/UP2	-16.3	-122	4-6
UZ14-94.8-95.4/T10/UP3	-16.2	-122	5-8
UZ14-94.8-95.4/T10/UP4	-16.3	-121	8-12
UZ14-94.8-95.4/T10/UP5	-16.4	-122	8-12
UZ14-94.8-95.4/T10/UP6	-16.4	-121	12-15
UZ14-94.8-95.4/T10/UP7	-16.4	-122	15-30
UZ14-94.8-95.4/T10/UP8	-16.3	-122	15-30
UZ14-94.8-95.4/T10/UP9	-16.3	-122	30-60
UZ14-94.8-95.4/T10/UP10	-16.1	-121	60-120

water and compressed water is that fractionation between the channel water of zeolite and bulk water occurred when the source water was imbibed into the dry core. The water that was more depleted went into channel spaces, resulting in enrichment of the bulk water (pore and residual water). These observations agree with the Karlsson and Clayton (1990) and Feng and Savin (1993) observations that the oxygen-18 of zeolite channel water is more depleted than bulk water. The compression method does not extract hydration waters of minerals and thus may be representative of the percolation water.

It is apparent that the compression method does not extract hydration water because the stable-isotope compositions do not change with pressure. The water extracted by the compression method is mainly drawn from large pore spaces. The stable-isotope composition of pore water in large pore spaces is similar to the residual water.

Isotopic Exchange Between Matrix Water and Percolating Water: Column Test

A column experiment was conducted to investigate the exchangeability of channel water in zeolite with the bulk water and to determine the exchange rate. The results also provide information on sources of zeolite channel water. Possible sources of water in zeolite channels include the most recent percolation water or paleowater. Araguàs-Araguàs and others (1995) used a column experiment with clay soil to reveal that weakly bound water in clay is easily exchangeable with isotopically different mobile water.

Table 17. Stable-isotope compositions of water extracted by the compression method from Calico Hills Formation and Prow Pass Tuff (zeolite-bearing) cores

[VSMOW, Vienna Standard Mean Ocean Water; Ksi, thousand pounds per square inch; NA, not applicable; *, not enough water for analysis]

Sample Identification	$\delta^{18}O$ (per mil) relative to VSMOW	δD (per mil) relative to VSMOW	Pressure (Ksi, 10^3 pounds per square inch)
TEST E: Core From Calico Hills ID: UZ16-1431.1-1431.6			
TST-1431.1-1431.6/source	-16.7	-125	N/A
TST-1431.1-1431.6/residual	-14.3	-118	N/A
TST-1431.1-1431.6/up1	*	119	0-15
TST-1431.1-1431.6/up2/A	-14.1	-119	15-30
TST-1431.1-1431.6/up2/B	*	-119	15-30
TST-1431.1-1431.6/up3/A	*	-119	30-45
TST-1431.1-1431.6/up3/B	*	-118	30-45
TST-1431.1-1431.6/up4	-13.6	-119	45-60
TST-1431.1-1431.6/up5	-14.0	-119	60-75
TST-1431.1-1431.6/up6	*	-119	75-105
TST-1431.1-1431.6/up7	*	-119	105-120
TEST F: Core From Prow Pass ID: UZ14-1764.2-1764.7			
TEST10/source	-16.3	-124	N/A
UZ14-1764.2-1764.7/T10/residual	-13.0	-114	N/A
UZ14-1764.2-1764.7/T10/up1	-13.0	-112	31-60
UZ14-1764.2-1764.7/T10/up2	-13.0	-112	60-120
UZ14-1764.2-1764.7/T10/up3	-13.0	-112	60-120
UZ14-1764.2-1764.7/T10/up/D	-17.2	-134	N/A

Zeolite Powder

The column experiment was performed with pure natural zeolite powder (95 percent clinoptilolite). Three kinds of eluant waters with different isotopic compositions were used: (1) Boulder (Colorado) tap water, (2) depleted Greenland ice water, and (3) enriched water. In the laboratory, the zeolite was placed in an oven at 250°C to dehydrate. It is important to note that clinoptilolite will rehydrate reversibly below 450°C (Feng, 1991). After dehydration, the zeolite was cooled in a desiccator. The dried and cooled zeolite was packed into the column (50 cm in height, 8 cm in diameter) and eluted with Boulder tap water at a rate of approximately nine column-volumes per day. The effluent was collected at the outlet. (The apparatus is shown in fig. 14.) The effluent was periodically sampled for isotope analysis. After elution, the rehydrated zeolite was removed from the column and divided into three parts—one part was taken for vacuum distillation to obtain the isotopic composition of zeolite water, and the other two parts were packed into two separate columns. The second part was eluted with depleted Greenland ice water and the third part with enriched water. Each effluent was periodically sampled for isotope analysis. Finally, the zeolite samples were removed from each column and vacuum distilled to obtain the isotopic composition of zeolite water.

The isotopic compositions of channel water were calculated by mass balance from the analytical data. Calculations were based on two assumptions (1) no ^{18}O exchange occurs between channel water and framework silicate minerals; and (2) the distillation method can extract water completely. In support of the first assumption, O'Neil (1987) reported that little oxygen isotope exchange occurred between silicate minerals and fluid water at temperatures below 100°C. To verify the second assumption, the dehydrated zeolite was imbibed with water of known isotopic composition (source water) and subsequently distilled under vacuum. If the recovery is 100 percent,

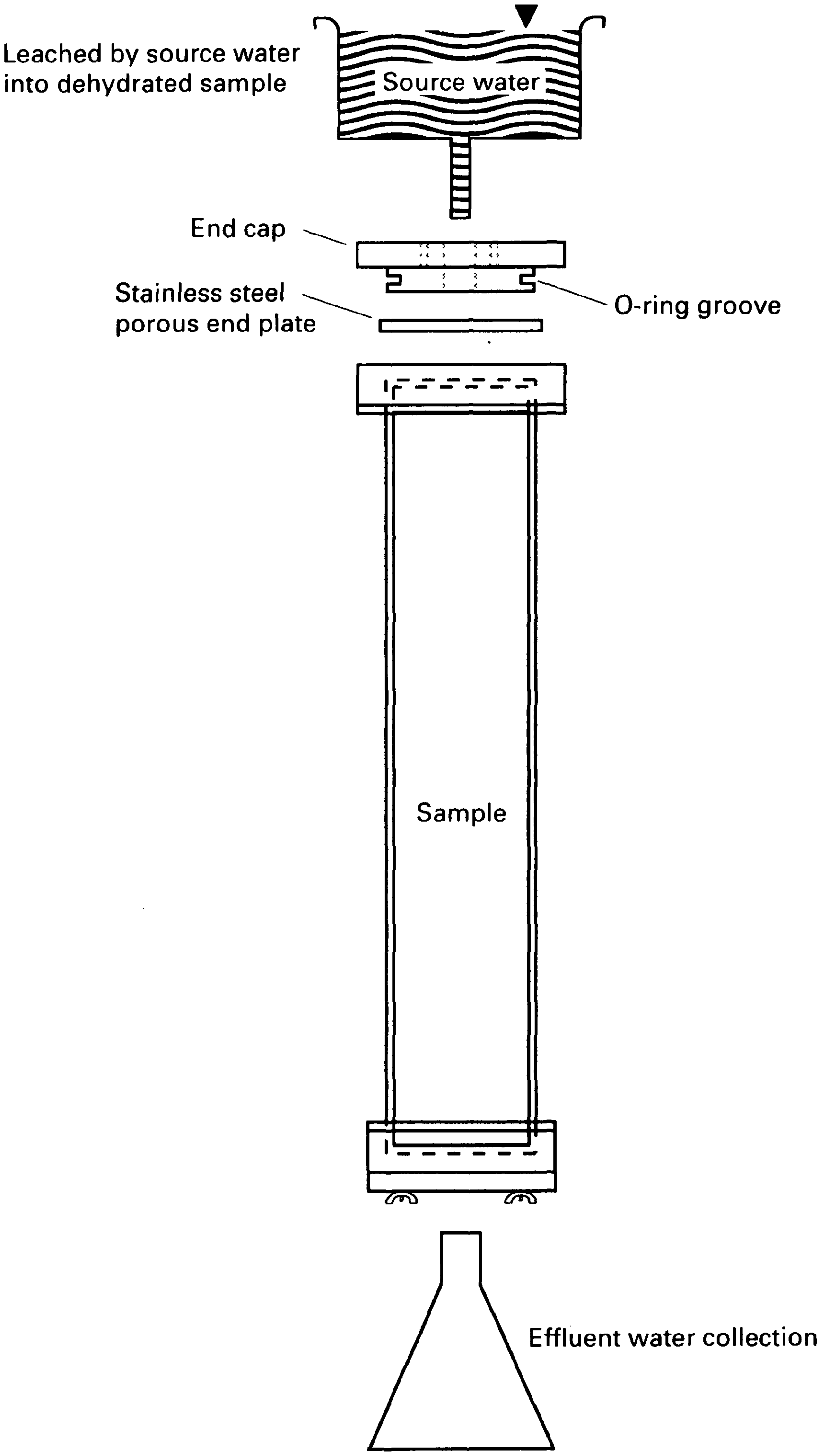


Figure 14. Apparatus for column test.

the distillation is complete. If not, corrections are needed for fractionation. Table 18 shows differences between the distilled water and source water of about 3 to 7 per mil for δD and 0.6 to 1.0 per mil for $\delta^{18}O$. The correction factors are, therefore, about 5 per mil for δD and 0.8 per mil for $\delta^{18}O$.

The results of column experiments are summarized in table 19. Effluents #1 to #8 are the periodic water samples collected when Boulder, Colorado, tap water (percolate I) was leached through the dehydrated sample. After the leaching, column packing was split into two parts and packed in separate columns. Effluents #1 to #9 in the middle of table 19 are the periodic water sample collected when the depleted Greenland ice water (percolate II) was flushed over the column leached with percolate I. Effluents #1 to #8 at the bottom of table 19 are the periodic water samples collected when more enriched water (percolate III) was flushed over the other column previously leached with percolate I.

The column experiments reveal several interesting relations. The isotopic compositions of effluents #1 to #6 leached with percolate I are more enriched than the source water, with the effluent #1 aliquot being the isotopically heaviest. The observed effect is due to isotope fractionation caused by uptake of lighter-water molecules by empty channels of clinoptilolite, leaving enriched-water molecules as effluent. As the leaching progressed, enriched isotopic water in the bulk water (pore space and intergranular spaces) was replaced by the leaching source water (effluents #7 and #8). This is evident by the isotopic compositions of effluents #7 and #8, which are the same as the bulk water collected by centrifugation. Source water in percolate I is more enriched than the percolate II source water (Greenland ice water). Leaching with the more depleted source water of percolate II on the column previously leached with percolate I resulted in a gradual decrease in δD and $\delta^{18}O$ values as the leaching progressed. Effluents #8 and #9 of percolate II in table 19 indicate the column is near equilibration with little change in $\delta^{18}O$ and δD values from the source water. The isotopic compositions of channel water, as indicated by the vacuum-distilled water, changed significantly by leaching from percolate I to percolate II. The percolate III case is very similar to that of percolate II, but the source water of percolate III is more enriched than the source water of percolate I. The δD and $\delta^{18}O$ of effluent waters became more enriched toward the source water of percolate III (effluents #7 and #8). The stable-isotope compositions of vacuum-distilled water of percolate I, II, and III are more depleted than their source waters by 6 to 8 per mil in δD and 0.9 to 1.7 per mil in $\delta^{18}O$.

Zeolite-Rich Core

Experiments with intact core were performed to further test the isotopic exchange characteristics of pore and channel waters. A zeolite-rich core from the Calico Hills Formation of Yucca Mountain (sample ID

Table 18. Comparison of stable-isotope compositions of water distilled from clinoptilolite imbibed with source water of known isotope composition

[VSMOW, Vienna Standard Mean Ocean Water]

Sample zeolite	Source water		Distilled water		Difference	
	$\delta^{18}O$ (per mil) relative to VSMOW	δD (per mil) relative to VSMOW	$\delta^{18}O$ (per mil) relative to VSMOW	δD (per mil) relative to VSMOW	$\delta^{18}O$ (per mil) relative to VSMOW	δD (per mil) relative to VSMOW
Zeolite #1	-17.1	-126	-18.1	-133	1.0	7
Zeolite #2	-25.1	-193	-26.0	-198	0.9	5
Zeolite #3	-9.1	-98	-9.7	-102	0.6	4
Zeolite #4	-39.3	-306	-40.0	-309	0.7	3
Average				4.75 (σ = 1.5)	0.8(σ = 0.16)	

The correction factors: 5‰ for δD, 0.8‰ for $\delta^{18}O$.

Table 19. Stable-isotope compositions of the effluents from the column experiment with clinoptilolite

[VSMOW, Vienna Standard Mean Ocean Water; ---, no data]

Sample ID	Volume (meter)	δD (per mil) relative to VSMOW	$\delta^{18}O$ (per mil) relative to VSMOW
Percolate I. (leached by Boulder, Colorado, tap water into dehydrated sample)			
Source water	---	-129	-17.6
Effluent #1	240	-127	-17.2
Effluent #2	240	-127	-17.3
Effluent #3	200	-128	-17.4
Effluent #4	60	---	---
Effluent #5	180	-128	-17.5
Effluent #6	60	---	---
Effluent #7	60	-129	-17.5
Effluent #8	60	-129	-17.5
Water extracted by:			
centrifugation	---	-129	-17.6
vacuum distillation	---	-137	-18.5
Percolate II: (flush percolate I sample by the more depleted Greenland ice water)			
Source water		-310	-39.6
Effluent #1	60	-186	-24.5
Effluent #2	60	-233	-30.2
Effluent #3	60	-268	-34.6
Effluent #4	60	---	---
Effluent #5	100	-299	-38.2
Effluent #6	80	---	---
Effluent #7	100	-306	-39.0
Effluent #8	60	-307	-39.1
Effluent #9	60	-308	-39.1
Water extracted by:			
vacuum distillation	---	-316	-40.6
Percolate III: (flush percolate I sample by the more enriched water)			
Source water	---	-79	-2.7
Effluent #1	60	-109	-10.0
Effluent #2	60	-90	-6.1
Effluent #3	60	---	---
Effluent #4	60	-82	-3.8
Effluent #5	100	-80	-3.1
Effluent #6	80	---	---
Effluent #7	100	-80	-3.8
Effluent #8	60	-79	-3.1
Water extracted by:			
vacuum distillation	---	-86	-4.4

UZ-14-1422.4-1423), which contains 45 percent zeolite (mostly clinoptilolite), was selected for this experiment. The selected core was dehydrated. After dehydration, 64.4 grams (g) of stable isotope water of known composition (source water I: Boulder, Colorado, tap water, $\delta^{18}O$: -17.2 per mil and δD: -128 per mil), was imbibed into the core to saturation, with some residual water remaining inside the container. The imbibed core was kept inside the container under vacuum for 10 days to attain equilibrium. At the end of 7 days, the residual water was sampled for isotope analysis. After 7 additional days, the residual water, 7.1 g, was completely removed and 37.0 g of a new source water (Greenland ice source water II, $\delta^{18}O$: -35.6 per mil and $\delta D = -272$ per mil), was injected into the container containing the core imbibed with source water I. Source water II did not enter the core because the core already was saturated. The residual water was sampled periodically for stable-isotope analysis to record the extent of exchange between pore water and residual water. Three samples were collected from the residual water for analyses after the fourth (8.1 g sampled), fifth (8.8 g sampled), and sixth days (19.0 g remaining) of equilibration. Finally, imbibed core was removed from the container, and core water was extracted using the compression method (18 g extracted). The remaining water, after compression, was extracted by vacuum distillation (38.8 g obtained) for isotope analysis. The data are shown in table 20.

Water mass balance is as follows: Boulder, Colorado, tap water (source water I) added to the container, 64.6 g; Greenland ice water (source water II) added to the container, 37.0 g, for a total of 101.6 g added to container; water removed (7.1 g + 8.1 g + 8.8 g + 19 g + 18 g + 38.8 g =) 99.8 g; and unrecovered, 1.8 g of water (held tightly inside the core by matrix potential). The stable-isotope compositions of periodically sampled residual water were gradually enriched. This implies that the pore water exchanged with the residual water through a diffusion mechanism. The exchange rate can be estimated by Einstein's random walk equation (Einstein, 1905; Ames, 1965):

$$X^2 = 2Dt$$

where X is mean travel distance, D is the diffusion coefficient, and t is travel time.

The diameter of core is about 6.1 cm. The self-diffusion coefficient of water is about 2.3×10^{-5} cm^2 s^{-1} at 25°C (Harris and Woolf, 1980). Calculations based on this equation indicate that the pore water in a 6-cm-diameter core will exchange in about 5 days. In this experiment, if the system reached equilibrium between pore water and residual water, the stable-isotope composition of pore water (TEST10/up) should equal the last sampled residual water (TEST10/R4). However, the stable-isotope compositions of compressed water (TEST10/up) are enriched relative to the last sampled residual water (TEST10/R4) and the compositions of compressed water changed slightly as a function of pressure. This indicates that the pore water and residual water have not reached equilibrium. The equilibration time of source water II with core sample was 6 days, apparently not long enough for equilibration. The disagreement between calculated and experimental equilibration times may be due to neglect of geometric effects (porosity and tortuosity) in the calculation. In any case, the results of the experiment indicate that the pore water is exchangeable with the residual water, and the exchange rate depends on the grain size of the core sample.

Table 20. Stable-isotope compositions of water from the imbibition experiment with two different source waters for zeolite-rich core

[%, percent; psi, pounds per square inch; VSMOW, Vienna Standard Mean Ocean Water]

Sample identification (UZ14/1422.4-1423.0)	$\delta^{18}O$ (per mil) relative to VSMOW	δD (per mil) relative to VSMOW	Pressure (10^3 psi)	Amount of water (grams)
Calico Hills Formation (zeolite 45%, amorphous material 35%, others 20%)				
TEST10/source I	-17.2	-128		64.6
TEST10/R1[a]	-16.4	-125		7.1
Source water II				
TEST10/source II	-35.6	-272		37.0
TEST10/R2 [b]	-27.6	-214		8.1
TEST10/R3 [c]	-26.2	-202		8.8
TEST10/R4 [d]	-25.3	-198		19.0
TEST10/up1	-22.9	-183	29-60	
TEST10/up2	----	-180	60-75	
TEST10/up3	-22.1	-178	75-120	
TEST10/up4	-22.5	-180	75-120	
TEST10/up/D	-21.6	-169		

Mass balance:

Total source water I added to container: 64.6 grams (g), residual water in container removed: 7.1 g.

Added source water II to container: 37.0 g, residual water in container: 8.1+8.8+19.0 g.

Compressed water from imbibed core: 18 g extracted.

Distilled water after compression: 38.8 g obtained.

Mass balance: 1.8 g of water unrecovered.

Oxygen-18 balance: 1.1 per mil.

Deuterium balance: 1.1 per mil.

[a]: imbibing source water I, sitting for 7 days, removed all the residual water (7.1 g).

[b, c, d]:adding source water II into above saturated cores container, sampled 8.1, 8.8, and 19.0 g water for analysis.

Applicability of the Extraction Methods to Yucca Mountain Cores

From the results of the vacuum-distillation and compression methods for extracting water from imbibed cores, it is apparent that the stable-isotope compositions of distilled water extracted by distillation are more depleted in δD and $\delta^{18}O$ than water compressed from core containing hydrated minerals. For the zeolite-bearing core, the isotopic composition of vacuum-distilled water is depleted in δD and $\delta^{18}O$ relative to bulk water by 9 to 15 per mil and 0.9 to 2.8 per mil, respectively. For the core containing clay minerals, the hydrated water is depleted about 5 per mil in δD and not depleted in $\delta^{18}O$ relative to bulk water. These data demonstrate that different water-extraction methods should be used for samples of different mineral content. For UZ-14 core-sample analysis, different water-extraction methods were used as appropriate for various lithologic units.

The Pah Canyon and the Topopah Spring Tuffs: Vacuum Distillation Method

Vacuum distillation is good for samples containing few hydrated minerals, such as the Pah Canyon Tuff. Complete distillation is necessary, however, to avoid fractionation. For the Topopah Spring Tuff, vacuum distillation also is the recommended method (water content of cores is typically less than 5 percent). Zeolite-bearing minerals occur above the basal vitrophyre (between the devitrified zone and the vitrophyre) within the Topopah Spring Tuff in a zone about 2 to 3 m thick (Bish and Vaniman, 1985). The vacuum distillation extraction is not a suitable technique for this zone.

Bedded Tuff and the Calico Hills Formation: Compression Method

For zeolite-bearing cores, vacuum distillation is not a suitable water-extraction method for stable-isotope analyses because the channel (hydrated) water will be partially removed during the distillation process. The compression method should be used. For the clay-bearing cores, the compression method is again better than the vacuum-distillation method. If the compression method cannot successfully extract sufficient amounts of water for analysis from low-moisture-content cores, however, then the distillation method can be used, but the data need to be corrected by addition of about +5‰ for δD and +1.0 ‰ for $\delta^{18}O$.

Interpretation of the Stable-Isotope Data

Appropriate pore-water extraction methods for stable-isotope analysis are dependent on the type of minerals present in the cores. Therefore, it was important to determine the mineralogy of the major stratigraphic units penetrated in borehole UZ-14. Table 21 shows the thickness and mineralogic data for each lithologic unit analyzed by the geochemistry laboratory of the U.S. Geological Survey in Denver, Colo., and by the Los Alamos National Laboratory (David Bish, oral commun., 1995).

The depth profiles of $\delta^{18}O$ and δD values of pore water extracted from UZ-14 cores by vacuum-distillation and compression methods are shown in figures 15 and 16. The $\delta^{18}O$ and δD data of pore water obtained by the compression method are limited—one measurement from Yucca Mountain Tuff, five from bedded tuff and the Pah Canyon Tuff, seven from the Calico Hills hydrogeologic unit, five from the Prow Pass Tuff, and one from the Bullfrog Tuff. These limitations arise because the compression method cannot extract water from the Topopah Spring Tuff or other lithologic units with a moisture content of less than 7 percent by weight. The δD profile (fig. 16) shows enrichment at shallow depth of the pore waters relative to the compositions of deeper samples. The figures exhibit more scatter in both $\delta^{18}O$ and δD values obtained by the vacuum-distillation method than by the compression method. Data for the Topopah Spring Tuff in both figures are less scattered and clustered in a narrow band.

The stable-isotope compositions of water distilled from the Calico Hills hydrogeologic unit, the Prow Pass Tuff, and Bullfrog Tuff cores are more depleted than those of other tuffs (for example, the Topopah Spring Tuff and Pah Canyon Tuff). The depletion is roughly proportional to the zeolite contents of core samples. At a depth of about 460 m in UZ-14, the zeolite content is about 67 percent, resulting in a significantly more depleted $\delta^{18}O$ value of -17.9 per mil and a δD value of -120 per mil. Also, water distilled from depths of 559.3 m to 575.5 m, where there is no zeolite in the cores, is more enriched than that from other adjacent zeolite-bearing cores. It previously has been shown that the vacuum-

Table 21. Depths and mineral contents in each lithologic unit of borehole USW UZ-14, Yucca Mountain area

[%, percent; m, meter; undifferentiated amorphous material includes volcanic glass, gels, and silica species such as opal]

Lithology (depth)	Sample identification	Major mineralogy
Yucca Mountain Tuff (12.1 to 23.8 m)	UZ14-69.0-69.5*	montmorillonite 39%, amorphous material 50%
	UZ14-77.4-78.0*	smectite 22%, amorphous material 40-50%
Bedded tuff (23.8 to 31.2 m)	UZ14-78.6-79.0*	smectite 22%, amorphous material 45-50%
	UZ14-94.8-95.4*	montmorillonite 30%, amorphous material 30%, plagioclase 20%
Pah Canyon Tuff (31.2 to 73.3 m)	UZ14-144.0-144.7*	plagioclase 30%, K-spar 19%, amorphous material 30%
Topopah Spring Tuff (80.9 to 427.6 m)	UZ14-869.1-869.7*	plagioclase 38%, K-spar 24%, amorphous material 15%
	UZ14-1049.4-1049.8*	plagioclase 36%, amorphous material 15%, K-spar 19%
	UZ14-1271.7-1271.9*	plagioclase 34%, K-spar 20%, amorphous material 15%
	UZ14-1277.4**	zeolite 58%, smectite 20%, opal-CT 20%
	UZ14-1298.6**	zeolite 32%, smectite 50%, opal-CT 9%
	UZ14-1312.5-1313.2*	magnetite 18%, plagioclase 17%, amorphous material 50%
Calico Hills Formation (427.6 to 531.6 m)	UZ14-1417.6**	zeolite 65%, opal-CT 12%, feldspar 12%
	UZ14-1422.4-1423.0*	zeolite 45%, amorphous material 35%
	UZ14-1422.4-1423.0*	zeolite 45%, amorphous material 35%
	UZ14-1465.5-1466.1*	zeolite 35%, amorphous material 35%
	UZ14-1514.8-1515.2*	zeolite 67%, amorphous material 20%
	UZ14-1666.3-1666.9*	zeolite 54%, amorphous material 25%
Prow Pass Tuff (531.6 to 623.9 m)	UZ14-1764.2-1764.7*	zeolite 32%, amorphous material 30%, plagioclase 15%
	UZ14-1854.4-1854.8*	plagioclase 30%, K-spar 28%, quartz 12%, pyroxene 8%
	UZ14-1904.3-1904.8*	zeolite 28%, plagioclase 11%, pyroxene 10%, amorphous material 30%
Bullfrog Tuff (623.9 to 672.4 m)	UZ14-2154.3-2154.8*	plagioclase 33%, amorphous material 15%, zeolite 6%

* Mineralogic analysis by Geochemistry Laboratory, Branch of Geochemistry, U.S. Geological Survey.

** Data From Los Alamos National Laboratory (David Bish, oral commun., 1995).

distillation method on zeolite-bearing cores can remove depleted channel water that does not represent the percolating water. Mineralogic data indicate large zeolite abundances in the Calico Hills Formation and parts of the Prow Pass Tuff. In comparison, the stable-isotope compositions of core water extracted by the compression method on these zeolite-bearing cores are in the range of -12.5 to -13.7 per mil for $\delta^{18}O$ and -98 to -103 per mil for δD, comparable to Topopah Spring Tuff values. The reason is that the compression process does not extract the channel water.

The shape of the vertical profiles of δD values relative to depth in figure 16 can be explained as follows. A series of precipitation events, all with the same δD composition, infiltrate episodically into the soil. Between rainfall events, the soil water has a chance to evaporate and, hence, to become more enriched in δD value near the surface. The next precipitation occurrence displaces this heavier water downward, and waters mix. The downward movement of the fluid in the matrix is controlled by two mechanisms—a concentration gradient of δD composition and a thermal gradient. Under quasi-steady-state conditions, with no appreciable temperature influence, an exponentially decaying δD profile would develop due to concentration-driven diffusion (Allison and others, 1984). The observed decaying δD compositions represented by four solid circles between depths of 45.7 m and 76.2 m (fig. 16) are products of this liquid-phase diffusion. This is consistent with the conclusion made by Yang and others (1996) on the UZ-1 ^{14}C gas data that the gas transport in the unsaturated zone beneath Pagany Wash was by a gas-diffusion mechanism.

The enrichment of $\delta^{18}O$ and δD values of compressed water from Prow Pass and Bullfrog Tuff

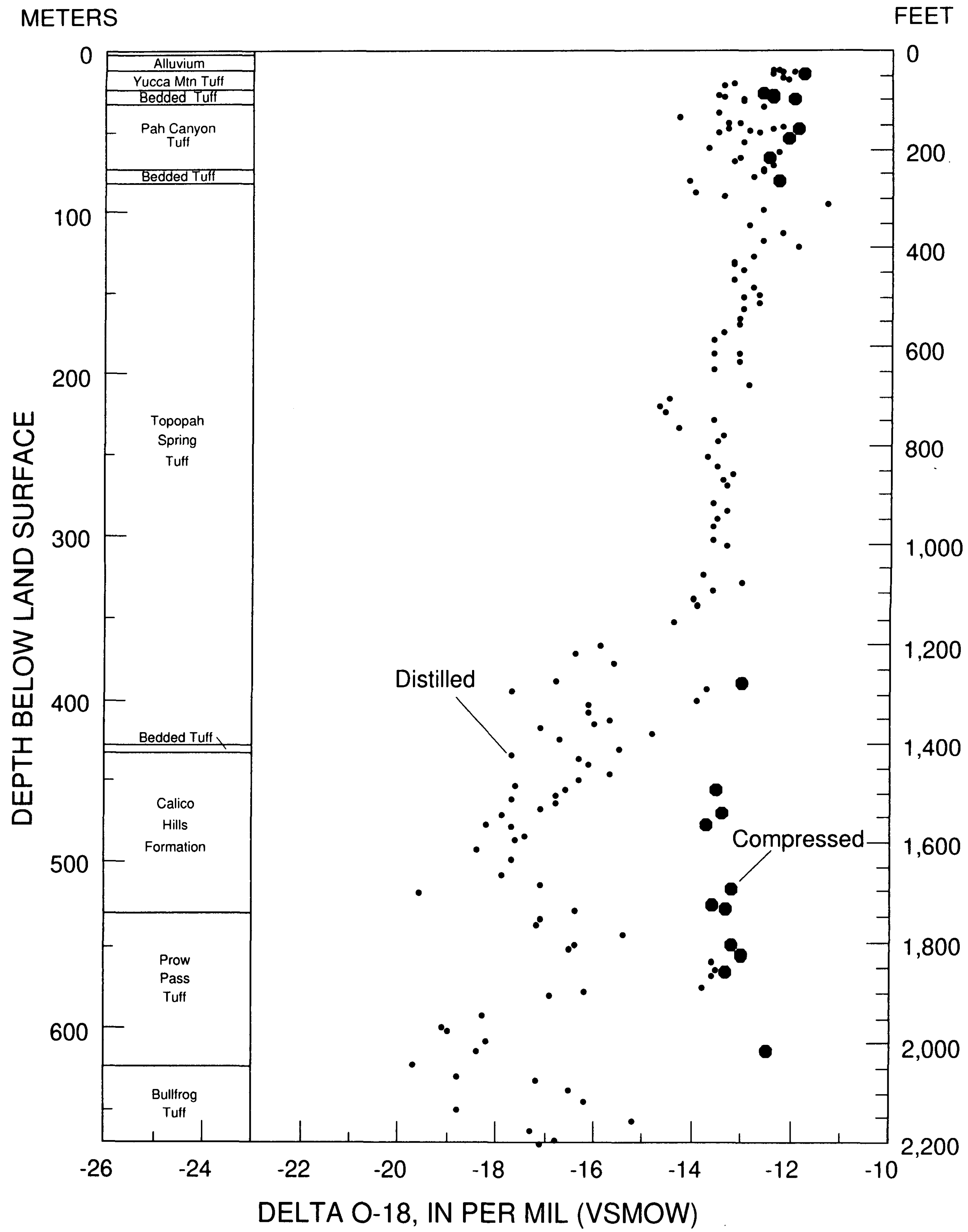


Figure 15. Lithologic units and $\delta^{18}O$ profile of compressed and distilled pore water from borehole USW UZ-14, Yucca Mountain area.

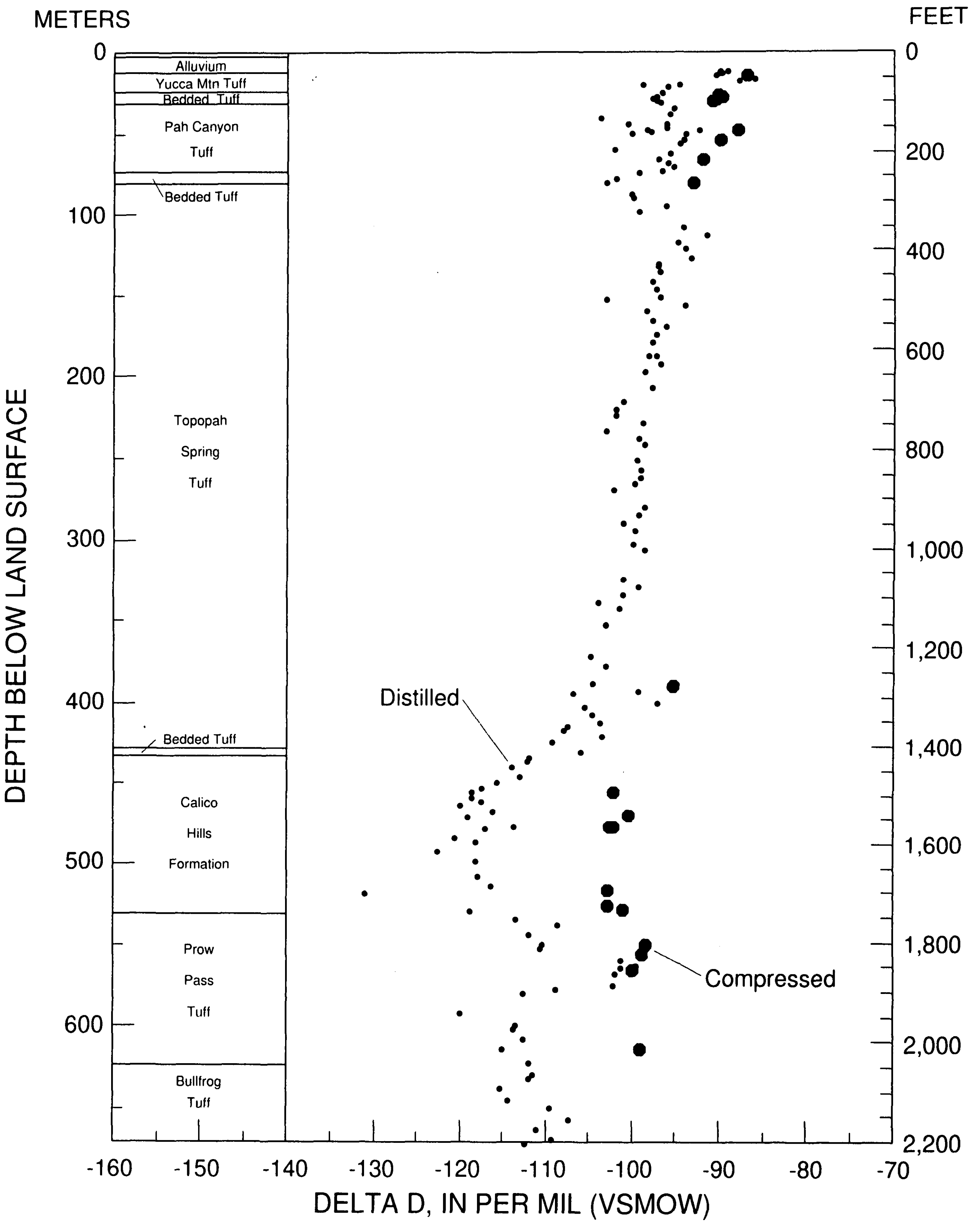


Figure 16. Lithologic units and δD profile of compressed and distilled pore water from borehole USW UZ-14, Yucca Mountain area.

cores compared with the Calico Hills Formation cores could be the results of (1) large amounts of zeolite in these tuffs, causing the fractionation between the channel water and the pore water, producing enriched pore water, or (2) mixing with other source water. It is not clear from the limited data which factor is causing this enrichment.

Source and Nature of Infiltrating Water in the Unsaturated Zone

The stable-isotope compositions of the Yucca Mountain UZ pore waters (UZ-water) from UZ-14 (using only those data that were obtained using a valid method on lithologic cores, that is, the compression method for the Calico Hills hydrogeologic unit and bedded tuff, and the vacuum-distillation method for the Topopah Spring Tuff) are plotted as δD compared to $\delta^{18}O$ in figure 17 along with the saturated-zone ground water (SZ-water) compositions beneath Yucca Mountain. The UZ-water data are scattered over a larger region than the SZ-water data but do overlap with part of the SZ-water data. This overlap probably occurs because the infiltrated pore water moved downward by piston flow representing various infiltration events (that is, variable δD and $\delta^{18}O$ values depending on the conditions of precipitation and evaporation history before infiltration), while the SZ water represents time-averages of well-mixed water from yet-to-be-determined sources. The SZ water is deep under Yucca Mountain. Therefore, this water could be a mixture of several source waters of different ages. In contrast, the shallow UZ water must come from local precipitation, either summer or winter precipitation or a combination of both.

Ingraham and others (1991) measured the stable-isotope compositions of precipitation in southern Nevada. They reported that the yearly weighted average ranged from -10.0 to -12.3 per mil for $\delta^{18}O$ and from -75 to -90 per mil for δD, while the winter precipitation (November to May) ranged from -12.5 to -14.5 per mil for $\delta^{18}O$ and from -92 to -106 per mil for δD. Milne and others (1987) measured the stable-isotope compositions of precipitation specifically at Yucca Mountain from 1984 to 1985. They reported that the yearly weighted average ranged from -9.4 to -11.8 per mil for $\delta^{18}O$ and -77 to -89 per mil for δD, while the winter precipitation ranged from -13.2 to -15.8 per mil for $\delta^{18}O$ and -93 to -114 per mil for δD. The UZ-water compositions ranged from -11.2 to -14.0 per mil for $\delta^{18}O$ and -87 to -104 per mil for δD (fig. 17). These data show that the stable-isotope compositions of UZ water are closer to the winter precipitation values and thus suggest that winter precipitation is the major source of recharge to the unsaturated zone at Yucca Mountain.

The stable-isotope composition of perched water, SZ water, and 1984 summer storms at Yucca Mountain are plotted as $\delta^{18}O$ relative to δD in figure 18. Four major storms that occurred in July and August of 1984 have δD and $\delta^{18}O$ values ranging from -67 per mil to -97 per mil for δD and from -10.5 per mil to -13.0 per mil for $\delta^{18}O$ (Milne and others, 1987). Waters from three of these four storm events are far heavier than the perched water or the UZ water values. Thus, summer rains appear to be a minor contribution to the UZ waters.

Stable-isotope data for UZ waters all plot to the right of the Yucca Mountain precipitation line (YMPL) but on a line that is approximately parallel to the YMPL (fig. 17). This offset is caused by near-surface evaporation resulting in enrichment of the remaining water. When this enriched water is displaced downward by a subsequent rainfall event of sufficient magnitude to remove it from the influence of evaporation, this parcel of water will move farther downward by piston flow. A following recharge event will repeat this cycle but with different initial isotopic composition. In this way soil water at depth (the recharge water) will fall on a line of a slope parallel to the YMPL, but displaced from it. The amount of this displacement is determined by a balance between the isotopic enrichment attained in the upper layers of the soil and the dilution of the rainfall. In arid conditions, low recharge rate and preferential winter precipitation may cause large displacement from the local precipitation line regardless of the climatic conditions under which the precipitation fell (Allison and others, 1984).

The stable-isotope data for perched waters also plot to the right of the YMPL (fig. 18) but are generally closer to the YMPL than the UZ waters, indicating little evaporative loss before recharging to perched-water bodies. This supports the conclusion of Yang and others (1996) based on chloride and dissolved-solid concentrations that perched waters were derived from rapid fracture flows instead of matrix flows. The SZ waters are isotopically lighter than the UZ waters, although there is some overlap between the two clusters. Although the average of all $\delta^{18}O$ and δD values in UZ waters may be different from the SZ $\delta^{18}O$ and δD

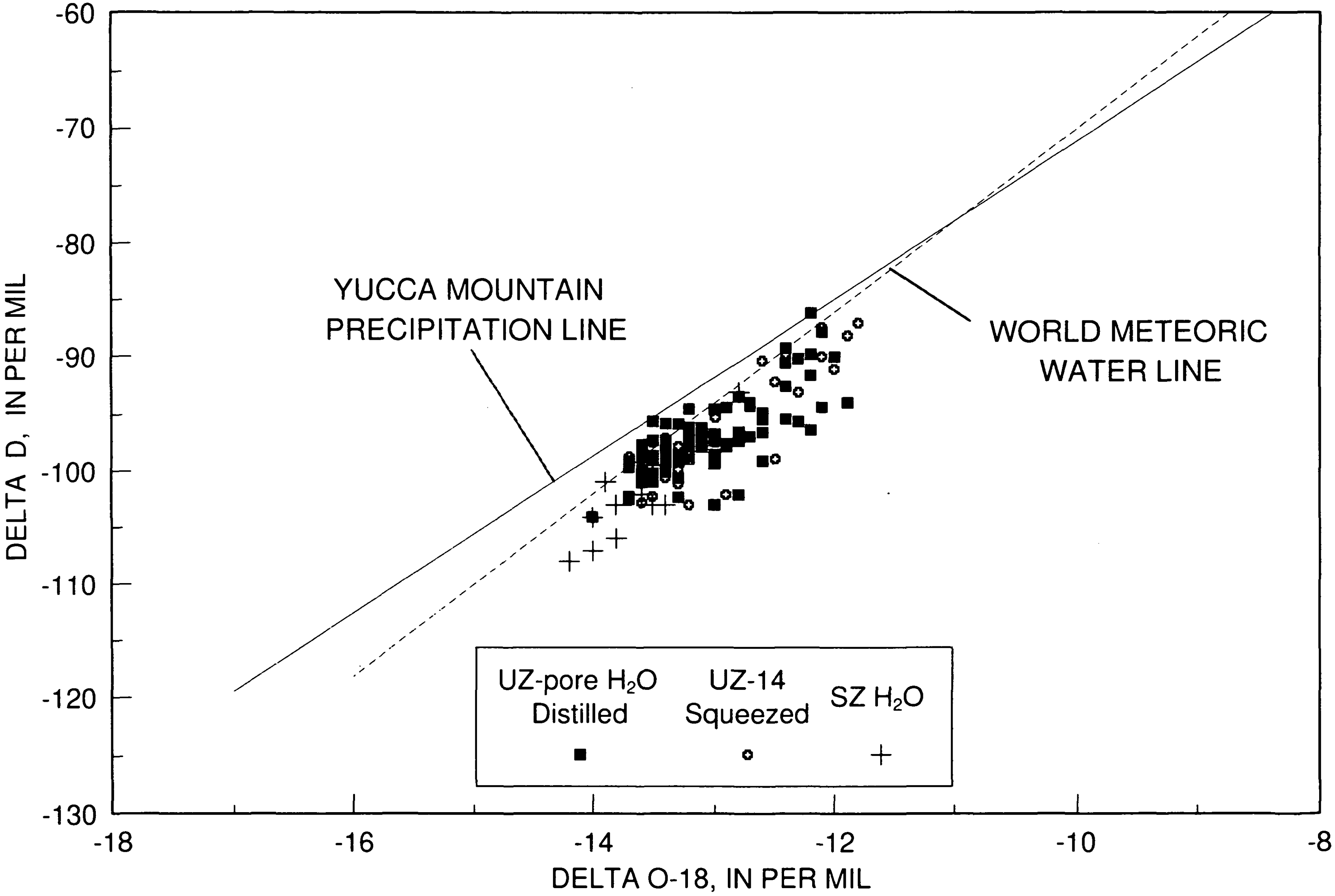


Figure 17. Relations of $\delta^{18}O$ and δD plot of USW UZ-14 unsaturated-zone pore water extracted by compression on bedded tuff and Calico Hills Formation and vacuum distillation on Topopah Spring Tuff, Yucca Mountain area.

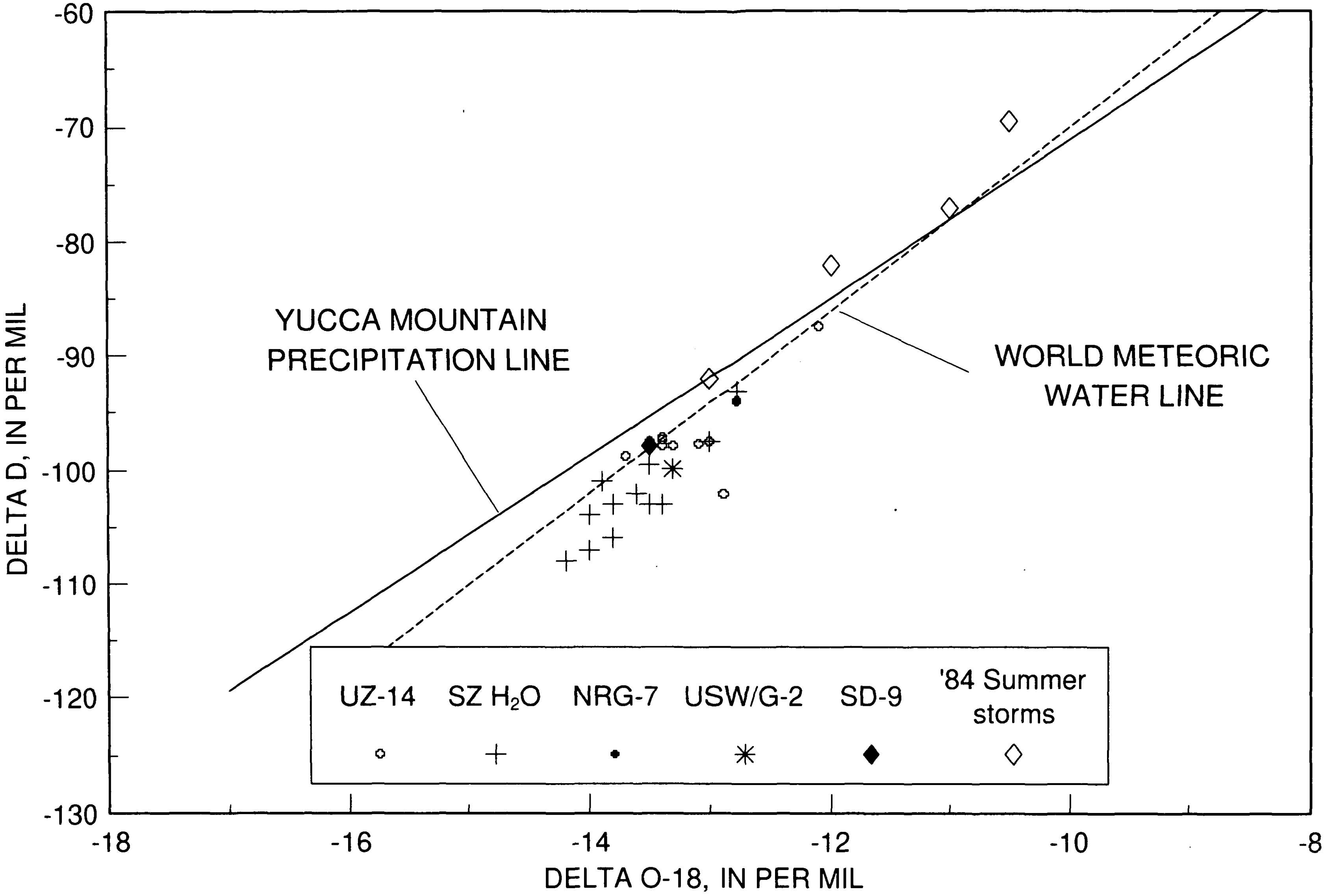


Figure 18. Relation of $\delta^{18}O$ and δD plot of 1984 storms, saturated-zone water, and perched water, Yucca Mountain area.

values, this overlap indicates matrix recharge to the SZ waters might be occurring to some extent from UZ waters.

These conclusions about Yucca Mountain hydrology are based on data from only a single borehole. Further investigations and additional data from other boreholes are needed to make generalized statements about the UZ water flow at Yucca Mountain.

Large Dissolved-Solids Concentrations and δD and δ^{18}O Values

In this section, the cause of the large dissolved-solids concentrations observed in three samples previously mentioned [NRG-6 (depth of 78 m), UZ-14 (3.8 m), and UZ-14 (614 m)] is reexamined with respect to their pore-water δD and δ^{18}O values. The δD versus δ^{18}O plot of these three samples is shown in figure 19. NRG-6 (78 m) and UZ-14 (614 m) plot farther away from the YMPL than the UZ-14 (13.8 m) sample, indicating more enrichment by evaporation. (Enrichment by high-temperature exchange between oxygen atoms of silicate and pore water is eliminated because δD values also are enriched, and there is no source of deuterium in the rock.) The question here is to what extent evaporation had occurred. The extent of evaporation for sample NRG-6 (78 m), which has the largest apparent loss of moisture by evaporation, is calculated here.

The δD and δ^{18}O values of precipitation that fell at Yucca Mountain were reported by Ingraham and others (1991) and Milne and others (1987). Their average δD and δ^{18}O values for winter precipitation are -103 per mil and -14.0 per mil. The NRG-6 (256 ft) sample pore-water values are -93.8 per mil for δD and -10.7 per mil for δ^{18}O. The winter precipitation values were used because it is the apparent source of infiltrating water at Yucca Mountain (as explained in the previous section). Evaporation under Rayleigh conditions is given by the following equation (Fontes and Garnier, 1979, p. 8):

$$\delta - \delta^{o} = (1/\alpha - 1)\ln f$$

where

δ = the composition of the remaining fraction of the pore water, δD(r)/1,000 or δ^{18}O(r)/1,000, at time t;

δ^{o} = the initial composition of pore water, δD(i)/1,000 or δ^{18}O(i)/1,000

α = fractionation factor; and

f = fraction of remaining water

At 20°C, $\alpha_{^{18}O} = 1.00925$ and $\alpha_D = 1.08$. When these values are substituted into the above equation along with precipitation values of -0.103 for δ^{o} (D) and -0.014 for δ^{o} (^{18}O), and pore-water values of -0.0938 for δD and -0.011 for δ^{18}O, the calculated value for f is about 0.88. That is, only about 12 percent of the original water volume has evaporated. This is the maximum value because Rayleigh conditions assume equilibrium between liquid water and vapor. This is one of several large f values because the pore water δD and ^{18}O data used in Rayleigh equation were affected by the kinetic evaporation, and this pair of δD and ^{18}O data has a very positive value. For more negative δD and ^{18}O data (less kinetic effect) the f value will be smaller. For the UZ-14(13.8 m) sample, the δD and δ^{18}O values are -90.5 per mil and -12.4 per mil, which are heavier than the UZ-14(614 m) sample (δD and δ^{18}O values of -99.0 per mil and -12.5 per mil), yet closer to the YMPL. Sources of precipitation that recharged this UZ water must be heavier in δD and δ^{18}O values, possibly from mixture of winter precipitation and spring or summer precipitation.

Did evaporation occur before infiltration or after infiltration? Most of the stable-isotope data presented here are from pore waters compressed from cores obtained from depths greater than 13.7 m, representing matrix water in the intact rock (not alluvium). Field investigation of core-moisture loss during core processing inside the field trailer is about 6 percent of total pore water (I.C. Yang, U.S. Geological Survey, unpub. data, 1993). Thus, about one-half of the 12 percent evaporation was lost in sample handling. Therefore, all δD and δ^{18}O values are systematically in error by a maximum of 5 per mil due to sample handling (12 percent evaporation causes 10 per mil difference in δD: -103 per mil - (-93 per mil) = 10 per mil). It may be concluded (fig. 16) that vapor transport in matrix water is not occurring. Therefore, the 6 percent pore-water loss can be attributed to evaporation before infiltration. This supports the previous conclusion that large dissolved-solids concentrations in the three samples are the result of water-rock interactions and not of evaporative concentration.

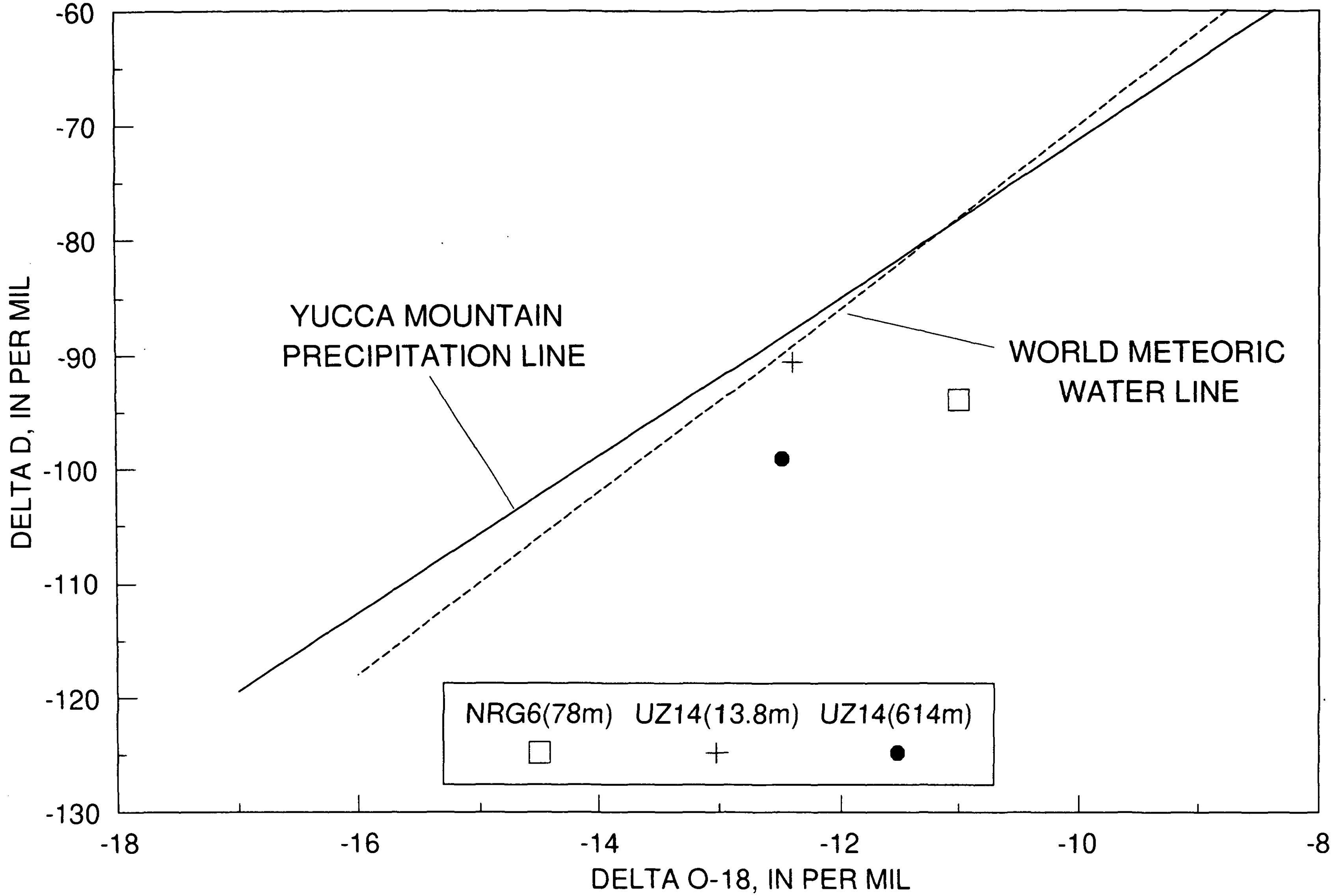


Figure 19. Relation of $\delta^{18}O$ and δD plot of data from samples containing large dissolved-solids concentrations in pore waters of USW UZ-14 and USW NRG-6 at different depths, Yucca Mountain area.

Interactions of Old Matrix Water with Younger Percolating Water

Rhyolitic volcanic ash, as erupted, contains 0.1 to 0.3 percent water (Friedman and others, 1993). After eruption, however, ash begins to react with infiltrating water that is incorporated into the tuff. If this secondary water of hydration does not undergo further isotopic exchange with the subsequently infiltrated water, it will represent the old matrix water. On the contrary, if this secondary water undergoes isotopic exchange, then the pore water will lose its old water signal and be replaced by a series of subsequently infiltrated waters. As stated previously in the section on column experiments, tuffs at Yucca Mountain do undergo isotopic exchange. Therefore, stable-isotope compositions of extracted pore water are representative of the most recently infiltrated percolating water.

The channel water of pure clinoptilolite powder exchanges with the percolating water within several hours to days. For crushed and ground tuffs from Yucca Mountain, the exchange rate also requires several hours to days, while intact cores take longer depending on the core size and grain size. The exchange processes for zeolite-bearing core can be divided into two steps: (1) the exchange between the pore water and the percolating water, and (2) the exchange between the pore water and channel water. If the system reached equilibrium, the stable-isotope compositions of pore water should equal those of percolating water, and those of channel water will differ from pore water by a fractionation factor. The first process appears to be diffusion-controlled. The equilibration time depends on the mean travel distance and the diffusion coefficient (Yu, 1996). The mechanism controlling the second step is unknown, but the reaction is rapid, as seen from column experiments. Therefore, the equilibration time is determined by the first process (Yu, 1996). For Topopah Spring Tuff that contains no zeolite, stable isotopes of water molecules exchange by diffusion mechanisms.

Preglacial (greater than 10,000-year ages) or Postglacial (2,000- to 10,000-year ages) Pore Water in the Topopah Spring Tuff

Both UZ-water and perched-water δD and $\delta^{18}O$ values are heavier than SZ water values. The SZ water uncorrected ^{14}C ages range from 9,000 to 18,000 years at Yucca Mountain (Benson and McKinley, 1985). Most UZ-water and perched-water stable-isotope values in figures 17 and 18 are larger than -99.8 per mil in δD and heavier than the last ice-age water δD values of -101 to -103‰ (uncorrected ^{14}C ages between 12,000 and 18,000 years) collected in the deeper SZ ground water of borehole H-1, which is near the UZ-14 borehole (Benson and Klieforth, 1989). If mixing of the last ice-age water (more than 10,000 years old) were involved in the matrix water of the Topopah Spring Tuff, the data would shift toward the left side in figures 15 and 16 (more negative) instead of remaining such constant values. Therefore, the pore waters of the Topopah Spring Tuff are interpreted to be consistent with the postglacial (2,000- to 10,000-year) water.

SUMMARY AND CONCLUSIONS

Pore-water compositions indicate that, in spite of large distances separating boreholes, chemical compositions are similar among boreholes and vary according to the lithologic units from which they were obtained. Chemical compositions are of the calcium-sulfate or calcium-chloride types in the Paintbrush Group (Tiva Canyon Tuff, Yucca Mountain Tuff, Pah Canyon Tuff, and bedded tuffs), and sodium-carbonate or sodium-bicarbonate types in the Calico Hills nonwelded unit. Several samples from the Calico Hills nonwelded unit in SD-7 and SD-12, however, are not true sodium-carbonate or sodium-bicarbonate types but rather trend toward calcium-sulfate or calcium-chloride types. Unsaturated-zone pore water has significantly larger concentrations of major ions and dissolved solids than do the saturated-zone water or the perched water. If the chemically dilute infiltrating waters were to recharge the perched or saturated-zone water, these waters must flow rapidly through fractures or permeable zones in the intervening PTn or Calico Hills nonwelded hydrogeologic units to avoid mixing (enrichment) with the chemically concentrated pore water in those units. This conceptual model is consistent with the observations of post-bomb tritium and ^{36}Cl in the deep UZ of Yucca Mountain—that is, consistent with rapid transport to the deep UZ.

Carbon-14 activities in the pore water of the Calico Hills nonwelded unit in SD-9 are between 82.3 to 95.3 pmc, with similar activities from the Calico Hills nonwelded unit in UZ-14, and activities of 50 to 60 pmc in the Calico Hills nonwelded unit of SD-7 and SD-12—considerably smaller (or older) than the

UZ-14 and SD-9 pore waters. The water with larger ^{14}C activities in UZ-14 and SD-9 could have been partly contaminated by the atmospheric $^{14}CO_2$ during drilling. More gaseous-phase ^{14}C data from the Calico Hills nonwelded unit are needed to confirm this possibility. A general trend is apparent from the distribution of borehole data, however, that younger water underlies the northern part of Yucca Mountain and older water underlies the southern part of the mountain. Perched waters reached in boreholes had large water masses, which are more likely to preserve their original chemical signatures than pore water.

Large tritium concentrations of about 30 to 150 TU were detected in the NRG-6 borehole at depths from 53.3 m to 74.7 m in the Pah Canyon Tuff and near the top of the Topopah Spring Tuff. One large tritium concentration of about 47 TU was detected in water from a depth of 108.7 m in NRG-7a. Only limited numbers of samples were analyzed from the SD-7, SD -9, and SD-12 boreholes, but no large tritium concentrations (greater than 30 TU) were detected.

The gaseous-phase ^{14}C activities of CO_2 gas from the entire unsaturated zone of borehole SD-12 show a trend similar to that observed at UZ-1; that is, ^{14}C activities decrease with depth, indicating gas transport by a diffusion mechanism. Gaseous-phase ^{14}C values in the Calico Hills nonwelded unit are, from SD-7 and from SD-9, respectively, 41.5 and 51.0 pmc.

Experiments showed that vacuum distillation of pore water for stable-isotope analysis produced reliable results from tuffs free of clay and zeolite minerals but not from tuffs with large hydrated mineral contents. Compression extraction of pore water from hydrated, mineral-rich tuffs did, however, produce fluids with isotopically unfractionated waters. Extraction methods need to be carefully chosen with regard to the mineralogic and lithologic composition of samples.

From the column experiments with pure clinoptilolite powder, the channel water was shown to be exchangeable with the bulk water, and the exchange is complete within hours to days. For core samples from Yucca Mountain containing large clinoptilolite components, the exchange is slower, ranging from days to months. This slower exchange rate is determined by the diffusion rate between the bulk water and pore water. Exchange between pore water and channel water is fast and is not a rate-determining factor. The isotopic compositions of the bulk pore water in the unsaturated-zone tuff at Yucca Mountain, pertaining to zeolite-rich core, will reflect the most recently infiltrated water. The channel water in zeolite is fractionated according to Rayleigh distillation.

Stable-isotopic composition of perched water generally plots close to the Yucca Mountain precipitation line (YMPL) indicating little evaporative loss before recharge of the perched-water bodies. Stable-isotopic composition of UZ-14 pore water, however, plots to the right of the YMPL, indicating slight evaporation before infiltration. Estimated quantities of evaporation under the Rayleigh conditions (the largest possible loss) were 12-percent volumetric loss, of which one-half is due to sample handling. Winter precipitation is likely the source of recharge to the UZ at Yucca Mountain.

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