Interpretation of Chemical and Isotopic Data From Boreholes in the Unsaturated Zone at Yucca Mountain, Nevada

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CONVERSION FACTORS

Metric (International System) units in this report may be converted to inch-pound units by using the following conversion factors:

Multiply metric unit	Ву	To obtain inch-pound unit
nanometer (nm)	3.937 × 10 ⁻⁸	inch
centimeter (cm)	3.937×10^{-1}	inch
cubic centimeter (cm^3)	6.102×10^{-2}	cubic inch
cubic meter (m ³)	6.102×10^4	cubic inch
gram (g)	2.2×10^{-3}	pound, mass
gram per cubic centimeter (g/cm ³)	3.6×10^{-2}	pound per cubic inch
kilometer squared (km ²)	1.076×10^{7}	square foot
kilometer (km)	6.214×10^{-1}	mile
kilopascal (kPa)	0.145	pound-force per square inch
liter (L)	0.2642	gallon
liter per minute (L/min)	0.2642	gallon per minute
megapascal (MPa)	144.7	pound per square inch
meter (m)	3.281	foot
meter per day (m/d)	3.281	foot per day
microgram per liter (µg/L)	1	part per billion
milligram (mg)	2.2×10^{-6}	pound
milligram per liter (mg/L)	1	part per million
milliliter (mL)	6.102×10^{-2}	cubic inch
millimeter (mm)	3.937×10^{-2}	inch

To convert degree Celsius (°C) to degree Fahrenheit (°F) use the following formula:

 $^{\circ}F = 9/5 (^{\circ}C) + 32$

Interpretation of Chemical and Isotopic Data from Boreholes in the Unsaturated Zone at Yucca Mountain, Nevada

By In C. Yang, Gordon W. Rattray, and Pei Yu

Abstract

Analyses of pore water from boreholes at Yucca Mountain indicate that unsaturatedzone pore water has significantly larger concentrations of chloride and dissolved solids than the saturated-zone water or perched-water bodies. Chemical compositions are of the calcium sulfate or calcium chloride types in the Paintbrush Group (Tiva Canyon, Yucca Mountain, Pah Canyon, and bedded tuffs), and sodium carbonate or bicarbonate type water in the Calico Hills Formation.

Tritium profiles from boreholes at Yucca Mountain indicate tritium-concentration inversions (larger tritium concentrations are located below the smaller tritium concentration in a vertical profile) occur in many places. These inversions indicate preferential flow through fractures. Large carbon-14 variations of about 53.0 to 97.7 percent modern carbon are seen in UE-25 UZ#16 bedded tuff and in the Calico Hills Formation. The larger value of 97.7 percent modern carbon and modern chlorine-36 values obtained from pore water and core cuttings from the Calico Hills Formation of UE-25 UZ#16 are in the same locations where large tritium concentrations are found.

The apparent carbon-14 ages of perched water range from 3,000 to 10,800 years. If age corrections are made to account for caliche dissolution, perched-water residence times all will be less than 7,000 years. Stable isotopic values of -12.1 to -13.8 parts per thousand for delta oxygen-18 and -87.4 to -100 per mil for delta deuterium in perched water are not consistent with recharge during colder climates and therefore strongly support carbon-14 mean ages of less than 7,000 years. Major-ion chemistry of perched water indicates similar chemical compositions to the saturated-zone ground water except for USW UZ-14 perched water, which is typical of Topopah Spring Tuff water.

Rock-gas compositions are similar to that of atmospheric air except that carbon dioxide (CO_2) concentrations are generally larger than those in the air. The delta carbon-13 values of gas from USW UZ-1 are fairly constant from surface to 365.8 meters, indicating little interaction between the gas CO2 and caliche in the soil. Carbon-14 data of gaseous and aqueous phases also show little interaction between gas CO_2 and caliche. With regard to gas-water exchange, an aqueous phase will affect a gaseous phase more because most carbon resides in the aqueous phase. The nonequilibrium condition observed between the two phases is likely caused by collecting most gas samples by pumping from dry fractures rather than from pore gas, which could have been in equilibrium with the pore water. Gas carbon-14 ages are significantly older than water carbon-14 ages in deep Topopah Spring Tuff and below. The observed apparent age differences may result from gravity-driven fracture flow of liquid, a process faster than the diffusion-controlled transport of gas.

Model calculations indicate that the gas transport in the unsaturated zone at Yucca Mountain agrees well with the gas-diffusion process. Tritium-modeling results indicate that the high tritium value of about 100 tritium units in the Calico Hills Formation of UZ–16 is within limits of a piston-flow model with a water residence time of 32 to 35 years. The large variations in tritium concentrations with narrow peaks imply piston flow or preferential fracture flow rather than matrix flow. In reality, the aqueous-phase flow in the unsaturated zone is between piston and well-mixed flows but is closer to a piston flow.

INTRODUCTION

The unsaturated zone (UZ) at Yucca Mountain in Nevada is being investigated as a potential site for a high-level nuclear-waste repository. A thorough understanding of geochemical and hydrologic processes in the UZ is essential for site characterization. The purpose of this report is to present gas and liquid hydrochemical data obtained to date and interpretations of these data related to the flow mechanisms and residence times of these fluids in the rock mass.

Data for the gaseous phase include carbon dioxide concentrations and carbon isotopic concentrations [carbon-13 (¹³C) and carbon-14 (¹⁴C)] of rock gas probably from fractured tuffs. Data for the aqueous phase include major cation and anion concentrations and isotopic concentrations and compositions, which include tritium (³H), ¹⁴C, ¹³C, deuterium (²H), and oxygen-18 (¹⁸O) of pore water in cores obtained from boreholes in the UZ. Pore-water compositions and carbon-14 data are mostly from bedded and nonwelded tuffs. In addition, perched-water bodies, when detected, also were analyzed for their chemical and isotopic compositions.

Most of the UZ boreholes are drilled in the washes on the east side of Yucca Mountain. From the present chemical and isotopic data, along with previously published USW UZ-1 data collected at Yucca Mountain (Yang and others, 1993), preliminary conceptual hydrologic-flow models are constructed from the data. Also, chemical compositions of pore water in different lithologic units are presented in Piper diagrams. The composition of pore water collected near the lithologic contacts and adjacent beds is reported and inferences to hydrologic flow are made. Finally, modeling of the gas-transport mechanism and tritium as a tracer in ground-water residence-time estimation was undertaken for the UZ of Yucca Mountain.

This investigation was conducted by the U.S. Geological Survey (USGS), in cooperation with the U.S. Department of Energy (DOE), under Interagency Agreement DE-AI08-78ET44802.

GEOHYDROLOGY OF THE STUDY AREA

Yucca Mountain is located near the western boundary of the Nevada Test Site in southern Nye County, Nevada. Along the crest of Yucca Mountain, altitudes generally range from 1,465 to 1,475 m (Montazer and Wilson, 1984). Yucca Mountain consists of a series of north-trending fault-block ridges composed of volcanic rocks that generally have an eastward tilt of 5° to 10° (Scott and Bonk, 1984). Numerous washes, generally underlain by alluvium, dissect the eastern side of the mountain. Average annual precipitation at the mountain is estimated to be about 150 mm, and nearly three-fourths of the annual precipitation falls from October through April (Quiring, 1983). An unsaturated zone that is 500-700 m thick is present beneath Yucca Mountain. This zone consists of ashflow tuff that is extensively fractured, densely welded, minimally porous but transmissive, and is interbedded with argillic and zeolitic bedded tuff and ash-flow tuff that are less fractured, nonwelded, porous, and transmissive (Scott and Bonk, 1984). A generalized section of hydrogeologic units at Yucca Mountain is given in figure 1.

	Stratigraphic unit	li	Tuff ithology	Hydrogeologic unit		
	Alluvium			Alluvium		
	Tiva Canyon Tuff		MD	Tiva Canyon welded unit		
	Yucca Mountian Tuff			Paintbrush		
	Bedded Tuff	1	NP,B	nonwelded		
group	Pah Canyon Tuff			unit		
Paintbrush Group	Bedded Tuff					
	Topopah Spring Tuff		MD	Topopah Spring welded unit		
	Calico Hills		(V)	Calico Hills		
	Formation	NP,B	(D)	nonwelded unit		
Group	Prow Pass Tuff		(in part zeolitic)	table cone		
Crater Flat Group	Bullfrog Tuff		D,NP,B ferentiated)	unit ologie Flat unit Crater Flat		

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 SAMPLED FOR CHEMICAL AND ISOTOPIC DATA

All UZ boreholes were drilled using the vacuum-reverse-air-circulation (VRAC) drilling method (Houghton, 1969). This method is intended to prevent the contamination of the unsaturated rocks with drilling fluids and thus allow the collection of native pore water and gas from the UZ for hydrochemical analyses. Sulfur hexafluoride (SF₆) was added to the compressed air stream injected into the annulus space between the inner and outer strings. The concentration of the SF₆ in the air mixture was about 1.5 parts per million by volume (ppmv). Atmospheric gas that enters the formation during the drilling process can be removed later by evacuation of the borehole. Disappearance of the SF₆ in the drilling air.

USW UZ-1 (fig. 2) was drilled from April through July of 1983 and completed to a total depth of 387.1 m. Coring was attempted but was unsuccessful due to the use of an inappropriate coring bit (Whitfield, 1985). Only two pieces of core less than 0.61 m long each were recovered. Rocks of Quaternary and Tertiary ages were penetrated during the drilling of the borehole. The stratigraphy of the lithologic units penetrated is described in Whitfield and others (1990). The top 17.4 m consists of alluvium, which is underlain by three units in the Paintbrush Group: Yucca Mountain, Pah Canyon, and Topopah Spring Tuffs. These are thick, ash-flow tuff beds separated by bedded tuff units that are each 6 m thick. The tuff units are variously welded and indurated. Black glass shards were recovered during bailing when the borehole was 383.3 m deep, indicating the presence of friable, nonwelded tuff at the base of the Topopah Spring Tuff (Whitfield and others, 1990). The borehole contained 15 instrument and sampling stations upon completion. Each sampling station has a pressure transducer, thermocouple psychrometer, and gas-sampling tubes, isolated by silica flour and cement grout. Details of construction were given by Montazer and others (1985).

UE-25 UZ#4 and UZ#5 are located in Pagany Wash on the north-northeast side of Yucca Mountain. Borehole UZ#4 is in the middle of the main wash and

is about 37.7 m north of borehole UZ#5. Borehole UZ#5 is on the southern bank of the wash and about 3 m higher than borehole UZ#4 (fig. 2). Borehole UZ#4 drilling started September 6 and was completed October 10, 1984, to a depth of about 111.8 m. The top 12 m of the borehole is in alluvial-colluvial material. Borehole UZ#5 drilling started October 11 and was completed November 19, 1984, to a depth of about 111.6 m. It is totally in bedrock. Details on the drilling of these two boreholes are given by Loskot and Hammermeister (1992). The predominant rock types penetrated by the two boreholes are ash-flow and ash-fall tuffs. These tuffs are part of the Paintbrush Group and, in descending order, are the Tiva Canyon Tuff, Yucca Mountain Tuff, Pah Canyon Tuff, and upper 18 m of Topopah Spring Tuff. Layers of bedded and reworked tuff separate each of the four tuffs. The tuffs show various degrees of welding, ranging from nonwelded to densely welded.

UE-25 UZ#16 borehole is located on the eastern side of the Yucca Mountain central block at the mouth of WT2 wash (fig. 2). Drilling of the borehole was started on May 27, 1992, and completed on March 11, 1993, to a total depth of 513.9 m, penetrating about 15.2 m into the water table. The predominant rock types penetrated by the UE-25 UZ#16 borehole are ash-flow and ash-fall tuffs. These tuffs are part of the Paintbrush Group and, in descending order, are the Tiva Canyon Tuff, Yucca Mountain Tuff, Pah Canyon Tuff, Topopah Spring Tuff, and the nonwelded tuffs that are interstratified with each of these tuffs, the Calico Hills Formation, and the Prow Pass Tuff. Details of the drilling of this borehole are given by Falah Thamir and others (U.S. Geological Survey, written commun., 1995).

The USW UZ–14 borehole is located in Drill Hole Wash, 26.2 m from USW UZ–1. Drilling of the borehole was started on April 15, 1993, 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. Predominant rock types are similar to those of USW UZ–1 reported by Whitfield and others (1990). Details of the drilling on this borehole were also given by Falah Thamir and others (U.S. Geological Survey, written commun., 1995).

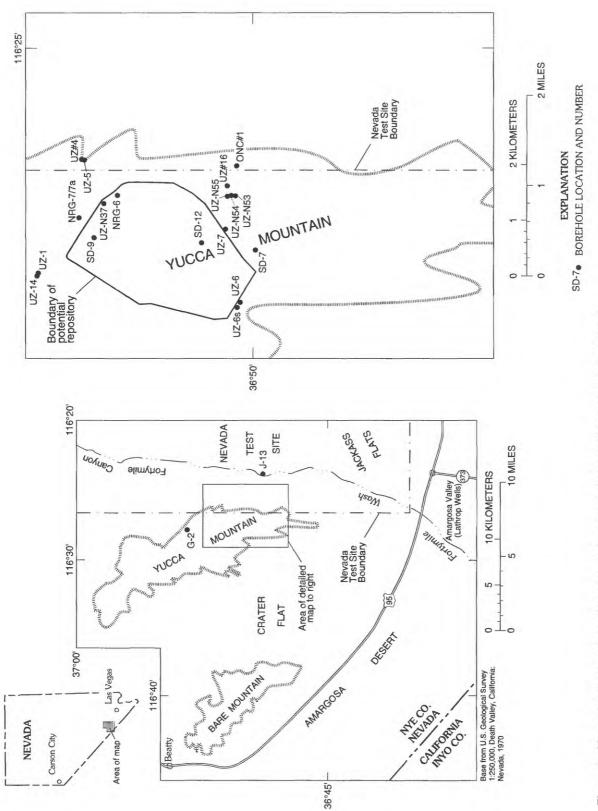


Figure 2. Maps showing locations of unsaturated-zone boreholes at Yucca Mountain, Nevada.

Other deep unsaturated-zone boreholes were drilled in addition to the UZ boreholes. North-ramp geologic boreholes NRG-6 and NRG-7a and systematic drilling geologic boreholes SD-7 and SD-9 have been completed (fig. 2). Drilling of NRG-6 was started on November 23, 1992, and cored to a total depth 335.3 m in the Topopah Spring Tuff on March 3, 1993. NRG-7a was drilled from October 21, 1993, and cored to a total depth of 461.3 m in the upper Calico Hills Formation on May 6, 1994. SD-9 was started on May 10, 1994, penetrating into the water table, and completed to a total depth of 677.6 m on September 26, 1994. SD-7 was started on October 3, 1994, and completed to a total depth of 497.4 m in the Calico Hills Formation on July 28, 1995.

METHODS OF SAMPLE COLLECTION AND ANALYSIS

Dry-drilling techniques were used to obtain all UZ cores from boreholes. The diameter of the rotary core was 6.10 cm. Cores from the rock formation were obtained using a 1.52-m core barrel with a split inner tube. Core recovery was typically more than 90 percent. Three to four pieces of unfragmented solid core, approximately 15 cm long, were selected from most core runs for pore-water extraction. The remainder of the cores were selected for other hydrologic-property tests and for archiving.

Aqueous-Phase Samples

Sample-handling procedures affect the success of extracting uncontaminated water from core samples. 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 carefully packed into plastic coolers and transported from the drill site to the Sample Management Facility (SMF) at Jackass Flats, Nev., for log-in and storage. The storage temperature was kept at 6° to 9°C until the cores were removed for pore-water extraction.

Extraction of Pore Water from Core Samples

Pore water was extracted from the cores by using a high-pressure one-dimensional (uniaxial) compression procedure (Mower and others, 1991, 1994; J.D. Higgins and others, Colorado School of Mines, written commun., 1995). Briefly, compression operations start with applying pressure to the first stress level of 103.4 MPa at a rate of 69 kPa/s. Loading continues in eight increments of 103.4 MPa (at the same loading rate) until the final stress level of 827 MPa is reached. Additional pore water can be 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. Water and gas samples are taken when adequate volumes are collected in the syringes. The extracted water was filtered through Nucleopore filters (0.45 µm) into suitable bottles. Samples for major ions were stored in polyethylene bottles, and samples for stable isotopes and ¹⁴C were stored in glass bottles.

The densely welded Topopah Spring Tuff, which generally has less than a 5-percent moisture content by weight, cannot yield water by compression. Therefore, the vacuum distillation method (Stewart, 1972; Walker and others, 1991) was used in this study. Cores which had undergone high-pressure compression were also distilled in a vacuum for the remaining water. That water can only be analyzed for ³H, ¹⁸O, and ²H.

In vacuum distillation, water from cores is distilled by heat in a vacuum system and captured in a cold trap at -78°C. A temperature of 150°C was maintained at the heating mantle, resulting in a core temperature of about 110°C. Vacuum-distilled water samples were stored in glass bottles for analysis of tritium. In samples with high zeolite contents (such as samples from the Calico Hills Formation), water may be fractionated and become more depleted in the heavy ¹⁸O isotope when it reacts with zeolites in cavities or channels. Therefore, pore-water samples for stable isotopic analyses (δD and $\delta^{18}O$) should be processed by vacuum distillation on a nonzeolitic core sample, while compressed water which represents percolating water should be used for zeolite samples. Further investigations on the extent of isotopic fractionation by the zeolite minerals are in progress using isotope-tagged (known stable isotopic values) water imbibed into dry core from the Calico Hills Formation and the bedded tuff.

Collection of Perched and Saturated-Zone Water Samples

Perched-water samples were collected from USW UZ-1, UZ-14, NRG-7a, SD-7, and SD-9. In addition, water samples were collected from the saturated zone immediately below the water table in J-13, ONC#1 (Office of Nye County), USW G-2, and UE-25 UZ#16. All water samples were collected using plastic bailers or stainless-steel bailers. Samples were stored inside an ice cooler after collection and transferred to the SMF at the end of the day for longterm storage in a 6-9°C cold room. Water-quality parameters, such as pH, specific conductance, and temperature (and occasionally bicarbonate concentration), were measured in the field laboratory. USW UZ-14 and USW SD-7 boreholes produced sufficient perched waters for hydraulic pumping tests. Consequently, only one complete set of perched-water samples was collected from each borehole except UZ-14 and SD-7, which were collected during pumping tests.

While drilling USW UZ-1 to a depth of 387.1 m, a body of perched-water was penetrated. During a 495-minute period, 491 L of water was removed by bailing (Whitfield and others, 1990). One sample was collected on July 7, 1983, using a plastic bailer. The other water sample was collected on July 11, 1983, using the same bailer. Prior to initiation of drilling operations, the unsaturated section had been estimated to be about 470 m thick at the USW UZ-1 location. During the drilling of USW G-1 in 1980, located 305 m to the southeast of USW UZ-1, operational difficulties were experienced at a depth of 303.9 m (Spengler and others, 1981). At this point, a portion of the drill rods and several types of retrieval tools were lost into the borehole. The borehole was reamed to a larger diameter and cemented from 239.3 to 308.8 m. The cement plug was then drilled through to a depth of 309.7 m. A total of 9,250 m³ of drilling fluids was lost to the formation during reaming and cementing operations.

On July 30, 1993, wet cores from UZ–14 were observed from 383.0 to 383.6 m (Falah Thamir and others, U.S. Geological Survey, written commun., 1995). A fracture was observed at 383.7 m. Core was dry below this fracture. A plastic bailer was left at the bottom of the borehole (384.6 m) over the weekend. On Monday morning (August 2, 1993), the bailer was full of water when it was pulled up. A whole set of hydrochemical samples was collected. A supplemental set was collected on the same day using a plastic bailer. The third set was collected on August 2, 1993, using a stainless-steel bailer. About 20 L of water was collected. All water samples were stored in a refrigerator at the SMF.

On August 3, 1993, the borehole was drilled from 386.1 to 387.7 m and wet cores were recovered. A plastic bailer was lowered down the borehole and 17 bailers of water samples were collected. On August 4, 1993, the borehole was drilled from 387.7 to 389.2 m and cores were wet throughout. Coring continued from 389.2 to 390.8 m. All cores were wet. Lithologically, the lower 1.3 m of this interval was composed of basal vitrophyre. On the morning of August 5, 1993, the water level was at 381.3 m. Eight bailers of water samples were collected.

Hydraulic drawdown and recovery tests were conducted on August 17, 1993, to estimate the size of the perched-water body. A Moyno pump was placed at the bottom of the borehole, and pump tests were concluded on August 27, 1993. Four sets of hydrochemical samples were collected during the tests, and a final set of hydrochemical samples was collected on August 31, 1993.

Pumping tests for USW SD-7 were conducted for 1 week, from March 16 through 21, 1995, at a rate of 11 L/min. Perched-water samples for hydrochemical analysis were collected on March 8, 1995, when perched water at USW SD-7 was first reached, then collected twice a day during the pumping tests.

One sample of all other perched water (NRG-7A, SD-9) was collected from each borehole by using a plastic bailer.

Analyses of Water Samples

The tritium was analyzed at the UZ hydrochemistry laboratory in building 56 of the Denver Federal Center using procedures published by Thatcher and others (1977). Tritium values were calculated by regressing back to the date of sample collection so that tritium decay was considered between sample collection and dates of analysis. Tritium errors were approximately ± 4 tritium units [1 tritium unit (1 TU) = 1 ³H atom per 10¹⁸ ¹H atoms]. Cation concentrations were measured using inductively coupled plasma emission spectroscopy, and anion concentrations were measured using ion chromatography at Huffman Laboratories, Inc., in Golden, Colo. Because only a small volume (3 to 30 mL) of pore water was obtained for each sample, complete measurements of water composition were not possible for individual samples. 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. Analysis by Tandem Accelerator Mass Spectrometer (TAMS) for ¹⁴C and δ^{13} C required about 30 to 60 mL of water. Samples were sent to Beta Analytic, Inc., in Miami, Fla., for analyses. Bicarbonate in water was converted to carbonate and then precipitated as strontium carbonate. Carbonate samples were acidified to yield carbon dioxide and subsequently converted to graphite for determination by TAMS. Uncertainty in δ^{13} C values was ±0.2 part per thousand (‰), and for ${}^{14}C$ was ±0.7 percent modern carbon (pmc). Stable isotopes of oxygen and hydrogen were analyzed by mass spectrometer at the U.S. Geological Survey Research Laboratory in Reston, Va., and at the Stable Isotope Laboratory, Institute of Arctic and Alpine Research, University of Colorado, Boulder, Colo. Precision for the measurements was $\pm 0.2\%$ for δ^{18} O and $\pm 1.0\%$ for δ D. All uncertainties quoted are one standard deviation.

Gas Samples

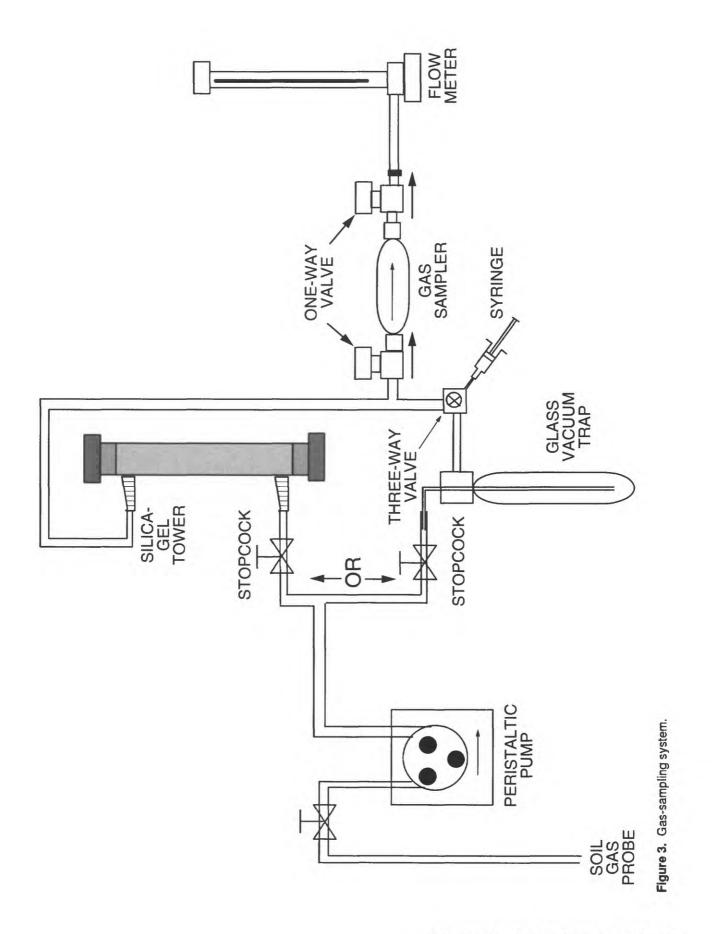
Gas samples were collected using a peristaltic pump connected through short silicone tubing to the downhole gas-sampling tubes. Gas-sampling tubes were pumped overnight before sample collection to purge the tubes of any atmospheric air that might have been introduced while connecting the pumps to the system. Generally, four types of gas samples were collected: gas composition, CO₂ concentration, δ^{13} C, and ¹⁴C. Gas-sampling devices used were 500 cm³-per-minute peristaltic pumps connected through 0.95-cm-diameter Teflon tubes to the pumping ports.

Collection from Borehole USW UZ-1

Rock-gas samples were collected using a syringe inserted into a three-way stopcock in the gas-sampling line of borehole USW UZ-1 (fig. 3), which is permanently instrumented for gas sampling. Gas-sampling lines were pumped overnight (20 hours) before gas samples were taken. The syringe was flushed with sample gas at least three times before collection of a sample. Gas was then drawn into the syringe, the syringe was transported to the laboratory, and gas was injected into a gas chromatograph for composition analysis. Each probe was sampled daily during a gas-sampling trip—more frequently when abnormal gas compositions were observed.

Two gas-sampling methods were used for determination of δ^{13} C ratio in carbon dioxide samples. In the first, the molecular-sieve (MS) method, the gas stream was initially passed continuously through a silica-gel tower to remove moisture (fig. 3), then through a 300-mL stainless-steel cylinder containing a 50-nanometer (50-nm), anhydrous (dehydrated under a vacuum at 350°C) molecular sieve to trap the CO₂ gas. The 50-nm molecular sieve strongly traps CO₂, which may be later recovered in the laboratory by heating to 350°C the stainless-steel cylinder (containing the molecular-sieve pellets) under a vacuum. This collection method was used from 1984 to 1991. In 1991, it was replaced by the whole-gas method described below.

The second method, the whole-gas (WG) method, was used for batch sampling. A gas stream was allowed to flow through a 500-mL glass container (or into a Mylar balloon) to purge the container several times before sampling (this "glass container" replaced the "gas sampler" in fig. 3). When the gas stream had attained a steady flow (indicated by flow meter), stopcocks at both ends were closed and the glass container removed from the flow line. The collection time was less than 5 minutes. This has become a preferred method and has been used continuously. Whole-gas samples collected in 500-mL glass containers are brought back to the laboratory for processing. About 99 percent of the gas collected is air. Separation of CO₂ from air required a specially designed, W-shaped glass coil trap (fig. 4). The gas sample from the field collection was allowed to flow slowly through an H₂O trap cooled with a dry-ice alcohol slurry to trap the water vapor, then through the W-shaped trap, cooled with liquid nitrogen to trap the CO₂. Noncondensable gases exited through the vacuum pump. The process was completed in 5 hours for 3 L of gas and 3 hours for 500 mL of gas.



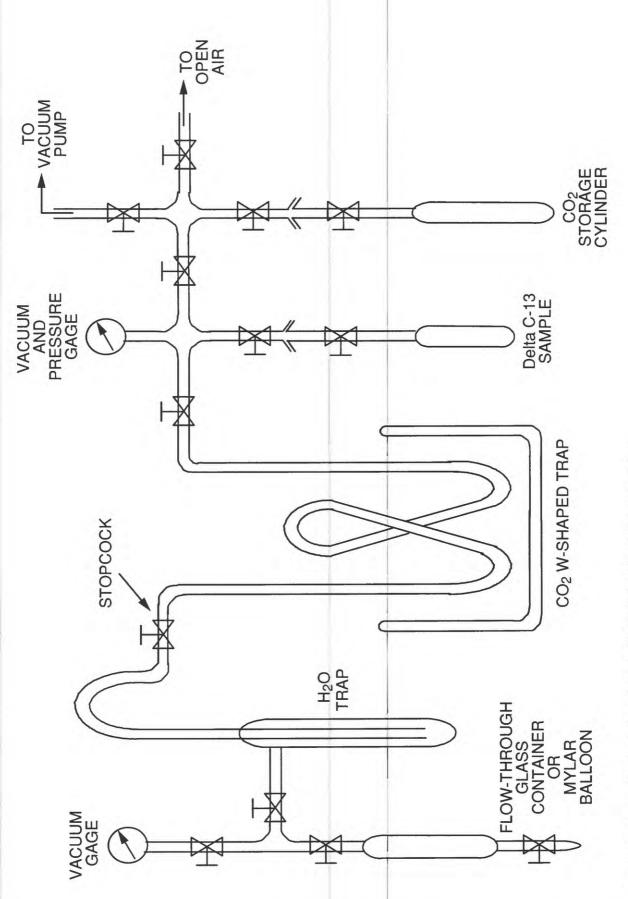


Figure 4. System for separation of carbon dioxide from air for whole-gas samples.

10 Interpretation of Chemical and Isotopic Data From Boreholes in the Unsaturated Zone at Yucca Mountain, Nevada

The method for ¹⁴C-sample collection was similar to the MS method used for δ^{13} C samples except that the collection time is 5–10 days depending on the CO₂ concentration of the gas. The CO₂ gas trapped in the MS was degassed in the laboratory, and heated in the vacuum line system to 350°C to release the trapped CO₂. Released carbon dioxide was collected in the cold trap, volume measured, and transferred to the storage cylinders. In the earliest stages of this study, some of the ¹⁴C samples were collected by sorption in concentrated KOH solution as described in Haas and others (1983) and Yang and others (1985).

Collection from Open Boreholes

After a borehole was drilled, the atmospheric air that entered the formation during the drilling process was removed by evacuation from the surface with a large-capacity pump. The tracer (SF₆) concentration in the evacuated air was continuously monitored. Disappearance of the SF₆ (concentration less than 0.1 ppm) assures the complete removal of the drilling air. Prototype tests for gas sampling from open boreholes was conducted by the U.S. Geological Survey near Superior, Ariz., in 1990, and results were reported by Peters and others (1991).

For UE-25 UZ#4 and UZ#5 boreholes, casing was retained inside the borehole for 6 years. Therefore, gas sampling was not conducted. Packers were installed inside the open boreholes in NRG-6, SD-12, and UZ#16 for gas-sample collections. Two intervals were packed in NRG-6 (one at the Tiva Canyon Tuff and one at the Topopah Spring Tuff), five intervals were packed in UZ#16 (one between the Tiva Canyon Tuff and Topopah Spring Tuff; two within the Topopah Spring Tuff, one between the Topopah Spring Tuff and Prow Pass Tuff, and one at the bottom of the borehole in the Prow Pass Tuff), and two intervals were packed in SD-12 (both within the Topopah Spring Tuff). In addition, a simple gassampling technique using clusters of nylon tubes hanging down the borehole at different depths was conducted at NRG-6, NRG-7a, and UZ#16.

Gas-composition samples were collected using a syringe inserted into a three-way stopcock in the gas-sampling line in the same way as described above. Each probe was sampled daily during a gas-sampling trip, more frequently when abnormal CO_2 concentrations were observed (usually rock-gas contains higher CO_2 concentration than atmospheric CO_2 , which is about 350 ppmv).

For the δ^{13} C samples, a 3-L Mylar balloon was used to collect a rock-gas sample. A deflated balloon was connected to the outlet of the pump and inflated with the sample gas.

Carbon-14 samples were collected the same as for the instrumented borehole. The gas stream was initially passed continuously through a silica-gel tower to remove moisture (fig. 3), then through a 300-mL stainless-steel cylinder containing a 50-nm, anhydrous (dehydrated under a vacuum at 350°C) molecular sieve to trap the CO₂ gas. The 50-nm molecular sieve strongly traps CO₂, which may be later recovered in the laboratory by heating the stainless-steel cylinder to 350°C (containing the molecular-sieve pellets) under a vacuum. The collection time is 5–10 days depending on the CO₂ concentration of the gas.

Analysis of Gas Samples

Gas chromatography was used for composition analyses. Sulfur hexafluoride (SF_6) was measured using an electron-capture detector with pure nitrogen gas as a carrier gas. Carbon dioxide was measured using a flame-ionization detector and pure nitrogen gas as a carrier gas. Nitrogen (N_2) , oxygen (O_2) , and argon (Ar) were measured using a thermalconductivity detector and pure helium gas as a carrier gas. Nitrogen, oxygen, and argon were analyzed at a U.S. Geological Survey laboratory in Reston, Va. Analytical errors are about ± 0.004 ppm for SF_6 in a concentration range of 0.5 to 1.5 ppm, ± 0.003 percent for CO₂ in a concentration range of 0.01 to 0.10 percent by volume, 0.1 percent for N_2 and O_2 , and ± 0.02 percent for Ar at atmospheric concentrations.

Samples for δ^{13} C were analyzed by mass spectrometry in the U.S. Geological Survey laboratory in Denver. The precision of δ^{13} C analysis was about ±0.2‰. Carbon-14 samples were sent to Geochron Laboratories (Krueger Enterprises, Inc.), Cambridge, Mass., for ¹⁴C determination by gas counting in a gas-proportional counter. Uncertainty in the ¹⁴C measurement was ±0.7 pmc. Conventional ¹⁴C determination (proportional counting, or liquid scintillation counting) requires about 1–2 L of pure CO₂ gas at one atmosphere and 25°C. Analysis by TAMS method requires only 10–20 mL of CO₂ gas at the same pressure and temperature; however, the cost of analysis is twice as great by TAMS than by the conventional method. Only a few samples from UZ–1 have been run by TAMS. Small ¹⁴C samples were sent to the University of Arizona in Tucson for analysis by TAMS. Uncertainty in the ¹⁴C measurement was ± 1.5 pmc.

INTERPRETATION OF CHEMICAL AND ISOTOPIC DATA

Understanding the unsaturated-zone gas and water transport and flow mechanism at Yucca Mountain is essential to the site-characterization program. Chemical composition of pore water (which reflects the extent of water-rock interactions between the recharge water and the matrix rock), tritium, and ¹⁴C ages, provide insight on the nature of flow mechanisms and residence times of the unsaturated-zone water. Carbon-14 concentration measurement in the gaseous phase can provide information relevant to the residence time of CO_2 in the unsaturated zone. Delta carbon-13 isotopic data can help to identify carbon sources, a necessary step in ¹⁴C age estimation. Also, a depth profile of gas carbon isotopic data can provide information on gas-flow mechanisms through the unsaturated zone as well as interactions with aqueous phase and calcite mineral. From the present chemical and isotopic data, along with previously published USW UZ-1 data collected at Yucca Mountain (Yang and others, 1993), preliminary conceptual hydrologicflow models are described.

Aqueous-Phase Data

Samples for aqueous-phase chemical data can only be acquired from drill cores where water contents are greater than 7.7% by weight (Mower and others, 1994). The water contents of cores vary according to geologic unit and to degree of welding. As indicated in table 1 (Loskot and Hammermeister, 1992), the densely welded units sampled in UE–25 UZ#4 and UZ#5 have the smallest water contents, ranging from 2.4% to 6.4% (gram weight of H₂O per gram of dry rock times 100) in the Tiva Canyon Tuff and ranging from 0.7% to 3.5% in the Topopah Spring Tuff. The nonwelded part of the Tiva Canyon Tuff had the largest water content of the nonwelded units sampled, with a maximum average water content of 36.3% in borehole UZ#4. Unnamed bedded tuff units generally have average water contents of about 16.7%. The Calico Hills Formation in USW UZ-14 has average water content of about 17.5%.

Pore-Water Chemistry

Water for chemical analyses was extracted from cores obtained from bedded tuff below the Pah Canyon Tuff in UE-25 UZ#4 at depths ranging from about 91 to about 100 m and from cores obtained near the top of the Topopah Spring Tuff in UZ#5 at depths ranging from about 103 to about 105 m. These data have been published previously (Yang and others, 1988; Yang, 1992). All other UZ-hole and NRG-hole pore-water compositions were obtained from nonwelded tuffs, bedded tuff, or the Calico Hills Formation because of higher moisture content in these units. These data are presented in tables 2, 3, and 4 for UE-25 UZ#16, USW UZ-14, and USW NRG-6 and NRG-7a, respectively. Also, precipitation (rainwater) near the neutron-access boreholes (UE-25 UZN#2) and ground water inside the neutronaccess boreholes (UE-25 UZN#2 and USW UZN-46) were collected whenever water was detected at the bottom of the neutron-access boreholes (water was detected during the spring snowmelts or after the summer rainstorms). However, water inside the neutronaccess boreholes usually remained there only for a couple of days and then seeped into depth. Results of these chemical analyses are also presented in table 2 for references.

Chemical changes induced by compression appear to be minor, as evidenced from results of compression and centrifugation-extraction procedures (Yang and others, 1990). Peters and others (1992) reported pore-water chemistry changes under greater compression loads. Complete analyses of major- and trace-element concentrations on individual samples were not possible because of limited volumes of water (^{14}C analysis requires about 70–80 mL of water for each sample); only major ions were selected for the chemical analyses.

A Piper diagram is a convenient graphical method for displaying the chemical composition of water. For example, in figure 5 it can be seen that major cations (sodium, calcium, and magnesium concentrations in percent milliequivalent) of one water sample are represented by one symbol in the lower left-hand side of the triangle, and major anions (chloride, sulfate, and bicarbonate plus carbonate in
 Table 1.
 Summary of relation of gravimetric water-content measurements of composite core to geologic unit and degree of welding for boreholes UE-25 UZ#4 and UE-25 UZ#5¹, Yucca Mountain, Nevada

Lithologic			content, n/gram		Degree of
unit	UE-25	UZ#4	UE	25 UZ#5	welding
-	Data range	Average	Data range	Average	-
Tiva Canyon	0.036-0.0642	0.039	0.024-0.036	0.030	Densely welded
	0.061-0.063	0.062			Moderately welded
	0.253-0.521	0.363	0.145-0.290	0.202	Partly to nonwelded
Yucca Mountain	0.101-0.210	0.157	0.059-0.143	0.110	Partly to nonwelded
Pah Canyon	0.092-0.182	0.134	0.084-0.221	0.122	Partly to nonwelded
Bedded tuff	0.069-0.391	0.167	0.078-0.365	0.176	
Topopah Spring			0.221-0.279	0.248	Nonwelded
	0.007-0.035	0.020	0.011-0.015	0.013	Densely welded

[All water-content data in gram per gram; --, indicates no data]

¹From Loskot and Hammermeister (1992).

percent milliequivalent per liter) of the same sample are also represented by the same symbol in the lower right-hand side of the triangle. When these two major cation and anion locations are projected upward parallel to their respective grids, they intersect at one point in the upper diamond diagram and are represented by the same symbol for both major cation and anion compositions of that sample. The locations in the diamond diagram represent the type of water composition for each sample. Calcium chloride or sulfate type water formed from recharging water interacting with near-surface or shallow-depth soils will be located near the top part of the diamond. The ground water that has interacted with deep Calico Hills Formation rocks will result in sodium carbonatebicarbonate type water located near the lower part of the diamond. The middle part of the diamond will represent intermediate chemical compositions for ground water in the Topopah Spring Tuff. Dissolved solids in pore water expressed in parts per million are represented by the circle size with the scale shown in figure 5.

Figures 5, 6A and 6B, and 7A and 7B are Piper diagrams for (1) the top 75 m (245 ft) of USW UZ-14 and saturated-zone chemical data; (2) USW NRG-6 and NRG-7a and lithologic contacts and adjacent beds; and (3) USW UZ-14 and UE-25 UZ#16. Figure 5 shows saturated-zone water chemistry (Benson and McKinley, 1985) compared to the composition of unsaturated-zone pore water in the top 75 m of USW UZ-14, between the Tiva Canyon

Tuff and pre-Pah Canyon bedded tuff. It is evident from the plot that dissolved solids are, in most cases, significantly higher in the unsaturated-zone pore water than in the saturated-zone ground water except in some saturated-zone carbonate aquifers, where both are about the same. This comparison is based on saturated-zone chemical-composition data that were collected prior to implementation of the approved U.S. Geological Survey Yucca Mountain Project quality-assurance program and, therefore, the data are not qualified. Furthermore, pore water in the Tiva Canyon, bedded tuff, and Pah Canyon tuffs are all grouped near the top of the diamond in the Piper diagram (that is, calcium sulfate or chloride type water), whereas saturated-zone ground waters are grouped near the bottom of the diamond (that is, sodium bicarbonate or carbonate type water). The composition of pore water from NRG-6 and NRG-7a boreholes is given in figure 6A; pore-water composition of lithologic contacts and adjacent beds is given in table 5 and in figure 6B. In figure 6A, sample G represents core obtained from borehole NRG-6 at a depth of 256 feet. The location of this core is in the upper Topopah Spring Tuff and contains about 3,500 mg/L in dissolved solids. It is too deep in the borehole to be explained as a result of surface evaporation. Rather, such a large value of dissolved solids probably resulted from prolonged contact of percolating water with the less permeable silicate rocks without replacement by fresher, younger water.

Table 2. Chemical composition of pore-water and ground-water samples from boreholes UE-25 UZ#16, UE-25 UZ-N2, and UZ-N46, Yucca Mountain, Nevada

 $[\mu S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; - - -, data not available; 0, values below detection limit; <, less than;$ *, contamination with sodium chloride during water-level measurement (accidentally dropped the measuring tape coated with sodium chloride); charge balance, (milliequivalent cation - milliequivalent anion)/(milliequivalent cation + milliequivalent anion) times 100]

Sample Identification	Symbol in Piper diagram (fig. 7B)	Average depth (meters)	Date	рН	Specific conductance (µS/cm)	Calcium Ca (mg/L)	Magnesium Mg (mg/L)	Sodium Na (mg/L)	Silica SiO ₂ (mg/L)
UZ-N2-Precip		0	03-31-92			0.7	0.5	0.8	0.9
UZ-N2Water		15.8	08-18-89	7.7	308	14	2.3	51	18
UZ-N2Water		15.8	02-14-92			1.4	0.5	1.7	0
UZ-N2-Water		15.8	031692			14.4	3.9	25.1	5.8
UZ-N2Water		15.8	03-31-92			25	4.7	16.2	11.8
UZ-N46-Water		30.1	02-14-92			0.8	0.5	1.6	0.2
UZ-16-Pore water									
UZ-16/163.5-163.9	1	49.90	120292	7.6	425	42.5	13.4	21.5	77.5
UZ-16/180.9-181.3	2	55.20	11-16-92	7.5	430	55	11	20	83
UZ-16/1166.19-1166.47	3	367.74	092794	8.7	710	28.9	13.7	83.6	57.1
UZ-16/1227.4-1227.7	4	374.17	08-09-93	8.1	430	26.5	6.2	47.9	62.2
UZ-16/1235.1-1235.41	5	376.52	08-11-93	8.2	480	33.5	7.9	51.3	52.9
UZ-16/1269.6-1269.9	6	387.04	08-04-93	8.5	430	14.1	2.4	67.5	57.1
UZ-16/1280.4-1280.8	7	390.33	09-02-93	8.3	530	20.5	3.7	92.0	71.8
UZ-16/1296.8-1297.06	8	395.33	09-23-93	7.4	930	32.4	19.7	98.2	46.7
UZ-16/1317.9-1318.2	9	401.76	09-09-93	7.3	420	20.6	5.1	60.1	131.6
UZ-16/1343.7-1344.0	Α	409.62	070193	8.4	530	17	2.4	99	62.1
UZ-16/1358.0-1358.4	В	413.98	05-06-93	7.5	550	3.4	0.3	76.7	47.9
UZ-16/1379.6-1379.9	С	420.56	062993	8.6	490	4.4	0.6	95	66.3
UZ16/1389.3-1389.6	D	423.52	05-18-93	7.0	530	3.6	0.9	114.6	62.5
UZ16/1395.5-1395.9	Ε	425.41	03-31-94	7.8	710	5.4	0.3	155	88.0
UZ-16/1397.7-1398.0	F	426.08	070793	8.7	550	5	0.5	124	79.2
UZ-16/1398.5-1398.7	G	426.29	040594	8.0	710	5	0.4	145	123
UZ-16/1408.2-1408.6	Н	429.28	07 <u>-</u> 2893	9.2	580	3.3	0.3	104	68.5
UZ-16/1412.9-1413.2	Ι	430.71	091693	8.7	450	1.2	0.1	101	75.9
UZ-16/1428.1-1428.4	J	435.35	09-14-93	8.8	570	1.9	0.1	134	80.5
UZ-16/1434.2-1434.6	К	437.21	071393	8.5	550	3.2	0.6	113	109.1
UZ-16/1442.8-1443.2	L	439.83	06-17-93	7.6	550	1.7	0.8	79.9	68.9
UZ-16/1486.9-1487.3	Μ	453.27	09-21-93	9.2	360	6.3	0.8	79.5	233.3
UZ-16/1601.1-1601.5	Ν	488.08	12-30-93	8.9	570	10	0.3	100	36
UZ-16/1607.7-1608.1	0	490.09	012494	9.0	660	25	0.3	108	34
UZ-16/1643.4-1647.2	Р	501.49	03-01-94	9.0	490	91	12	34	70
UZ-16/1651.6-1651.7	R	503.44	031594	8.4	420	17.3	0.3	66	47.4
UZ-16 ground water #1									
(1609.0-1614.0)		491.19	02 — 24—93			11.4	1.6	7 9 .2	36.2
UZ-16 ground water #2									
(1609.0-1614.0)		491.19	022593			19.2	2.1	175.1*	25.5
UZ-16 ground water #3									
(1609.0-1614.0)		491.19	022593			30.1	2.9	360.5*	27.2

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Table 2. Chemical composition of pore-water and ground-water samples from boreholes UE-25 UZ#16, UE-25 UZ-N2, and UZ-N46, Yucca Mountain, Nevada-Continued

[µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; - - -, data not available; 0, values below detection limit; <, less than; *, contamination with sodium chloride during water-level measurement (accidentally dropped the measuring tape coated with sodium chloride); charge balance, (milliequivalent cation – milliequivalent anion)/(milliequivalent cation + milliequivalent anion) times 100]

Sample Identification	Symbol in Piper diagram (fig. 7B)	Average depth (meters)	Date	рН	Specific conductance (µS/cm)	Caicium Ca (mg/L)	Megnesium Mg (mg/L)	Sodium Na (mg/L)	Silica SiO ₂ (mg/L)
UZ-16 ground water #1								· · · · · · · · · · · · · · · · · · ·	-
(1649.3-1659.2)		504.22	030893			10.3	1.8	76.1	170.6
UZ-16 ground water #2									
(1649.3-1659.2)		504.22	03 -09-9 3			8.6	0.7	65.4	18.4
UZ-16 ground water									
(1649.3-1686.2)		508.33	03-15-93			8.4	1.3	87.2	16.5

Sample Identification	Aiuminum Ai** (mg/L)	Bicarbonate HCO ₃ (mg/L)	Carbonate CO ₃ (mg/L)	Chiorine Ci (mg/L)	Bromine Br (mg/L)	Nitrate NO ₃ (mg/L)	Sulfate SO ₄ (mg/L)	Charge balance
UZ-N2-Precip	0	23.3	0	2.4	0	2	4.1	-0.5
UZ-N2-Water		112	0	10	0.54		29	0.4
UZ-N2-Water	0	11.7	0	12.2	0	8.2	7.8	-0.6
UZ-N2-Water	0.0	58.2	0	10	1.7	27.3	21	0.0
UZ-N2Water	0	127.6	0	5.8	0.9	19.7	15.6	-0.6
UZ-N46-Water	0.0	23.3	0	3.3	0	1.6	4.7	-0.5
UZ-16-Pore water								
UZ-16/163.5-163.9	0.5	114.7	45.0	32.4	0.0	23.1	72.3	-2.0
UZ-16/180.9-181.3	0.1	120	0.0	38	<1	33	38	0.2
UZ-16/1166.19-1166.47	0	1 96	0	82	0	17	28	-1.4
UZ-16/1227.4-1227.7	0.3	137.0	0	24	0	23	26	1.2
UZ-16/1235.1-1235.41	0	154	0	52	0	26	29	-4.7
UZ-16/1269.6-1269.9	0	139	13	27	0	18	14	-2.7
UZ-16/1280.4-1280.8	1.5	192.0	0	28	0	19	19	6.9
UZ-16/1296.8-1297.06	0	324	12	50	0	19	18	-1.9
UZ-16/1317.9-1318.2	1.1	171	0	32	0	20	18	-4.0
UZ-16/1343.7-1344.0	1.7	47.6	58.8	56	0.0	18	23	6.5
UZ-16/1358.0-1358.4	1.1	140.3	0	22.8	0.0	16.1	18.7	-0.1
UZ-16/1379.6-1379.9	2.6	72	46.8	21	0.0	18	25	0.3
UZ-16/1389.3-1389.6	2.0	122	36.0	23.5	0.0	18.5	23.8	0.6
UZ-16/1395.5-1395.9	3.9	216.0	24.0	17	0	16	22	11.9
UZ-16/1397.7-1398.0	4.7	131.8	35.4	45	0.0	25	45	-0.3
UZ-16/1398.5-1398.7	7.8	237.0	31.0	14	0	16	20	4.8
UZ-16/1408.2-1408.6	3.4	72	70.8	20	0.0	14	16	0.1
UZ-16/1412.9-1413.2	1.0	165.0	0	26	0	24	30	0.1
UZ-16/1428.1-1428.4	3.4	160.0	43.0	23	0	19	23	3.9
UZ-16/1434.2-1434.6	6.1	72	70.8	23	0.0	16	19	0.3
UZ-16/1442.8-1443.2	1.2	18.3	87.6	18.9	0.0	11.3	13.7	-0.6
UZ-16/1486.9-1487.3	26.2	137.0	0	38	0	6	11	2.7
UZ-16/1601.1-1601.5	0.7	181.0	0	53	0	13	27	-3.6
UZ-16/1607.7-1608.1	1.0	170.0	0	71	0	10	33	2.8
UZ-16/1643.4-1647.2	3	162.0	0	70	0	8	28	13.6

Table 2. Chemical composition of pore-water and ground-water samples from boreholes UE-25 UZ#16, UE-25 UZ-N2, and UZ-N46, Yucca Mountain, Nevada-Continued

[µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; - - -, data not available; 0, values below detection limit; <, less than; *, contamination with sodium chloride during water-level measurement (accidentally dropped the measuring tape coated with sodium chloride); charge balance, (milliequivalent cation – milliequivalent anion)/(milliequivalent cation + milliequivalent anion) times 100]

Sample Identification	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-16/1651.6-1651.7	0.7	87.0	19.0	27	0	6	20	6.1
UZ-16 ground water #1				I				
(1609.0-1614.0)	1.2	210.6	0	10.6	0.6	0.2	29.1	-0.2
UZ-16 ground water #2								
(1609.0-1614.0)	0	196.7	0	188.0*	0.6	0	31.8	-0.4
UZ-16 ground water #3								
(1609.0-1614.0)	0.2	200.0	0	488*	0.7	0.5	34.6	0.3
UZ-16 ground water #1								
(1649.3-1659.2)	19.9	164.2	0	13.4	0	0.3	27.7	0.3
UZ-16 ground water #2								
(1649.3-1659.2)	0	151.6	0	10.6	0	0	25.5	0.0
UZ-16 ground water								
(1649.3-1686.2)	0.1	197.3	0	8.6	1	0	27.7	0.3

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

Table 3. Chemical composition of pore-water samples from borehole USW UZ-14, Yucca Mountain, Nevada

[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; N/A, not analyzed; up1, uniaxial pressure stage #1; charge balance, (milliequivalent cation - milliequivalent anion)/(milliequivalent cation + milliequivalent anion) times 100]

Sample Identification	Symbol in Piper dlagram (fig. 7B)	Average depth (meters)	Date	pН	Specific conductance (µS/cm)	Calcium Ca (mg/L)	Magnesium Mg (mg/L)	Sodium Na (mg/L)	Silica SiO ₂ (mg/L)
UZ-14/45.0-45.4/up1	1	13.78	09-19-94	8.6	1,320	19.6	6.1	249.3	59.5
UZ-14/85.2-85.6/up1	2	26.03	032494	6.9	630	49.9	13.2	43.5	89.8
UZ-14/91.0-91.3/up1	3	27.80	03 –17–94	7. 6	530	40.7	10.1	37.1	80.6
UZ-14/95.5-95.9/up1	4	29.17	04-2194	7.2	600	53.3	13.2	38.1	81.5
UZ-14/96.2-96.6/up1	5	29.38	05-03-94	6.9	550	46 .9	12.7	33.6	79.6
UZ-14/100.4-100.8/up1	6	30.66	03-22-94	7.0	600	51.1	13.8	41.3	91.8
UZ-14/114.8-115.0/up1	7	35.02	09-01-94	6.6	540	49.0	10.5	35.9	93.9
UZ-14/135.5-135.8/up1	8	41.36	04-12-94	6.9	690	68.5	14.3	56.2	92.0
UZ-14/144.8-145.2/up1	9	44.20	08-11-94	7.7	650	65.5	12.0	48.2	81.5
UZ-14/147.7-148.1/up1,2	Α	45.08	04-14-94	6.9	640	54.8	11.5	51.6	77.3
UZ-14/177.6-177.9/up1	В	54.19	09-12-94	6.5	730	67.8	11.3	48.7	77.5
UZ-14/178.1-178.4/up1	С	54.35	04-19-94	6.8	740	64.0	10.6	49.1	93.1
UZ-14/215.7-216.1/up2	D	65.81	04-21-94	6.9	710	65.5	10.7	39.4	97.8
UZ-14/225.9-226.2/up1	Е	68.92	10-31-94	7. 9	640	58.6	10.4	48.4	91.2
UZ-14/235.1-235.4/up1	F	71.72	03-02-94	7.1	630	67	10.5	29	63
UZ-14/240.8-241.1/up1	G	73.46	03-02-94	7.6	810	32	1	103	61
UZ-14/245.5-245.8/up1	Н	74.89	0207 9 4	6.8	580	65	12	9	46
UZ-14/1258.5-1258.8/up1vb	Ι	383.65	01-14-94			43	3.7	67	35
UZ-14/1277.4-1277.7/up1	J	389.41	01-14-94	N/A	N/A	62	4.5	49	44
UZ-14/1277.7-1278.0/up1	К	389.50	01-14-94	N/A	N/A	74	5.1	45	38
UZ-14/1409.4-1409.8/up1	L	429.65	013095	7.8	720	30.0	0.7	88.0	57.0

Table 3. Chemical composition of pore-water samples from borehole USW UZ-14, Yucca Mountain, Nevada-Continued

|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; N/A, not analyzed; up1, uniaxial pressure stage #1; charge balance, (milliequivalent cation – milliequivalent anion)/(milliequivalent cation + milliequivalent anion) times 100]

Sample Identification	Symbol in Piper diagram (fig. 7B)	Average depth (meters)	Date	рН	Specific conductance (µS/cm)	Calcium Ca (mg/L)	Magnesium Mg (mg/L)	Sodium Na (mg/L)	Silica SIO ₂ (mg/L)
UZ-14/1419.5-1419.8/up1	M	432.72	122294	8.3	410	20.0	0.6	68.0	60.0
UZ-14/1461.9-1462.1/up1	Ν	445.62	04-04-95	7.6	570	9.2	0.1	128	68.7
UZ14/1495.81496.0/up1	0	455.95	04-11-95	8.4	500	2.1	0.0	122	56.7
UZ-14/1524.55-1524.75/up1	Р	464.73	04-14-95	7.7	560	1.1	0.1	137	54.8
UZ-14/1542.3-1542.8/up1,2,3	R	470.18	07-25-94	8.6	760	3.6	0.5	207	143.0
UZ-14/1563.6-1563.8/up1,2,3	S	476.62	08-30-94	8.7	660	1.2	0.2	155.0	72.0
UZ14/1564.6-1564.8/up1,2,3	Т	476.92	08-23-94	9.0	590	1.3	0.2	129	140.4
UZ-14/1564.9-1565.0/up1	U	477.01	08-1794	8.3	690	1.7	0.5	169.0	54.0
UZ-14/1585.0-1585.2/up1	v	483.14	09-14-94	8.9	460	0.9	0.3	106.8	74.5
UZ-14/1585.3-1585.6/up1,5	W	483.23	10-03-94	9.3	400	1.2	0.5	85.0	75.0
UZ14/1605.91606.1/up1	Х	489.51	10-07-94	8.9	470	1.0	0.3	87.8	67.2
UZ-14/1644.3-1644.5/up1	Y	501.21	011995	8.8	420	2.2	0.7	110.0	74
UZ-14/1674.8-1675.1/up1	Z	510.54	10-24-94	7.2	N/S	1.8	0.6	58.0	64.6
UZ-14/1695.4-1695.6/up1	\$	516.79	12-29-94	7.9	N/A	1.4	1.1	115.8	55.9
UZ-14/1715.0-1715.3/up1	&	522.79	032895	7.3	390	0.2	0.0	88	52.9
UZ-14/1734.5-1734.7/up1	*	528.71	05-02-95	8.7	750	2.0	0.3	184	50.7
UZ-14/2104.05/well bottom	+	641.33	04-22-94	9.4		2.1	0.7	143	352

Sample Identification	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/up1	1	245	18	245	0	35	33	-1.8
UZ14/85.285.6/up1	0.3	131	0	60	0	22	66	-0.9
UZ-14/91.0-91.3/up1	0.0	87	0	47	0	26	81	-4.1
UZ-14/95.5-95.9/up1	0	73	0	79	0	29	83	-1.9
UZ-14/96.2-96.6/up1	0	79	0	59	0	26	75	-0.9
UZ-14/100.4-100.8/up1	0.0	128	0	44	0	23	83	0.5
UZ-14/114.8-115.0/up1	0	67	0	61	0	25	90	-2.1
UZ-14/135.5-135.8/up1	0	105	0	83	0	23	96	4.6
UZ-14/144.8-145.2/up1	0	118	0	77	0	22	102	-1.7
UZ-14/147.7-148.1/up1,2	0	79	0	83	0	22	102	-1.5
UZ-14/177.6-177.9/up1	0	49	0	100	0	23	130	-2.0
UZ-14/178.1-178.4/up1	0	62	0	97	0	21	120	-3.0
UZ-14/215.7-216.1/up2	0	55	0	85	0	14	130	-3.0
UZ-14/225.9-226.2/up1	0	55	0	93	0	16	116	-2.6
UZ-14/235.1-235.4/up1	0.0	96	N/S	84	0	15	94	-5.7
UZ-14/240.8-241.1/up1	3	162	N/S	99	0	17	100	-11.7
UZ-14/245.5-245.8/up1	0	66	N/S	77	0	12	79	-4.7
UZ-14/1258.5-1258.8/up1vb	0.0	170	N/S	88	0	16	19	-4.9
UZ-14/1277.4-1277.7/up1	0.0	170	N/S	87	0	17	45	-7.1
UZ-14/1277.7-1278.0/up1	0.0	170	N/S	130	0	15	38	-10.3
UZ-14/1409.4-1409.8/up1	0.1	160	0	75	0.0	5	106	-13.2
UZ-14/1419.5-1419.8/up1	1.4	166	0	24	0.0	6	21	1.0
UZ-14/1461.9-1462.1/up1	1.2	265	0	24.2	0	6.2	37.3	1.1
UZ-14/1495.8-1496.0/up1	0.3	228	0	28.0	0	10.8	14.3	3.9

Table 3. Chemical composition of pore-water samples from borehole USW UZ-14, Yucca Mountain, Nevada-Continued

[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; N/A, not analyzed; up1, uniaxial pressure stage #1; charge balance, (milliequivalent cation - milliequivalent anion)/(milliequivalent cation + milliequivalent anion) times 100]

Sample Identification	Aluminum Ai* (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)	Suifate SO ₄ (mg/L)	Charge balance
UZ-14/1524.55-1524.75/up1	1.1	232	0	26.2	0	12.5	22.3	7.2
UZ-14/1542.3-1542.8/up1,2,3	13.8	384	46	20	0	4	28	1.0
UZ-14/1563.6-1563.8/up1,2,3	13.9	160	97	16	0.0	4	14	1. 2
UZ-14/1564.6-1564.8/up1,2,3	9.4	6 1	113	16	0	4	17	0.4
UZ-14/1564.9-1565.0/up1	15.5	376	0	23	0.0	1	30	0.1
UZ-14/1585.0-1585.2/up1	5	98	67	14	0	7	10	1.6
UZ-14/1585.3-1585.6/up1,5	16.3	148	18	11	0.0	6	9	2.4
UZ-14/1605.9-1606.1/up1	6	178	0	18	0	6	9	2.4
UZ-14/1644.3-1644.5/up1	30.9	74.0	79	14	0.0	0	9	5.5
UZ-14/1674.8-1675.1/up1	18	104	0	10	0	4	9	8.6
UZ-14/1695.4-1695.6/up1	10	203	18	21	0	5	26	0.6
UZ-14/1715.0-1715.3/up1	0.6	168	0	11.9	0	3.1	16.0	5.1
UZ-14/1734.5-1734.7/up1	0.1	211	79	39.4	0	5.6	17.5	2.9
UZ-14/2104.05/well bottom	38	229	19	10	0	4	23	10.1

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

Table 4. Chemical composition of pore-water and ground-water samples from borehole NRG-6/7a, Yucca Mountain, Nevada

 $[\mu S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; -, data not available; 0, values below detection limit; up1, uniaxial pressure stage #1; charge balance, (milliequivalent cation - milliequivalent anion)/(milliequivalent cation + milliequivalent anion) times 100]$

Sample Identification	Symbol in Piper diagram (fig. 7B)	Averege depth (meters)	Date	pН	Specific conductance (µS/cm)	Calcium Ca (mg/L)	Magneslum Mg (mg/L)	Sodium Na (mg/L)
NRG-6/158.2-158.6/up1	A	48.28	07-06-94	6.4	1070	122	23.3	35.6
NRG-6/160.8-161.2/up1	В	49.07	011795	7.0	860	1 04	18	35.0
NRG-6/171.0-171.3/up1	С	52.18	07–21–94	7.0	620	70.5	11.5	29.2
NRG-6/175.6-176.0/up1	D	53.58	0801 9 4	6.6	520	49.2	8.6	29.4
NRG-6/219.9-220.2/up1	Е	67.09	11- -309 4	7.0	660	24.3	4.2	99.3
NRG-6/244.6-245.0/up1	F	74.62	01-10-95	6.6	630	33	4.9	72.0
NRG-6/255.9-256.1/up1	G	78.03	011295	6.7	19 20	176	19	215.0
NRG-7a/1492.7-1493.1/up1	Н	455.04	052694			30.6	0.3	74.7
NRG-7/1498.6-1498.9/up1	Ι	456.83	062894	7.5	500	28.7	0.5	73.2

Sample Identification	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)
NRG-6/158.2-158.6/up1	97.4	0	34	0	185	1	32	159
NRG-6/160.8-161.2/up1	84.0	1.6	55	0	148	0.9	35	139
NRG-6/171.0-171.3/up1	79.4	0	48	13	58	0	43	94
NRG-6/175.6-176.0/up1	78.1	0	60	0	47	0	42	64
NRG-6/219.9-220.2/up1	61.4	1	9 2	0	77	0	47	77
NRG-6/244.6-245.0/up1	51.0	0.6	61	0	49	0.1	40	115
NRG-6/255.9-256.1/up1	68.0	0.9	61	0	115	0.0	35	840
NRG-7a/1492.7-1493.1/up1	71.5	0.0	104	34	39	0	18	23
NRG-7/1498.6-1498.9/up1	83.0	1	156	0	50	0	17	18

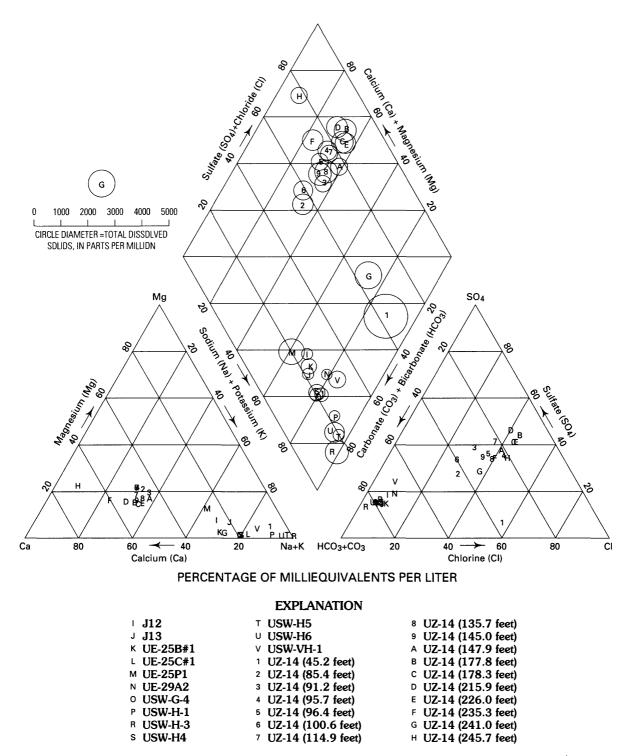


Figure 5. Piper diagram showing top 75 meters of USW UZ-14 pore water (1-9, and A-H) and saturated-zone water compositions (I-V).

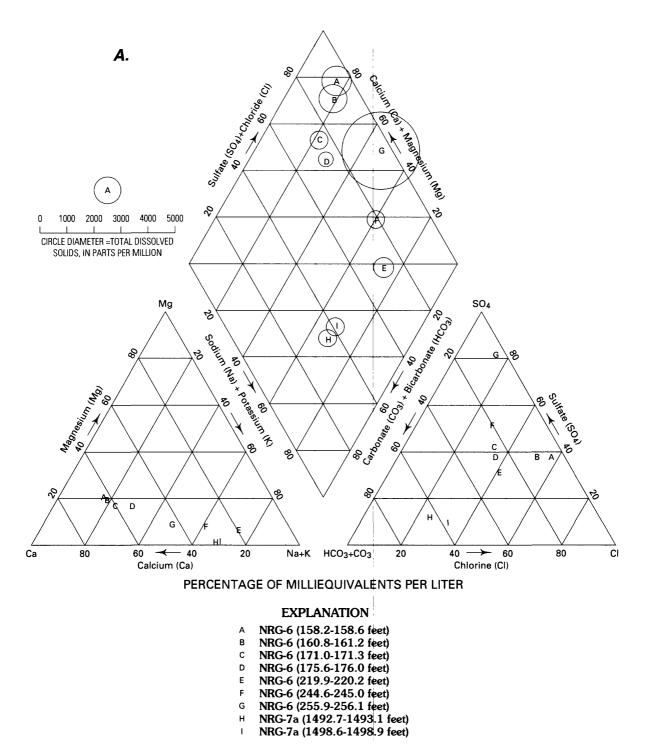


Figure 6. Piper diagram showing (A) USW NRG–6 and 7a pore-water composition, and (B) composition of lithologic contacts and adjacent beds from USW NRG–6, 7a, and unsaturated-zone boreholes.

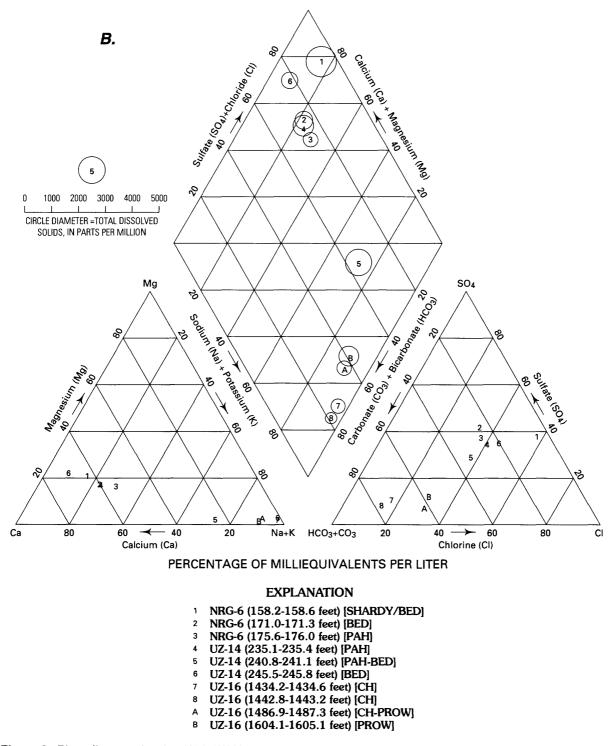


Figure 6. Piper diagram showing (A) USW NRG-6 and 7a pore-water composition, and (B) composition of lithologic contacts and adjacent beds from USW NRG-6, 7a, and unsaturated-zone boreholes—Continued.

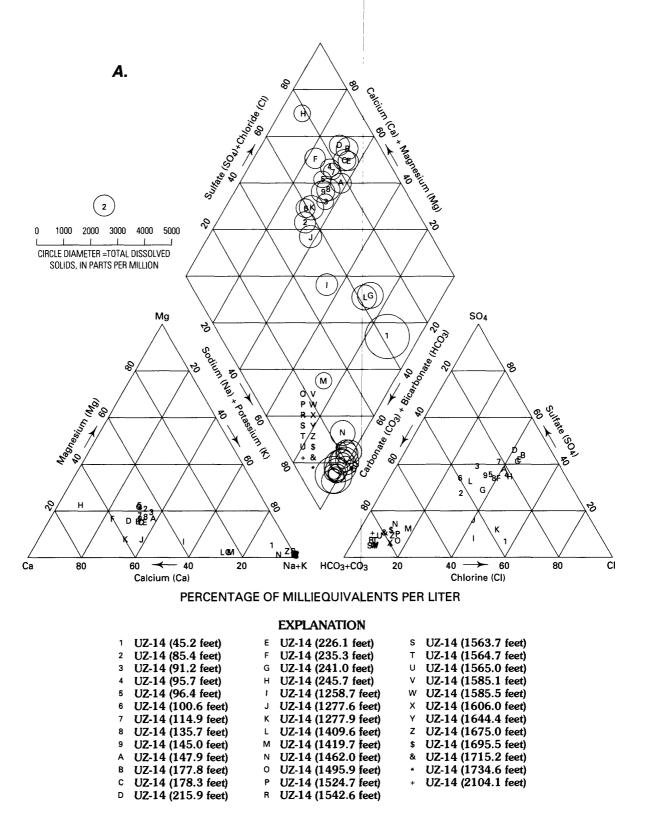


Figure 7. Piper diagram showing pore-water composition of (A) USW UZ-14 and (B) UE-25 UZ#16.

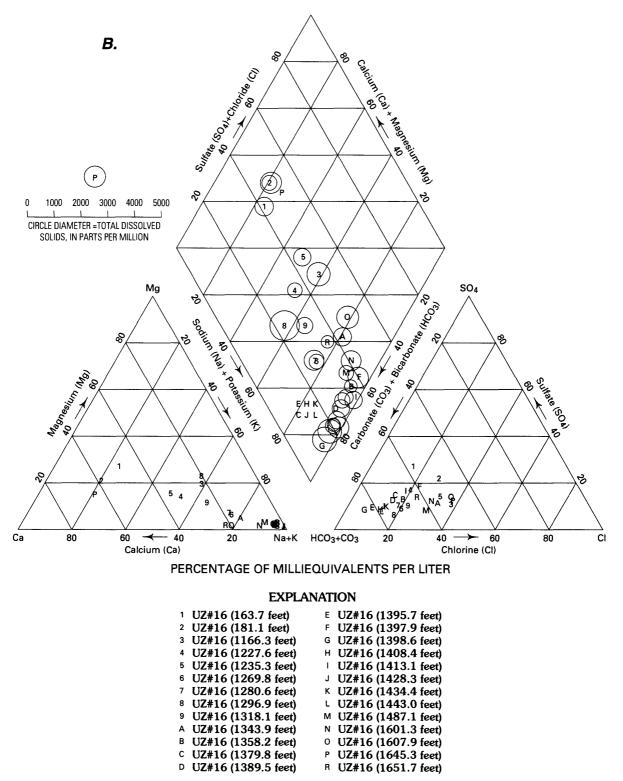


Figure 7. Piper diagram showing pore-water composition of (A) USW UZ-14 and (B) UE-25 UZ#16-Continued.

Table 5. Comparison of pore-water composition in lithologic contacts and adjacent beds, Yucca Mountain, Nevada

[m, meters; mg/L, milligrams per liter]

Sample identification	Symbol in Piper diagram (fig. 6B)	Average Depth (m)	Aluminum Al* (mg/L)	Caicium Ca (mg/L)	Magnesium Mg (mg/L)	Sodium Na (mg/L)	Bicarbonate HCO ₃ (mg/L)
NRG-6/158.2-158.6 (Shardy base/bedded)	1	48.28	0	122	23.3	35.6	34
NRG-6/171.0-171.3 (Bedded)	2	52.18	0	70.5	11.5	29.2	48
NRG-6/175.6–176.0 (Pah Canyon)	3	53.58	0	49.2	8.6	29.4	60
UZ-14/235.1–235.4 (Pah Canyon)	4	71.72	0.0	67	10.5	29	96
UZ-14/240.8-241.1 (Pah Canyon/Bedded)	5	73.46	3	32	1	103	162
UZ-14/245.5-245.8 (Bedded)	6	74.89	0	65	12	9	66
UZ-16/1434.2-1434.6 (Calico Hills)	7	437.21	6.1	3.2	0.6	113	59
UZ-16/1442.8-1443.2 (Calico Hills)	8	439.83	1.2	1.7	0.8	79.9	15
UZ-16/1486.9-1487.3 (Calico Hills/Prow Pass)	Α	453.27	26.2	6.3	0.8	79.5	137
UZ-16/1601.1-1601.5 (Prow Pass)	В	488.08	0.7	10	0.3	100	181

Sample identification	Carbonate CO ₃ (mg/L)	Chioride Ci (mg/L)	Bromine Br (mg/L)	Nitrate NO ₃ (mg/L)	Sulfate SO ₄ (mg/L)	Silica SiO ₂ (mg/L)
NRG-6/158.2-158.6 (Shardy base/bedded)	0	185	1	32	159	97.4
NRG-6/171.0-171.3 (Bedded)	13	58	0	43	94	79.4
NRG-6/175.6–176.0 (Pah Canyon)	0	47	0	42	64	78.1
UZ-14/235.1-235.4 (Pah Canyon)	N/S	84	0	15	94	63
UZ-14/240.8-241.1 (Pah Canyon/Bedded)	N/S	99	0	17	100	61
UZ-14/245.5-245.8 (Bedded)	N/S	77	0	12	79	46
UZ-16/1434.2-1434.6 (Calico Hills)	118	23	0	16	19	109.1
UZ-16/1442.8-1443.2 (Calico Hills)	146	18.9	0	11.3	13.7	68.9
UZ-16/1486.9-1487.3 (Calico Hills/Prow Pass)	0	38	0	6	11	233.3
UZ-16/1601.1-1601.5 (Prow Pass)	0	53	0	13	27	36

*0.45-µm filter paper was used, hence, particulate aluminum is likely included in these values.

For pore water extracted from lithologic contacts and adjacent beds, the pore-water compositions are shown in figure 6B. A shardy base/bedded tuff contact in the NRG-6 borehole is shown by symbol 1 and a Pah Canyon/bedded tuff contact in the USW UZ-14 borehole is shown by symbol 5. Both of these pore waters have larger dissolved-solids values (about 1,200 mg/L) than the adjacent bed pore waters represented by symbols 4 and 6 in figure 6B. This is likely due to the fact that more water is flowing through the adjacent beds than along contacts. More water flow will cause pore water to be dilute. A water from a lithologic contact of the Calico Hills Formation/Prow Pass in the UE-25 UZ#16 borehole is shown by A in figure 6B, which does not show a larger value of dissolved solids. However, this pore water

is very high in aluminum (Al, 26.2 mg/L) and silica $(SiO_2, 233.3 mg/L)$ concentrations (table 5). In most pore waters from bedded tuff and the Calico Hills Formation, aluminum (Al) concentrations are from zero to 2 mg/L, and silica (SiO_2) concentrations are from 50 to 100 mg/L. These pore-water compositions and total dissolved solids in the lithologic contacts and adjacent beds are interesting observations. Although more data are needed to substantiate these observations, they may imply that percolating water is rerouted above the lithologic contacts and flows laterally through tilted porous tuffs (such as bedded tuff or Calico Hills Formation).

Finally, figures 7A and 7B present the compositions of pore water from USW UZ-14 and UE-25 UZ#16 boreholes. In general, the trends are consistent in that ground waters are calcium bicarbonate, sulfate, or chloride type of shallow depths (top of diamond in the Piper diagram) and sodium bicarbonate or carbonate types (near the bottom of diamond) in the Calico Hills Formation. The composition of the porewater sample from 13.8 m (45.2 ft) in USW UZ-14 is an exception to this trend shown by point 1 in figure 7A. This core sample is in the Yucca Mountain Tuff, and the pore water has very high concentrations of dissolved solids. The chemical composition is not the calcium chloride or sulfate type typical of the shallow-depth pore water, but it is similar to the Topopah Spring Tuff pore water, which has an intermediate composition on the diagram (points G and L). Repeated concentration of pore water by evaporation and/or extended water-rock interactions might result in the observed larger dissolvedsolids concentration.

Compositions of pore water from the upper Calico Hills Formation of UE-25 UZ#16 are shown by symbols 4 and 5 in figure 7B. These waters have less water-rock interactions in the Calico Hills Formation and are similar to the water type of a Topopah Spring Tuff. Also, a core at 501.5 m (1,645 ft) deep in the Prow Pass Tuff of UZ#16 is shown by symbol P in figure 7B, which shows a chemical composition similar to symbol 1 at a shallow depth of only 49.8 m (164 ft) in the same borehole (fig. 7B). This suggests that young waters are rapidly transported through fractures with little waterrock interaction and are present in the upper Calico Hills Formation or Prow Pass Tuff of UE-25 UZ#16. This is chemical evidence that preferential flow occurred around UE-25 UZ#16. The faults and fault zones and Sundance fault near this borehole may contribute to fast-flow paths (Spengler and others, 1994).

Tritium

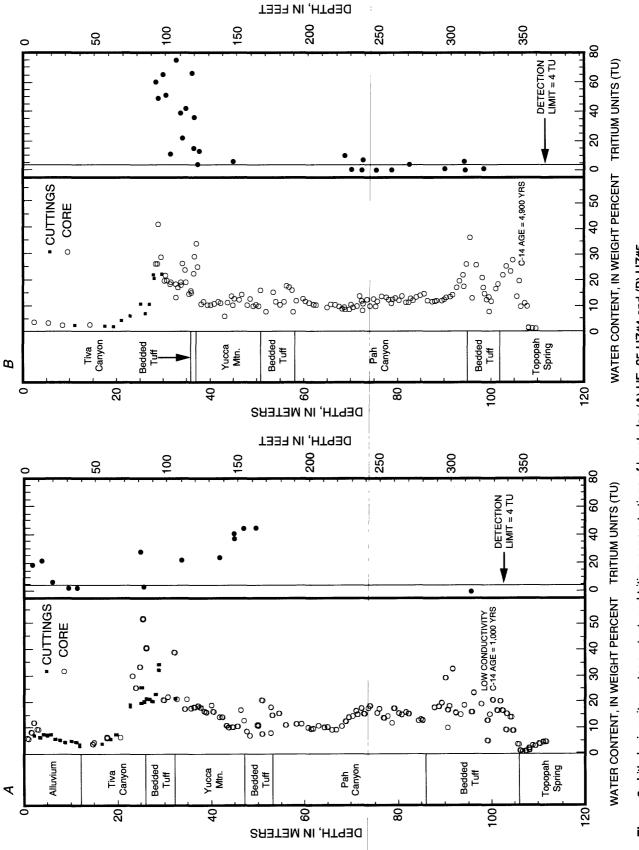
The tritium concentration in precipitation before the atmospheric nuclear tests (pre-1952) was about 10 TU (Davis and Bentley, 1982). However, between 1952 and 1963, the United States and the Union of Soviet Socialist Republics conducted a series of atmospheric nuclear tests in the northern hemisphere that produced significant amounts of tritium in the Earth's atmosphere. As a result, the tritium concentration in precipitation increased rapidly from 1952 and peaked in the early 1960's. Michael (1989) reported a yearly tritium-concentration average of 2,700 TU in precipitation collected in 1963 at a Salt Lake City, Utah, station. A nuclear-test ban in 1963 stopped further tests in the atmosphere, and the tritium concentration gradually decreased to the present level of about 10 to 40 TU measured in precipitation at the Nevada Test Site (Milne and others, 1987).

Water content and tritium data for pore water extracted from cores from UE-25 UZ#4 and UZ#5 are shown in figures 8A and 8B. The tritium concentrations range from zero to 45 TU in UZ#4, and the peak concentration is at about 46-49 m (fig. 8A). In UZ#5, the peak concentration of 75 TU is at about 32 m (fig. 8B). The larger tritium concentrations at these depths relative to the tritium concentrations of 30 to 40 TU in precipitation during the 1980's are likely the result of water infiltrated in the early 1960's. No tritium data were obtained from the surface to a depth of 25 m in borehole UZ#5 because the cores were not available for pore-water extraction. Similarly, no tritium data are available between 50 and 95 m in UZ#4 and between 47 and 67 m in UZ#5. (Tritium data for UZ#4 and UZ#5 were collected prior to implementation of the approved U.S. Geological Survey Yucca Mountain Project quality-assurance program and, therefore, the data are not qualified.)

USW UZ-14 tritium-concentration profiles from pore waters are shown in figure 9. They do not show any significantly large concentrations. However, there are several peaks at 18 to 30 TU in the Pah Canyon Tuff that likely are from the postbomb era.

Only small intervals of the NRG-6 and NRG-7a cores were analyzed for pore-water tritium and ¹⁴C. The data are shown in figures 10A and 10B. High tritium concentrations of about 30 to 150 TU in a broad peak are observed in NRG-6 boreholes (fig. 10A) from 53.3 m to 74.7 m in the Pah Canyon Tuff, and near the top of Topopah Spring Tuff.

Tritium concentrations from UE–25 UZ#16 are plotted in figure 11. An extremely high concentration of about 150 TU is observed at a depth of 48 m just above the bedded tuff unit, which is similar in location to the high tritium values in UZ#4, UZ#5, and NRG–6 near the bedded and Pah Canyon Tuffs. In addition, several postbomb peaks are observed in the Topopah Spring Tuff at depths of 80 m, 204 m, and 317 m to 357 m in UE–25 UZ#16. Other large peaks, in figure 12, are seen in the Calico Hills Formation at depths of 426 m (44 TU) and 437 m (103 TU).





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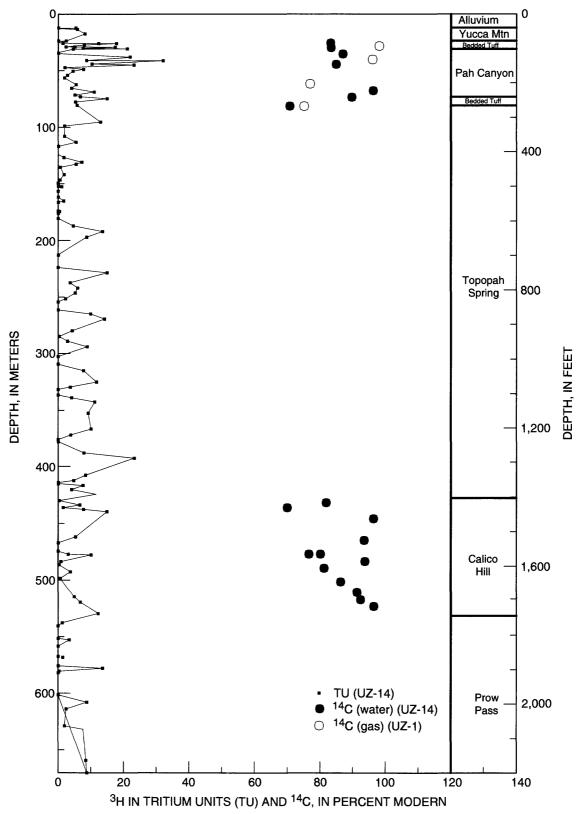
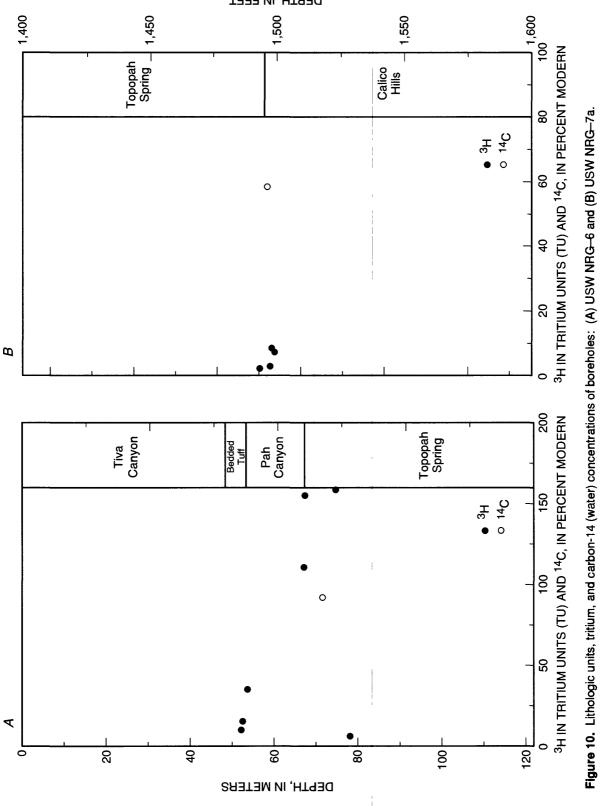


Figure 9. Tritium and carbon-14 data from USW UZ-14 pore water and rock-gas carbon-14 data from USW UZ-1.





28 Interpretation of Chemical and Isotopic Data From Boreholes in the Unsaturated Zone at Yucca Mountain, Nevada

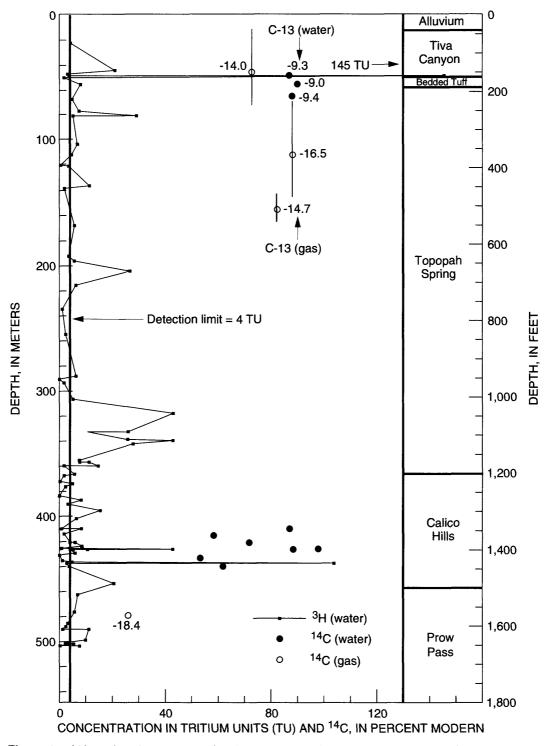


Figure 11. Lithologic units, tritium, and carbon-14 (gas and water) concentrations of borehole UE-25 UZ#16. Lines through gas data indicate zone of sample collection.

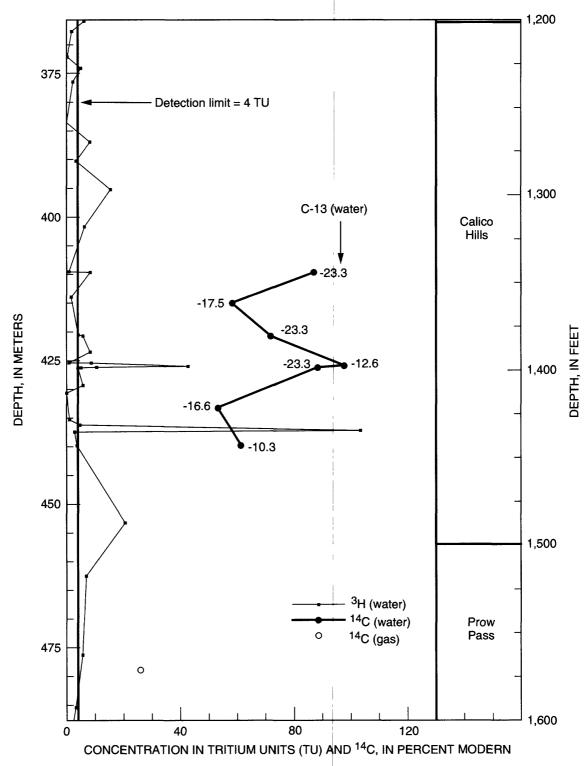


Figure 12. Expanded graph of tritium, carbon-14, and carbon-13 data from figure 11, UE-25 UZ#16.

Postbomb tritium concentrations down to the depth of 60 m were observed in the past (Yang, 1992). However, the large postbomb tritium concentrations found in the Calico Hills Formation of UZ#16 were unexpected. Possible laboratory contaminations were initially suspected, and much effort was devoted to identifying possible sources of contamination. Measurements were made on the laboratory air and storage room (cold room) air in Denver for tritium concentrations, which were about 60 to 100 TU. If contamination occurred, it should affect all samples, not just a few. If radon contamination was present, then the high activity should disappear after a month due to a short half-life of radon gas (3.5 days). A recount of the same sample after a month still showed the high activity. Therefore, radon contamination was ruled out. Possible Pb-210 contamination was considered but was unlikely because water samples for tritium measurements were distilled from cores. Inorganic lead (Pb) compounds are nonvolatile at these temperatures.

From the tritium data observed in the boreholes mentioned above, tritium-concentration inversions (larger tritium concentrations located below the smaller tritium concentration in a vertical profile) occurred in many places. These inversions indicate that vertical water percolation through the matrix is not a normal flow mechanism at Yucca Mountain. Postbomb tritium concentrations were observed down to bedded tuff or Pah Canyon Tuff in many boreholes. The occurrence of postbomb tritium waters (recent water) below old water in a vertical profile is strong evidence of fracture flows occurring at Yucca Mountain. With regard to postbomb tritium concentrations observed at the Calico Hills Formation of UZ#16, we believe these postbomb tritium peaks are real unless they can be proven otherwise. However, the flux is very small because the tritium-peak shape is so narrow. A large flux should result in a broader peak.

Supporting evidence of the above conclusions can be seen from the ${}^{14}C$ and ${}^{36}Cl$ data. Liu and others (1995) reported modern ${}^{36}Cl$ values in the Calico Hills Formation of UZ#16. The ${}^{14}C$ values obtained from pore water of UZ#16 in the Calico Hills Formation also showed young ages near the locations where the high tritium concentrations were found. It has been reported by Spengler and others (1994) that the Sundance fault, trending from northwest to southeast at Yucca Mountain, crosses near the UE-25 UZ#16 borehole. Only fracture flow can explain the observed rapid percolation.

Field observations have shown that: (1) several neutron-access boreholes in washes accumulated 30 to 60 cm of water at the bottom of the boreholes after storms or periods of spring snowmelt and disappeared the next day (Alan Flint, U.S. Geological Survey, oral commun., 1993); and (2) in boreholes USW SD-9 and UE-25 UZ#4, water was dripping down from a borehole wall near fractures (SD-9 and UZ#4 from field log books). Also, many fractures (although not all) are coated with calcite minerals, as reported by Whelan and others (1992, 1994). These calcite deposits indicate that water has flowed through the fractures, depositing the minerals as they became saturated. These fractures are possible conduits for the rapid flow of young water to significant depths.

Carbon isotopes (δ^{13} C and ¹⁴C)

Only one carbon-isotope value was obtained for each borehole of UE-25 UZ#4 and UZ#5 because of the large amounts of time involved in compressing 50 to 90 mL of pore water from cores for each ^{14}C age determination. For other deeper boreholes, such as UE-25 UZ#16 and USW UZ-14, core compression was conducted mostly on the high-moisture-content intervals (or units) (bedded tuff and Calico Hills Formation). Therefore, ¹⁴C data from pore waters are mainly available from these intervals. The ¹⁴C residence time of 1,000 years is indicated for water at a depth of 96.0 to 100.6 m (bedded unit above Topopah Spring Tuff) at UE-25 UZ#4. The water 14 C residence time of 4,900 years at a depth of 103.5 to 105.2 m (in upper Topopah Spring Tuff) in borehole UE-25 UZ#5 is older than water from the corresponding depth in UZ#4 by nearly a factor of five (Yang, 1992). These abrupt changes in ¹⁴C residence times support a rapid flow of younger water through fractures to the location where younger ¹⁴C ages are observed (Yang, 1992).

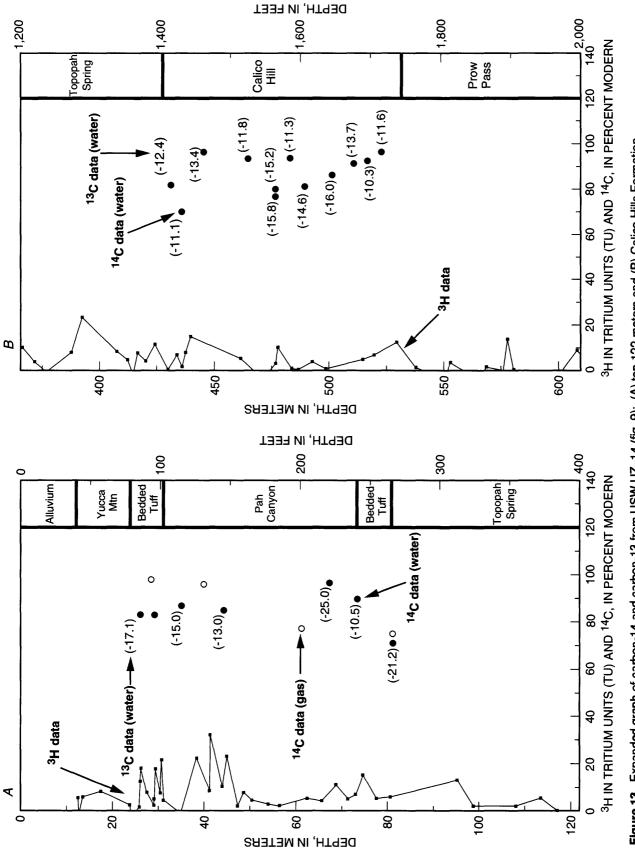
For borehole USW UZ-1, there was no core recovered. Therefore, pore-water isotopic data are not available. However, because borehole USW UZ-14 is about 26.2 m (86 ft) away from USW UZ-1, pore-water isotopic data from USW UZ-14 and UZ-1 should be representative of both boreholes. Carbon-14 data of pore water compressed from borehole USW UZ-14 cores are shown in figure 9 along with gaseous ¹⁴C data from USW UZ-1. Water ¹⁴C values (uncorrected) from the top 91 m (300 ft) ranging from 70 to 95 pmc and are similar to values for the Calico Hills Formation pore-water ¹⁴C values, which are between 70 and 96 pmc (uncorrected) between depths of 426.7 and 522.4 m. It was unexpected to see ¹⁴C values in the Calico Hills Formation of USW UZ-14 between 80 and 96 pmc even at a depth below 500 m. This is guite different from borehole UE–25 UZ#16 where seven 14 C values in the Calico Hills Formation of UE-25 UZ#16 ranged from 53 to 98 pmc, with three of the values between 53 and 61 pmc (see fig. 11 and discussion below). The apparent young ${}^{14}C$ or high ${}^{14}C$ pmc values could be related to: (1) young ${}^{14}CO_2$ 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 (1,257 ft) in order to seal off a borehole wall and prevent perched-water leakage (portland cement contains a small amount of Ca(OH)2, which will absorb atmospheric CO₂ during mixing with water and release the CO₂ during exothermic curation).

Figures 13A and 13B are expanded versions of the top 91 m ¹⁴C data and the Calico Hills Formation ¹⁴C data, respectively, for borehole UZ-14. From figure 13A, gas ¹⁴C values are different from water ¹⁴C values. This indicates that a nonequilibrium condition may exist between gaseous and aqueous phases. ¹³C from gaseous and aqueous phases, and the CO₂(g)-H₂CO₃ (liq.)-HCO₃ (liq.) system also shows a nonequilibrium condition (this will be explained in detail later in the section on δ^{13} C Isotopic Ratio in Gaseous-Phase Chemistry of USW UZ-1). There are no gaseous-phase data in the Calico Hills Formation at present (1995). When borehole UZ-14 is instrumented, gaseousphase chemical and isotopic data will be collected and studied. If the gaseous-phase ¹⁴C age from the Calico Hills Formation is significantly older than the aqueous-phase ¹⁴C values, the apparent young ¹⁴C ages in the aqueous phase will not be the result of gas CO₂ and liquid bicarbonate exchange. The existence of cement in the borehole could release

 CO_2 gas during cement curation. If enough CO_2 gas was released, potential contamination to pore water ¹⁴C age could be significant.

Delta carbon-13 values of pore water are shown in parenthesis in figures 13A and 13B near the respective ¹⁴C data. It is unexpected to see δ^{13} C data so widely spread (-10.3 to -25%) compared to perched water or saturated-zone waters. Soil CO₂ δ^{13} C values have been measured at the Nevada Test Site in the last 3 years by E.A. McConnaughey (Science Applications International Corp., Denver, Colorado, written commun., 1995). Their measured δ^{13} C values vary from year to year depending on the vegetation growth (-10 to -25%), which in turn depends on the amount of precipitation. Therefore, ¹⁴C ages of pore waters will be more variable if these changes exist. Furthermore, due to wide variations in ¹⁴C ages of caliche that dissolved partially or totally into subsurface water, the uncertainty will be larger. It would be difficult to make a good age correction. However, a possible range of ages with some uncertainty can be assigned in the future when more data become available. At present, apparent ages will be used to make preliminary interpretations.

Carbon-14 and δ^{13} C data from UE–25 UZ#16 are plotted in figures 11 and 12. Pore-water ¹⁴C data (uncorrected) from depths between 45.7 and 76.2 m (150–250 ft) are all close to 88 pmc, and δ^{13} C values range from -9.0 to -9.4%, indicating dissolution of caliche. The deeper ¹⁴C data (uncorrected) in the Calico Hills Formation have a wider range of ¹⁴C values (53 to 97 pmc): three in the range of 53 to 61 pmc, three in the range of 72 to 87 pmc, and one at 97 pmc. This wide scatter of ¹⁴C values indicates preferential flow rather than a well-mixed unsaturatedzone water. The flux of the fast-flowing water is small judging from the narrow shape of the tritium peaks. One important consideration is the mixing of young ¹⁴C age water with the old ¹⁴C age water. As calculated by Liu and others (1995), for 99% volume of pore water (matrix water) having an age of 5,000 years mixed with a 1% volume of bomb-pulse component from the fracture fluid, the effect to the matrix ¹⁴C age would be negligible. This mixing effect would not be significant until matrix water ages are more than 35,000 years.





The other consideration is the exchange of younger $^{14}CO_2$ gas with the pore-water bicarbonate, resulting in younger pore water. Due to limited data at present, further confirmation from other boreholes is needed. The gaseous-phase ¹⁴C data shown in figure 11 are not conclusive because the measured δ^{13} C data are between -14‰ and -16.5‰, whereas the USW UZ-1 stemmed-borehole gas data are -18 to -20%. A possible air leak in the inflated packer system and the borehole wall or incomplete removal of air-contaminated rock gas can cause the shift in δ^{13} C to the measured heavier values. However, one value in the Prow Pass from a depth of 477-481 m (1,565–1,578 ft) using a commercially constructed packer system has a ¹⁴CO₂ gas value of 25.8 pmc and $\delta^{13}C$ of -18.4‰, similar to the USW UZ-1 value at depth.

Perched Water

Perched-water compositions from boreholes USW UZ-14, USW NRG-7a, USW SD-9, and SD-7 are presented in table 6. The data are plotted in a Piper diagram in figure 14 along with ONC#1 and USW G-2 samples collected from the saturated zone. Most of these perched-water zones were in the upper Calico Hills Formation, with the exception of UZ-14, which is in the Topopah Spring Tuff. As can be seen from table 6, major cation and anion concentrations were fairly constant throughout the pumping tests for USW UZ-14 and USW SD-7. Chloride concentration, which is hydrologically conservative, is fairly small ranging from about 4 to 8 mg/L except one at 15 mg/L.

The composition of perched water located near or in the upper part of the Calico Hills Formation is, in general, closer to the pore-water composition of the Calico Hills Formation from UE-25 UZ#16 and USW UZ-14 and also similar to saturated-zone water. But the chloride concentrations in all pore water are significantly larger than in the perched water. For example, perched waters collected from USW UZ-14 all have chloride concentration between 6 and 15 mg/L (represented by symbols C through J in fig. 14). In contrast, the chloride concentration of pore water compressed from USW UZ-14 cores obtained from perched-water zone (represented by symbols I and J in fig. 7A) are about 87.5 mg/L. If matrix pore water contributes significantly to the perched-water body, then the chloride concentration of perched water

should be similar to that of the pore water. This was not observed. The smaller concentration of chloride in perched water means that there is less interaction of fluid with rock, and that the source of the perched water flows through fractures. This is another point of evidence that fracture flows are the principal source of perched-water bodies at Yucca Mountain. In addition, the large chloride difference also indicates nonequilibrium conditions between the perched water and pore water. Furthermore, the compositions of the perched water are also different from pore water. Analyses of a USW UZ-14 perched-water sample collected before the pumping test (sample UZ-14C) indicated that the perched water contained a polymer that was used in the drilling of USW G-1 (Whitfield and others, 1990). If the polymer-contaminated perched water had a different chemical composition than the noncontaminated pore water, the chemical compositions between the two phases should be equilibrated after 10 years (USW UZ-1, which is only 26.2 m away from USW UZ-14, was drilled in 1985). It could be that trapped air in the porous medium prevents perched water from equilibrating with the pore water.

Perched-water isotopic-composition data are given in table 7. All perched waters contain background tritium concentration. If postbomb fracture waters are mixed in these perched waters, they are small in volume and subsequently are diluted by the large quantity of perched water, resulting in an undetectable tritium concentration.

Carbon-14 and δ^{13} C values are plotted in figures 15A and 15B. As can be seen from the figures, the ¹⁴C values range from 66.9 to 27.2 pmc, corresponding to apparent ¹⁴C residence times of about 3,500 years to 11,000 years. Water ¹⁴C ages are affected by the dissolution of older caliche by the infiltrating water. This dissolution can be identified by the $\delta^{13}C$ isotopic values since caliche has δ^{13} C values in the range of -3 to -9%(Szabo and Kyser, 1985; Whelan and Stuckless, 1992), while biogenic CO₂ has δ^{13} C values of -18to -23% (UZ-1 data in this report). The heavier $\delta^{13}C$ values in the water will indicate the dissolution of caliche in the ground water. Carbon-14 ages of caliche at Yucca Mountain have been dated and range from 20,000 to several hundred thousands of years (Whelan and others, 1994; Szabo and Kyser, 1985).

Table 6. Chemical composition of perched water at Yucca Mountain, Nevada

 $[\mu S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; - -, data not available; 0, values below detection limit; charge balance, (milliequivalent cation – milliequivalent anion)/(milliequivalent cation + milliequivalent anion) times 100]$

Sample identification	Symboi in Piper diagram (fig. 14)	Average depth (meters)	Date	Temperature (degree Celsius)	pН	Specific conductance (µS/cm)	Aluminum Al (mg/L)	Calcium Ca (mg/L)	Magnesium Mg (mg/L)	Potassium K (mg/L)
NRG7a	Α	460.25	03-07-94	•	8.7	224	0.0	3	0	6.8
SD-9/TS	В	453.85	07-17-94	27.0	8.6	445	2.1	2.9	0.2	9.8
UZ14 A	С	384.60	08-02-93	27.1	7.6	312	0.7	23	1.8	5.6
UZ14 A2	D	384.60	08-02-93	27.1	7.8	308	1.0	24	1.8	3.9
UZ14 B	Ε	387.68	08-03-93	23.8	8.1	335	6.1	31	2.7	4.4
UZ14 C	F	390.75	080593	24.2	8.3	518	0.0	45	4.1	5.8
UZ-14 PT-1	G	390.75	08-17-93				0.0	37	3.1	6.3
UZ14 PT2	Н	390.75	08-19-93				0.0	30	2.4	3.3
UZ14 PT4	Ι	390.75	08-27-93				0.0	27	2.1	1.8
UZ14 D	J	390.75	08-31-93		7.8		0.0	31	2.5	4.1
ONC#1	L	432.97	12-15-94		8.7	302	11	13.3	1.1	3.6
USW G-2	М	649.22	020895		7.7	259		7 .9	0.5	5.2
SD-7(3/8)	х	479.76	030895				0.28	14.2	0.13	5.3
SD-7(3/16)	х	488.29	031695	21.8	8.1	239	0.44	13.3	0.13	5.3
SD-7(3/17)	х	488.29	03-17-95	22.6	8.2	285	0	12.8	0.08	5.5
SD-7(3/20)	x	488.29	032095	23.3	8.0	265	0	12.9	0.07	5.4
SD-7(3/21)	х	488.29	03-21-95	23.2	8.2	259	0	13.5	0.08	5.5

Sample identification	Sodium Na (mg/L)	Silica SiO ₂ (mg/L)	Bicarbonate HCO ₃	Carbonate CO ₃ (mg/L)	Chlorine CL (mg/L)	Bromine Br (mg/L)	Nitrate NO ₃ (mg/L)	Sulfate SO ₄ (mg/L)	Charge baiance
NRG-7a	42	9	114		7	0	1	4	-1.9
SD-9/TS	98	64.2	1 9 7	10	5.6	0	3.3	27.6	-6.6
UZ14 A	39	34.2	150	0	7.9	0.2	8.6	14.3	-0.1
UZ-14 A2	38	36.4	148.8	0	9.1	0.1	12.5	13.8	-0.2
UZ14 B	40	51.4	147.6	0	8.3	0.4	16.9	16.3	0.2
UZ14 C	88	7.7	106.1	0	15.5	0.4	0	223	-0.4
UZ-14 PT-1	40	21.4	144.0	0	7.2	0.1	12.7	57.3	-0.1
UZ14 PT2	35	25.7	144.0	0	7.0	0.1	15.4	22.9	-0.1
UZ14 PT4	34	32.1	141.5	0	6.7	0.1	14.5	14.1	0.1
UZ14 D	35	40.7	146.4	0.	7.0	0.1	17.1	24.2	-0.3
ONC#1	50.6	26.5	115	8.8	7.1	0	5.2	23.6	8.4
USW G-2	46	51	116		6.5	0.1		13	6.9
SD-7(3/8)	45.5	62.3	112	0	4.4	0	33.8	9.1	-6.1
SD-7(3/16)	45.3	57.4	128	0	4.1	0	33.8	9.1	-4.6
SD-7(3/17)	45.8	50.9	130	0	4.1	0	22.8	8.6	-2.4
SD-7(3/20)	45.5	55	127	0	4.1	0	13.4	8.5	0.6
SD-7(3/21)	44.6	55.9	128	0	4.1	0	13.2	10.3	-1.0

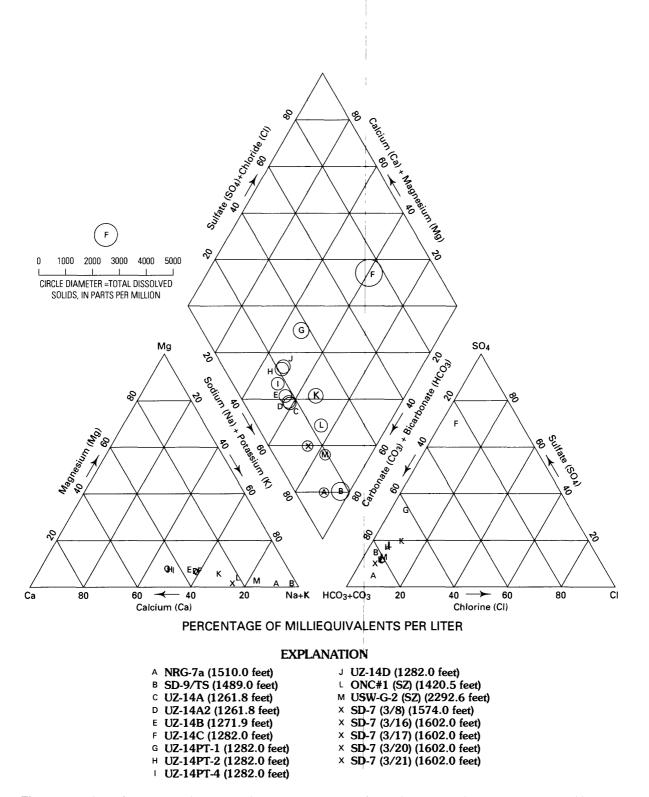


Figure 14. Piper diagram showing perched-water composition, along with saturated-zone water compositions (ONC#1, L, and USW G-2, M).

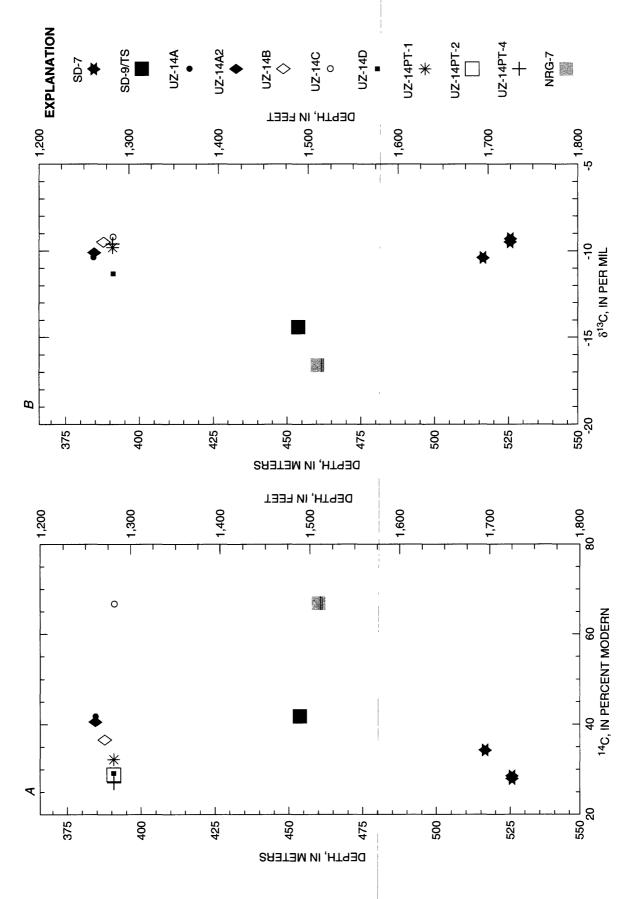
Table 7. Isotopic composition of perched w	Nater
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[m, meter; ‰, parts per thousand; pmc, percent modern carbon; - - -, data not available; PDB, Pee Dee Belemnite standard; SMOW, Standard Mean Ocean Water]

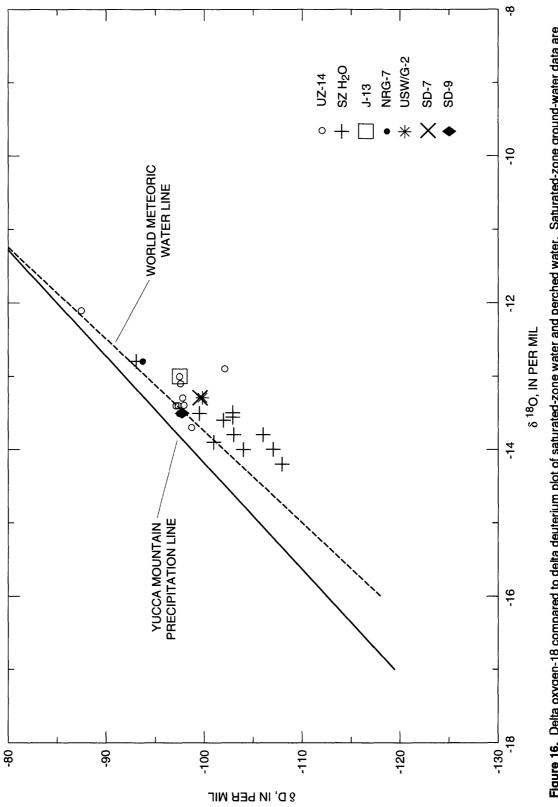
Sample identification	Depth (m)	Date	Carbon-13 ¹³ C (%., PDB)	Carbon-14 ¹⁴ C (pmc)	Tritlum ³ H (tritlum units)	Deuterium D (% ., SM OW)	Oxygen-18 ¹⁸ O (% -, SM OW)
SD-7(3/8)	479.76	03-08-95	-10.4	34.4	6.2	-99.8	-13.4
SD-7(3/16)	488.29	031695	-9.4	28.6		-99 .7	-13.3
SD-7(3/17)	488.29	03-17-95	-9.5	28.4		-99.6	-13.4
SD-7(3/20)	488.29	03-20-95	-9.5	27.9		99.6	-13.4
SD-7(3/21)	488.29	03-21-95	-9.5	28.4		-99.6	-13.3
SD9/TS	453.85	07–17– 9 4	-14.4	41.8	0.0	-97.8	-13.3
UZ14 A	384.60	080293	-10.2	41.7	0.3	- 9 8.6	-13.8
UZ14 A2	384.60	080293	-10.1	40.6	3.1	-97.5	-13.5
UZ-14 B	387.68	080393	-9.5	36.6	0.0	-97 .1	-13.4
UZ14 C	390.75	080593	-9.2	66.8	0.4	-87.4	-12.1
UZ14 PT1	390.75	08–17–93	-9.8	32.3	1.8	-9 7.8	-13.3
UZ-14 PT-2	390.75	081993		28.9	3.1	-97.9	-13.4
UZ14 PT4	390.75	08–27–93	-9.6	27.2	0.0	-97.3	-13.4
UZ14 D	390.75	08-3193	-11.3	29.2	0.0	-97.6	-13.1
NRG-7a	460.25	0307 9 4	-16.6	66.9	10.4	-93.9	-12.8

Perched-water δ^{13} C values range from -9.2 to -14.4‰ (except NRG-7a, which is -16.6%), which indicates older caliche was dissolved into the ground water, making water ages look older than their actual ages. For NRG-7a perched water, because the 13 C value is -16.6%, it implies that gas-liquid exchange might have occurred after caliche dissolution, causing the apparent age to look younger than its real age. If age corrections are applied to account for dilution by the older caliche and gas-liquid exchange after caliche dissolution, the implied perched-water residence times will probably be in the range of 2,000 to 7,000 years. Further investigations for ¹⁴C-age corrections will be made using geochemical model "NETPATH" in the near future. Since δ^{13} C values for perched waters are very consistent, and their large water volumes were presumably little affected by the gas-water exchanges, relative ¹⁴C residence times within the perched-water samples can be compared without correction.

Stable isotopic data (oxygen-18 and deuterium) are plotted as δ^{18} O relative to δ D in figure 16. Perched-water values are slightly heavier than the saturated-zone values and generally are closer to the Yucca Mountain precipitation line, indicating little evaporation before infiltration (Craig, 1961; Dansgaard, 1964). Moreover, it can be seen that δ^{18} O and δ D values in table 7 for USW SD-7 pumping tests (from March 16 through 21) are fairly constant. If mixing of older waters (more than 10,000 years old, last ice age) is involved, stable δ^{18} O and δ D isotopic values will be significantly more negative than -15% for δ^{18} O and -105%for δD [last ice age $\delta^{18}O$ value is about -15 to -20‰, and between -115 to -120% for δD (I.C. Yang, U.S. Geological Survey, unpub. data, 1996)]. All perched-water stable-isotopic values shown in table 7 are between -12.8 and -13.8% for $\delta^{18}O$ and -94 and -99.8% for δD . These values are consistent with a ¹⁴C residence time of less than 7,000 years for the perched waters.



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Gaseous-Phase Data from Borehole USW UZ-1

Gas sampling at USW UZ-1 is ongoing (1995). The data in this report are those collected from 1983 through 1994. Data from 1983 through mid-1985 and from 1988 to 1991 were published by Yang and others (1985, 1993). From 1983 through 1987, gas samples from each probe were collected twice a year. It was several years before sample composition stabilized in the borehole. Once stabilized, sample collections were reduced to once a year (since 1988). (Gaseous-phase chemical and isotopic data for 1983-88 were collected prior to implementation of the approved U.S. Geological Survey Yucca Mountain Project quality-assurance program and, therefore, the data are not qualified. However, the data collected from 1989-94 are qualified.)

Dry-Gas Composition

When USW UZ-1 drilling was completed, the borehole was evacuated for a few hours before stemming and instrumentation. No SF₆ concentration check was undertaken at that time. During all subsequent sampling, each probe was pumped at a rate of 250 to 500 mL per minute continuously for about 10 days. As shown in figure 17, SF_6 concentrations measured in 1984 were generally about 0.15 ppmv except for large values near the surface and small values of about 0.09 and 0.1 ppmv at 189 m and 228 m. The probes above 45 m have concentrations of 0.3 to 0.45 ppmv. Since 1988, the SF_6 concentration has decreased steadily to less than 0.15 ppmv in all but the 1989 measurements. The reason for the large values in 1989 is unknown. In general, the drilling air appears to have been removed by 1986-87, and data collected since that time should be representative of the rock-gas composition.

Results of gas chromatographic analysis on gas composition (April 1984, September 1986, and July 1994) of USW UZ–1 samples are shown in table 8. The gas composition is similar to atmospheric air, with slightly more CO_2 .

Carbon-Dioxide (CO₂) Concentrations

As shown in figures 18A and 18B, CO₂ concentrations are rather large (greater than 0.15 percent) at shallow depths (probes 1, 2, 3, and 4) and near the bottom (probe #15) relative to others in the profiles (less than 0.15 percent). The larger concentrations at the shallow depths (more than 0.3 percent by volume) are also larger than other environments near and around Yucca Mountain (Thorstenson and others, 1990). This is attributed to the biologically produced CO₂ from burial of vegetation during construction of the USW UZ-1 drilling pad. The larger CO₂ concentrations at the bottom probe may be attributed to the breakdown of organic polymers from the drilling-fluid contamination. The CO₂-concentration profiles as a function of time (fig. 18A) indicate that low CO_2 concentrations were measured in 1983 and that, except for probe 13, concentrations steadily increased until 1987. The atmospheric CO_2 concentration (0.034 percent) is significantly lower than most of the soil CO₂ concentration in USW UZ-1. Thus, the early CO₂ samples, diluted by drilling air in the borehole, showed relatively low CO_2 concentrations. As the semiannual gassampling process proceeded, more drilling air was removed from the borehole and the pristine rock-gas composition was revealed. From 1988 through 1994, the CO_2 concentration from 100 to 360 m showed little change (fig. 18B). The invariant CO_2 concentrations at probe 13 are puzzling. This probe yielded the lowest amount of CO_2 gas for 10 days of pumping.

Deita Carbon-13 Value

Delta carbon-13 values, relative to depth (fig. 19A) showed large variations in 1984 and 1985. As was explained previously concerning the CO₂ concentration, the 1984 shift was the result of the drillingair contamination in the borehole. The δ^{13} C value of the atmospheric CO₂ at Yucca Mountain is about -8.5‰ (Thorstenson and others, 1990, 1995). The presence of atmospheric air in collected samples would thus lead to larger δ^{13} C values. Between 1986 and 1987 (fig. 19A), and 1988 through 1994 (fig. 19B), all δ^{13} C values were fairly constant, ranging from -18 to -23‰ except for probes 9 and 10 in 1992 and near the bottom of the borehole (probes 13 and 14), where occasional departures from the average value were observed.

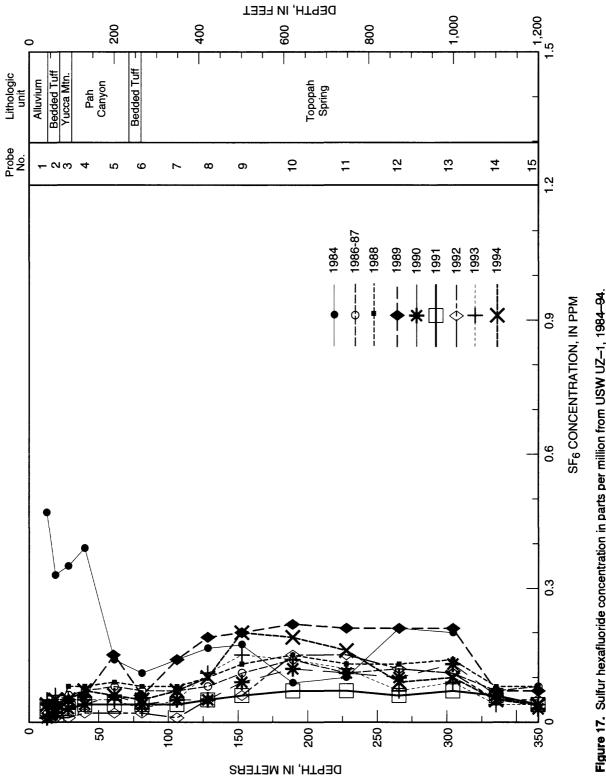


Figure 17. Sulfur hexafluoride concentration in parts per million from USW UZ-1, 1984-94.

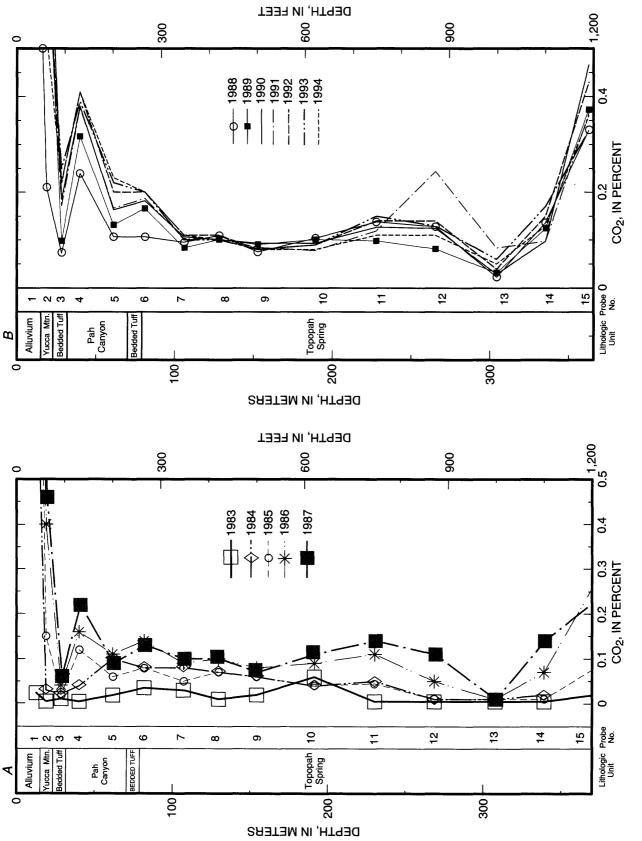
Table 8. USW UZ-1 dry-gas composition (percent by volume)

^{[---,} data not available]

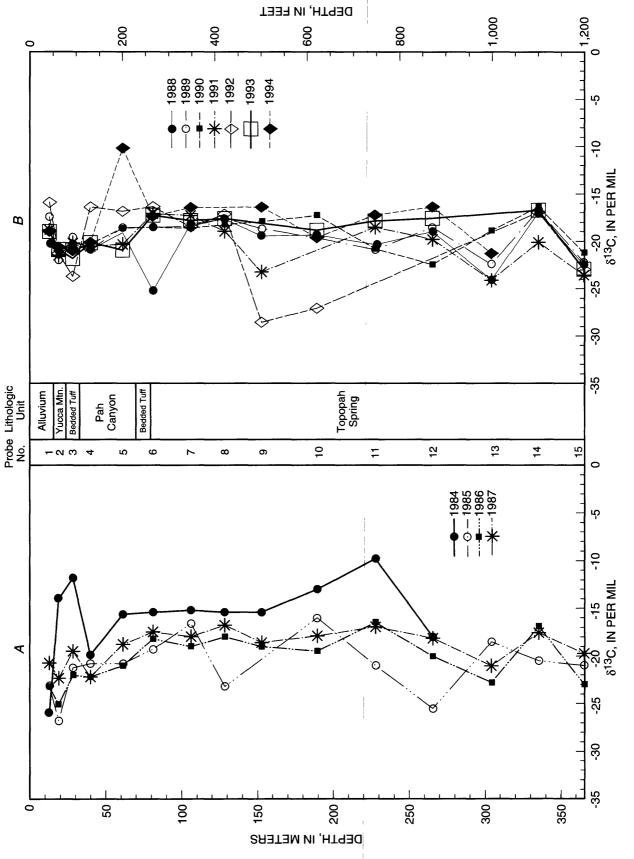
			April 198	4	
Probe no.	Depth (meters)	Nitrogen N ₂	Oxygen O ₂	Argon Ar	Carbor dioxide CO ₂
1	12.8	79.6	18.5	0.99	0.83
2	18.9	79.7	19.3	1.01	0.02
3	28.3	79.2	19.8	1.01	0.03
4	39.9	79.1	20.1	0.90	0.03
5	61.3	78.5	20.3	0.92	0.24
6	81.1	78.4	20.5	0.98	0.08
7	106.1	78.4	20.6	0.95	0.07
8	128.3	78.4	20.5	1.01	0.09
9	152.7	78.4	20.6	0.96	0.05
10	189.3	78.6	20.4	0.96	0.04
11	227.7	78.7	20.3	0.96	0.03
12	265.5	78.5	20.6	0.98	0.01
13	304.2	78.5	20.5	1.02	0.01
14	335.3		·		
15	367.9				

		Septem	ber 1986			July 1994	
Probe no.	Nitrogen N ₂	Oxygen O ₂	Argon Ar	Carbon dloxide CO ₂	Nitrogen N ₂	Oxygen O ₂	Carbon dioxide CO ₂
1	78.4	19.4	0.97	1.30	78.2	20.8	0.79
2	79.0	19.7	0.98	0.39	77.8	20.6	0.53
3	79.1	19.9	0.99	0.05	77.1	20.4	0.22
4					77.1	20.4	0.41
5					77.7	20.4	0.23
6					78.5	20.8	0.20
7	78.4	20.6	0.97	0.10	78.1	20.8	0.11
8					77.9	20.8	0.10
9					78.0	20.8	0.08
10					77.7	20.6	0.08
11					77.4	20.4	0.11
12					76.7	20.5	0.11
13	78.5	20.6	0.96	0.02	76.9	20.5	0.05
14	78.6	20.4	0.97	0.07	78.1	20.9	0.13
15	80.3	18.5	0.99	0.26	78.1	20.6	0.36

The δ^{13} C value of about -20‰ at shallow depths is representative of biogenic CO₂ (CO₂ gas respired from plant roots). The average δ^{13} C value of near -20‰ at all depths indicates that the CO₂ gas in the UZ has not exchanged with or is in equilibrium with in-situ calcite or caliche because the solid fracturefilling carbonates have a δ^{13} C value generally between -9 and -3‰ in the UZ (Szabo and Kyser, 1985; Whelan and Stuckless, 1992). If exchange had occurred, the CO_2 gas $\delta^{13}C$ values would have become larger, which was not observed (fig. 19B). Also, the ¹⁴C age of the CO_2 gas would be older than its real age because of the old ¹⁴C age of calcite and caliche [greater than 20,000 years to as much as several hundred thousand years (Szabo and Kyser, 1985; Whelan and others, 1994)].







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Figure 19. Delta carbon-13 values in per mil from borehole USW UZ-1: (A) 1984-87 and (B) 1988-94.

On the other hand, the extent of interactions between the gaseous-phase CO_2 and the pore-water bicarbonate can be seen from the following data analysis. The concentration of dissolved CO₂, as bicarbonate, analyzed from pore water of UZ boreholes has values ranging from 30 mg/L at shallow depth to about 250 mg/L at a depth of about 500 m with some exceptions. These bicarbonate concentrations are equivalent to 0.5-4.0 millimoles per liter (mmol/L). Volumetrically, the pore-water volume to the pore-air volume can be estimated as follows. According to Montazer and Wilson (1984), saturation in the Yucca Mountain cores ranges from 60 percent in the Paintbrush Tuff to 90 percent in the Calico Hills Formation. Therefore, the volume ratio of pore water to pore air will range from (60/40=) 1.5 to (90/10=) 9. The concentration of CO₂ in pore air is about 0.1 percent (fig. 18B). Thus, the amount of CO_2 in a liter of pore air at 25°C and one atmosphere is $(11) \times (0.001)/(24 \text{ l/mole}) = 0.00004 \text{ mol or } 0.04 \text{ mmol}.$ Since pore-water volume is about 1.5 to 9 times greater than the pore air, the amount of carbon in an aqueousphase reservoir relative to carbon in the CO₂ gaseousphase reservoir is about $\{[(0.5+4.0)/2] \times 1.5/0.04\} = 84$ to $\{[(0.5+4.0)/2] \times 9/0.04 =\}$ 506 times greater. Therefore, most carbon present in the underground UZ is in the aqueous phase. Consequently, an aqueous phase will dominate the gaseous phase if any exchange occurs. Preliminary $\delta^{I3}C$ values for pore water from UZ cores ranged from -10 to -25% (this report). If CO₂ gas is in equilibrium with the pore-water bicarbonate, the equilibrium fractionation factor (Friedman and others, 1977) for the CO₂(g)-HCO₃(aq.) system predicts a δ^{13} C value about -8.5% lighter for $CO_2(g)$ relative to the $\delta^{13}C$ value of bicarbonate in an aqueous phase. If so, $\delta^{13}C$ values of CO_2 gas in the borehole would be between -18.5%and -33.5%, which is not always the case in figure 19B. The CO_2 -gas ¹⁴C values are also not in equilibrium with the aqueous-phase ¹⁴C values, as mentioned previously (figs. 11 and 13A). Drilling air in the borehole of USW UZ-1 in 1984 through 1987 may have an effect on this disequilibrium between gaseous and pore-water phases. Furthermore, many open boreholes are known to inhale or exhale throughout the year. This could also affect the disequilibrium. However, the fact that the ¹⁴C values of rock gas are decreasing steadily with depth infers little effect by inhalation or exhalation (if topographic effect is significant, ¹⁴C values will scatter instead of steadily decreasing). The nonequilibrium condition in a $CO_2(g)$ -HCO₃(aq.) system could be due to the fact that gas samples were collected mainly from dry

fractures with little contribution from pore gas, which is in equilibrium with pore water. Thus, interactions between pore gas and pore water are not detected. Thorstenson and others (1990) also observed that approximately 2×10^6 m³ of gas was exhausted by USW UZ–6s borehole without compositional changes in rock gas. If the gas CO₂ was interacting with a large aqueous-phase carbon reservoir, a gas-phase CO₂ concentration would be modified, which was not observed. It is conceivable that such nonequilibrium conditions exist between gaseous and aqueous phases in many parts of Yucca Mountain. Due to insufficient gaseous-phase data and knowledge of the fractured system at the mountain, this statement is preliminary.

Carbon-14 Data

The ¹⁴C data plotted in figure 20A also indicate large variations in 1984 and 1985. The values tend to lie on the right-hand side of the 1986 values (that is, higher ¹⁴C activity values). This is consistent with the previous explanation of the drilling-air contamination in the borehole. Presentday ¹⁴C activity in the atmospheric air is about 120 pmc, which would cause the ¹⁴C activity of soil CO_2 gas to shift toward higher values. After pumping for 2 years, the ¹⁴C data are very consistent for the last 7 years (fig. 20B), with a gradual decrease in ¹⁴C activity with depth to about 23 pmc at 368 m.

The ¹⁴C profile in figure 20B shows that there is an abrupt change in the slope at probe 5. The transport velocity (¹⁴C concentration gradient over distance) between probes 1 and 5 is smaller than the transport velocity between probes 5 and 15. The smaller transport velocity may be due to higher porosity and moisture content in this zone. An estimate of the traveltime in the Topopah Spring Tuff (between probes 5 and 15) based on the apparent ¹⁴C ages and the distance yields gas movement of 3.26 cm/yr. This is a minimum value because the distance used for the calculation is simply depth in the borehole.

A gas-diffusion effect would cause ${}^{12}CO_2$ to diffuse downward faster than the heavier ${}^{14}CO_2$ molecules and would result in an older ${}^{14}C$ age at a greater depth than if the ${}^{14}C$ decay alone were considered. However, the effect is small and can be neglected.

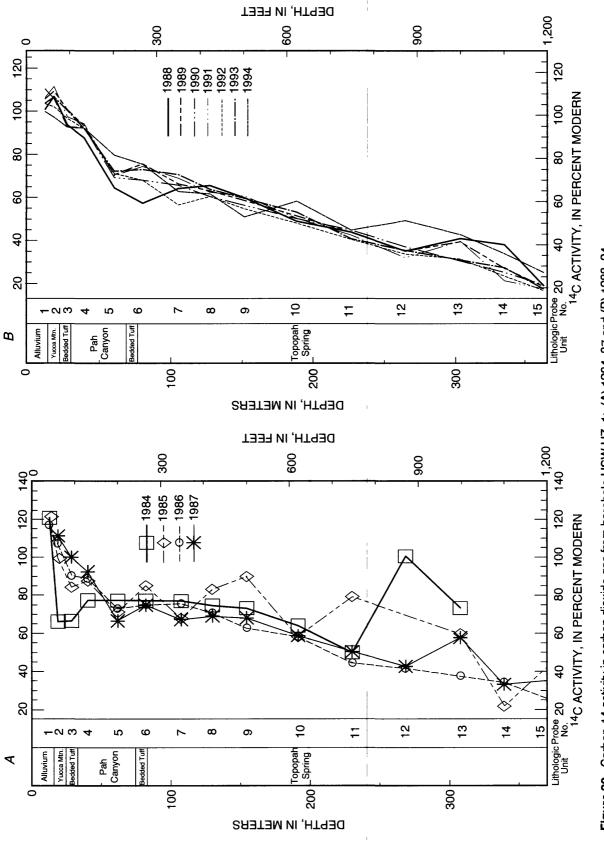


Figure 20. Carbon-14 activity in carbon dioxide gas from borehole USW UZ-1: (A) 1984-87 and (B) 1988-94.

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Gaseous-Phase Data from Selected Open Boreholes

Dry-gas composition was measured in the instrumented borehole of UZ-1. Since the gas composition was essentially the same as the atmospheric air composition, no attempt was made to repeat the measurement. Carbon dioxide and carbon isotopic data were measured in selected open boreholes (NRG-6, NRG-7a, UZ#16, and SD-12) and are given in table 9. As can be seen from the table, δ^{13} C values are heavier, in many cases, than the values for UZ–1. Also, 14 C values do not show a steady decrease with depths, as seen in UZ-1. The reason for the heavier δ^{13} C values and younger ¹⁴C values at depths could be due to contamination with atmospheric air as a result of a leaking packer or incomplete removal of drilling air. It has been observed in many locations at Yucca Mountain that topographic effects cause the gas to inhale or exhale through the open boreholes. This will also result in possible contamination of formation gas by air. In one case at the Prow Pass zone in UE-25 UZ#16 where the air-K test packer system was used, the rock-gas ¹⁴C age is about 10,000 years, similar to the gas age obtained from the deepest probe in USW UZ-1, an instrumented borehole. This could be due to the packer used in this zone having a tight seal, or alternatively gas inhalation or exhalation in the borehole does not reach to this depth. The δ^{13} C value of -18.4% strongly supports this argument. We have not collected any gas data from NRG-6 and NRG-7a boreholes because instrument tests are still in progress. The long-term carbon isotopic data (more than I0 years' data) from USW UZ-1, which show steady decrease in 14 C ages as a function of depth with consistent δ^{13} C values, are the only dependable rock-gas data so far in the Topopah Spring unit and below.

MODEL CALCULATIONS

A gas-diffusion and two aqueous-flow models were applied to explain the observed gaseous ^{14}C distributions in USW UZ–1 and tritium concentrations in pore-water samples of UE–25 UZ#16.

The gas-diffusion model: A steady-state diffusion of ${}^{14}\text{CO}_2$ from a constant source at the surface with firstorder radioactive decay was considered. In this case, the finite depth of the UZ must be taken into account because of the length of times possibly available for diffusion. The equation for steady-state diffusion and first-order homogeneous reaction in a finite layer is taken from Bird and others (1960, p. 533, eq. 17.4–7). The equation assumes that the reactant and product species are present in very small concentrations and that the net gas flux is zero. Thus, multicomponent effects (Thorstenson and others, 1989) and advective transport due to local topographic effects (Weeks, 1987) are not considered.

The aqueous-flow model: Piston-flow and wellmixed models were used to determine if observed tritium concentrations are feasible, given estimated tritium input functions for the Yucca Mountain site. Numerous studies of surface- and ground-water ages and mixing rates have been conducted over the years with the use of tritium (Carmi and Gat, 1973; Pearson and Truesdell, 1978; Simpson and Carmi, 1983; Egboka and others, 1983; Knott and Olimpio, 1986; Vuataz and Goff, 1986; and Shevenell, 1991). Discussions of piston-flow compared to well-mixed flow behavior have been abundant in these and other studies. Simpson and Carmi (1983) focused on a simple exponential model of piston flow while studies by Nir (1964) discussed the concepts of well-mixed and piston-flow reservoirs, utilizing hydrodynamic dispersion coefficients in describing the well-mixed endmember. Carmi and others (1973) simulated wellmixed behavior with the use of an age function that incorporates a recharge weighting function to determine ages from the combination of tritium input over a given number of years. Pearson and Truesdell (1978) and Shevenell (1991) applied this model to the geothermal systems.

Gas-Transport Model

To a first approximation, the $\delta^{13}C$ data suggest that there is no systematic CO₂ reaction with solid carbonate in the USW UZ–I borehole. Thus, the possibility must be considered that the gas in the borehole is stagnant and that the decrease of ¹⁴C with depth is due to radioactive decay and that the ¹⁴C data thus imply substantial "ages" of the CO₂ at depth.

The CO₂ concentrations in the upper few probes (probes I through 4, figs. 18A and 18B) are anomalously high relative to concentrations observed in other environments at the NTS (Thorstenson and others, 1990). The UZ–1 data also suggest that these high concentrations are migrating downward with time (fig. 18). It is likely that construction of the UZ–I drill pad caused some effects on these CO₂ concentrations, for example, through burial of vegetation during construction. Consequently, gas ¹⁴C data from the upper few probes will not be considered here. Table 9. Carbon-14 (¹⁴C) and delta carbon-13 (gas) data from boreholes NRG-6, NRG-7a, UZ-16, and SD-12

[---, data not analyzed; pmc, percent modern carbon; ‰, parts per thousand; PDB, Pee Dee Belemnite standard]

Borehole	Depth (meters)	Lithologic unit	Carbon dioxide (CO ₂)	¹⁴ C (pmc)	¹³ C/ ¹² C (‰, PDB)	Isotopic analytical laboratory
NRG-6	6.1	Tiva Canyon	0.07		-12.83	USGS stable isotope
NRG-6	6.1	Tiva Canyon			-15.18	USGS stable isotope
NRG-6	6.1	Tiva Canyon			-15.15	USGS stable isotope
NRG-6	24.4	Tiva Canyon	0.11		-14.25	USGS stable isotope
NRG-6	24.4	Tiva Canyon	ļ	92.1	-15.2	Geochron
NRG-6	26.8-38.1	Tiva Canyon	0.07		-14.60	USGS stable isotope
NRG-6	26.8-38.1	Tiva Canyon		61.0	-13.9	Geochron
NRG-6	26.8-38.1	Tiva Canyon	ţ.		-14.62	USGS stable isotope
NRG-6	26.8-38.1	Tiva Canyon			-14.61	USGS stable isotope
NRG-6	26.8-38.1	Tiva Canyon			-14.63	USGS stable isotope
NRG-6	26.8-38.1	Tiva Canyon			-14.99	USGS stable isotope
NRG-6	26.8-38.1	Tiva Canyon			-15.02	USGS stable isotope
NRG-6	61.0	Pah Canyon	0.10		-14.14	USGS stable isotope
NRG-6	61.0	Pah Canyon			-14.24	USGS stable isotope
NRG-6	61.0	Pah Canyon		91.0	-14.9	Geochron
NRG-6	83.8	Topopah Spring	0.05		-15.05	USGS stable isotope
NRG-6	83.8	Topopah Spring			-15.05	USGS stable isotope
NRG-6	107	Topopah Spring			-17.24	USGS stable isotope
NRG-6	183	Topopah Spring	0.10	83.2	-15.5	Geochron
NRG-6	183	Topopah Spring			-14.06	USGS stable isotope
NRG-6	221	Topopah Spring	0.07		-14.69	USGS stable isotope
NRG-6	221	Topopah Spring			-14.69	USGS stable isotope
NRG-6	233-238	Topopah Spring			-10.14	USGS stable isotope
NRG-6	233–238	Topopah Spring			-10.31	USGS stable isotope
NRG-6	282	Topopah Spring	0.11	94 .2	-16.1	Geochron
NRG-6	282	Topopah Spring	•		-14.14	USGS stable isotope
NRG-6	305	Topopah Spring	0.07		-14.43	USGS stable isotope
NRG-6	305	Topopah Spring	1		-14.34	USGS stable isotope
NRG7a	42.7	Yucca Mountain	0.12	108.0	-16.8	Geochron
NRG7a	42.7	Yucca Mountain			-17.24	USGS stable isotope
NRG7a	149	Topopah Spring	0.19		-17.69	USGS stable isotope
NRG7a	149	Topopah Spring			-17.68	USGS stable isotope
NRG7a	149	Topopah Spring		111.7	-18.2	Geochron
NRG-7a	271	Topopah Spring	0.15	111.0	-19.0	Geochron
NRG-7a	271	Topopah Spring			-17.75	USGS stable isotope
NRG7a	271	Topopah Spring			-17.73	USGS stable isotope
NRG-7a	370	Topopah Spring	0.19		-17.61	USGS stable isotope
UZ-16	45.7	Tiva Canyon		73.2	-15.5	Geochron
UZ-16	45.7	Tiva Canyon			-13.82	USGS stable isotope
UZ-16	45.7	Tiva Canyon	1		-13.72	USGS stable isotope
UZ-16	14.3–74.1	Tiva to Topopah		72.7	-14.0	Geochron
UZ-16	14.3-74.1	Tiva to Topopah			-12.32	USGS stable isotope
UZ-16	73.1	Topopah Spring			-13.19	USGS stable isotope
UZ-16	73.1	Topopah Spring			-13.14	USGS stable isotope

 Table 9. Carbon-14 (¹⁴C) and delta carbon-13 (gas) data from boreholes NRG-6, NRG-7a, UZ-16, and SD-12-Continued

 [- - -, data not analyzed; pmc, percent modern carbon; ‰, parts per thousand; PDB, Pee Dee Belemnite standard]

Borehole	Depth (meters)	Lithologic unit	Carbon dioxide (CO ₂)	¹⁴ C (pmc)	¹³ C/ ¹² C (%-, PDB)	is otopic analyticai laboratory
UZ-16	82.3	Topopah Spring			-12.97	USGS stable isotope
UZ16	82.3	Topopah Spring			-12.94	USGS stable isotope
UZ-16	74.1–148	Topopah Spring		87.0	-16.5	Geochron
UZ-16	74.1–148	Topopah Spring			-19.71	USGS stable isotope
UZ16	74.1–148	Topopah Spring			-20.07	USGS stable isotope
UZ-16	74.1–148	Topopah Spring			-20.86	USGS stable isotope
UZ-16	148163	Topopah Spring		81.6	-14.7	Geochron
UZ-16	148–163	Topopah Spring			-18.31	USGS stable isotope
UZ-16	163-512	Topopah Spring to Prow Pass		89.2	-17.0	Geochron
UZ-16	163-512	Topopah Spring to Prow Pass			-15.63	USGS stable isotope
UZ-16	477-481	Prow Pass			-17.60	USGS stable isotope
UZ16	477-481	Prow Pass		25.8	-18.4	Geochron
UZ-16	477-481	Prow Pass			-16.32	USGS stable isotope
UZ-16	477-481	Prow Pass			-16.26	USGS stable isotope
UZ-16	477-481	Prow Pass			-15.51	USGS stable isotope
SD-12	216-220	Topopah Spring		74.33	-11.6	Geochron
SD-12	342347	Topopah Spring		60.17	-16.1	Geochron

Surface ¹⁴CO₂ concentration is calculated with $CO_2 = 0.125\%$ and a ¹⁴CO₂ = 100 pmc. The steadystate diffusion of ¹⁴CO₂ from a constant source at the surface with first-order radioactive decay was considered by Thorstenson and others (U.S. Geological Survey administrative report, 1995). Calculations were made with a depth of 500 m for values of diffusivity ranging from 10⁻⁶ to 10⁻⁷ m²/s. A good visual fit is obtained with D = 10^{-6.7} m²/s (D = 2.0 × 10⁻⁷ m²/s).

The calculated and observed concentrations of ${}^{14}\text{CO}_2$ are plotted in figure 21. The calculations do not explicitly take into account solubility or reactions. While simple Fickian diffusion may not be the only process that is operative, it appears that it can account for the observed depth distribution of ${}^{14}\text{CO}_2$ in the fractured Topopah Spring. (This conclusion is supportable using solely the data that were collected in compliance with the approved U.S. Geological Survey Yucca Mountain Project quality-assurance program.) This is in marked contrast to the observations in the open boreholes at the Yucca Mountain crest, where it appears impossible to account for observations without major advection in the system (Weeks, 1987; Thorstenson and others, 1990).

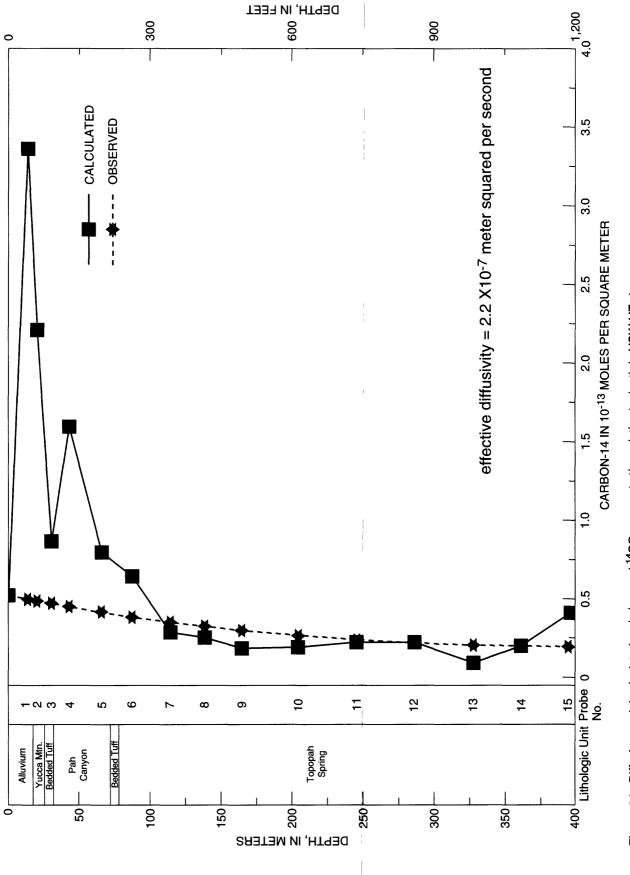
Use of Tritium in Ground Water to Determine Water Mean Residence Times

Tritium generally behaves conservatively in the ground-water system. Therefore, its concentration in water is a reliable indicator of mixing and relative ground-water ages. The flow type is assumed to be either piston flow, well-mixed flow, or some combination of the two. The piston flow (no mixing between fluids of different ages) provides an upper limit, and the well-mixed model (complete mixing of fluids of different ages) provides the lower limit on mean residence times of ground water in the system.

Piston-Flow, or Preferential-Flow, Model

This flow model does not take into account hydrodynamic-dispersive mixing within the unsaturated-zone reservoir system, nor from other sources of water. Output tritium concentrations depend only on the input concentration at recharge and the elapsed time since the recharge. The relationship between input and output concentration is simply a standard decay equation:

$$C_{out}(t) = C_{in}(t-T)e^{-\lambda T}$$





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where

- $C_{out}(t)$ = output tritium concentration at time t, expressed in calendar year 19xx (not number of years);
- $C_{in}(t)$ = tritium concentration of fluid recharging the system;
 - T = residence time; and
 - λ = tritium decay constant (5.576 × 10⁻²/yr).

This equation can be solved by the analytical method for tritium concentrations relative to residence times with known tritium input function.

Well-Mixed Model

On the other hand, the well-mixed model assumes that all sources of water input to the reservoir are completely mixed with the water already in the reservoir. For such a reservoir, it is assumed that volume does not change with time and input rate equals the output rate $(Q_{in}=Q_{out})$. The mass-balance equation presented by Pearson and Truesdell (1978) is given as follows:

$$\frac{dC(t)}{dt} = \frac{Q_{in}C_{in}(t)}{V} - \frac{Q_{out}C(t)}{V} - \lambda C(t)$$

where

C(t) = the tritium level in the reservoir, and at the discharge point, at time t;

 $C_{in}(t)$ = input tritium concentration;

 Q_{in} = recharge flow rate, $Q_{in} = Q_{out}$;

- Q_{out} = discharge flow rate; V = volume of reservoir, constant;
 - t = residence time, V/Q; and
 - λ = decay constant of tritium (5.576 × 10⁻²/yr).

This differential equation can easily be solved by the numerical method with a known tritium input function.

Tritium Input Function

In order to evaluate the end-member models, the tritium concentration of recharge water before and after nuclear testing must be estimated in the study area. Prior to 1952, little tritium data were reported. A few measurements were made on lake water, ground water, and wines from Chicago and New York areas. These measurements indicate that the average natural background tritium value for the interior of North America is about 6 TU, depending on the latitude and altitude (Craig and Lal, 1961; Kaufman and Libby, 1954). Also, tritium values in precipitation were reported by Payne (1972) to be between 2

and 25 TU prior to the 1950's. Tritium data in precipitation at Yucca Mountain were reported by Milne and others (1987) from November 1983 to June 1985 only. Other reported data, not from Yucca Mountain but from States neighboring Nevada, are available from stations set up by the International Atomic Energy Agency (IAEA) in Menlo Park, Calif., Albuquerque, N. Mex., Flagstaff, Ariz., and Salt Lake City, Utah. The averaged data from these four stations were taken to represent the Yucca Mountain area even though there are differences in latitude, altitude, and local climatic conditions between these four stations and Yucca Mountain. The average monthly tritium concentration in precipitation has been reported by IAEA for these four stations since 1963 (International Atomic Energy Agency, 1969–1986). However, no data were reported from 1953 to 1962. To estimate the pre-1963 tritium concentrations for the four stations, the IAEA data from Ottawa in Canada, which has a complete record of tritium values in precipitation since 1953, were used to formulate the tritium input data. This same method was also used by Pearson and Truesdell (1978), Campana and Mahin (1985), Knott and Olimpio (1986), and Shevenell (1991).

The IAEA tritium data, reported as a monthly average, increases in concentration during the spring and summer. The long-term precipitation records of Las Vegas, Nev., also show increases in tritium concentrations in spring and summer (Cayan and others, 1991). Annual average value and maximum monthly value of each year from IAEA were used as input functions for these models.

To estimate the missing tritium data at these stations between 1953 and 1962, trends of tritium concentration at these stations are assumed to be similar to the tritium concentrations in the Ottawa station. The best-fit linear regression equations for four stations and their correlation coefficient (R^2) are shown below. Using annual average:

- $Y_1 = 0.960393 X_1 0.07485 R^2 = 0.9015$ (estimated linear equation at Flagstaff)
- $Y_2 = 1.168409 X_1 0.36611 R^2 = 0.9622$ (estimated linear equation at Salt Lake City)
- $Y_3 = 1.080147 X_1 0.37512 R^2 = 0.944$ (estimated linear equation at Albuquerque)
- $Y_4 = 0.745824 X_1 0.36611 R^2 = 0.799$ (estimated linear equation at Albuquerque)

where

 Y_1 =log (annual ³H concentration at Flagstaff), X_1 =log (annual ³H concentration at Ottawa) Y_2 =log (annual ³H concentration at Salt Lake City) Y_3 =log (annual ³H concentration at Albuquerque) Y_4 =log (annual ³H concentration at Menlo Park) Similarly, using maximum monthly value of each year:

 $Y_1=1.099583 X_1 - 0.36034 R^2 = 0.904$ (estimated linear equation at Flagstaff) $Y_2=1.195766 X_1 - 0.45923 R^2 = 0.908$ (estimated linear equation at Salt Lake City)

 $Y_3=1.129000 X_1 - 0.44896 R^2 = 0.887$ (estimated linear equation at Albuquerque) $Y_4=0.905918 X_1 - 0.29431 R^2 = 0.790$

(estimated linear equation at Albuquerque) where

- $Y_1 = \log (maximum monthly value of {}^{3}H concentration at Flagstaff),$
- Y₂=log (maximum monthly value of ³H concentration at Salt Lake City)
- Y₃=log (maximum monthly value of ³H concentration at Albuquerque)
- Y_4 =log (maximum monthly value of ³H concentration at Menlo Park)

The average of the tritium concentration at the four stations is assumed to represent the concentration at Yucca Mountain (figs. 22A and 22B). The most notable feature of the concentration profile is that the maximum tritium concentrations in precipitation, approximately 250 times above background levels, occurred in 1963. The estimated annual average tritium concentration of 1984 is 23.0 TU, which is close to the measured tritium concentration (19.7 TU) in precipitation at Yucca Mountain (Milne and others, 1987).

Results of Tritium Model Calculations

Pre-1952 tritium concentrations in precipitation ranging from 5 to 20 TU are used as an initial concentrations for input into the well-mixed model sensitivity analyses. The results indicate that the output tritium concentrations change insignificantly. Therefore, a pre-1952 tritium concentration of 6 TU was adopted for the annual average value, and 12 TU was adopted for the maximum monthly average value.

Figures 23A and 23B show the calculated tritium concentrations relative to mean residence times for the two end-member cases for the samples

collected in 1993 at Yucca Mountain (a) using an annual mean value, and (b) using the highest monthly tritium value in a year in precipitation as input functions. The curve for the piston-flow model indicates several peak concentrations of tritium, reflecting the various nuclear-test series begun in 1953. On the other hand, mixed-reservoir curves show smooth increases in the tritium content of a reservoir caused by high tritium inputs from the mid-1950's to 1963, followed by a decrease to the present (1995) level. It is important to note that the piston-flow model using the highest monthly value in figure 23B gives the highest tritium concentrations of up to 700 TU, in 1993 with residence time of 30 years, from 1963 nuclear-test fallout. The highest tritium concentration in the well-mixed reservoir is only about 55 TU. Using the annual mean value from the closest four stations for tritium concentration in precipitation, the piston-flow model gives 350 TU as a maximum, and the well-mixed model gives 25 TU as a maximum in ground water in 1993. The piston-flow model with either type of input function can account for the observed tritium peaks of more than 100 TU in the Calico Hills Formation of UE-25 UZ#16. However, the well-mixed model cannot account for the observed values.

In reality, no hydrologic system should be expected to exhibit pure piston-flow or pure wellmixed flow behavior. The results of piston-flow and well-mixed flow models only give the lower and upper limits of peak tritium concentrations for various residence times. Although tritium, with its short half-life, cannot be used rigorously to obtain an accurate mean residence time of an older water, this study demonstrates that it can be used to obtain an order of magnitude estimate of a residence time.

Extremely variable tritium values in the USW UZ-14 and UE-25 UZ#16 profiles indicate unsaturated-zone waters are not well mixed (as seen from tritium model calculation) but are transported in large part by piston flow (between piston and well-mixed flows, but closer to a piston flow). Therefore, preferential flow through fractures is the dominant mechanism. Other evidence of fracture flow is supported by the presence of many calcite and silica deposits in fractures, boreholes, and the Exploratory Study Facilities. Also, water was observed to seep out from the fractures in several boreholes. Large tritium concentrations in borehole UZ#16 in the Calico Hills Formation are within limits of piston-flow-model calculation (about 30 years' residence time).

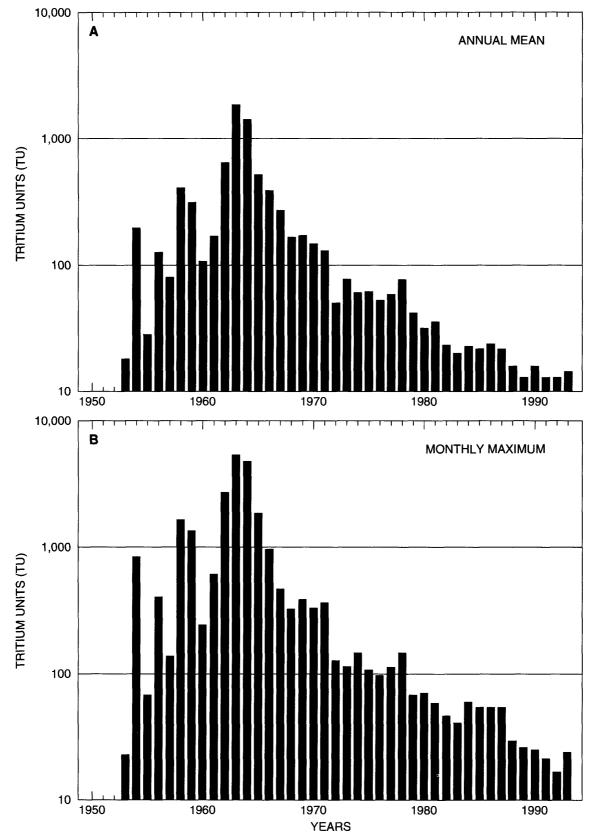


Figure 22. Tritium input function derived from (A) annual mean value, and (B) highest monthly value in a year of tritium concentration in precipitation from four stations: Albuquerque, New Mexico; Flagstaff, Arizona; Menlo Park, California; and Salt Lake City, Utah.

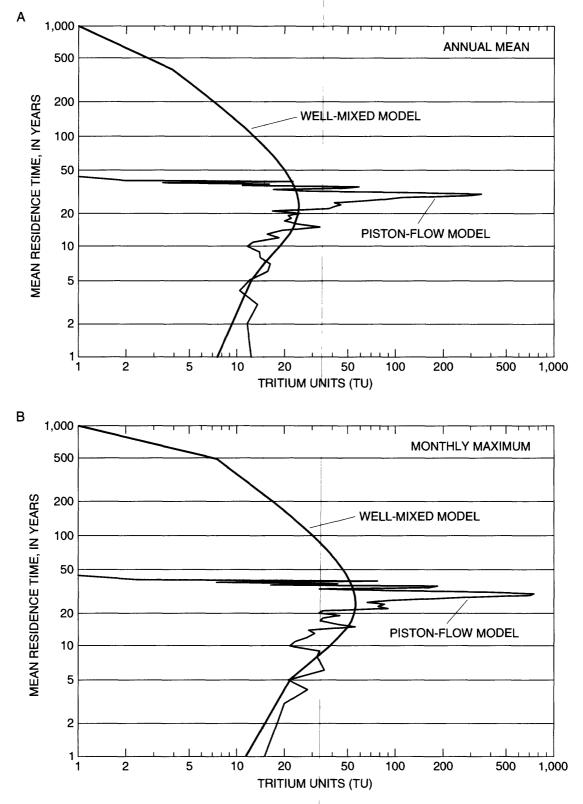


Figure 23. Calculated tritium contents of water in the unsaturated zone by piston-flow and well-mixed models using (A) annual mean value of tritium input function (fig. 22A), and (B) highest monthly value of tritium input function (fig. 22B).

SUMMARY AND CONCLUSIONS

Unsaturated-zone pore water generally has significantly larger concentrations of dissolved solids than either the saturated-zone water or perched water. Pore-water composition plotted on Piper diagrams define groups related to lithologic units. Pore waters in the Tiva Canyon, Yucca Mountain, Pah Canyon, and bedded tuffs are calcium sulfate or calcium chloride types that group together near the top of the diamond on the Piper diagram. Calico Hills Formation waters are sodium carbonate or bicarbonate type and plot near the bottom of the diamond. Pore waters in the Topopah Spring Tuff are at the middle of the diamond.

Tritium profiles show inversions occurred in several places. These inversions indicate that vertical water percolation through the matrix is not the normal flow mechanism at Yucca Mountain. Rather, fracture flow is the dominant fluid-flow mechanism. The postbomb tritium concentrations observed in the Calico Hills Formation of UE–25 UZ#16 are also supported by the young ¹⁴C ages and modern ³⁶Cl signals found in the same locations. However, total water flux to the Calico Hills Formation is small.

Large ¹⁴C variations of about 53 to 97.7 pmc are seen in UE–25 UZ#16 bedded tuff and in the Calico Hills Formation. Three values ranging from 53 to 61 pmc values in the Calico Hills Formation are in agreement with observed values in perched water. Many of the ¹⁴C values in the Calico Hills Formation of USW UZ–14 are between 80 and 95 pmc (equivalent to apparent ¹⁴C ages of about 1,800 and 400 years), although one value is 70 pmc. Further investigations are in progress to confirm these apparent young ¹⁴C ages.

Chemical and isotopic compositions of the perched water indicated that (1) the apparent ¹⁴C ages of perched water are similar to apparent ¹⁴C ages of the Calico Hills Formation pore water in UE–25 UZ#16, ranging from 3,000 to 7,000 years; (2) stable isotopic values of -12.1 to -13.8% for δ^{18} O and -87.4 to -100%for δ D in perched water strongly support the postglacial ¹⁴C ages; (3) the hydrogen and oxygen isotopic compositions of perched-water samples indicate that perched water rapidly infiltrated into fractures; (4) chloride concentrations of the perched water indicate that perched waters were recharged mainly from fracture waters with little contribution from matrix water; and (5) major-ion chemistry indicates that most perched waters have similar chemical compositions to the saturated-zone ground water except the perched water in USW UZ-14, which is typical of Topopah Spring Tuff water.

Rock-gas compositions are similar to the atmospheric air except that CO₂ concentrations are generally larger than in air. The $\delta^{13}C$ (gas) values of USW UZ-1 are fairly constant from the surface to 365.8 m, indicating little interaction between the gas CO₂ and caliche in the soil. With regard to gas-water exchange, most of the carbon is in the aqueous phase. Consequently, an aqueous-phase ¹⁴C age will affect a gaseous-phase ¹⁴C age more than the converse. The reason for the nonequilibrium condition observed between the two phases is probably due to the fact that most of the gas was collected from fractures rather than from pores where equilibrium conditions may exist. Carbon-14 ages in the gaseous phase are significantly older than the water ¹⁴C ages in the deep Topopah Spring Tuff and subadiacent units. The observed apparent age differences may result from liquid-gravity fracture flow, a process faster than gas-diffusion flow.

Model calculations indicate that gas transport in the unsaturated zone of Yucca Mountain agrees well with the steady-state diffusion and decay process, based on the ¹⁴C data from USW UZ–1. Tritiummodeling results indicate that the high tritium value of about 100 TU in the Calico Hills Formation of UZ#16 is within limits of a piston-flow model with residence time of about 30 years. The large variations in tritium values with narrow peaks suggest an aqueous-phase flow in the unsaturated zone that is closer to a piston or preferential fracture flow than to a matrix flow.

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[m, meters; mg/L, milligrams per liter] Revisions in the outlined cells below have been checked and accepted by: Z 2 2 2 2 2 2			Revisio	ons in the o	utlined celk	s below hav	e been che	Revisions in the outlined cells below have been checked and accepted by:	cepted by:	Ň	le s	Z	8/24	10
										I. C. Yang			Date	
Ceils with changes are outlined	outlined										~			
Sample		Symbol in Piper Average	4	Aluminum*	Calcium N	Aagnesium	Sodium E	Aluminum* Calcium Magnesium Sodium Bicarbonate	Carbonate Chloride Bromide	Chloride	Bromide	Nitrate Sulfate		Silica
Identification		diagram (fig.6B)	Depth (m)	AI (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	HCO ₃ (mg/L)	CO ₃ (mg/L)	CL (mg/L)	Br (mg/L)	.NO ₃ (mg/L)	SO4 (mg/L)	SiO ₂ (mg/L)
Compression stage codes have been added to the sample Identification	been added	F							-					
NRG-6/158.2-158.6/up1 Shardy b	Shardy base/bedded		48.28	0	122	23.3	35.6	34	0	185	-	32	159	97.4
		7	52.18	0	70.5	11.5	29.2	8	13	58	0	43	94	79.4
NRG-6/175.6-176.0/up1 Pah Canyon	iyon	e	53.58	0	49.2	8.6	29.4	60	0	47	0	42	64	78.1
UZ-14/235.1-235.4up1 Pah Canyon	ы	4	71.72	0	67	10.5	29	96	na	84	0	15	94	63
UZ-14/240.8-241.1/up1 Pah Cany	Pah Canyon/ Bedded	S	73.46	e	32	-	103	162	na	66	0	17	0	61
UZ-14/245.5-245.6/up1 Bedded		9	74.89	0	65	12	თ	99	na	11	0	12	79	46
UZ-16/1434.2-1434.6/up1 Calico Hills	Hills	7	437.21	6.1	3.2	0.6	113	72 [a]	70.8 [a]	23	0	16	19	109.1
UZ-16/1442.8-1443.2/up1 Calico Hills	Hills	80	439.83	1.2	1.7	0.8	79.9	18.3 [a]	87.6 [a]	18.9	0	11.3	13.7	68.9
UZ-16/1486.9-1487.3/up1 Calico Hills UZ-16/1601.1-1601.5/up1 Prow Pass	Calico Hills/Prow Pass Prow Pass	< ₪	453.27 488.08	26.2 0.7	6.3 10	0.8 0.3	79.5 100	137 181	00	38 23	00	6 13	11 27	233.3 36
roomores.												ſ		
[a] Values reported by the laboratory for these samples were for CaCO ₃ equivalent. The table values posted her bicarbonate and carbonate concencentration. Compression code: /up1 indicates first-stage uniaxial compression.	oratory for these a encentration. Con	samples w npression (ere for Ci code; /up	aCO ₃ equiv 1 indicates	alent. Th i first-stac	e table valı 1e uniaxial	ues poste compres:	The table values posted here have been mathematically converted to stage uniaxial compression.	been math	ematicall	y converte	ed to		
*0.45 µm fitter paper was used, hence, particulate aluminum is likely included in these values	ce, particulate alum	inum is likel	ly Included	d in these va	ilues.									

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Corrected Table 2, WRIR 96-4058. Chemical composition of pore-water and ground-water samples from boreholes UE-25 UZ#16, UE-25 UZN#2 and UZN46

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								۔ -	Bue	-	Date					
	Symbol									•						
	diagram	Average			Snecific	Calcium 1	Calcium Mannesium	Sodium	Silica A	Aluminum	Ricarhonate	Carbonate [Chloride	Bromide	Nitrate	Sulfate
Sample Identification	(fig.7B)	Depth	Date	Ħ	Conductance	Ca	BM	ą			HCO3	ŝ	G	ā	ő	so.
		(meters)			(InS/cm)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
UZ-N2-Area Precipitation	:	0	03/31/92	:	:	0.7	0.5	0.8	6.0	0	23.3	0	2.4	0	0	4
UZ-N2-Water	:	15.8	08/18/89	17	308	4	2.3	51	18	• :	112	0	9	0.54	:	29
UZ-N2-Water	:	15.6	02/14/92			1.4	0.5	1.7	0	0	11.7	0	12.2	0	8.2	7.8
UZ-N2-Water	i	15.8	03/16/92	;	:	14.4	3.9	25.1	5.8	0	58.2	0	10	1.7	27.3	21
UZ-N2-Water	;	15.8	03/31/92	;	:	25	4.7	16.2	11.8	0	127.6	0	5.8	0.9	19.7	15.6
UZ-N46-Water	ł	30.1	02/14/92	;	,	0.8	0.5	1.6	0.2	0	23.3	0	3.3	0	1.6	4.7
UZ 16 Pore Water Compression stage codes have been adder	codes have	e been adde	d to the sample	ipie identi	dification for UZ	Z-16 samples										
117-18/183 5-183 Qhin 1	-				425		124	21 E	77 5	7	1147 [a]	45 n (a)	10.4	c	23.1	773
02-10-100-0-100-0-0-0-0-0-0-0-0-0-0-0-0-	- ~	55.20	11/16/92	, r	430		<u>1</u>	2,5	2) -	146 4 [a]		38	• ⊽	3	88
LIZ-16/1166 19-1166 47/m1		355 AB	P0/7C/00	5.8	710	28.9	13.7	83.6	57.1	, c	196			Ċ	1	28
UZ-16/1227 4-1227 7/m1	, 4	374.17	08/09/93	5	430	285	6.5	47.9	62.2	۶°	137	• •	54	, c	23	26
UZ-16/1235 1-1235 41/up1	r ua	376.52	08/11/93	82	480	33.5	1.0	513	52.9	}	154		23		26	39
UZ-16/1269.6-1269.9/up1	. 6	387.04	08/04/93	85	430	141	24	67.5	57.1		139	13	27		18	4
UZ-16/1280.4-1280.8/up3	-	390,33	09/02/93	8.3	530	20.5	3.7	92.0	71.8	1.5	192	0	28	0	19	19
UZ-16/1296.8-1297.06 /up1	- 60	395,33	09/23/93	7.4	930	32.4	19.7	98.2	46.7	0	324	12	3	0	19	18
UZ-16/1317.9-1318.2/up1	9	401.76	26/60/60	7.3	420	20.6	5.1	60.1	131.6	1.1	121	0	32	0	20	18
UZ-16/1343.7-1344.0/up1	۲	409.62	07/01/93	8.4	530	17	2.4	66	62.1	1.7	47.6	58.8	56	0	18	23
UZ-16/1358.0-1358.4/up1	æ	413.98	05/06/93	7.5	550	3.4	0.3	78.7	47.9		140.3 [a]	0 [8]	22.8	0	16.1	18.7
UZ-16/1379.6-1379.9/up1	ပ	420.56	06/29/93	8.6	490	4.4	0.6	95	66.3	2.6 7	72	46.8	51	0	18	25
UZ-16/1389.3-1389.6/up3	۵	423.52	05/18/93	7.0	530	3.6	0.9	114.8	62.5	2.0	122 [a]	36.0 [a]	23.5	0	16.5	23.8
UZ-16/1395.5-1395.9/up1	ш	425.41	03/31/94	7.8	710	5.4	0.3	155	88	3.9	216	24	17	0	16	33
UZ-16/1397.7-1398.0/up1	Ľ	426.08	07/07/93	8.7	550	S	0.5	124	79.2	4.7	131.8	35.4	45	0	25	45
UZ-16/1398.5-1398.7/up1	ບ :	426.29	04/05/94	8.0	710	ŝ	4.0	145	123	7.8	237	31	7	0 (16	23
UZ-16/1408.2-1408.6/up1	I	429.28	07/28/93	9.2	580	3.3	0.3	2	66.5	34	72 [a]	70.8 [a]	ຊ :	0 (4	92 92
UZ-16/1412.9-1413.2/up1		430.71	09/16/93	8.7	450	1.2		5	75.9	- 3	165	0 9	2 6		5	3 8
UZ-16/1428.1-1428.4/up1	- , :	435.35	09/14/93	8.8	570	9. J	0.1	100	80.5	4	160	43	8 8 _	5 0	61	3 9
UZ-16/1434.2-1434.6/up1	¥ .	437.21	56/51//0	0 0 20 1	000	3.2	9.0	502	1.601	5.5	12 21	/0.8 8	3		₽ ;	2 5
UZ-10/1442.9-1443.2/Up0	J :	409.00	00/11/90		000		0.0	R.D.1	00.9	7 8	10.0 10		<u> </u>			2
UZ-10/1480.9-148/ Jupi	Ξ 2	453.27	56/17/60	7.6	005	5.0	8.0	C.R.	233.3	7.07	131	.	5 8	. .	• ;	: ;
UZ-10/10/1.1-10/1.2/UP1 1.17 14/14/7 7 14/18 1/1-14	zc	468.08	12/30/93	5 C	0/0	2 %	5 6	3	8 8	- c	101	- C	3 5		2 🗧	28
UC-101001.1-1000.1401	0	07 103	10/10/00	0.0		3 5	;; ;	3 2	ך ג ג		51	.		,	2α	30
UZ-16/1651.6-1651.7/up1	- 02	503.44	03/15/94	6 8 7 9	420	17.3	- 0 3	58	5 4 4 4	}	87	5 6	21	• •	0 00	2 8
										ب ا						
UZ-10 ground water #1 (1609.0-1614.0)	:	491.19	02/24/93	:	;	4,11	9.	7.67	38.2	7	5.012	5	0.01	0.0	7 n	7 3.1
UZ-16 ground water #2	:	491.19	02/25/93	:	:	19.2	2.1	175.1*	25.5	0	196.7	0	188*	0.6	0	31.8
(1609.0-1614.0)																
UZ-16 ground water #3	:	491.19	02/25/93	:	:	30.1	2.9	360.5*	27.2	0.2	200	0	488*	0.7	0.5	34.6
(1008.0-1014.U)		504.33				с с т т	0	1 91	9041	007	6 191	c	¥ 6 †	c	5	770
02-10 ground water #1 (1649.3-1659.2)	;	77.600	02/00/20		:	0.01	0.		0.071	a.a	7.40	5	t. -	5	2	1
UZ-16 ground water #2	:	504.22	03/09/93	:	:	8.6	0.7	65.4	18.4	0	151.6	0	10.6	0	0	25.5
(1649.3-1659.2)																
UZ-16 ground water	!	508.33	03/15/93	:	ł	8.4	1.3	87.2	16.5	0.1	197.3	0	8.6		0	27.7

Is a reverse reported by the approximate your uses satisfies were to decug squareant. The publicates first, second, third stage compression and so forth. Stage codes; /up indicates sample was extracted by unlaxial compression; /up2, /up2, etc. indicates first, second, third stage compression and so forth. The publicated footnotes for the table have not changed and still apply. Change balance values have not changed and the column has been intentionally omitted from this revised table.

Corrected Table 1, WRIR 96-4058. Summary of relation of gravimetric water-content measurements of composite core to geologic unit and degree of welding for boreholes UE-25 UZ#4 and UE-25 UZ#5¹, Yucca Mountain, Nevada

Cells with changes are outlined

[All water-content data in gram per gram; - -, indicated no data]

The revision in the outlined cell below has been checked and accepted by: $\frac{2u \cdot hu^2}{1. C. Yang} \frac{8/2x/\delta_0}{Date}$

Lithologic		Water Co gram/g			Degree of
Unit	UE-25 U2	Z# 4	UE-25 U2	Z#5	Welding
	Data Range	Average	Data Range	Average	
Tiva Canyon	0.036-0.042	0.039	0.024-0.036	0.030	Densely welded
Tiva Canyon	0.061-0.063	0.062			Moderately welded
Tiva Canyon	0.253-0.521	0.363	0.145-0.290	0.202	Partly to nonwelded
Yucca Mountain	0.101-0.210	0.157	0.059-0.143	0.110	Partly to nonwelded
Pah Canyon	0.092-0.182	0.134	0.084-0.221	0.122	Partly to nonwelded
Bedded Tuff	0.069-0.391	0.167	0.078-0.365	0.176	<u>-</u> -
Topopah Spring			0.221-0.279	0.248	Nonwelded
Topopah Spring	0.007-0.035	0.020	0.011-0.015	0.013	Densely welded

¹ From Loskot and Hammermeister (1992)



United States Department of the Interior

U. S. GEOLOGICAL SURVEY Box 25046 M.S.<u>421</u> Denver Federal Center Denver, Colorado 80225

MEMORANDUM

Date: August 31, 2000

To: Distribution

From: T. Brady, USGS, WRD, YMPB, Denver, CO

Subject: Publications -- Errata for USGS Water-Resources Investigations Report 96-4058 "Interpretation of Chemical and Isotopic Data from Boreholes in the Unsaturated Zone at Yucca Mountain, Nevada

This errata sheet corrects Tables 1, 2, and 5 of this report.

Please enclose this errata sheet with the distribution of this report.

Thank you for your cooperation with this request. If you have any questions that pertain to this matter, please contact Tim Brady at (303)236-5050, ext 249.

ini Brook

Tim Brady, Reports Specialist For Bob Craig, Chief, YMPB

BTM/mm Enclosure

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