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**GEOCHEMISTRY OF THERMAL WATER FROM SELECTED WELLS, BOISE, IDAHO**

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**Abstract**

Samples of thermal water from selected wells in the Boise area were analyzed for chemical composition; stable isotopes of hydrogen, oxygen, and dissolved carbon; radioactive carbon; and dissolved-gas concentrations. Chemically, the waters are virtually identical to those of the adjacent Idaho batholith. Isotopically, the thermal waters are more depleted in deuterium and oxygen-18 than cold-water springs in the presumed recharge area. Chemical and isotopic data indicate the presence of two separate geothermal systems. Radioactive carbon and dissolved helium concentrations are interpreted to indicate recharge during the Pleistocene. Hot water in or southeast of Boise probably recharged 20,000 to 30,000 years ago, and warm water 2.5 miles northwest of Boise probably recharged at least 15,000 years ago. Recharge to the system during the Pleistocene would have been more depleted in deuterium and oxygen-18 than modern precipitation because of the colder climate during the Pleistocene.

**Introduction**

The geologic and structural setting of the geothermal system in Boise has been described by Wood and Burnham (1983); early geothermal development in Boise has been reviewed by Wells (1971). Although some chemical and isotopic data are available for the thermal waters discharging in and near Boise, Idaho, they are variable in quality and many are incomplete. This sampling was designed to provide a complete chemical and isotope data set for the geothermal systems in and near Boise, and was funded in part by the U.S. Department of Energy. Recent utilization of the resource has increased and many wells that were artesian must now be pumped. From January to April 1988, 37 thermal-water wells in the Boise area were inventoried. Water levels were measured where possible, and water samples were collected from 18 of the thermal-water wells. Most wells were located at the base of the Boise foothills at an altitude of about 2,800 feet above sea level. Three cold-water springs also were inventoried and sampled to provide data on local meteoric water. The springs are in the Boise foothills at altitudes of about 4,500, 5,100, and 6,300 feet. Well-inventory, water-level, and water-chemistry data for all thermal-water wells and cold-water springs are compiled and presented in a separate report (Young and others, 1988). Data were collected to provide a baseline against which future changes in chemical and isotopic composition of the system (or systems) can be compared. This paper describes the results of a study to determine the relation of the thermal waters along the Boise front to one another, and to estimate circulation times for the thermal waters.

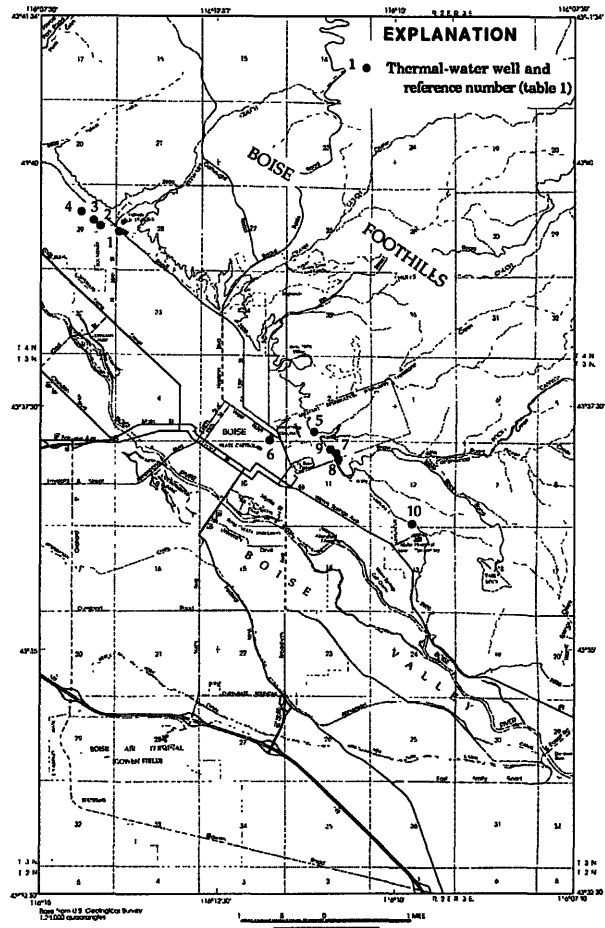


Figure 1.—Locations of selected thermal-water wells.

Thermal-water samples from 10 of the 18 wells were analyzed for stable isotopes of hydrogen, oxygen, and dissolved carbon; radioactive carbon; and dissolved-gas concentrations. Samples for dissolved-gas analysis were collected in flow-through tubes. Locations of the sampled wells are shown in figure 1. Cold-water samples from springs were analyzed for chemical composition, and stable isotopes of hydrogen, oxygen, and carbon. Spring locations are northeast of the area shown in figure 1; township-range-section locations are 4N-3E-10BDCB1S, -11BBAA1S, and -35CCDD1S. Spring 4N-3E-10BDCB is 8 miles northeast of

Table 1.--Chemical composition of selected thermal-water wells and cold-water springs

[Concentrations are in milligrams per liter (mg/L); --, no data]

Reference number	Local number	Collection date	Temperature (°C)	pH	Ca	Mg	Na	K	Li	Cl	F	SO <sub>4</sub>	Alkalinity as HCO <sub>3</sub> <sup>-</sup>		
													Total	True	SiO <sub>2</sub>
Thermal waters															
1	4N-2E-28CBBB1	1-28-88	42.5	9.2	1.7	0.02	66	0.7	0.022	3.9	9.8	25	129	112	38
2	4N-2E-29ACDB1	1-25-88	47.5	8.9	1.6	.01	65	.7	.021	4.3	10	25	131	120	39
3	4N-2E-29ADCC1	2- 2-88	45.5	9.0	1.7	.03	67	.8	.023	3.6	10	22	128	114	41
4	4N-2E-29BADD1	2- 2-88	46.5	9.2	1.7	<.01	67	.8	.024	3.9	10	22	129	109	40
5	3N-2E- 2CDCD1	1-26-88	72.0	8.6	1.6	<.01	80	1.1	.036	8.6	12	23	157	139	64
6	3N-2E-10AABB1	1-26-88	67.5	8.4	1.6	.13	81	.8	.034	7.2	12	21	154	145	55
7	3N-2E-11ABBC1	1-27-88	76.0	9.0	1.7	.04	84	1.4	.043	8.7	19	23	156	111	74
8	3N-2E-11ABCB2	1-27-88	79.5	8.8	1.4	<.01	84	1.5	.050	8.2	19	23	154	125	59
9	3N-2E-11BAAA1	1-27-88	71.5	8.9	1.6	.06	82	1.0	.038	8.1	18	23	135	104	63
10	3N-2E-12CDD1	1-25-88	77.5	8.5	1.8	.02	86	1.6	.047	8.6	12	22	168	149	78
Cold springs															
11	4N-3E-10BDCB1S	5-10-88	3.5	5.8	5.3	1.2	3.5	.3	--	.9	.2	5.2	22	22	22
12	4N-3E-11DDAA1S	4- 8-88	7.5	6.2	5.6	.66	5.2	.5	--	.6	.2	3.6	32	32	28
13	4N-3E-35CCDD1S	3-11-88	10	7.2	30	2.0	8.5	.4	--	3.8	.2	25	90	90	27

Boise, -11BBAA is 8.9 miles northeast of Boise, and -35CCDD is 6.6 miles east-northeast of Boise.

#### Geochemistry

Temperatures of thermal waters in the area ranged from about 42.5 to 79.5 °C (table 1). Hot water (about 75 °C) is present on the east and southeast sides of Boise, near or on the Old Fort Boise Military Reservation and at the Idaho Historical State Penitentiary (wells 5-10). Warm water (about 45 °C) is also present at the mouth of Stewart Gulch, approximately 2.5 miles northwest of Boise (wells 1-4). Temperatures of cold-water springs in the mountains to the east ranged from 10 °C at 4,500 feet to 3.5 °C at 6,300 feet.

Thermal waters encountered in wells drilled in or near Boise (wells 1-10) are dilute, slightly alkaline, and of sodium-bicarbonate type (table 1). Chemically, they are practically indistinguishable from the thermal waters of the Idaho batholith described by Young (1985). Fluoride concentrations are relatively high and range from 12 to 19 mg/L in Boise and 9.8 to 10 mg/L at Stewart Gulch. Chloride concentrations ranged from 7.2 to 8.6 mg/L in Boise and 3.6 to 4.3 mg/L at Stewart Gulch.

A series of geologically reasonable reactions, which could convert the cold water (sample 11) to the composition of the hot water in Boise (average of samples 5-10), are listed in table 2. Aluminum is not included in the table but is conserved in the total reaction set. Stilbite has been identified by X-ray diffraction in altered rocks at several hot springs in the Idaho batholith. Production of stilbite or other zeolites is highly probable in such alkaline waters. Plagioclase is assumed to be An<sub>22</sub> based on values given by Fisher and others (1983). The "possible reactions" listed in the table are intended to represent, in a general way, the reactions by which the cold recharge water could be changed chemically to the composition of the thermal water. Rigorous calculations are not possible because the chemical and isotopic composition of the cold water which recharged the geothermal system and the composition of the minerals which dissolved are unknown.

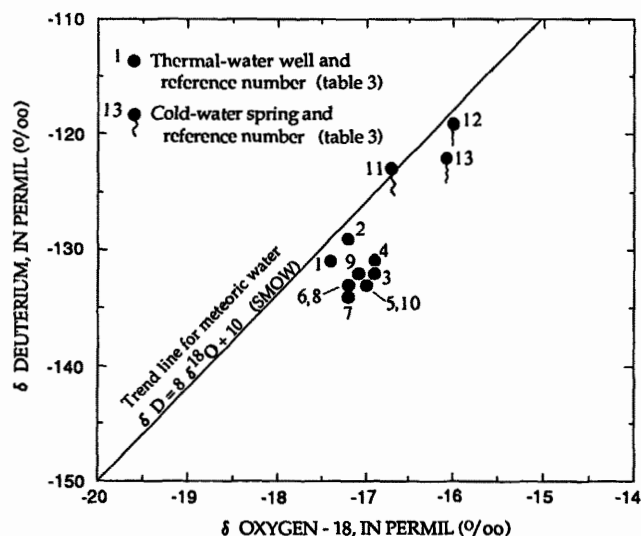


Figure 2.--Relation between concentrations of deuterium and oxygen-18.

#### Stable Isotopes

Stable-isotope data for thermal waters in the area (table 3) show some variation (figure 2). The average composition of the hot water in or near Boise was -133 permil in  $\delta D$  and -17.1 permil in  $\delta^{18}O$ . The warm water at Stewart Gulch was not as depleted in deuterium and displayed a larger range of  $\delta D$  values, -129 to -132 permil. A plot of  $\delta D$  as related to  $\delta^{18}O$  (figure 2) shows that the cold waters of the Boise foothills cannot be the recharge for the current geothermal waters in the Boise area. A plot of  $\delta D$  as related to chloride (figure 3) shows that the hot water in Boise

Table 2.--Possible reactions controlling solution chemistry in the thermal waters at Boise, Idaho

[Concentrations are in milligrams per liter; --, no data]

Possible reaction	SiO <sub>2</sub>	Ca	Na	K	Cl	F	SO <sub>4</sub>	CO <sub>2</sub>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>=</sup>
Cold water (sample 11)	22	5.3	3.5	0.3	0.9	0.2	5.2	116	22	0
Dissolved NaCl			+4.7		+7.3					
Dissolved CaF <sub>2</sub>		+15.6				+14.8				
Oxidized FeS <sub>2</sub>							+17.8			
Dissolved K-feld.	+4			+0.8						
Dis. plag. (An <sub>22</sub> )	+686	+36.2	+73.8							
Ppt. stilbite <sup>1</sup>	-502	-47.8								
Ppt. Ca-clay <sup>2</sup>	-254	-7.7								
Dissolved SiO <sub>2</sub>	+110									
Calculated composition	66	1.6	82	1.2	8.2	15	23	--	<sup>3</sup> 132	4
Hot water (average of samples 5-10)	66	1.6	82	1.2	8.2	15	23	--	123	6

<sup>1</sup> Stilbite composition CaAl<sub>2</sub>Si<sub>7</sub>O<sub>18</sub>·7H<sub>2</sub>O

<sup>2</sup> Ca-montmorillonite Ca<sub>0.16</sub>Al<sub>2.33</sub>Si<sub>3.67</sub>O<sub>10</sub>(OH)<sub>2</sub>

<sup>3</sup> The total reaction set consumes 1.9 x 10<sup>-3</sup> moles of hydrogen per liter of water. This results in the conversion of all H<sub>2</sub>CO<sub>3</sub> to HCO<sub>3</sub><sup>-</sup> and 4 mg/L of HCO<sub>3</sub><sup>-</sup> to CO<sub>3</sub><sup>=</sup>.

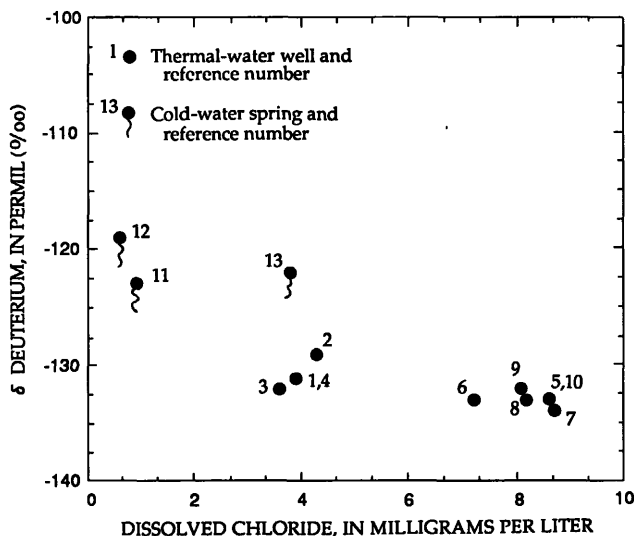


Figure 3.--Relation between concentrations of dissolved chloride and deuterium.

cannot be related to the warm water at Stewart Gulch by mixing because no cold waters as depleted as -128 to -130 permil occur in the local area. Cold waters this depleted in deuterium occur 50 or more miles to the east and northeast in the Idaho batholith (Young, 1985). The depleted isotopic composition of the hot water could be due to more depleted precipitation at the time of recharge, to recharge at a higher altitude, or to recharge at least 50 miles to the east or northeast. The minor differences in chemical composition of the thermal waters could be due to different amounts of

water-rock reaction or differences in the composition of the confining rock.

Values of  $\delta^{13}\text{C}$  for the cold waters show considerable variability (-20 to -15 permil), whereas those for the thermal waters are about -10 permil. The total dissolved carbon in the cold water is relatively constant; thus, changes in  $\delta^{13}\text{C}$  cannot be attributed solely to dissolution of mineral carbonate from the soil. The principal differences among the cold waters are the values of pH. Isotopic fractionation between soil gas CO<sub>2</sub> and dissolved CO<sub>2</sub> is negligible, but the fractionation between HCO<sub>3</sub><sup>-</sup> and dissolved CO<sub>2</sub> is appreciable. At 10 °C the fractionation is about +10 permil, based on the equation of Mook and others (1974). Thus, as hydrolysis of the feldspars in the soil zone results in more alkaline pH, the  $\delta^{13}\text{C}$  of the total dissolved carbon becomes less depleted. This must occur if isotopic equilibrium is maintained between soil gas carbon dioxide and dissolved carbon because bicarbonate makes up a larger part of the total dissolved carbon. The  $\delta^{13}\text{C}$  values of the cold water (samples 11 and 13) can be produced from the measured pH, temperature, and fractionation factors if a soil gas  $\delta^{13}\text{C}_{\text{CO}_2}$  of -23 permil is assumed. Soil gas carbon dioxide typically ranges from -13 to -27 permil (Mook and others, 1974). The more depleted values are usually associated with environments in which trees predominate, and the more enriched values are usually associated with environments in which grasses predominate. During cooler time periods, trees would have been less common relative to grasses in the probable recharge area. As soil gas carbon dioxide is a function of the plant community, the difference in  $\delta^{13}\text{C}$  between the cold and thermal waters could be due to differences in the plant communities present when the respective waters recharged. The composition of the plant communities is determined largely by the temperature of the environment.

Table 3.--Isotope analyses of water from selected thermal-water wells and cold-water springs

[Values are in permil, except as noted; --, not analyzed]

Reference number	Local number	Temperature (°C)	$\delta D$ (SMOW)	$\delta^{18}O$ (SMOW)	$\delta^{13}C$ (PDB)	Percent modern carbon
Thermal waters						
1	4N-2E-28CBBB1	42.5	-131	-17.4	-9.9	9.1
2	4N-2E-29ACDB1	47.5	-129	-17.2	-10.0	--
3	4N-2E-29ADCC1	45.5	-132	-16.9	-10.3	--
4	4N-2E-29BADD1	46.5	-131	-16.9	-9.9	--
5	3N-2E- 2CDD1	72.0	-133	-17.0	-10.5	5.4
6	3N-2E-10AABB1	67.5	-133	-17.2	-10.4	6.2
7	3N-2E-11ABBC1	76.0	-134	-17.2	-9.4	--
8	3N-2E-11ABCB2	79.5	-133	-17.2	-9.8	--
9	3N-2E-11BAAA1	71.5	-132	-17.1	-9.5	--
10	3N-2E-12CDD1	77.5	-133	-17.0	-10.7	3.2
Cold springs						
11	4N-3E-10BDCB1S	3.5	-123	-16.7	-20.0	--
12	4N-3E-11DDAA1S	7.5	-119	-16.0	-16.1	--
13	4N-3E-35CCDD1S	10.0	-122	-16.1	-14.8	--

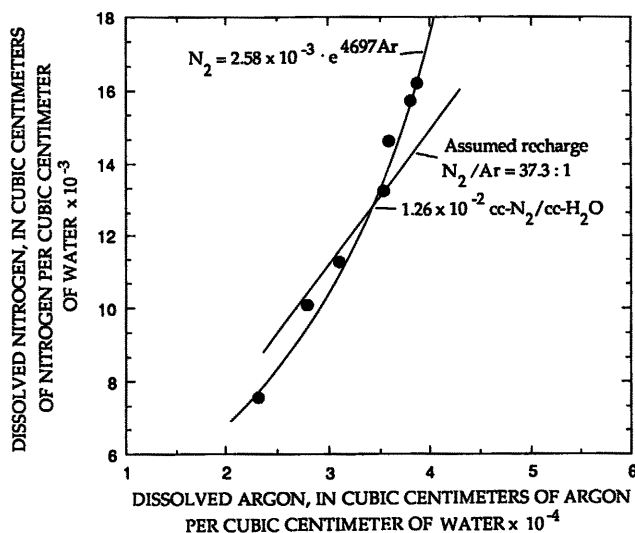


Figure 4.--Relation between concentrations of dissolved nitrogen and argon.

#### Circulation Times

Circulation times of thermal water may be estimated from carbon-14 and dissolved radiogenic helium. Carbon-14 is difficult or impossible to use for age dating in most thermal waters because of uncertainty about loss or gain of carbon during circulation. However, it appears that total dissolved carbon does not change appreciably as the water circulates through this particular geothermal system. In addition, carbonate minerals are very rare in the rock of the batholith so exchange is improbable. For purposes of calculation, it is assumed that the recharge water contained at most 100 percent, and at least 50 percent modern carbon.

Calculated water ages range from 23,000 to 28,000 years for the hot waters in or southeast of Boise and 15,000 to 20,000 years for the warm water from the system northwest of Boise.

Dissolved helium concentrations can be used to estimate water age only if rock porosity, density, uranium content, and thorium content can be measured or estimated. Estimation of dissolved-gas concentrations in the thermal water is complicated because the water degasses at the well head.

Dissolved-gas data for thermal water in the Boise area (table 4) does not follow an ideal Rayleigh distillation curve. Mazor and Wasserberg (1965) demonstrated that gas discharge from thermal springs approximates a Rayleigh distillation process. Data for nitrogen, argon, and helium in the Boise area fit exponential or power curves reasonably well (figures 4 and 5). Differences in using exponential or power curves to estimate dissolved helium concentrations prior to gas loss are not significant relative to other uncertainties in the helium age-dating technique.

Where replicate dissolved-gas samples were collected, differences in collection pressures resulted in various amounts of gas exsolution and dissolution. Dissolved-gas samples collected during January 1988 contain more nitrogen and argon than the presumed recharge water. Pressure in the collection vessel nearly equaled well-head pressure after the collection system was filled with water, but apparently, degassing of the first water to enter the collection apparatus lined the walls of the collection vessel and tubing with gas bubbles. These gas bubbles slowly redissolved in the mixture of Rayleigh degassed and new water to produce water that contained more gas than the water initially discharged by the well. Therefore, variations in measured nitrogen, argon, and helium are due to the different pressures, temperatures, and times of collection.

Ratios of dissolved nitrogen to argon shift slightly with temperature of the recharge water. Air-saturated water at 5 °C contains dissolved gas with a nitrogen to argon ratio

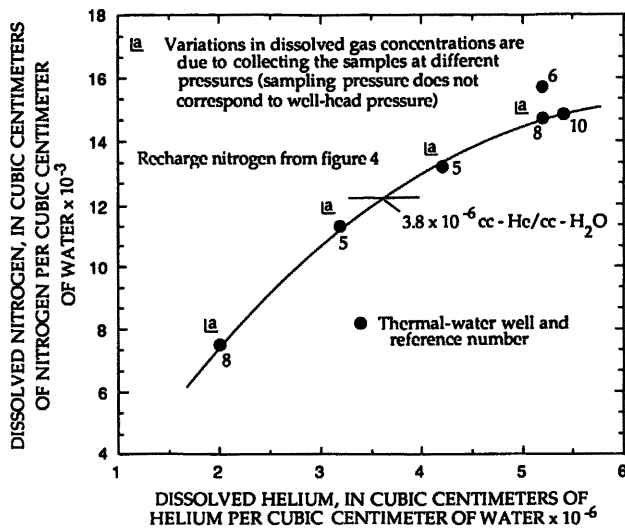


Figure 5.--Relation between concentrations of dissolved nitrogen and helium.

of 37.3:1 (Weiss, 1970). Dissolved nitrogen and argon in these thermal waters have a ratio of 37.3:1 when concentrations are  $1.26 \times 10^{-2}$  cc-N<sub>2</sub>/cc-H<sub>2</sub>O and  $3.37 \times 10^{-4}$  cc-Ar/cc-H<sub>2</sub>O, respectively (figure 4). These values are assumed to represent the recharge concentrations of nitrogen and argon in all of the thermal waters. Plots of nitrogen and helium for the wells in or southeast of Boise also produce a smooth curve (figure 5) with a helium concentration of  $3.8 \times 10^{-6}$  cc-He/cc-H<sub>2</sub>O at the nitrogen concentration corresponding to the nitrogen-argon ratio of the presumed recharge water. Data for the well sampled near Stewart Gulch do not plot on the He-N<sub>2</sub> curve for hot waters in or near Boise. This is another indication that the warm-water system at Stewart Gulch is separate and distinct from the hot-water system in Boise.

Assuming rock porosity of 1 percent and density of  $2.65 \text{ g/cm}^3$ , average values for granites from Wolff (1981), and assuming that the water circulated through rock with a uranium and thorium content of the local granodiorite (Swanberg and Blackwell, 1973), the equation of Andrews and Lee (1979) can be used to estimate an age of 20,000 years for the hot waters in and southeast of Boise. The age for the warm-water system at Stewart Gulch, based on a single gas sample from well 4N-2E-28CBBB1, is about 13,000 years. The carbon-14 age for the same water was about 20,000 years. Neither the helium nor carbon-14 ages can be interpreted to be the absolute circulation times for the thermal waters. However, both techniques indicate recharge during the Pleistocene.

#### Conclusions

Relations between the chemical and isotope data for thermal waters in and near Boise indicate that two distinct thermal systems are present. Hot water (about 75 °C) is present in and southeast of Boise, and warm water (about 45 °C) is present 2.5 miles northwest of Boise at the mouth of Stewart Gulch. Chemically, the thermal waters are dilute, slightly alkaline, and a sodium-bicarbonate type with high dissolved fluoride concentrations. These thermal waters are virtually identical to the thermal waters of the Idaho batholith to the east. Thermal waters in the Boise area are more depleted in deuterium than cold water at the presumed recharge area in the Boise foothills. Circulation time for the hot water is between 20,000 and 30,000 years, based on carbon-14 and dissolved helium age-dating techniques. Circulation time for warm water discharging near Stewart Gulch northwest of Boise is apparently between 15,000 and 20,000 years. The most likely explanation for the differences in deuterium between cold and thermal waters in and near Boise, the carbon-14 content of the thermal waters, and the dissolved-helium concentrations of the thermal waters is that it has taken 15,000 to 30,000 years for the waters to circulate through the respective geothermal systems. Water ages are approximate because of uncertainty about the conditions during recharge and reactions which produced the chemical composition of the thermal waters. Cold-water springs and thermal waters encountered along the Boise front may differ in  $\delta^{13}\text{C}$  because different plant communities were present at the time the respective waters recharged.

Table 4.--Dissolved-gas data for selected thermal-water wells

[cc-gas/cc-water; --, no data]

Reference number	Nitrogen N <sub>2</sub> x 10 <sup>-2</sup>	Argon Ar x 10 <sup>-4</sup>	Methane CH <sub>4</sub> x 10 <sup>-6</sup>	Carbon Dioxide CO <sub>2</sub> x 10 <sup>-6</sup>	Helium He x 10 <sup>-6</sup>	Oxygen O <sub>2</sub> x 10 <sup>-6</sup>
1	1.62	3.86	3.8	1.8	3.0	9.0
15	1.32	3.57	7.0	5.8	4.2	4.0
	1.13	3.11	6.9	4.5	3.2	18.0
16	1.57	3.86	7.4	3.6	5.2	4.0
	1.01	2.80	6.0	3.8	--	1.1
18	1.47	--	8.5	--	5.2	4.0
	.75	2.35	6.0	4.7	2.0	1.8
10	1.48	3.62	8.7	4.7	5.4	4.0

<sup>1</sup> Variations in dissolved-gas concentrations for individual sites are due to different collection pressures; sampling pressure did not correspond to well-head pressure.

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