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**ANALYSIS OF GASEOUS-PHASE STABLE AND RADIOACTIVE ISOTOPES  
IN THE UNSATURATED ZONE, YUCCA MOUNTAIN, NEVADA**

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**MASTER**

**Abstract**

The Nevada Nuclear Waste Storage Investigations Project of the U.S. Department of Energy provides that agency with data for evaluating volcanic tuff beneath Yucca Mountain, Nevada, to determine its suitability for a potential repository of high-level radioactive waste. Thickness of the unsaturated zone, which consists of fractured, welded and nonwelded tuff, is about 1,640 to 2,460 feet (500 to 750 meters). One question to be resolved is an estimate of minimum ground-water traveltime from the disturbed zone of the potential repository to the accessible environment. Another issue is the potential for diffusive or convective gaseous transport of radionuclides from an underground facility in the unsaturated zone to the accessible environment.

Gas samples were collected at intervals to a depth of 1,200 feet from the unsaturated zone at Yucca Mountain, Nevada. Samples were analyzed for major atmospheric gases; carbon dioxide in the samples was analyzed for carbon-14 activity and for  $\delta^{13}\text{C}$ ; water vapor in the samples was analyzed for deuterium and oxygen-18. These data could provide insight into the nature of unsaturated zone transport processes.

Two different collection techniques and analytical methods were used for determination of  $\text{CO}_2$  concentration, carbon isotopes, and water vapor. The results indicate that  $\text{CO}_2$  concentrations measured by both methods were not consistent, possibly because of continual fluctuations of unknown origin. Data for  $^{14}\text{C}$  indicate general agreement between the molecular sieve and KOH methods for comparable samples, and significantly different

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results for  $\delta^{13}\text{C}$  samples. More data are needed to resolve the differences. The majority of post-bomb  $^{14}\text{C}$  was observed to a depth of 40 feet (12.2 meters) below surface, and less than pre-bomb activity was measured at and below a depth of 60 feet (18.3 meters). Data for  $\delta^{18}\text{O}_v$  indicate exchange of oxygen atoms between the water and the molecular sieve occurred during degassing and affected the oxygen-isotope values. Data for  $\delta\text{D}_v$  seem to be unaffected by exchange processes. Values of  $\delta\text{D}_l$  are close to those in ground water at Yucca Mountain and at nearby areas, although values of  $\delta\text{D}_l$  determined by molecular-sieve and cold-trap methods are not consistent in direction or magnitude.

## Introduction

The Nevada Nuclear Waste Storage Investigations (NNWSI) Project of the U.S. Department of Energy provides that agency with data for evaluating volcanic tuff beneath Yucca Mountain, Nevada, to determine its suitability for a potential repository of high-level radioactive waste. This investigation is being conducted in cooperation with the U.S. Department of Energy, Nevada Operations Office, under Interagency Agreement DE-AI08-78ET44802.

One of the questions to be resolved is an estimate of minimum ground-water traveltime from the disturbed zone of the potential repository to the accessible environment. The U.S. Nuclear Regulatory Commission's (1983) siting criteria state that a site would be favorable if the pre-waste-emplacment ground-water traveltime from the disturbed zone to the accessible environment substantially exceeds 1,000 years. The U.S. Department of Energy's (1984) siting guidelines on this issue state that a site would be disqualified if the expected pre-waste-emplacment ground-water traveltime from the disturbed zone to the accessible environment is less than 1,000 years; a site would be favorable if ground-water traveltime is more than 10,000 years. Another question is the potential for diffusive or convective transport of gaseous radionuclides from an underground facility in the unsaturated zone to the accessible environment. The U.S. Nuclear Regulatory Commission's (1984) proposed rule on this issue states that a site would have a potentially adverse condition if there is a risk of vapor transport (radioactive gases) from the underground facility, located in the unsaturated zone, to the accessible environment.

The concept of storing nuclear waste in the arid-climate vadose zone appeared in the literature more than a decade ago (Winograd, 1972, 1974), and in more recent papers by Winograd (1981) and Roseboom (1983). However, little detail exists of the hydrogeology of Yucca Mountain. No isotopic and chemical data have been reported for the unsaturated-zone water of Yucca Mountain. The purpose of this study is directed at evaluating analytical methods for determining gas constituents in the unsaturated zone of Yucca Mountain.

## Physiographic and Geologic Description of Yucca Mountain

The Yucca Mountain study area is located near the southwestern corner of the Nevada Test Site in southern Nevada, within the Great Basin physiographic province, and in the most arid region of the United States. Average annual precipitation at the mountain is estimated to be about 5.9 in. (150 mm), and the average annual recharge rate is estimated to range from 0.02 to 0.18 in. (0.5 to 4.5 mm) (Montazer and Wilson, 1984). The altitude of the mountain is 4,823 ft (1,470 m). A very thick, 1,640 to 2,460 ft (500 to 750 m), unsaturated zone occurs beneath Yucca Mountain. The zone consists of extensively fractured, densely welded, minimally porous, but transmissive, ash-flow tuff, interbedded with less fractured, nonwelded, porous, but less transmissive, argillic and zeolitic bedded tuff and ash-flow tuff. The mountain consists of a series of north-trending fault-block ridges with an eastward tilt of about 5° to 30°. The proposed high-level nuclear-waste repository would be emplaced in the densely welded fractured tuff in the central block of Yucca Mountain.

### Sample Collection

Gas samples were collected from the borehole USW UZ-1 located at the northern end of the central block on Yucca Mountain (fig. 1). Borehole USW UZ-1 was drilled by a reverse-vacuum method to a depth of 1,269 ft (387 m) in 1983 (Whitfield, 1985, this proceedings).

During drilling, air was withdrawn through the inner string of the concentric dual-string pipe by vacuum at a rate of about 1,400 ft<sup>3</sup>/min (39.6 m<sup>3</sup>/min). Air was injected into the annulus of the inner string at a rate of about 315 ft<sup>3</sup>/min (8.9 m<sup>3</sup>/min) and air also circulated downward through the annulus between the borehole wall and the drill-string to make up the difference between the injected and withdrawn volumes. Sulfur hexafluoride (SF<sub>6</sub>) was added to the injected air or to the air stream in the hole annulus or to both at a rate of 40 to 50 mL/min except for occasional increases to a rate of 100 mL/min or more. If perfect mixing is assumed, the resulting mixture should have contained about 1 ppmv (part per million by volume) SF<sub>6</sub>. However, the vacuum rate varied somewhat, particularly when the inner string became partly plugged, and may have decreased to a few hundred cubic feet per minute at times. At those times, the SF<sub>6</sub> concentrations may have increased to as much as a few parts per million by volume.

The hole was completed with 15 sampling stations, including gas probes, isolated from each other by silica flour and cement grout. Details of probe construction are given by Montazer et al. (1985, this proceedings).

### Samples for Analysis of Sulfur Hexafluoride

Samples were collected and analyzed for SF<sub>6</sub> onsite on March 31-April 2, 1984, by personnel of Tracer Research, Inc., Tucson, Arizona, using a gas chromatograph equipped with an electron-capture detector. In addition, later samples were collected and shipped to Tracer Research, Inc., for analysis. For the samples collected and analyzed on March 31, each probe

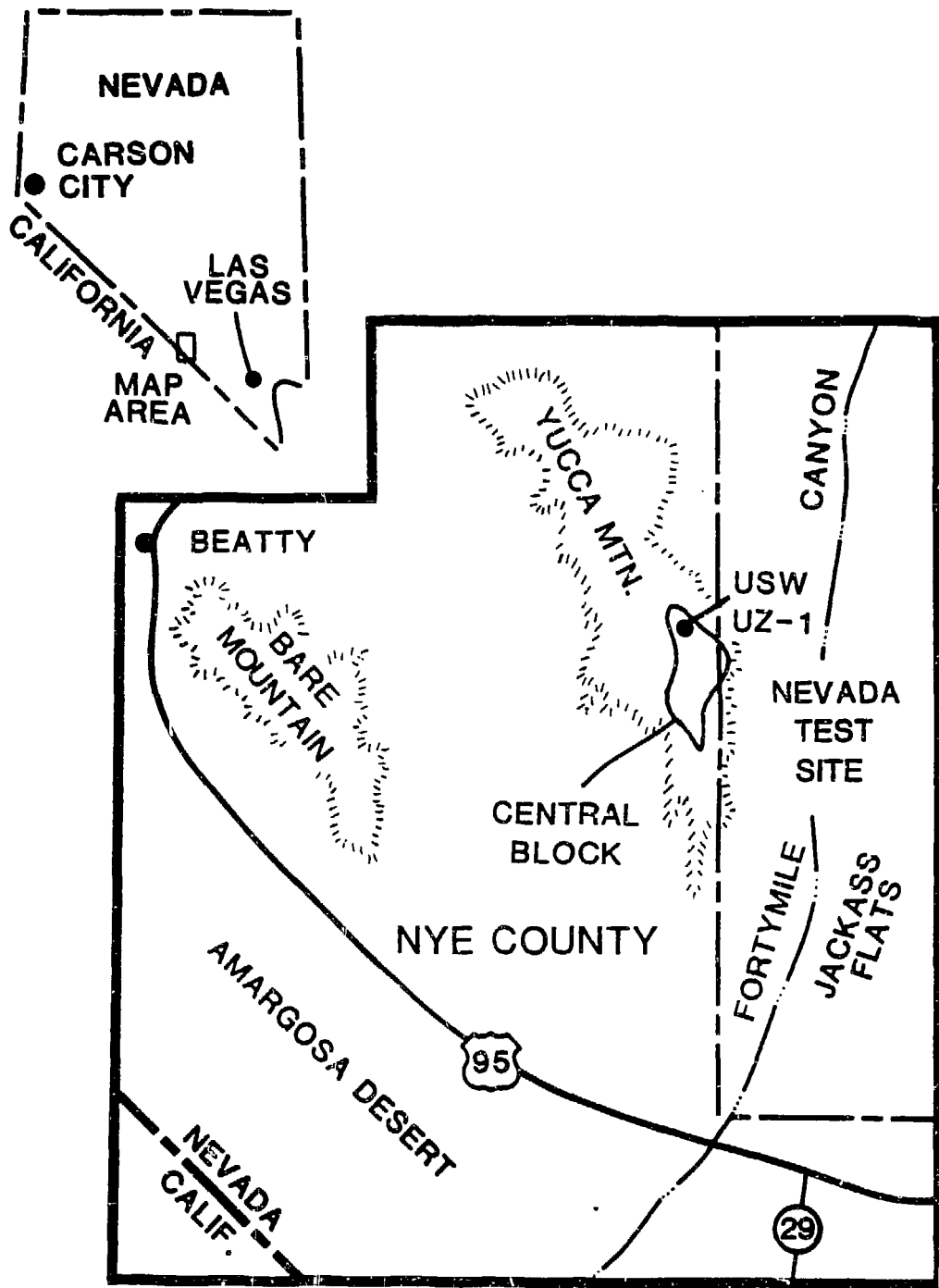


Figure 1. Location of borehole USW UZ-1

was pumped for 30 min (more than 30 times the volume of probe) prior to collecting a sample for analysis. Samples were collected through silicone tubing by syringe and injected directly into the gas chromatograph. After sampling was completed on March 31, probes 1-13 were connected through manifolds to two rotary-vane pumps and pumped overnight. The probes were resampled on April 1, the sampled probes being pumped individually, using a peristaltic pump for about 15 min prior to sampling. The deeper probes were pumped overnight on April 1 and again resampled on April 2.

Samples for analysis of SF<sub>6</sub> also were collected on September 17, 1984. These samples were collected in previously evacuated stainless-steel containers and shipped to Tracer Research, Inc., for analysis.

#### Samples for Analysis of Carbon Dioxide

Samples were collected for analysis of CO<sub>2</sub> by gas chromatography (thermal-conductivity detector) in November 1983; January, March, April, September, and December 1984; and May 1985. In addition, gas samples were analyzed onsite for CO<sub>2</sub> by gas chromatography on April 1-2, 1984. Concentrations of CO<sub>2</sub> also were computed for March and May 1985 from the volume of CO<sub>2</sub> recovered during molecular sieve trapping, as described below, divided by the volume of soil gas pumped through the molecular sieve.

For the gas-chromatography method, gas samples were collected in 15.25-in.<sup>3</sup> (250-mL) flow-through gas collector (glass tube), with stopcocks on both ends. For those samples not collected for <sup>14</sup>CO<sub>2</sub> analysis, the gas collector was installed upstream of a rotary-vane vacuum pump, which was operated for 30 min before the sample was collected. After that time, the downstream stopcock was closed and the pump was shut off. After 5 min, the upstream stopcock was closed. The stopcocks were taped to insure against accidental opening during shipping, and were shipped to the U.S. Geological Survey at Reston, Virginia, for analysis. For samples collected for <sup>14</sup>CO<sub>2</sub> analysis, a similar procedure was followed, except that a peristaltic pump was used.

#### Samples for Analysis of Carbon Isotopes

Samples were collected for the analysis of <sup>14</sup>CO<sub>2</sub> activity and for determination of <sup>13</sup>C/<sup>12</sup>C ratios in April 1984 and in March and April-May, 1985. In 1984, samples were collected from probes 1-13 by trapping with KOH solution, using a method described by Haas et al. (1983). In 1985, samples were collected using molecular-sieve traps for all 15 probes and by KOH for 5 probes.

The KOH method: For this method, described in detail by Haas et al. (1983), soil gas is pumped through KOH solution by a peristaltic pump installed downstream from the bubbler. The soil gas is dispersed through a fritted plate into 15.25 in.<sup>3</sup> (250 mL) of 5.0 molar KOH solution at a rate of 30.5 in.<sup>3</sup> (500 mL/min), and the CO<sub>2</sub> is absorbed in the solution. Ideally, about 48.8 in.<sup>3</sup> (800 mL) of CO<sub>2</sub> is trapped. However, CO<sub>2</sub> concentrations were so small in the soil gas from all probes except probe 1 that they were pumped for 10 d to obtain about 4.9 to 18.3 in.<sup>3</sup> (80 to 300 mL) for analysis.

Molecular-sieve (MS) method: Gas-collection cylinders with a volume of 18.3 in.<sup>3</sup> (300 cm<sup>3</sup>), filled with Linde 5A molecular-sieve pellets, 1/16 in. (0.159 cm), were used for gas sampling. Details of the sampler are shown in figure 2a. The cylinder was made of 304L stainless steel, connected to Nupro<sup>1</sup> B4HK2 valves attached to hosebarbs at both ends. In addition, one end of the cylinder was equipped with a check-valve between the hosebarb and valve to prevent backflow of air during sample collection.

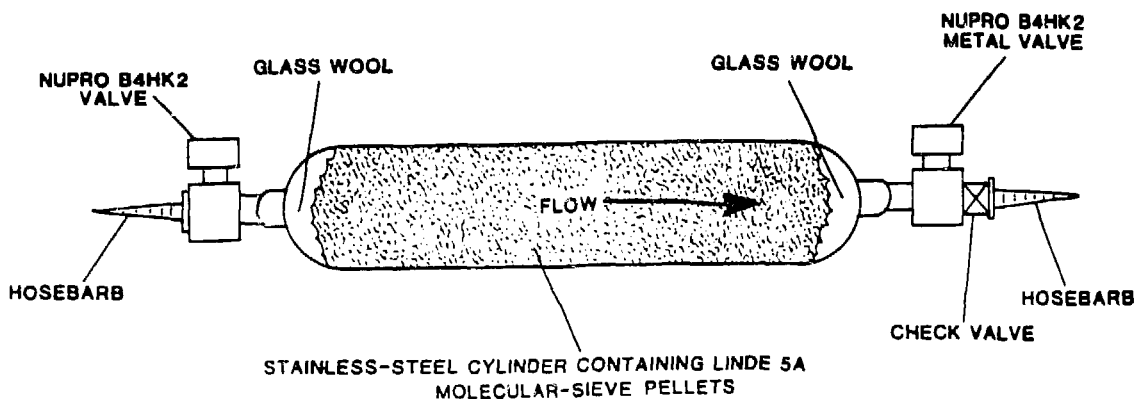


Figure 2a. Gas sampler

The onsite setup of equipment for soil-gas collection by the MS method is shown in figure 2b. Soil-gas probes were pumped overnight before sample collection to purge the lines and probes of any atmospheric air that might have been introduced while connecting the pumps to the system. During sample collection, the sample gas was pumped at a flow rate of 30.5 in.<sup>3</sup>/min (500 mL/min). The date, start, and end times of pumping were recorded, so that total volumes of gas flow through the sampler could be calculated. The MS trapped both water vapor and CO<sub>2</sub>. If saturation of the MS were to be attained during the process, water vapor would displace CO<sub>2</sub>. Therefore, a small ascarite-filled glass tube was attached to the downstream side of the system to monitor CO<sub>2</sub>-gas escape (formation of white NaHCO<sub>3</sub> on the ascarite). The uncertainty in this gas detection was about 5 mg CO<sub>2</sub>. A sampler of this size should trap about 0.84 ft<sup>3</sup> (24 L) of CO<sub>2</sub> at 25°C and 1 atmosphere in the absence of water, and about 100 mL of liquid water. This capacity is sufficient for CO<sub>2</sub> sampling at the Yucca Mountain site. If gases with substantial moisture content are expected, a larger capacity cylinder, 30.5 in.<sup>3</sup> (500 mL), needs to be used. The collection efficiency and performance data are given in a paper by Yang (1983). Limited equipment and space allowed sampling only 5 to 8 probes at a time, with each sample requiring 4 to 5 d to collect. The 15 probes were sampled in 2 onsite trips with probes 9, 11, and 15 being resampled.

<sup>1</sup>Any use of trade name is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

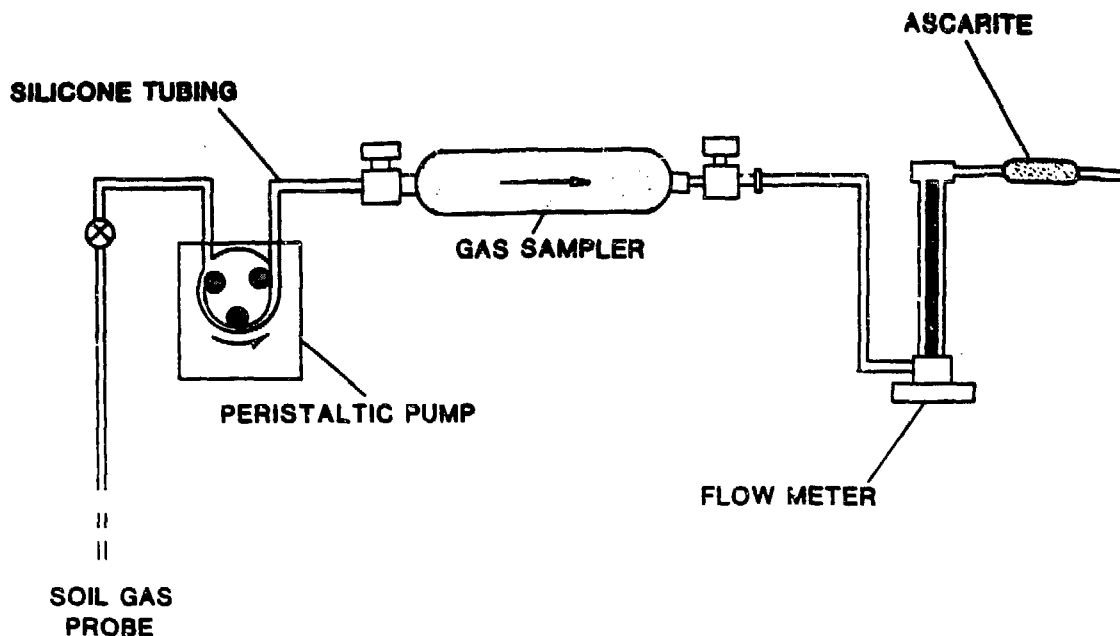


Figure 2b. Onsite apparatus for soil-gas collection.

### Samples for Analysis of Water Vapor

Dry-ice acetone trap: For samples collected for analysis of water vapor, a dry-ice acetone slush was used. A glass-vacuum trap, immersed into the slush contained in the dewar, replaced the gas sampler in figure 2b. Collection time of 36 to 48 h yielded about 0.61 in.<sup>3</sup> (10 mL) of liquid water.

MS method: Water vapors and CO<sub>2</sub> were collected simultaneously. The MS was heated under vacuum at 350°C overnight prior to collection, to ensure that no moisture from previous collections was trapped in the sieve. Collection efficiency was not determined.

### Sample Analyses

#### Sulfur-Hexafluoride Samples

Sulfur-hexafluoride (SF<sub>6</sub>) samples were analyzed both onsite and in the laboratory by personnel of Tracer Research, Inc., Tuscon, Arizona, using a gas chromatograph equipped with an electron-capture detector.

#### Carbon-Dioxide Samples

Carbon-dioxide samples collected by the gas collector were analyzed by gas chromatography (thermal-conductivity detector) at the U.S. Geological Survey Laboratory in Reston, Virginia. Concentrations of CO<sub>2</sub> determined by the MS method were computed from the volume of CO<sub>2</sub> recovered during molecular-sieve trapping divided by the volume of soil gas pumped through the sieve.

## Carbon-Isotope Samples

**KOH method:** The  $\text{CO}_2$  collected in the KOH solution was released by acidification and converted into benzene for  $^{14}\text{C}$  analysis by scintillation counting at the Southern Methodist University (SMU) radiocarbon laboratory. Details of the method were described by Haas et al. (1983). The ratio of  $^{13}\text{C}/^{12}\text{C}$  also was determined at the SMU isotope laboratory. For small-size samples (less than 15.25 in.<sup>3</sup> or 250 mL  $\text{CO}_2$  gas at 25°C and 1 atmosphere),  $^{14}\text{C}$  concentrations were measured using the Tandem accelerator mass spectrometer at the University of Arizona.

**MS method:** The  $\text{CO}_2$  gas trapped in the MS was degassed at the U.S. Geological Survey laboratory in Denver. Because both  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were trapped in the MS, a system was designed to separate the two components; this system is shown in figure 3. The MS was heated to 350°C in a vacuum

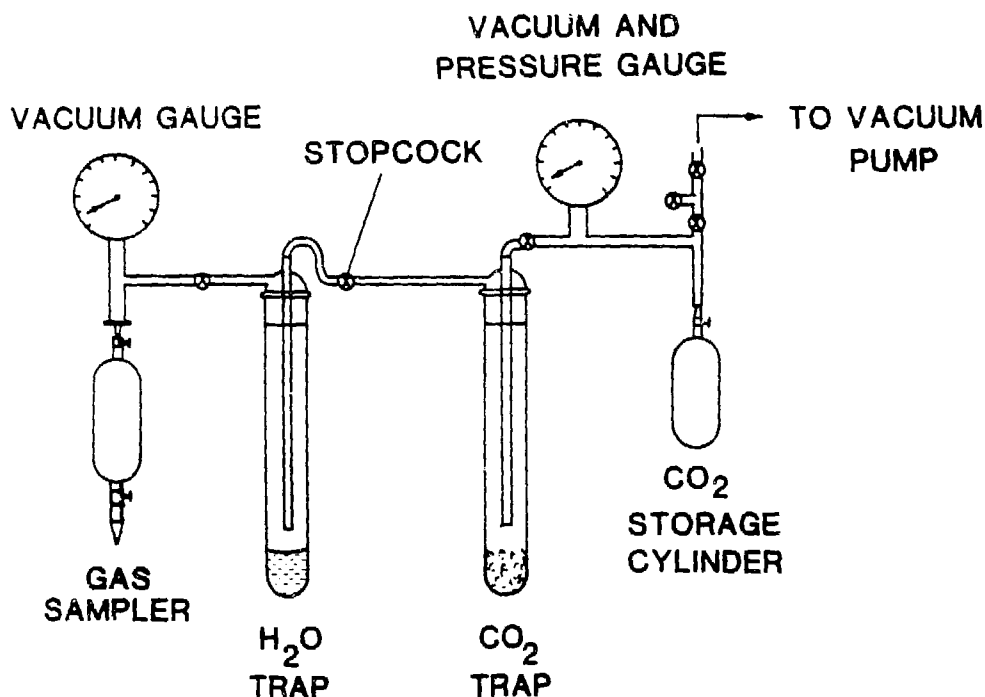


Figure 3. Degassing system

system. Water was collected in a dry-ice acetone trap;  $\text{CO}_2$  was collected in a liquid-nitrogen trap. Complete degassing took 10 h or longer. The volume of the collected  $\text{CO}_2$  was measured in a calibrated flask equipped with a pressure gage. The gas was then transferred to a storage cylinder. Carbon-dioxide samples of more than 36.6 in.<sup>3</sup> (600 mL) at 25°C and 1 atmosphere were sent to Geochron Laboratory (Krueger Enterprise, Mass.) for  $^{14}\text{C}$  analyses, by conventional gas counting of  $\text{CH}_4$ . Two samples with volumes of 30.5 and 24.4 in.<sup>3</sup> (300 and 400 mL) were dated at the SMU radiocarbon laboratory. Even smaller samples have been submitted to the



University of Arizona (Tucson) for analyses by using the Tandem accelerator mass spectrometer. Results were not available at the time of preparation of this paper.

### Water-Vapor Samples

Water samples collected by cold trap and by MS (degassed, as mentioned in the previous section) were sent to the U.S. Geological Survey laboratory in Reston, Virginia, for determination of  $^3\text{H}$ , and  $^{18}\text{O}/^{16}\text{O}$  and D/H ratios.

## Results and Discussion

### Sulfur-Hexafluoride Concentrations

The results of the  $\text{SF}_6$  analyses are given in table 1. Based on the introduced atmospheric air having an  $\text{SF}_6$  concentration of 1 ppmv, soil gas would contain 10 to 30% residual atmospheric air. However, the measured  $\text{CO}_2$  concentrations and carbon-isotope data indicate that the proportion of residual atmospheric air should be significantly less. Hence it is likely that the effective concentration of  $\text{SF}_6$  in the drilling air was greater than 1 ppmv, and may have been as much as 2 ppmv, resulting in a contamination level of 5 to 15% as of September 1984. Air contamination should be successively less during subsequent sampling.

### Carbon-Dioxide Concentrations

Concentrations of  $\text{CO}_2$  measured at borehole USW UZ-1 are given in tables 2a and 2b. Concentrations were large in probe 1, which is in alluvium. Such concentrations are typical of soil gas at other sites (Thorstenson et al., 1983, for example), and results from root respiration and microbial activity in the soil zone. However, at probe 2, located in nonwelded tuff a few feet below its contact with alluvium, and in all lower probes, concentrations were much smaller, and at several screens, concentrations were less than atmospheric.

The  $\text{CO}_2$  concentrations also show substantial variations with time since sampling began in November 1983. The November 1983 samples are particularly anomalous, possibly because they were collected only several days after the hole had been instrumented, and  $\text{CO}_2$  in the soil gas may have been sorbing and equilibrating with the stemming materials. However, large variations in  $\text{CO}_2$  concentrations with time were measured even after large volumes of soil gas were pumped for  $^{14}\text{CO}_2$  sampling in April 1984. Moreover, the trends are inconsistent, with concentrations of samples from some probes alternately increasing and decreasing; other samples showed trends of steadily increasing concentrations, and still others showed steadily decreasing concentrations. Such variations with depth were unanticipated, and generally are not detected at other locations (Thorstenson et al., 1983, for example). Continued sampling may help determine the causes of the variations, or concentrations may eventually stabilize.

Table 1. Summary of SF<sub>6</sub> data for borehole USW UZ-1 March 31-April 2, 1984, and for September 17, 1984

[ppmv = parts per million by volume]

Probe No.	Date	SF <sub>6</sub> Concentration (ppmv)	Probe No.	Date	SF <sub>6</sub> Concentration (ppmv)
1	3/31	1.47	8	3/31	0.16
	4/1	.60		4/1	.16
	9/17	.34		4/2	.18
		9/17		.16	
2	3/31	.08	9	3/31	.19
	4/1	.58		4/1	.16
	9/17	<sup>1</sup> 1.018		4/2	.15
3	3/31	.49	10	3/31	.15
	4/1	.30		4/1	.06
	9/17	.27		4/2	.07
4	3/31	.58	11	3/31	.15
	4/1	.33		4/1	.06
	9/17	.26		4/2	.07
5	3/31	.18	12	3/31	.25
	4/1	.16		4/1	.19
	9/17	.09		4/2	.19
6	3/31	.13	13	3/31	.25
	4/1	.12		4/1	.18
	9/17	.09		4/2	.18

<sup>1</sup>Bad sample (?).

Concentrations of CO<sub>2</sub> also were measured in the molecular-sieve samples. These should, assuming 100% trapping efficiency, represent integrated values for a large volume of soil gas. However, separate samples from a given probe also indicated large variations in CO<sub>2</sub> concentrations, varying by as much as a factor of 5. Agreement with the later gas chromatography data, particularly December 1984 and May 1985, ranges from good to poor. When the correspondence between methods is poor, the results of the MS analyses are consistently less than those of the GC analyses.

Table 2a. Carbon-dioxide concentrations from soil gas by molecular-sieve method, borehole USW UZ-1

[CO<sub>2</sub> concentrations are percent (%) by volume; dashes indicate no data]

Probe No.	Depth		Collection date (1985)	CO <sub>2</sub> (%)	Collection date (1985)	CO <sub>2</sub> (%)
	(ft)	(m)				
1	42	12.8	--	--	4/30-5/1	0.790
2	62	20.3	--	--	4/30-5/2 5/3	.029 .088
3	93	28.3	--	--	4/30-5/2 5/3	.014 .013
4	131	39.9	--	--	--	--
5	201	61.3	--	--	4/30-5/2 5/3	.021 .033
6	266	81.1	3/26-27	0.030	--	--
7	348	106.1	3/23-24	.016	--	--
8	421	128.3	3/25-26 3/27	.064 .052	--	--
9	501	152.7	3/25 3/26	.011 .007	5/2-3	.014
10	621	189.3	3/23-24 3/27	.014 .053	--	--
11	747	227.7	3/19-21 3/23	.011 .010	4/29-30 5/1-2	.035 .055
12	871	265.5	3/19-20 3/21	.016 .009	--	--
13	998	304.2	3/19-21 3/24-25	.004 .002	--	--
14	1,100	335.3	3/19-21 3/22-23 3/23-25	.012 .001 .019	--	--
15	1,207	367.9	3/19-21	.039	4/29-30 5/1-3	.046 .027

Carbon Isotopes (<sup>14</sup>C and <sup>13</sup>C/<sup>12</sup>C ratio)

Carbon-14 activity and δ<sup>13</sup>C values from individual probes obtained by both KOH and MS methods are presented in table 3. In addition, volumes of CO<sub>2</sub> gas collected and measured at 25°C and 1 atmosphere also are tabulated.

Table 2b. Carbon-dioxide concentrations from soil gas by gas-chromatography method, borehole USW UZ-1

[CO<sub>2</sub> concentrations are percent (%) by volume; dashes indicate no data]

Probe No.	Depth		CO <sub>2</sub> (%) on indicated collection date							
	(ft)	(m)	11/9/83	1/18/84	3/12/84	4/1-2/84 <sup>1</sup>	4/9-10/84	9/17/84	12/17/84	5/4-6/85
1	42	12.8	0.024	0.32	0.67	1.1	0.83	0.58	1.05	1.64 1.37
2	62	20.3	<.005	.01	.02	.03	.023	.037	.045	.15
3	93	28.3	.011	.02	.016	.035	.026	.023	.022	.01
4	131	39.9	<.005	.004	.013	.02	.033	.077	.079	.09
5	201	61.3	.019	.06	.085 .076	.06	.24	.107	.10	.04
6	266	81.1	.035	.08	.13	.12	.08	.07	.026	--
7	348	106.1	.032	.10	.065	.075	.07	.08	.08	.06
8	421	128.3	.105	.06	.059 .061	.10	.09	.06	.09	.06 .11
9	501	152.7	.024	.04	.063	.05	.05	.09	.07	.06 .11
10	621	189.3	.006	.06	.009	.04	.04	.04	.04	--
11	747	227.7	<.005	.05	.006 .007	.025	.026	.05	.05	.08 .10
12	871	265.5	<.005	.003	<.006	<.004	<.004	--	<.003	<.02
13	998	304.2	<.005	<.003	.006	ND <sup>2</sup>	.009	--	<.003	<.01
14	1,100	335.3	<.005	.020	--	--	-	--	--	.02
15	1,207	367.9	.020	--	--	--	--	--	--	.18

<sup>1</sup> Samples analyzed onsite by Tracer Research, Inc.

<sup>2</sup> ND = not detectable.

Table 3. Summary data for gas-phase CO<sub>2</sub> and δ<sup>13</sup>C and <sup>14</sup>C, borehole USW UZ-1[Errors for δ<sup>13</sup>C values = ± 0.2‰; CO<sub>2</sub> %-volume are weighted values; dashes indicate no data; blank indicates sample being analyzed]

Probe No.	Depth		Molecular-sieve method <sup>1</sup>				KOH-method <sup>2</sup>				
	(ft)	(m)	Collection Date	CO <sub>2</sub> (% vol.)	CO <sub>2</sub> vol. (l)	δ <sup>13</sup> C (‰)	<sup>14</sup> C (% modern)	Collection Date	CO <sub>2</sub> vol. (l)	δ <sup>13</sup> C (‰)	<sup>14</sup> C (% modern)
		Air	--	--	--	--	--	4/05-10/84	1.87	- 8.91	125.63 ± 1.01
		Surface	--	--	--	--	--	(4/29-5/6)85	1.71	- 8.56	124.43 ± 1.78
								4/06-11/84	6.40	-16.63	124.29 ± 0.38
								(4/30-5/6)85	3.60	-14.62	123.39 ± 1.55
1	42	32.8						4/2-7/84	8.1	-25.68	120.55 ± 0.66
								4/7-12/84	13.2	-26.30	120.99 ± 0.38
			(4/30-5/2)85	0.789	5.680	-22.3	121.8 ± 1.8	(4/30-5/2)85	8.9	-24.04	120.23 ± 0.64
								5/5-6/85	6.9	-23.04	120.75 ± 0.62
2	62	20.3	(4/30-5/4)85	.043	1.230	-26.2	99.3 ± 1.7	4/1-10/84	0.87	-14.58	67.42 ± 0.87
3	93	28.3						4/1-10/84	0.88	-11.70	62.57 ± 1.95
			(4/30-5/6)85	.014	1.18	-25.0	85.3 ± 2.3 <sup>3</sup>	(4/30-5/6)85	1.18	-17.68	79.96 ± 1.45
4	131	39.9						4/1-10/84	1.10	-19.96	77.37 ± 1.52
								(4/30-5/6)85	3.0	-20.79	87.57 ± 1.08
5	201	61.3						4/1-10/84	2.6	-15.68	77.35 ± 0.79
			(4/30-5/4)85	.024	.640	-23.8	70.3 ± 3.3	(4/30-5/6)85	2.30	-17.87	72.15 ± 0.88
6	266	81.1	3/26-28/85	.030	.430	-19.2	85.1 ± 4.0 <sup>3</sup>	4/1-10/84	1.50	-15.27	77.24 ± 1.48
7	348	106.1						4/1-10/84	2.70	-14.79	76.98 ± 0.90
			3/27-28/85	.016	.235			(4/30-5/6)85	2.60	-16.59	72.88 ± 0.74
8	421	128.3	3/25-27/85	.059	.430	-23.3	88.3 ± 2.5	4/1-10/84	3.70	-15.18	74.62 ± 0.67
9	501	152.7	3/25-26/85	.009				4/1-10/84	2.1	-15.13	73.23 ± 0.94
			5/2-4/85	.013	.185						
10	621	189.3	3/27-28/85	.024	.210	-15.8		4/1-10/84	1.7	-12.82	64.02 ± 0.90
11	747	227.7	3/19-23/85	.011				4/1-10/84	1.64	- 9.69	49.94 ± 1.23
			5/1-4/85	.045	.800	-20.1	61.7 ± 1.8				
12	871	265.5	3/19-22/85	.013	.185	-25.4		4/8-10/84	0.014	-18.09	100.4 ± 3.7 <sup>4</sup>
13	998	304.2	19-22; 24-26/85	.003	.104	-11.0		4/9-10/84	.004	--	73.3 ± 2.5 <sup>4</sup>
14	1,100	335.3	3/19-25/85	.011	.385	-21.6					
15	1,207	367.9	3/19-22/85	.039	.540	-21.0	34.2 ± 1.5				
			(4/29-5/1)85	.034							

<sup>1</sup> All <sup>14</sup>C and δ<sup>13</sup>C under molecular-sieve method were measured by Geochron Laboratory, Kruger Enterprise, Inc., Cambridge, Massachusetts, except as otherwise noted.  
<sup>2</sup> All <sup>14</sup>C and δ<sup>13</sup>C under KOH method were measured by Southern Methodist University (SMU) radiocarbon laboratory, Dallas, Texas, except as otherwise noted.  
<sup>3</sup> All <sup>14</sup>C and δ<sup>13</sup>C under molecular-sieve method were measured by SMU radiocarbon laboratory.  
<sup>4</sup> All <sup>14</sup>C and δ<sup>13</sup>C under KOH method were measured by the Tucson accelerator, University of Arizona, Tucson, Arizona.

**Carbon-14 activities:** Several of the probes showed large changes between 1984 and 1985, and may still be changing. Comparing data by the KOH method, values for samples from probes 1 virtually were the same, those for probes 3 and 4 had large increases from 1984 to 1985, and that for probe 7 had a small decrease. For the three probes for which 1985 data from both the KOH and MS methods are available, the results of two (probes 1 and 5) compare well, and for one (probe 3), the MS method resulted in somewhat larger values. However, the magnitude of the difference is not totally out of the range that might be expected from statistics, and more comparisons are needed.

The results of the three other samples (probes 2, 8, and 11) collected by the MS method in 1985 indicate a substantially greater  $^{14}\text{CO}_2$  activity than those from the same probes determined by the KOH method in 1984. It is not known whether these discrepancies result from temporal changes or from differences in the methods.

A plot of  $^{12}\text{CO}_2$  and  $^{14}\text{CO}_2$  mole fractions versus depth is presented in figure 4 for samples collected in March and May 1985 by the MS method. The  $^{14}\text{CO}_2$  mole fractions were calculated from a formula derived by Thorstenson et al. (1983). The  $^{14}\text{CO}_2$  mole fractions were plotted at  $10^{-12}$  the scale of the  $^{12}\text{CO}_2$  mole fractions. The data presented in figure 4 are considered to be preliminary, because the gas concentrations continue to change at the site, and the changes in  $^{14}\text{C}$  noted above may still be occurring. However, one conclusive statement can be made regarding  $^{14}\text{CO}_2$  in the unsaturated zone. The mole fraction of  $^{14}\text{CO}_2$  at probe 1 is significantly greater than that at the land surface or other depths. This large value is the result of a series of atmospheric-nuclear tests conducted in the early 1960's, that introduced significant quantities of  $^{14}\text{CO}_2$  into the atmosphere, which subsequently were incorporated into the soil gas through plant respiration. Therefore, this large value is a good indicator of the penetration of gaseous  $\text{CO}_2$  from the early 1960's to that depth. A general trend of rapidly decreasing  $^{12}\text{CO}_2$  mole fractions followed by small decreases with depth occurred as noted above, except in probes 8, 11, and 15. Larger  $^{12}\text{CO}_2$  concentrations at probes 8 and 15 also are indicated by the GC method. More data are needed to confirm these variations with depth.

**Carbon-13/Carbon-12 Ratios:** Carbon 13/Carbon-12 ratios are presented in table 3 for 12 of the 13 samples collected by the KOH method in 1984, the 5 samples collected by the KOH method in 1985, and 12 of the 15 samples collected by the MS method in 1985. Results for the samples collected in 1984 have a tendency toward a fairly uniform profile distributed about  $\delta^{13}\text{C}$  values ranging from -15 to -17‰ (7 samples, with 4 substantially heavier and 3 substantially lighter). Results for probe 1 indicate exceptionally light values among these samples. Of the samples collected by the KOH method in 1985, the  $\delta^{13}\text{C}$  value for probe 1 became heavier, and  $\delta^{13}\text{C}$  values for the other 4 probes were somewhat to substantially lighter than those measured in 1984. The values for  $\delta^{13}\text{C}$  in samples collected by the MS method tend to be lighter (-19 to -26‰) but values for probes 10 and 13 are somewhat heavier.

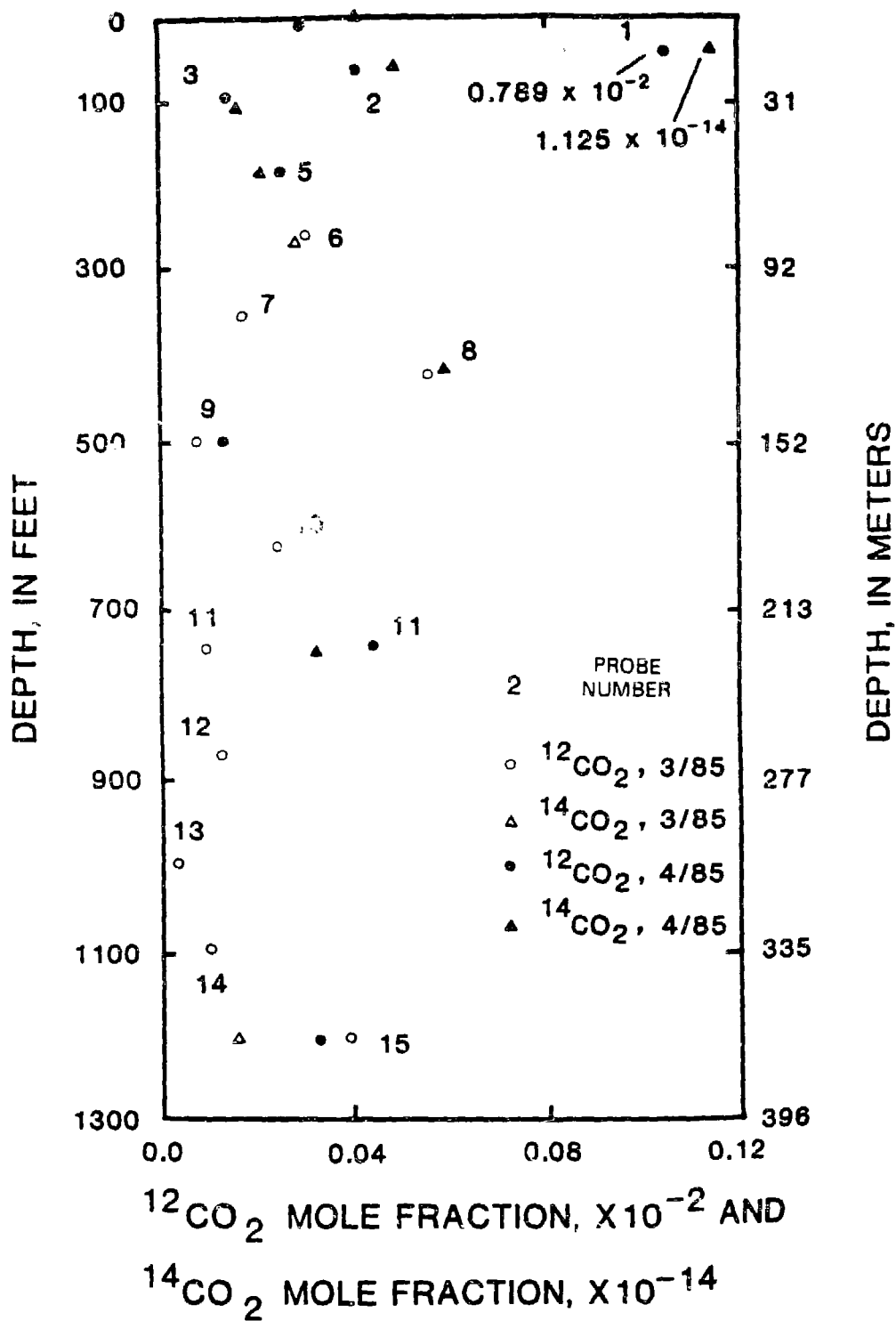


Figure 4.  $^{12}\text{CO}_2$  and  $^{14}\text{CO}_2$  mole fraction versus depth

Comparisons of the  $\delta^{13}\text{C}$  values for samples collected by the two methods are only possible for probes 1, 3 and 5. The  $\delta^{13}\text{C}$  value for the sample collected by MS for probe 1 is somewhat heavier than that for the sample collected by KOH. For the other two probes, the  $\delta^{13}\text{C}$  values for the samples collected by MS are lighter by 6 to 7%. Discrepancies between the methods are under investigation.

### Water Vapor

Stable isotopic data of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  in water vapor collected from individual probes by the MS and cold-trap methods are given in table 4. In addition, the calculated in-situ, liquid-phase isotopic data of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  are provided, assuming the vapor is in equilibrium with the water phase at 25°C. As indicated in the table, the difference in isotopic ratios of  $\delta\text{D}_v$  in samples collected by the cold-trap and molecular-sieve methods is reasonably comparable for probes 7 and 8, whereas they are significantly different for probes 1, 11, and 13. Moreover, the direction and magnitude in  $\delta\text{D}_v$  values determined by the two methods are not consistent. Apparent differences in  $\delta\text{D}_v$  by the two methods may be due to fractionation of vapor during pumping from depth to the land surface through several stages of condensation and evaporation in the small (0.118-in. or 3-mm) probe tubes. In any case, the overall calculated values of  $\delta\text{D}_v$  values are close to those in ground water at Yucca Mountain and at nearby areas (-97 to -110 ‰), obtained by Benson et al. (1983) and Claassen (1983). However, the  $\delta^{18}\text{O}_v$  values determined by the two methods were very different in all cases, with the MS-method results being much heavier. This heavier tendency is attributed to the exchange of oxygen atoms between the water and MS ( $\text{SiO}_2$ ) materials during degassing at 350°C.

Repeated sampling of water vapor by both methods or other improved methods will be continued to ensure that consistent values are obtained. These data also will be compared with isotopic data obtained by squeezing and centrifuging of pore fluids from cores to be collected at other areas on Yucca Mountain.

### Conclusions

#### Evaluation of Molecular-Sieve Method

The principal advantage of the MS method of  $\text{CO}_2$  gas and water-vapor sampling is its simple design and insured nonbreakable shipping between the sampling site and the laboratory. For water-vapor collection, an exchange of oxygen atoms between the water and the molecular sieve occurred during degassing and affected the oxygen-isotope values. The hydrogen-isotopic data seem to be unaffected by exchange processes, and values were close to those in ground water at Yucca Mountain and at nearby areas. Thus,  $\delta\text{D}$  data (and possibly tritium data) can be obtained by the MS method simultaneously with  $\text{CO}_2$  samples, whereas the KOH method cannot be used to collect both samples at the same time.



Table 4. Stable-isotope ratios in water vapor, borehole UG-1, Grinnell, Antarctica.

[ $\delta$  values are in parts per thousand (‰) relative to V-SMOW standard, errors for  $\delta D = \pm 2$ , and  $\delta^{18}O = \pm 0.2$ ; CT = cold-trap method; MS = molecular-sieve method; dashes indicate no data]

Probe No.	Depth		Collection date	Collection method	$\delta D_v$ (‰)	$\delta^{18}O_v$ (‰)	$\delta D_1^1$ (‰)	$\delta^{18}O_1^1$ (‰)
	(ft)	(m)						
1	42	12.8	4/10/84	CT	-169.5	-19.7	-108.0	-10.7
			4/30/85	MS	-151.0	- 6.4	- 88.2	+ 2.7
2	62	20.3	5/02/85	MS	-173.5	-12.3	-112.3	- 3.2
3	93	28.3	5/02/85	MS	-170.5	-13.9	-109.1	- 4.8
4	131	39.9	--	--	--	--	--	--
5	201	61.3	5/02/85	MS	-161.0	- 7.5	- 98.9	+ 1.6
6	266	81.1	3/26/85	MS	-185.0	-10.6	-124.7	- 1.5
7	348	106.1	4/10/84	CT	-187.0	-23.6	-126.8	-14.6
			3/25/85	MS	-188.5	-12.6	-128.4	- 3.5
8	421	128.3	4/10/84	CT	-170.0	-22.0	-108.6	-13.0
			3/25/85	MS	-175.5	- 9.5	-114.5	- 0.4
			3/27/85	MS	-172.0	- 7.0	-110.7	+ 2.1
9	501	152.7	3/25/85	MS	-189.0	-15.6	-129.0	- 6.5
			3/26/85	MS	-194.0	-13.4	-134.4	- 4.3
			5/02/85	MS	-174.5	-14.4	-113.4	- 5.3
10	621	189.3	3/23/85	MS	-176.5	-13.8	-115.6	- 4.7
11	747	227.7	5/01/85	CT	-175.5	-22.7	-114.5	-13.7
			3/21/85	MS	-191.0	-14.5	-131.1	- 5.4
			4/29/85	MS	-159.0	- 5.7	- 96.8	+ 3.4
12	871	265.5	3/20/85	MS	-164.0	- 7.3	-102.1	+ 1.8
13	998	304.2	4/10/84	CT	-188.0	-24.7	-127.9	-15.7
			3/21/85	MS	-176.5	-14.7	-115.6	- 5.6
14	1,100	335.3	3/21/85	MS	-172.0	-17.9	-110.7	- 8.9
15	1,207	367.9	3/19/85	MS	-172.0	-14.4	-110.7	- 5.3
			4/29/85	MS	-157.0	- 8.0	- 94.6	+ 1.1
			5/01/85	MS	-142.5	-13.9	- 79.0	- 4.8

Note:  $^1\delta D_1$ ,  $\delta^{18}O_1$  are calculated liquid-phase isotopic data, assuming water-vapor equilibrium at 25°C.

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### Biographical Sketch

A native of Taiwan, Dr. In Che Yang received his bachelor of science degree in chemical engineering from National Taiwan University, master of science in nuclear chemistry (1966) from Carleton University, Canada, and doctor of philosophy degree in isotope geochemistry (1971) from the University of Washington. He worked at the Department of Geology, University of Washington as a post-doctor (1971-73), Research Assistant (1973-75), and Research Assistant Professor (1975-78) after graduation. Dr. Yang joined the U.S. Geological Survey in April 1978. He was section chief of the Radiochemical Section (1980-84), and joined the Nuclear Hydrology Program (1984 to present). He is currently a Project Chief in Hydrochemistry. His address : U.S. Geological Survey, Box 25046, MS 416, Denver Federal Center, Denver, CO 80225.

Edwin P. Weeks received his bachelor of science degree in geological engineering from Colorado School of Mines, Golden, Colorado, in 1958. He has worked in various aspects of ground-water research at the Water Resources Division of the U.S. Geological Survey from 1958 to present. Since 1958, he has served as the chief of various projects involving studies of the impacts of irrigation on ground-water systems, development of air-permeability techniques to characterize unsaturated zones, investigation of artificial recharge methods, studies of anisothermal vapor-transport and gaseous diffusion in the unsaturated zone, and measurement of evapotranspiration. He has also taught courses at the U.S. Geological Survey Training Center in various ground-water related subjects. He is currently Chief of the Unsaturated Zone Field Studies in Denver, Colorado. His address is: U.S. Geological Survey, Box 25046, MS 413, Denver Federal Center, Denver, CO 80225.

(Biographical information for H.H. Haas and D.C. Thorstenson was unavailable at time of printing.)

## Carbon-Dioxide and Carbon-Isotope Concentrations

The CO<sub>2</sub> concentrations measured by MS and GC methods were not consistent, possibly because of continued fluctuations of unknown origin. In theory, the MS method should have fewer fluctuations by integrating long-term (4 to 5 d) average values.

The <sup>14</sup>C data indicate general agreement between the molecular-sieve and KOH methods for comparable samples, and significant differences for δ<sup>13</sup>C values between samples. More data are needed to resolve these differences. Post-bomb <sup>14</sup>C was detected to a depth of 40 ft (12.2 m) below land surface, and less than pre-bomb activity was measured at and below a depth of 60-ft (18.3 m).

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