WM DOCKET CONTROL
CENTER

'85 APR 15 P[illegible]

UCRL- 15667
SANL 126-016

HYDROLOGY DOCUMENT NUMBER 103

Permeability and Fluid Chemistry Studies of the Topopah Spring Member of the Paintbrush Tuff, Nevada Test Site: Part II

D. E. Moore
C. A. Morrow
J. D. Byerlee

March 1985

Lawrence
Livermore
National
Laboratory

UCRL-15667
SANL 126-016

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

PERMEABILITY AND FLUID CHEMISTRY STUDIES OF THE TOPOPAH SPRING MEMBER OF THE PAINTBRUSH TUFF, NEVADA TEST SITE: PART II

D. E. Moore, C. A. Morrow, and J. D. Byerlee

Open-File Report
84-848

This report is preliminary and
has not been reviewed for conformity
with Geological Survey editorial standards
or stratigraphic nomenclature

ABSTRACT

The Topopah Spring Member of the Paintbrush Tuff is being considered as a possible emplacement horizon for the disposal of nuclear waste. The permeability and pore-fluid chemistry of the Topopah Spring Member have been investigated experimentally. The work reported here represents a continuation of previous permeability studies on the Topopah Spring Member. Three experiments were run, to test the effect of pore pressure, sample orientation, and flow direction on permeability and pore fluid chemistry. In the experiments, water flowed either up or down a temperature gradient established across the tuff sample in response to a small pore pressure gradient. The maximum temperature of the gradient was 150°C, and the minimum was 43-45°C. The confining pressure was 100 bars, corresponding to a disposal depth of 400 meters. J13 water was the starting pore fluid. The heated tuff samples showed few changes in permeability from their initial, room-temperature values. In addition, the fluids discharged from both the low and high-temperature sides of the tuff samples were dilute, nearly neutral solutions whose compositions did not differ greatly from the starting J13 compositions.

INTRODUCTION

The Topopah Spring Member of the Paintbrush Tuff, Nevada Test Site, is being considered as a possible emplacement horizon for the disposal of nuclear waste. The permeability and pore-fluid chemistry of the Topopah Spring Member are being investigated experimentally, as a support study for the Nevada

Nuclear Waste Storage Investigations Project. An initial group of experiments, in which the relationship between temperature and permeability was examined, has been described by Moore et al. (1984) and Morrow et al. (1984). This paper reports the results of a second set of experiments dealing with the effects of pore pressure, sample orientation, and flow direction on the permeability and pore fluid chemistry of this tuff. The tuff samples used in the experiments were obtained from outcrop material collected at Fran Ridge; this material is described in detail by Knauss (1984b).

EXPERIMENTS CONDUCTED

The sample assembly is depicted in Figure 1. The general experimental procedure has been described previously (Moore et al., 1984) and is not reported here in detail. Briefly, cylindrical samples of the tuff were prepared with a central borehole, so that a resistance heater placed in the borehole produced a temperature gradient between the center and outside of the rock. Water flowed through the tuff due to a small differential pore pressure gradient that was applied between the center and outside of the sample. The water used in the experiments was a natural groundwater (J13) collected at the Nevada Test Site. Its chemical composition, listed in Table 1, differs slightly from that of previous J13 water supplies (Byerlee et al., 1983; Moore et al., 1984) in the lower pH and the presence of measurable amounts of phosphorus, reported as hydrogen phosphate (HPO_4^{-2}).

The initial permeability of each tuff sample was measured at room temperature. Following that, fluid flow was halted while the sample was heated, and then flow was resumed once a stable temperature gradient had been established across the tuff. Samples of the fluids discharged from the

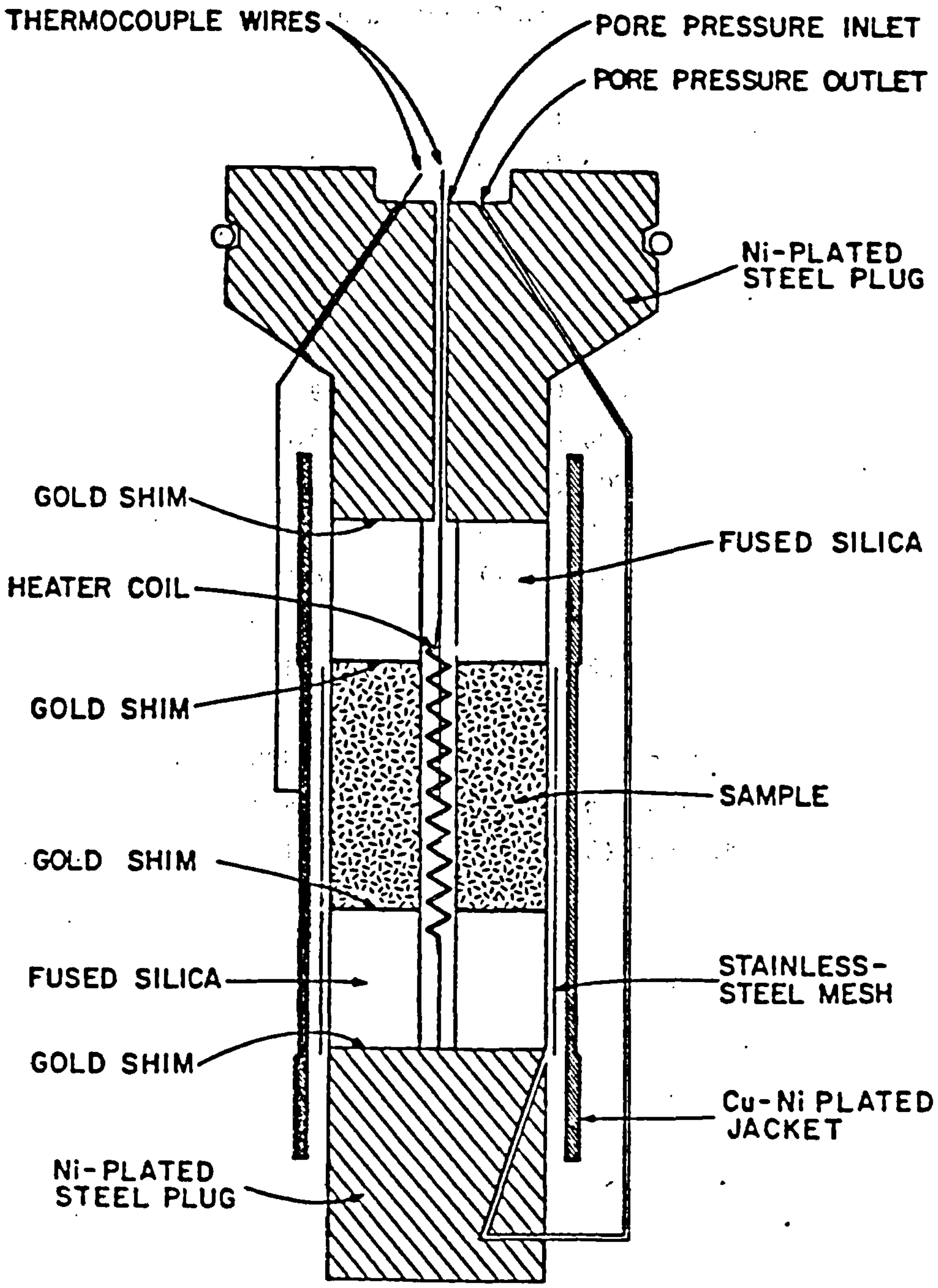

Figure 1. Schematic sample assembly.

Table 1. Composition of J13 Groundwater from the Nevada Test Site used in Topopah Experiments 4, 5, and 6.

SiO_2 (mg/1)	-	60
Na (mg/1)	-	45
K (mg/1)	-	4.9
Mg (mg/1)	-	1.9
Ca (mg/1)	-	13
HCO_3 (mg/1)	-	120
SO_4 (mg/1)	-	19
NO_3 (mg/1)	-	9.6
HPO_4 (mg/1)	-	1.8
F (mg/1)	-	2.2
Cl (mg/1)	-	6.8
pH	-	7.17
Anion Sum (meq/1)	-	2.888
Cation Sum (meq/1)	-	2.883
Balance (%)	-	+0.17

cylinders were collected during the measurement of permeability at room-temperature and after heating, to determine any changes in water chemistry resulting from interaction with the tuffs.

The conditions of the three experiments conducted for this study (numbered 4, 5, 6), are summarized in Table 2. All three experiments were run at a borehole temperature of 150°C and a confining pressure of 100 bars. This pressure corresponds to a disposal depth of 400 meters. During the first part of experiment 4, the pore pressure was held at 34 bars to provide a direct correlation with the previous Topopah experiments (Moore et al., 1984), which were run at a 1:3 pore-to-confining pressure ratio. After 8 days, the pore pressure was reduced to 10 bars. This lower pore pressure is still greater than that expected at the potential disposal site in the Topopah Spring Member. However, for the heated permeability experiments the fluid pressure had to be high enough to prevent the pore fluid from flashing to steam in the high-temperature borehole area. The sample orientation of experiment 4 was the same as that of the earlier Topopah experiments (Moore et al., 1984); that is, the samples were cored in such a way that fluid flow would be along the bedding direction, simulating a lateral migration of groundwater away from the canisters at the disposal site.

Experiment 5 repeated the conditions of the second part of experiment 4, except that the bedding planes were perpendicular to the orientation of previous experiments, so that some of the flow would be directed across rather than along the bedding. Such a flow direction would approximate the path of groundwater as it percolates downward from the disposal horizon. Experiment 6 was run with the same sample orientation as experiment 5 but with flow directed from the lower-temperature, outer edge of the sample towards the higher temperature borehole. This flow direction would approximate the

Table 2. Experimental Conditions and Permeability Results.

experiment	4	5	6
Borehole Temperature (°C)	150	150	150
Jacket Temperature (°C)	43	44	45
Confining Pressure (bars)	100	100	100
Pore Pressure (bars)	34 (0-8 days) 10 (8 days-end)	10	10
Differential Pore Pressure (bars)	1	1	1
Pore Fluid	J13 water	J13	J13
Flow Path	$\parallel$ bedding	$\perp$ bedding	$\perp$ bedding
Flow Direction	high → low T	high → low T	low → high T
Duration (days)	10	14	17
Room-Temperature Permeability (μda)	5.3	10.1	0.85
Final Heated Permeability (μda)	5.0 at 33b 4.6 at 10b	8.2	0.60
Approximate Flow Rate (cm^3/sec)	5.1(10^{-4}) at 33b 5.0(10^{-4}) at 10b	7.85 (10^{-4})	5.5 (10^{-5})

movement of groundwater from the earth's surface down to the disposal horizon in the tuff.

With the exception of bedding orientation (Table 2), the three tuff cylinders used in the experiments have very similar physical characteristics. The bedding direction is indicated principally by flattened lithic fragments; some short, discontinuous veinlets filled with a grayish-white material also are oriented in the bedding direction. One of these filled fractures intersects the borehole of sample 5. On one side, this veinlet extends to the outer edge of the cylinder; on the other side, however, the veinlet terminates before reaching the edge. Samples 5 and 4 each have a large, relatively soft and porous lithic fragment on their outer edges. Neither of these fragments extends as far as the borehole; therefore, no highly porous path connects the borehole and edge of these cylinders. Sample 6 contains a narrow, apparently open fracture that cuts diagonally from the outer edge to the bottom of the sample. At its closest point this fracture is more than 15 mm away from the borehole.

RESULTS

PERMEABILITY

The variations in permeability with time for experiments 4-6 were determined from measured changes in the mass flow rate while the pore pressure gradient was held constant. The calculation procedures are described in Morrow et al. (1984) and Moore et al. (1984) and are not repeated here. The measured changes in permeability with time are shown in Figure 2, and the room temperature and final heated permeability values are listed in Table 2.

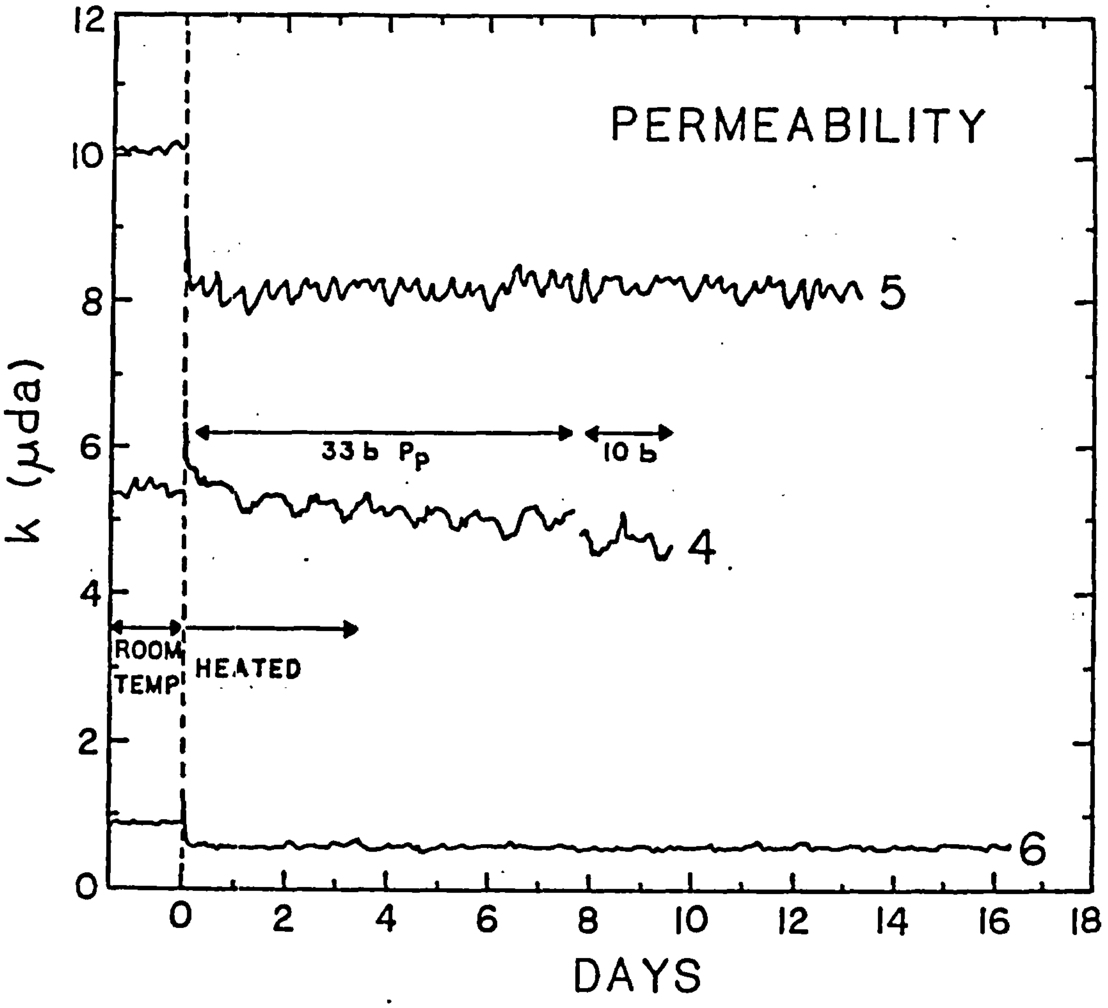

Figure 2. Permeability of the Topopah Spring Member as a function of time. Conditions of experiments 4, 5, and 6 are listed in Table 2.

The room-temperature permeabilities of samples 4, 5, and 6 ranged from approximately 0.8 to 10 μda. With heating, the samples showed an initial, transient disturbance in permeability, which probably was caused by thermal cracking. Soon after, however, the permeabilities of samples 5 and 6 levelled out at values somewhat below their room-temperature permeabilities. The tuff sample in experiment 4 showed a slight overall decrease in permeability with time throughout the experiment. Decreasing the pore pressure from 33 to 10 bars caused a slight additional decrease in permeability. Even so, the final permeability of experiment 4 remained very close to the room-temperature value.

FLUID CHEMISTRY

At intervals during the experiments a 2 ml sample of the fluids discharged at the low-temperature, outer edge of the tuff cylinder was collected for chemical analysis. Sample treatment procedures and analytical techniques are the same as described in Moore et al. (1984). The results of these analyses are listed in Table 3.

Selected fluid compositions were analyzed at room-temperature with the SOLMNEO computer program (Kharaka and Barnes, 1973) which, among other things, computes the equilibrium distribution of the aqueous species present in the waters. The SOLMNEO results indicate that aluminum, which is reported as Al^{+3} in Table 3 in accordance with standard practice, actually occurs in solution as the complex $Al(OH)_4^{-1}$. This anion complex, rather than the cation Al^{+3}, was used to calculate the solution balances in Table 3. In addition, phosphorus in solution is distributed by SOLMNEO between hydrogen phosphate (HPO_4^{-2}) and dihydrogen phosphate ($H_2PO_4^{-1}$). The results show that hydrogen phosphate is usually the principal of the two ions. Because of the predominance of hydrogen phosphate and because the total amount of phosphorus in solution is

Table 3. Chemical Analyses of Fluids Collected During Permeability Experiments on the Topopah Spring Member of the Paintbrush Tuff. (Concentrations in mg/L.)

	Days	pH (25°C)	SiO_2	Na	K	Mg	Ca	Al	HCO_3	SO_4	NO_2	NO_3	HPO_4	F	Cl	Bal. (%)
EXPERIMENT 4																
Room-Temperature	-	7.42	38	93	59	2.5	26	0.15	140	54	1.0	67	2.7	16	44	+ 5.7
Heated Run (150°C borehole; 43°C jacket)	0.8	7.92	70	81	73	2.0	31	0.06	240	58	2.7	0.55	4.6	2.1	32	+11.6
	1.8	7.83	82	64	62	1.5	31	0.10	220	53	-	Tr	5.5	2.0	24	+7.4
	2.8	7.80	88	60	55	1.2	26	0.12	200	46	-	-	4.4	1.8	18	+9.2
	3.8	7.75	91	54	46	0.92	24	0.07	180	41	-	-	5.1	2.4	14	+7.9
	6.8	7.54	100	50	38	0.68	20	0.09	170	33	-	Tr	4.4	1.9	12	+4.7
	7.8	7.56	101	46	35	0.56	19	0.11	160	30	-	-	2.1	1.9	9.3	+6.2
	8.8	7.59	103	48	32	0.61	18	1.45	160	29	-	-	2.7	1.8	8.3	+5.0
	9.8	7.59	103	49	30	0.54	17	0.08	160	27	-	-	2.4	1.9	8.3	+6.0

Table 3. (Continued)

	Days	pH (25°C)	SiO_2	Na	K	Mg	Ca	Al	HCO_3	SO_4	NO_2	NO_3	HPO_4	F	Cl	Bal. (%)
<u>EXPERIMENT 5</u>																
Room-Temperature	-	7.38	32	70	45	0.76	10	0.07	170	20	-	31	2.0	2.7	22	+4.3
Heated Run (150°C borehole; 44°C jacket)	1.0	7.42	82	48	43	0.41	8.8	0.12	170	21	Tr	3.2	4.4	2.5	16	-7.7
	2.0	7.63	85	50	40	0.49	12	0.16	170	21	-	0.66	2.5	2.6	13	+1.1
	3.0	7.36	84	48	35	0.47	14	0.04	170	21	0.30	1.8	2.6	2.3	13	-2.7
	4.0	7.60	82	49	32	0.43	15	0.08	160	20	2.5	1.8	4.9	2.4	12	+1.2
	5.0	7.59	85	50	30	0.42	15	0.17	140	21	2.2	1.1	3.0	2.8	11	+11.4
	6.0	7.52	85	49	26	0.42	16	0.08	160	20	0.83	1.2	2.9	2.5	11	+1.4
	7.0	7.52	86	49	33	0.43	16	0.10	160	20	0.22	0.27	2.9	2.2	11	+0.5
	10.0	7.03	86	47	20	0.37	16	0.05	150	19	-	Tr	2.4	2.1	8.7	+3.6
	11.0	7.46	83	45	19	0.40	16	0.04	150	19	-	Tr	2.3	2.2	8.2	+0.7
	12.0	7.19	90	49	20	0.31	15	0.06	150	19	-	-	2.0	3.3	8.3	+3.3
	13.0	7.38	88	46	18	0.37	15	0.38	150	19	-	Tr	2.3	2.2	8.8	+5.3
	14.0	7.30	93	46	17	0.40	15	0.11	150	19	-	0.50	1.7	2.2	8.4	+5.5

Table 3. (Continued)

	Days	pH (25°C)	SiO_2	Na	K	Mg	Ca	Al	HCO_3	SO_4	NO_2	NO_3	HPO_4	F	Cl	Bal. (%)
<u>EXPERIMENT 6</u>																
Room-Temperature	–	7.49	51	48	7.9	2.1	13	0.04	140	19	0.09	6.0	2.2	2.7	10	–4.7
Heated Run (150°C borehole; 45°C jacket; flow is from jacket to borehole)	2.1	7.73	70	62	90	0.44	13	0.03	190	31	13	2.7	3.3	12	26	+5.9
	2.9	7.61	77	64	110	0.33	13	0.04	200	36	0.38	0.89	3.4	16	33	+6.2
	3.9	7.67	84	65	120	0.30	14	0.08	280	40	–	0.27	2.1	16	39	–11.3
	4.9	7.52	96	66	130	0.33	15	0.35	210	41	–	0.35	5.0	20	43	+4.2
	5.9	7.31	90	62	120	0.45	15	0.11	180	39	–	0.22	1.6	19	42	+8.9
	6.9	7.17	87	61	130	0.34	16	0.04	280	38	–	0.66	0.93	1.9	44	+0.8
	9.1	7.35	85	57	110	0.28	13	0.05	250	34	–	1.4	–	1.6	42	–2.2
	10.9	6.90	94	57	110	0.26	13	0.07	240	34	–	–	–	6.2	38	–0.8
	11.9	6.87	90	53	100	0.38	12	0.90	210	29	–	0.89	–	11	34	–2.5
	12.9	6.83	69	49	95	0.31	11	0.04	140	27	–	Tr	–	16	31	+11.5
	13.9	6.81	64	49	90	0.22	8.8	0.06	190	28	–	0.20	–	6.6	28	+1.1
	16.9	6.84	42	49	82	0.13	5.0	0.03	190	29	–	–	–	0.94	21	+2.9

small, total phosphorus is reported as hydrogen phosphate in Table 3 and solution balances were calculated using these values.

Solution balances (sums of equivalents of anions and cations) for experiment 5 and the second half of experiment 4 are nearly all within ±6%. The samples collected during the first 4 days of experiment 4 have somewhat higher positive balances, indicating low anion totals for those analyses. The pH of the early-collected fluid samples, although higher than that measured later in experiment 4, is not sufficiently high to cause some of the dissolved silica to be ionized to $H_3SiO_4^{-1}$ or $H_2SiO_4^{-2}$. The regular improvement of the balance with time suggests that some additional anion that was not detectable by ion chromatographic techniques may be present in these fluids, and that the concentration of this anion in solution decreased significantly during the experiment.

Most of the fluids analyzed from experiment 6 and one sample from experiment 5 contain two unidentified species, whose presence was indicated by ion chromatography. These species were closely associated with the normal fluoride peak in the analytical results, and they may represent fluorine-bearing complexes. Based on solution chemistry considerations that are discussed in the Appendix, the two species have been tentatively identified by T.S. Presser (written communication, 1984) as CaF^+ and CaF_2°. The fluoride contents and solution balances reported in Table 3 for the fluid samples of experiment 6 were calculated in accordance with this identification.

The fluid compositions analyzed at room temperature with SOLMNEQ also were analyzed at the temperature of discharge from the tuff. For experiments 4 and 5 the jacket temperatures were used, and for experiment 6, the reverse-flow experiment, the borehole temperature was used. The SOLMNEQ program computes the degree of saturation of a given solution with respect to many minerals as a function of temperature; positive values of ΔG_R indicate that the solution is supersaturated with respect to the mineral considered. Table 4 lists positive values of ΔG_R for some of the possible alteration minerals in tuff. The results give an indication of the kinds of minerals that potentially could precipitate from the pore fluids at the point of exit from the tuff.

DISCUSSION

PERMEABILITY

The combined results of this study and the earlier Topopah experiments (Moore et al., 1984) show that the initial permeability of this tuff is quite variable. The measured room-temperature permeability ranges from 0.8 to 65 μda, a variation of nearly two orders of magnitude. These values are essentially independent of confining and pore pressures and of sample orientation. Instead, this wide range of permeabilities probably reflects sample-to-sample differences in the density, distribution, and configuration of cracks and pores. For example, the slightly higher room-temperature permeability measured during experiment 5 may be caused by the through-going fracture in that sample. The effect of initial heating is variable, some samples showing increases and others decreases in permeability. These temperature-related changes may be caused by the creation of new cracks or the modification of existing cracks in the samples. Whatever the direction of change in permeability, however, the proportional variation is small compared to the range of room-temperature permeability values. Therefore, heating the tuff samples does not affect their overall permeability.

Table 4. Reaction States (ΔG_R, in Kcal) of Selected Fluid Samples of the Low-Temperature Sides of the Tuff Cylinders. Only Positive Values of ΔG_R, Indicating Supersaturation, are Included in the Table.

Sample / Mineral	EXPERIMENT 4 (43°C)			EXPERIMENT 5 (44°C)				EXPERIMENT 6 (150°C)			
	0.8 Days	2.8 Days	8.8 Days	2.0 Days	5.0 Days	7.0 Days	14.0 Days	2.1 Days	4.9 Days	10.9 Days	16.9 Days
Adularia	4.77	5.34	7.08	5.42	5.24	4.70	4.79				
Albite, low	1.60	2.17	4.10	2.34	2.34	1.95	2.19				
Boehmite	0.46	0.93	3.40	1.53	1.58	1.29	1.72				
Calcite	0.62	0.26						1.05	1.22	0.24	
Chalcedony	0.59	0.74	0.85	0.71	0.71	0.72	0.78				
Chlorite-Mg								4.76	8.85		
Cristobalite A	0.32	0.47	0.58	0.44	0.44	0.45	0.50				
Gibbsite			2.35	0.46	0.52	0.22	0.65				
Illite	7.27	8.51	13.49	9.28	9.22	8.35	9.06				
Kaolinite	5.12	6.36	11.53	7.48	7.59	7.01	7.98				
Laumontite	9.06	10.18	13.92	10.37	10.53	9.80	10.21		0.68		
Montmorillonite-Ca	7.18	8.76	14.65	9.88	10.03	9.34	10.43				
Phillipsite	16.03	16.60	18.40	16.71	16.62	16.16	16.32	6.56	9.86	8.45	5.20
Prehnite	3.53	4.08	6.06	3.43	3.64	2.73	2.43		0.58		
Quartz	1.13	1.28	1.39	1.25	1.25	1.26	1.31				
Silica, Amorphous			0.09				0.01				
Wairakite	1.86	2.98	6.72	3.19	3.35	2.63	3.04				

The combination of heat and fluids also has little effect on the permeability of the tuff. In the time of the experiments, almost no permeability changes were measured as heated groundwater flowed through the Topopah cylinders. As was observed at room-temperature, the results are independent of confining and pore pressure and of sample orientation. In addition, changes in temperature and in the direction of fluid flow relative to temperature also have no effect on permeability.

FLUID CHEMISTRY

Ionic Concentrations. Figure 3 plots the changes with time in the sum of cations in solution, expressed in milliequivalents per liter, for experiments 4, 5, and 6. The results of the 150°C experiment 1 (Moore et al., 1984) are included for comparison. This plot illustrates the changes in the overall ionic concentrations that occurred during the experiments. Cation sums throughout experiment 5 are very similar to those for experiment 1. The final cation sums for experiment 4 are near those of 1 and 5; however, the first few heated fluid samples collected during experiment 4 contain about twice the amount of dissolved ionic material as the corresponding fluids in the other two experiments. The room-temperature fluid sample from experiment 4 also contains more dissolved material than the room-temperature samples from experiments 1 and 5. This material may have been derived from salts deposited from evaporating groundwater along the major voids or fractures in the sample. Such deposits have been found in the Bullfrog Member of the Crater Flat Tuff (Morrow et al., 1983; Byerlee et al., 1983; Oversby and Knauss, 1983). Another possibility is that Topopah cylinder 4 contained some slightly more saline pore fluids that were flushed from the sample during the first few days of fluid flow.

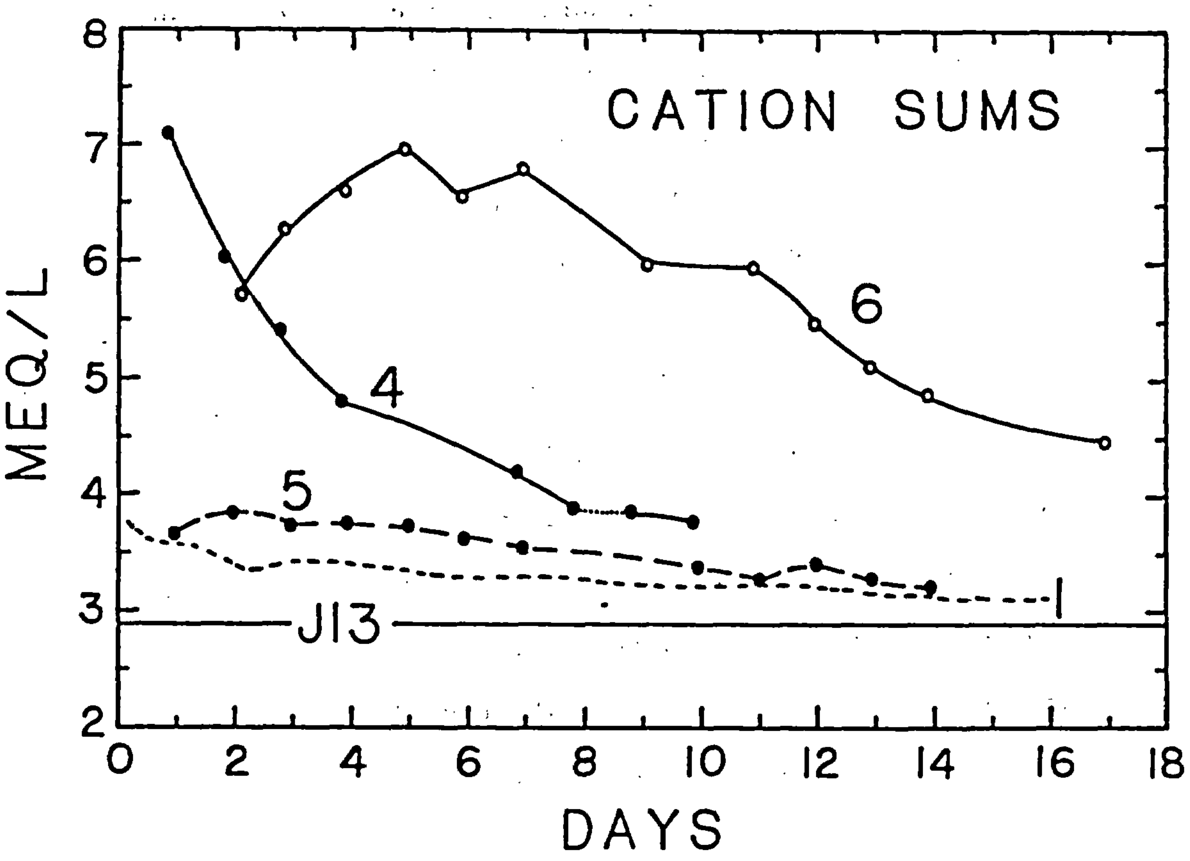

Figure 3. Changes with time in the sum of cations (expressed as milliequivalents per liter) in the discharged fluids, compared to the starting J13 composition. The dotted line shown in the trends for experiment 4 (in this and subsequent figures) separates the 0 to 8-day fluid samples, at 34 bars pore pressure, from the last 2 samples, at 10 bars pore pressure.

Few evaporation deposits or pore fluids were removed in the room-temperature fluids during reverse-flow experiment 6 (Table 3). Nevertheless, the ionic concentrations of fluid samples from the heated run are high compared to the other three 150°C experiments. The ionic concentrations in experiment 6 go through a maximum after about 5 days and subsequently decrease; even so, the final values are still well above the final concentrations measured in the other experiments.

pH. In Topopah experiments 1, 2, and 3 (Moore et al., 1984) the general conclusions about pH were that: 1) the pH of the discharged fluids tended to decrease with time during an experiment; and 2), the fluids collected during the higher temperature experiments had a lower pH than those from the lower temperature experiments. The results of experiments 4, 5, and 6, shown in Figure 4, are consistent with these earlier conclusions. In all three experiments, the final pH is lower than the initial pH. In addition, the final measured pH of fluids from reverse-flow experiment 6, with its high discharge temperature, is lower than the final pH of the other experiments. The pH of each of the last five fluid samples collected during experiment 6 is below the J13 level.

The decrease in pH with time during each experiment may be related to the progressive removal of the salt deposits or saline pore fluids from the tuff, as was observed during previous experiments on the Bullfrog tuff (Byerlee et al., 1983; Morrow, et al., 1983). Also consistent with this interpretation is the measurement of higher pH values during experiment 4 than during experiment 5, despite the similarity of temperature and pressure conditions. As described previously, the tuff sample used in experiment 4 contained more of these readily leached materials than did the other samples. The decrease

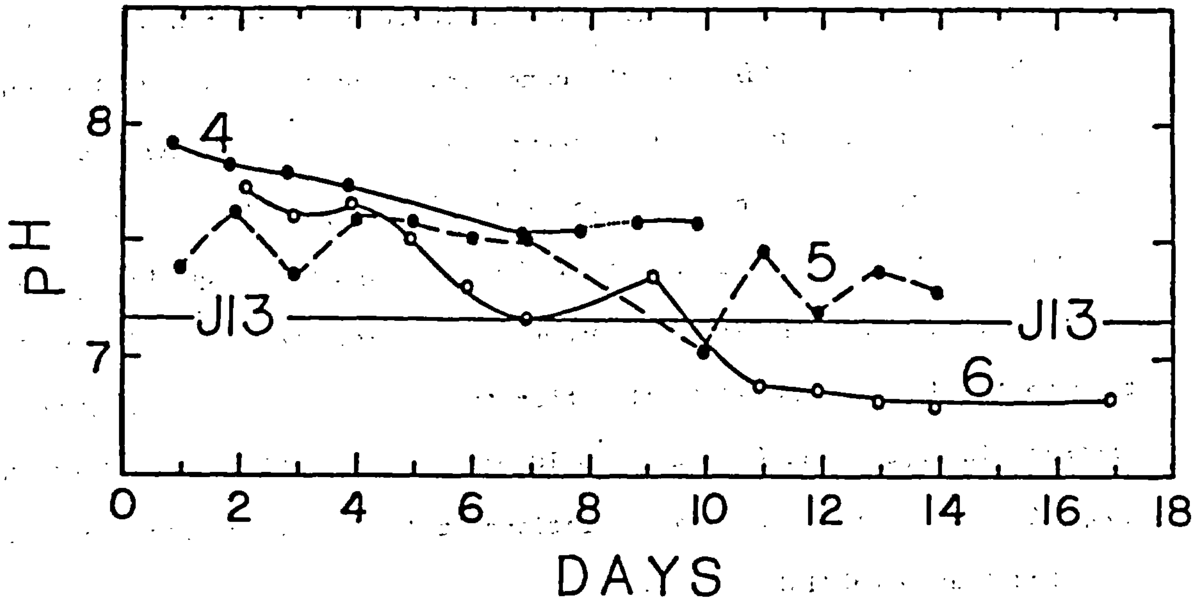

Figure 4. Changes in pH of the discharged fluids with time during the permeability experiments on the Topopah Spring Member.

in pH with increasing temperature is probably caused by temperature-related differences in tuff-water reactions.

Individual Dissolved Species. Figures 5 to 13 show the changes with time of nine of the dissolved species listed in Table 3. The results from experiment 1 also are included in several of the figures for comparison. For the majority of the graphs, the compositional trends of any given ionic species are similar to the changes in the overall ionic concentrations for the experiment (Figure 3). In addition, the compositions of the individual species in the fluids collected during experiments 5 and 1 are very similar to each other. With the exception of silica and hydrogen phosphate, the concentrations of all the species in the first heated samples of experiment 4 are high relative to those of experiments 5 and 1; however, the values decrease with time to the levels reached in the other two experiments. Changing pore pressure in experiment 4 from 33 to 10 bars had no noticeable effect on fluid composition. Instead, the concentrations at 10 bars vary along the trends that had been established at 33 bars.

Looking in more detail at experiments 4 and 5, the final concentrations of potassium, calcium, bicarbonate and silica (Figures 5 to 8) are above J13 levels. These species appear to have been added to the fluids through interaction with minerals in the tuff (Moore et al., 1984). For the most part, it is not possible to determine whether the increase of a given species during these two experiments is the result of a single dissolution reaction or the net product of competing reactions. However, the behavior of calcium during experiment 5 indicates that both calcium-consuming and calcium-generating reactions were taking place. In experiment 5, the room-temperature fluids as well as the first heated samples have calcium concentrations below J13 levels. The room-temperature loss of calcium suggests that it may have

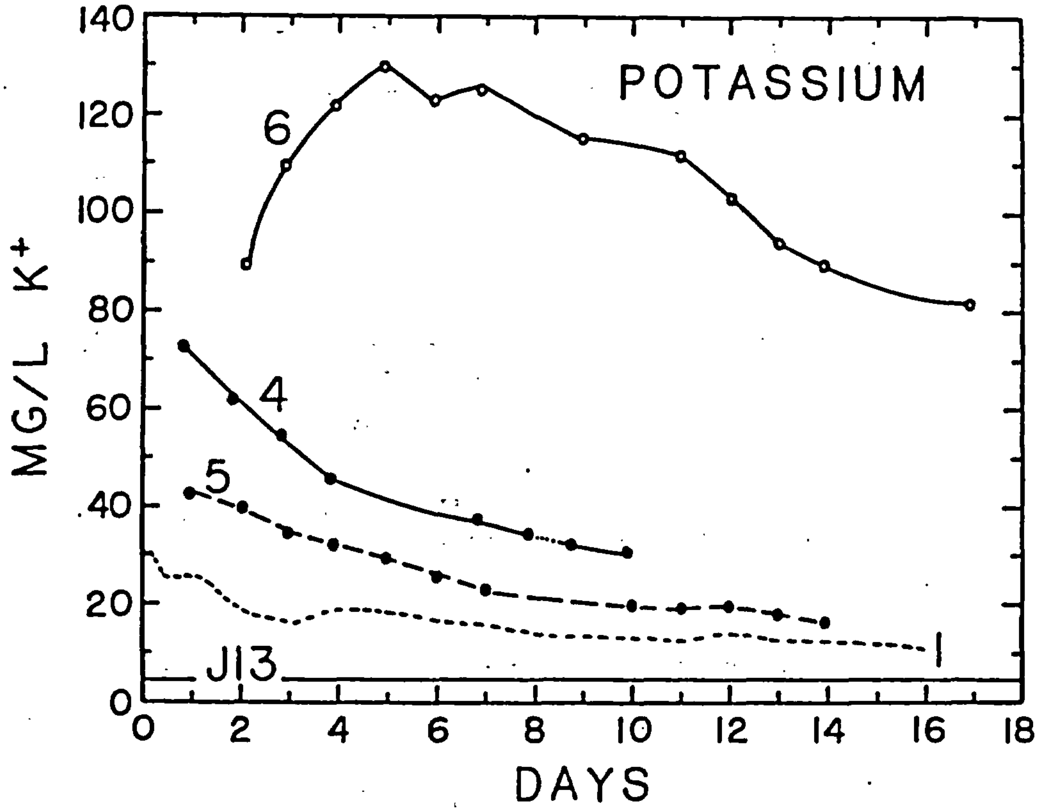

Figure 5. Changes in potassium contents of the discharged fluids with time during experiments 4, 5, and 6. Also included in this and several subsequent figures are the results from the earlier Topopah experiment #1 (Moore et al., 1984), which also was run at a borehole temperature of 150°C.

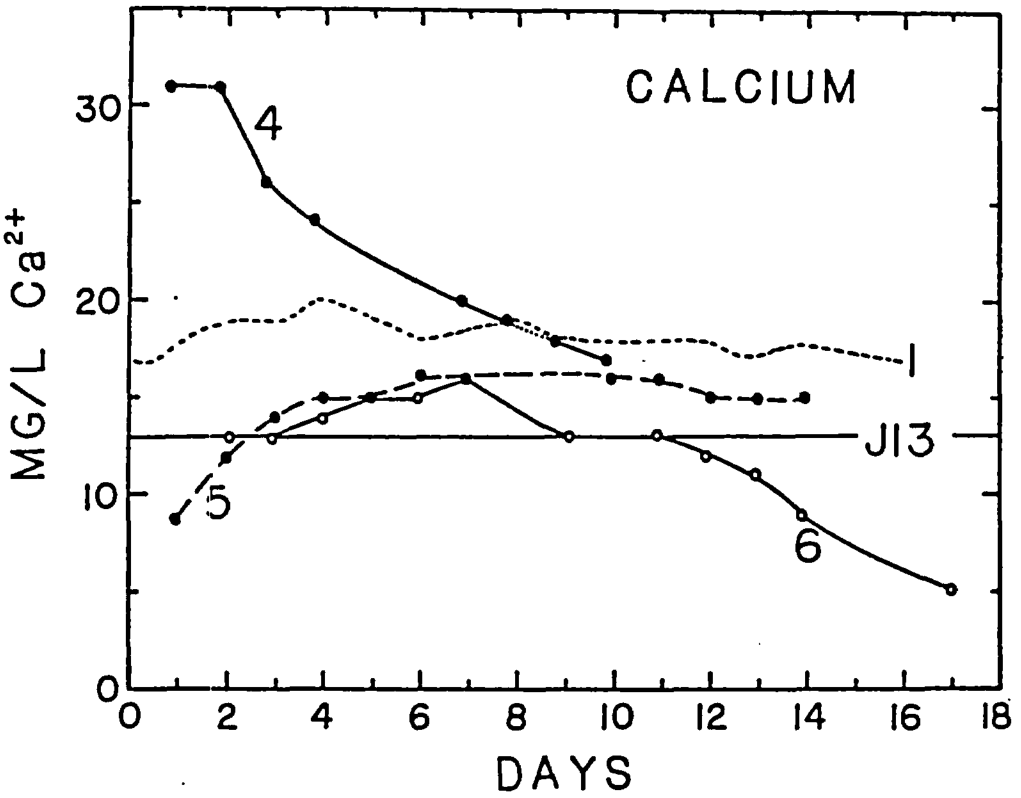

Figure 6. Calcium contents of the fluids collected during experiments 4, 5, and 6 as well as the earlier 150°C experiment 1.

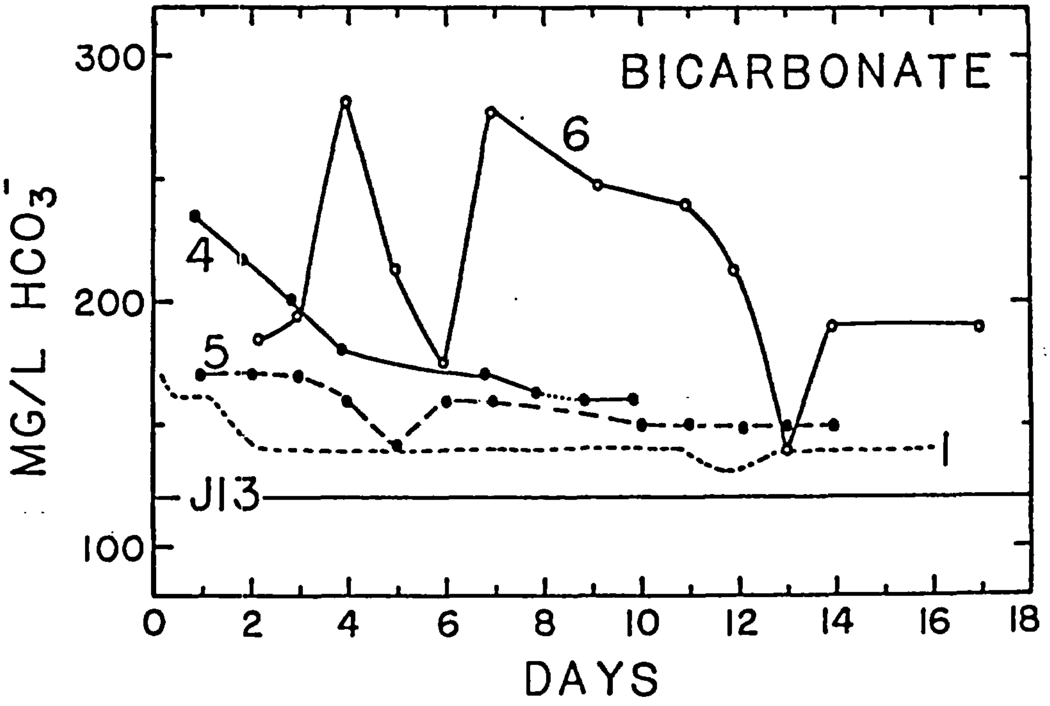

Figure 7. Changes in bicarbonate content of the discharged fluids.

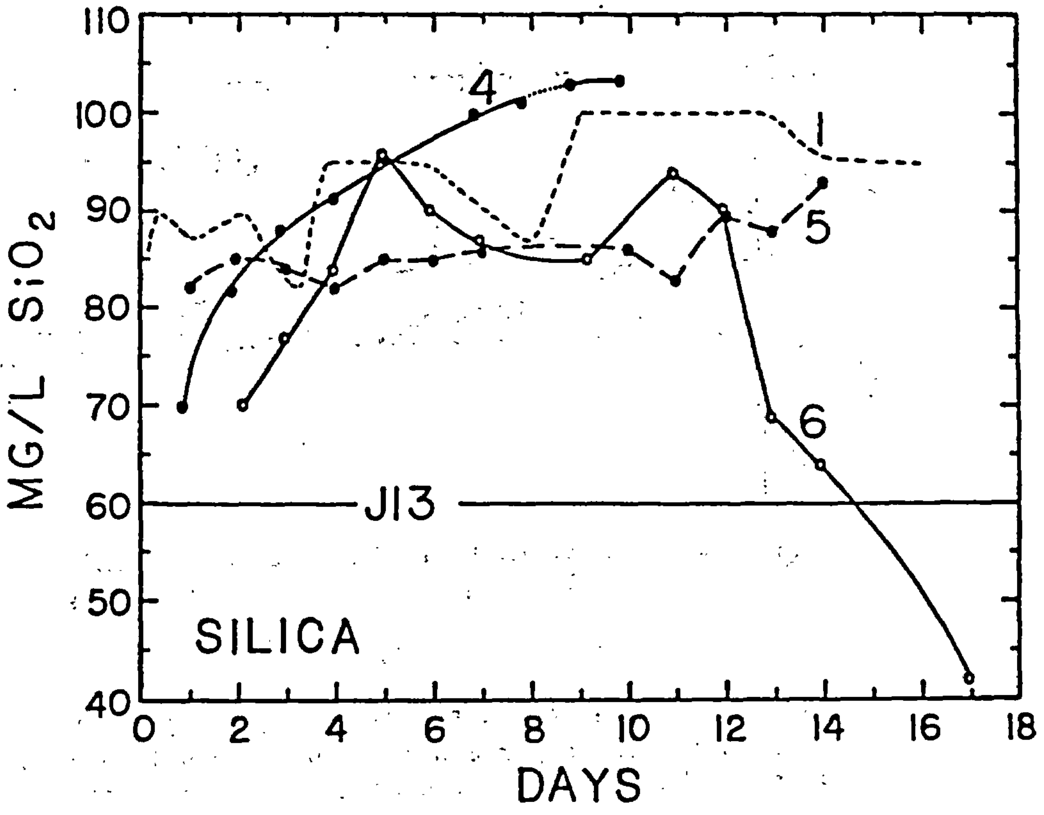

Figure 8. Dissolved silica contents of the fluids discharged from the Topopah samples during experiments 1, 4, 5, and 6.

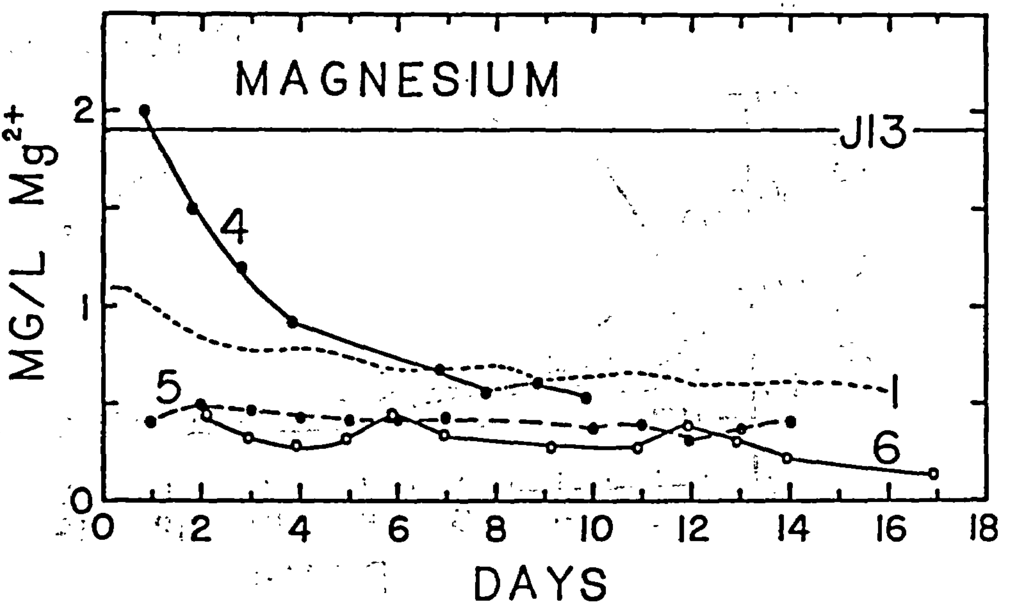

Figure 9. Magnesium contents of the discharged fluids, compared to the starting J13 Mg concentration.

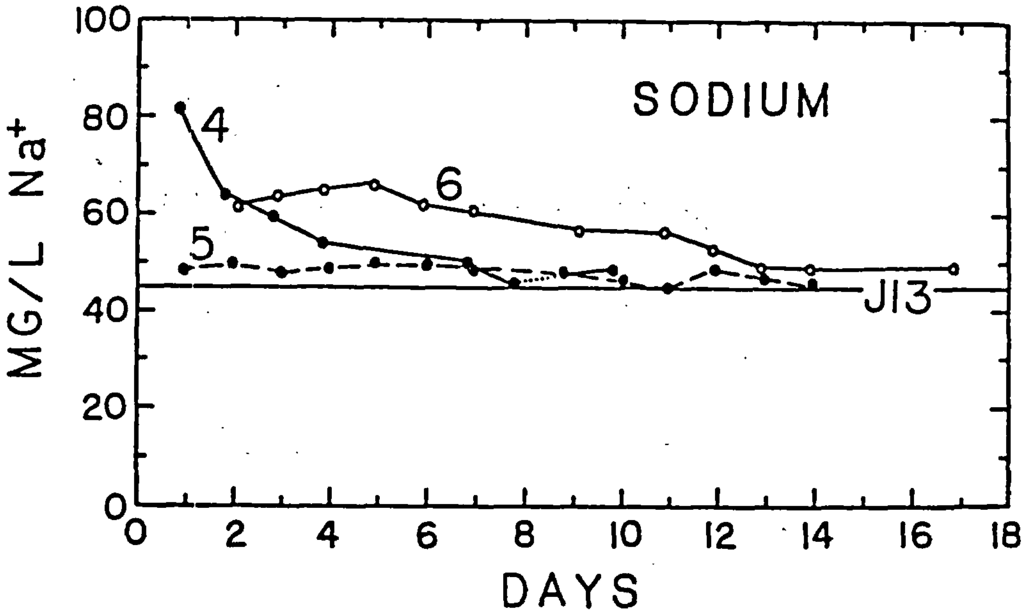

Figure 10. Sodium contents of the fluids discharged from the Topopah cylinders during the experiments. Fluid compositions for experiment 1 plot on the J13 line for most of the experiment.

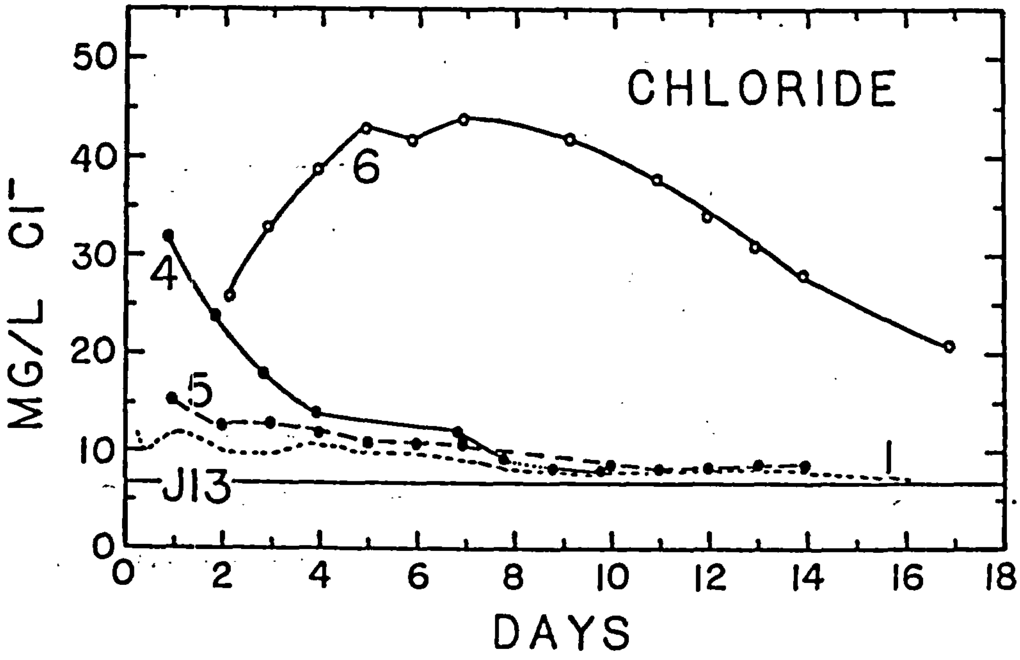

Figure 11. Changes in chloride content of the discharged fluids with time during the permeability experiments.

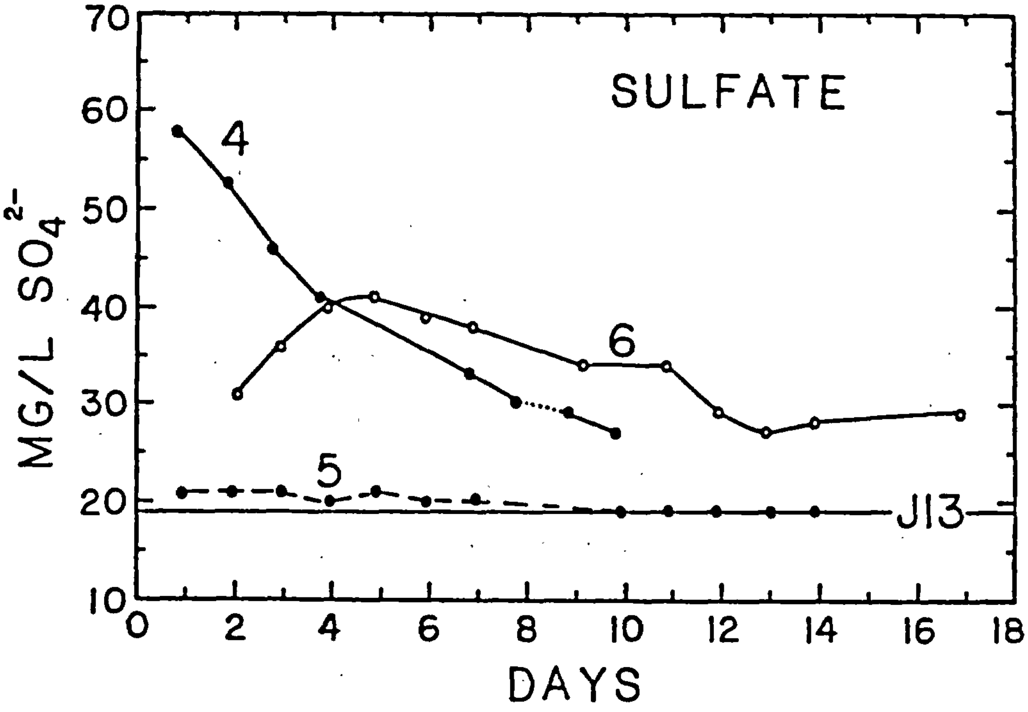

Figure 12. Sulfate concentrations of the fluids discharged from the Topopah cylinders. Compositional trends for experiment 1 almost completely overlap those of experiment 5.

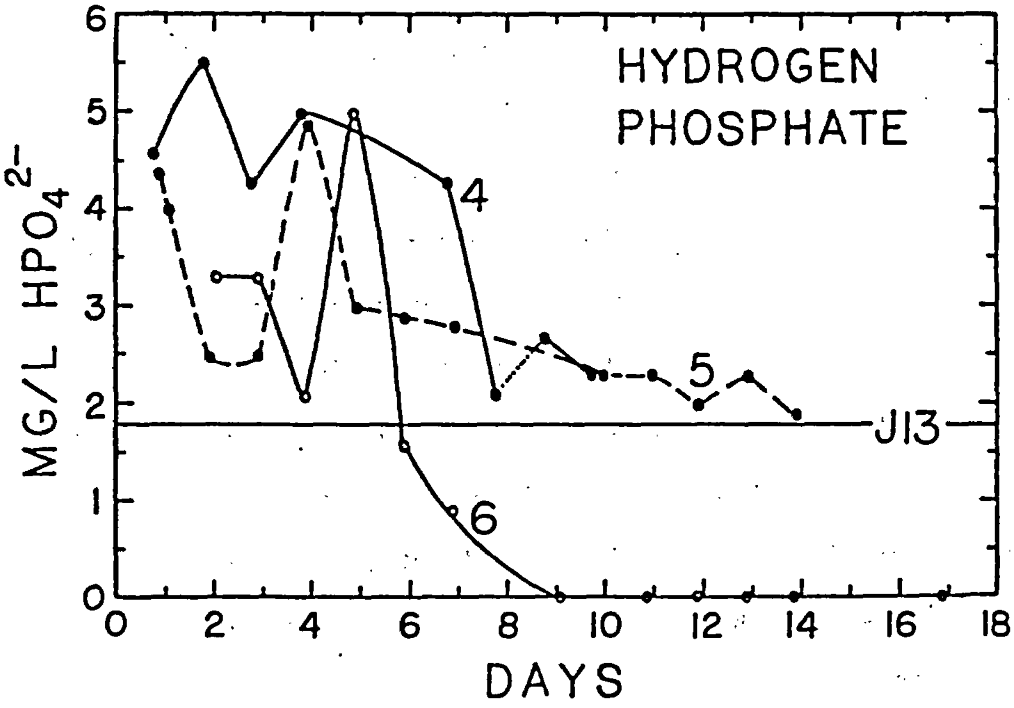

Figure 13. Changes in the concentration of hydrogen phosphate ion with time. Compositional trends for experiment 1 are not shown because the J13 supply used in that experiment did not contain measurable amounts of phosphorus in solution.

been involved in some type of adsorption or other surface reaction. Knauss (1984) describes a reaction of this type in an experiment at 150°C, in which J13 water was reacted with a core sample of Bullfrog tuff. During that experiment, calcium from the heated J13 water was deposited as a coating on plagioclase phenocrysts in the tuff. After the first few days of heating during experiment 5, a second, calcium-generating reaction predominated over the calcium-consuming reaction. One possible source of calcium to solution would be the calcite fillings found in some fractures and vugs. The increase in bicarbonate concentrations with heating during experiment 5 is consistent with the dissolution of calcite.

The concentrations of fluoride during experiment 4 (Table 3) and of magnesium throughout experiments 4 and 5 (Table 3, Figure 9), decrease to values below the original J13 levels. These reductions also suggest the occurrence of mineral reactions. Magnesium is known to be readily incorporated into alteration minerals during basalt-seawater interaction experiments at elevated temperatures (e.g., Hajash, 1975; Mottl and Holland, 1978, Seyfried and Bischoff, 1981). In a similar way, the magnesium in the J13 groundwater may have been incorporated into a clay mineral in the tuff; indeed, Knauss et al. (1984) have observed abundant "illite/montmorillonite" clays forming on samples of Topopah Spring tuff that were reacted with J13 water at 150°C. The results of an earlier Topopah experiment at 250°C borehole temperature (Moore et al., 1984) indicated that some magnesium also was added to solution as a result of a mineral reaction. If such a reaction also takes place in the 150°C experiments, it is less important than the magnesium-consuming reaction in controlling the net magnesium concentration.

With respect to the low fluoride concentrations in experiment 4, all of the fluids that were analyzed with SOLMNEQ at the discharge temperature were undersaturated with fluorite (Table 4), which is the only probable fluorine-bearing mineral to form in the tuff. However, fluorite has a negative solubility relationship with temperature; therefore, some fluorite could have precipitated near the borehole. Alternatively, the fluoride in the J13 water may have been incorporated as a minor element into an existing mineral in the tuff.

Nitrate concentrations in experiments 4 and 5 (Table 3) also are below J13 levels. However, nitrate is not a mineral-forming species, and the disappearance of this anion more likely is caused by the instability of nitrogen species in solution (e.g., Byerlee et al., 1983; Moore et al., 1984). Similar arguments hold for the nitrite in solution.

The final concentrations of sodium, chloride, sulfate and hydrogen phosphate (Figures 10-13) in experiments 4 and 5 are at or near J13 levels. These species probably did not come from minerals in the tuff but rather were present in small quantities in pore fluids or evaporation deposits in vugs or cracks (Moore et al., 1984). The results of experiments 4 and 5 for these species do not suggest that any reactions took place other than the simple dissolution of this material and its subsequent removal from the tuff.

The results of the reverse-flow experiment 6 (Table 3) show that sodium (Figure 10) and magnesium (Figure 9) are the only species whose solution concentrations are similar at all times to those from the other 150°C experiments. The initial trends of calcium (Figure 6), silica (Figure 8), and hydrogen phosphate (Figure 13) correspond to the trends in experiments 4 and 5; after several days, however, the concentrations of these species drop below J13 levels. Hydrogen phosphate is completely absent from the final six fluid samples of experiment 6. Overall, the minor component aluminum (Table 3) is present in slightly lower concentrations in experiment 6, whereas the other species are at higher concentrations.

Interpreting the chemical results of reverse-flow experiment 6 is complicated by the fact that the rate of fluid flow through this sample was about an order of magnitude lower than that for the other two tuff cylinders (Table 2, Figure 2). If the concentration of a given species in these solutions is a function of competing, temperature-dependent reactions, then the path of the fluids relative to temperature will affect the composition of the discharged fluids. Decreasing the rate of fluid flow will increase the amount of time available for tuff-water reactions at all temperatures to occur, which also will affect the final solution concentrations.

The higher chloride, sulfate, fluoride, and sodium concentrations of experiment 6 may be explained by the removal of the deposited salts in the tuff in a much smaller fluid volume. The room-temperature fluids of experiment 6 did not have high concentrations of these species despite the low flow rates; this suggests that the total amount of salts or saline pore fluids initially present in this sample was actually relatively low. This is also borne out by calculations of the total masses of chlorite and sulfate removed in solution during the experiments; the totals were much lower for experiment 6 than for experiment 5.

The decrease in calcium concentrations below J13 levels during experiment 6 may possibly be a function of flow direction. Calcite shows a negative solubility relationship with temperature; and the early-discharged fluids were supersaturated with respect to calcite (Table 4), including the 10.9-day sample which has the same calcium concentration as the J13 water. Another possible reaction is the formation of apatite, which would also account for the removal of hydrogen phosphate from solution (Figure 13).

The low silica concentrations of experiment 6 may be a function of the low flow rate as well as the flow path. It was previously proposed (Moore et al., 1984) that silica concentrations in solution were a function of competing silica-generating and silica-consuming reactions. The principal silica-generating reactions were the dissolution of quartz and cristobalite; these reactions were kinetically favored over the silica-consuming reaction. In experiment 6, none of the fluid samples were supersaturated with respect to any silica polymorph at the discharge temperature (Table 4); even so, the silica concentrations dropped below J13 levels during this experiment. A possible explanation for this behavior is that the flow rate was sufficiently low that the silica-consuming reaction was also kinetically favored. In addition, the silica-consuming reaction must occur near the high-temperature borehole; otherwise, quartz and cristobalite dissolution in the borehole area would lead to higher silica concentrations in the discharged fluids.

Several possibilities exist for the identity of the silica-consuming reaction. According to the SOLMNEQ results (Table 4), the only silicate minerals that potentially might precipitate from the early-discharged fluids and that might reasonably be forming in the tuff are magnesian-chlorite and phillipsite, which is a potassium-bearing zeolite. However, the amount of magnesium in solution is not high enough to account for any significant decrease in dissolved silica concentrations. In addition, the magnesium concentrations decrease immediately upon heating, whereas the decrease in silica does not occur until about 12 days later. Therefore, if a silicate mineral was forming from a supersaturated solution, phillipsite would appear to be the best choice among those analyzed by SOLMNEQ. Potassium concentrations do decrease along with silica, although the reduction in potassium begins several days before that of silica (Table 3). It is not necessarily true, however, that a new silicate mineral was precipitating from solution during experiment 6. Instead, the silica may have been incorporated into one or more minerals in the tuff groundmass that were undergoing compositional changes during the experiment.

A modest relationship between aluminum and silica concentrations is apparent when the results of experiments 4, 5, and 6 are compared (Figure 14). An area of overlap between 80 and 100 mg/L silica exists where the aluminum concentration of a given sample may be low or high. However, fluid samples with less than 80 mg/L dissolved silica also contain 0.06 mg/L aluminum or less, whereas samples with more than 100 mg/L silica have aluminum concentrations of 0.08 mg/L or greater. This relationship is consistent with the fact that essentially all the aluminum in the tuff is contained in silicate minerals.

Comparison With Other Permeability Studies. In contrast to the tuff experiments, significant permeability reductions have been measured during similar experiments conducted on granitic rocks (Morrow et al., 1981; Moore et al., 1983), and also on quartzite, gabbro, and anorthosite (Morrow et al., 1985). Scanning electron microscope examination of some of the post-test granite samples showed the presence of mineral deposits that were not found in the starting material (Morrow et al., 1981; p. 3006). These mineral deposits were considered by Morrow et al. (1981) to be the source of the permeability decreases. Preliminary modeling of some of the granite experiments by Lichtner and Helgeson (1983) supports the suggestion that solution-deposition processes could account for the observed permeability changes. Although few changes in permeability accompanied fluid flow during the tuff experiments, the fluid chemistry results show that some fluid-tuff interactions did take place. The dissolution of minerals in the tuff added some species to the

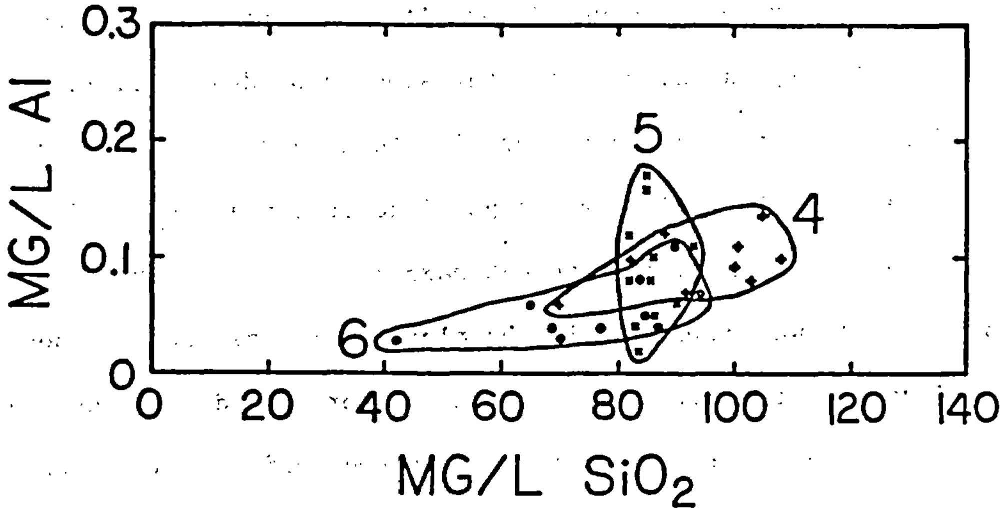

Figure 14. Plot of Al against SiO_2 for the fluid samples of experiments 4, 5, and 6. Omitted from the figure are 3 samples with the unusually high Al concentrations (Table 3), which are considered to result from the dissolution of very fine-grained particulate matter in the acidified sample.

groundwaters. In addition, species such as magnesium, calcium, silica, and hydrogen phosphate were removed from the pore fluids by mineral reactions during one or more of the experiments.

The lack of permeability decrease in the tuffs despite the occurrence of these mineral reactions may be a function of differences in the geometry of cracks and pores between the two rock types. Fluid flow through the granite samples, for example, was restricted to narrow microcracks and grain boundaries. Only a small volume of deposited material would be needed to restrict fluid flow in the granite. Much of the flow through the Topopah samples is along interconnected porosity. If the pores in the Topopah samples are sufficiently large, much greater amounts of deposited material would be needed in the tuff than in the granite to constrict the flow path and thereby reduce permeability. It also is possible that the amount of material deposited in cracks in the Topopah samples is low compared to that in the granites. As was described in the fluid chemistry section, some of the reactions that removed material from the pore fluids may involve changes in the composition of existing minerals in the tuff instead of the formation of crack-filling deposits. For example, the removal of some species from the J13 pore fluid at room-temperature (Table 3) is suggestive of adsorption by an existing mineral rather than the growth of a new mineral, because most mineral-forming reactions are extremely sluggish at room temperature. The combination of large pores and a small volume of pore-filling minerals would explain the lack of permeability change in the Topopah cylinders. Detailed SEM examinations of the Topopah cylinders should be conducted to test this hypothesis.

CONCLUSIONS

The results of this second series of permeability experiments on the Topopah Spring Member of the Paintbrush Tuff are consistent with the results of the earlier Topopah studies. The tuff cylinders showed little variation in permeability during the experiments, which were conducted at temperature and pressure conditions approximating those expected at the potential disposal site. The fluid chemistry results also were consistent with the earlier Topopah experiment conducted at the same borehole temperature, in that the fluids were dilute, nearly neutral solutions that did not differ significantly from the starting J13 groundwater composition.

ACKNOWLEDGEMENTS

This work was performed for Lawrence Livermore National Laboratory under Contract Number SANL 126-016.

APPENDIX. FLUORIDE CONCENTRATIONS OF EXPERIMENT 6

Because of the necessarily small fluid sample size, fluoride determinations had to be made using ion chromatographic rather than standard ion specific electrode techniques. Whereas in the electrode determinations the samples can be treated to yield total fluoride concentrations in solution, problems can arise with the ion chromatographic determinations if some of the fluoride in solution forms complexes. Such complexing of fluoride appears to have occurred in the fluids collected during reverse-flow experiment 6 and in the room-temperature sample of experiment 5.

The ion chromatography charts for all but the last heated sample of experiment 6 contain 2 unknown peaks, at 2.35 and 2.55 minutes (Figure A). The close proximity of these two peaks to the normal 2.15 minute fluoride peak suggested that the two unknown peaks were fluoride-bearing complexes of some kind. At the present time, little information is available concerning the behavior of different fluoride-bearing complexes during ion chromatographic analysis. As described below, however, it is suggested that the 2.35 minute peak measures the amount of CaF_2^o in solution and the 2.55 minute peak measures CaF^{+1} concentrations (T.S. Presser and I. Barnes, written communication, 1984).

The occurrence and heights of the three peaks among the fluid samples of experiment 6 are listed in Table A. This table shows the following significant features:

1) The 2.15 minute peak is the only one present in all the fluid samples. When found with one or both of the other peaks, the 2.15 minute peak is at a relatively uniform height. When associated with a large 2.35 minute peak, the 2.15 minute peak appears as a shoulder on the larger peak.

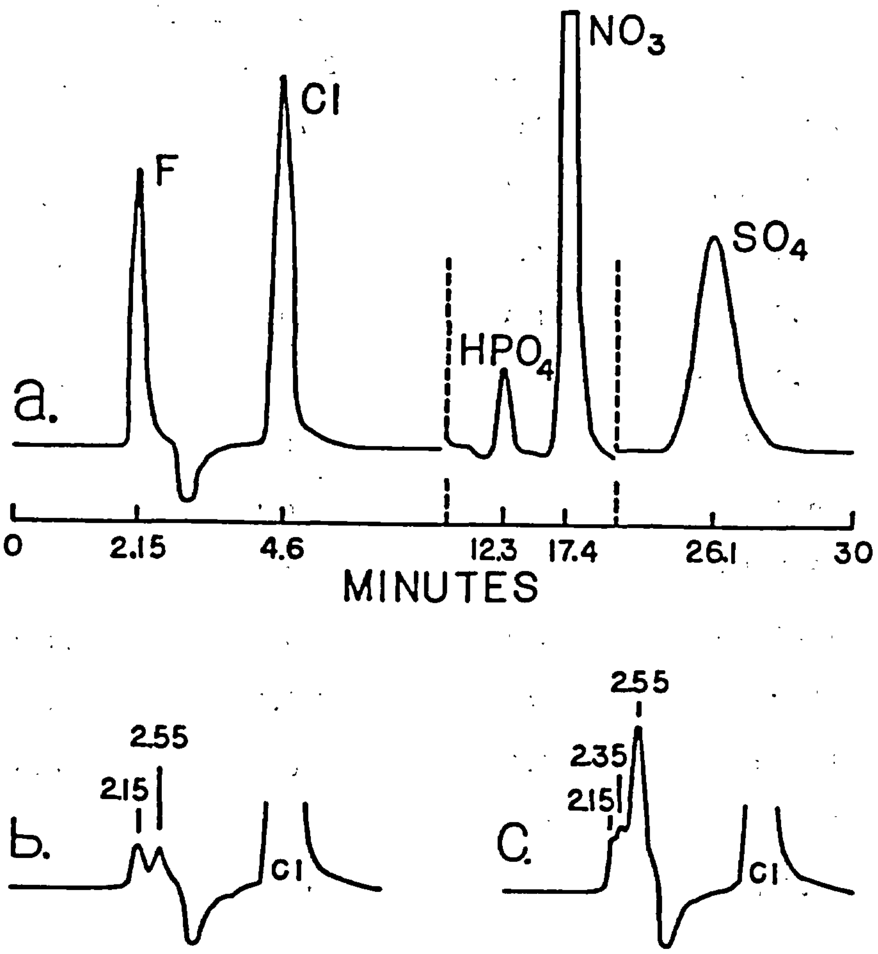

Figure A. Ion chromatography charts. a) Results for J13 groundwater, showing the regular fluoride peak at 2.15 minutes. The two dashed lines correspond to changes in chart speed and other recording conditions. b) 9.1 day sample from experiment 6, showing a new peak at 2.55 minutes. c) 10.9 day sample from experiment 6, showing three peaks between 7.15 and 2.55 minutes.

Table A. Peak Heights of Probable Fluoride Species from Ion Chromatographic Analyses, Experiment 6

Sample	Dilution	Peak Heights (mm) 2.15 min.	2.35 min.	2.55 min.
Room-Temperature	1:2	45.5	-	9
Heated - 2.1 days	1:4	11	36.5	39.8
2.9 days	1:4	10.5	48	56
3.9 days	1:4	10	49	65
4.9 days	1:5	10	38	78
5.9 days	1:5	9	33	90
6.9 days	1:5	6.5	-	7.5
9.1 days	1:4	8	-	7
10.9 days	1:4	9	11.2	29
11.9 days	1:4	9.5	14.7	74
12.9 days	1:4	10	26.5	119
13.9 days	1:3	12	-	83.5
16.9 days	1:3	14	-	-

2) The 2.35 minute peak is only present in samples that contain both a 2.15 and a 2.55 minute peak.

3) With the exception of the 13.9 day sample, the height of the 2.55 minute peak is low in the samples that lack a 2.35 minute peak.

Solution balances for the fluid samples in experiment 6 were calculated assuming that the two extra peaks represented complexes with a single fluoride ion and that the amount of fluoride in each complex could be estimated by comparison with the 2.15 minute fluoride standards. A good balance was achieved for the samples containing only the 2.15 and 2.55 minute peaks. Samples with a large 2.55 minute peak and a small 2.35 minute peak also gave good balances; however, samples with a large 2.35 minute peak had a deficiency of anions.

Calcium is the most likely cation to form complexes with fluoride in these solutions. Using the fluoride concentrations that were estimated for the initial balance computations, nearly all the samples showed supersaturation with respect to fluorite at 25°C. Therefore, it is possible that some complexing between Ca and F did occur in the fluid samples. The possible reactons are:

$$Ca^{+2} + F^{-1} \rightleftharpoons CaF^{+1} \qquad (1)$$

$$CaF^{+1} + F^{-1} \rightleftharpoons CaF_2^{\circ}\ (aq) \qquad (2)$$

The proposed identification (T.S. Presser, written communication) is that the complex CaF^{+1} appears as the 2.55 minute peak and the CaF_2° as the 2.35 minute peak on the ion chromatograph charts.

This identification explains the distribution of peaks shown in Table A, and it also satisfies the need for more than one fluoride ion in the 2.35 minute complex to improve the solution balances. Therefore the fluoride concentrations of experiment 6 that are reported in Table 3 are a total of all the fluoride-bearing peaks, with the contribution of the 2.35 minute peak being calculated as double the concentration determined by direct comparison to the heights of the fluoride standards. (The species CaF_2° itself is uncharged and as a whole does not add to the anion balance. However, atomic absorption analysis of the diluted, acidified sample yields a total calcium concentration. Since the calcium in the CaF_2° complex is being counted in the cation total, the two fluorides must be added to the anion total.)

The two complexes, particularly CaF_2°, might be expected to be unstable in the solutions. A second ion chromatographic analysis of the samples conducted 5 months after the first did indeed show that in many cases the 2.35 and 2.55 minute peaks were significantly reduced. In most of the samples, the 2.15 minute peak was unchanged; for these samples, the mineral fluorite apparently was being precipitated. In a few cases, however, the size of the 2.15 minute peak was enhanced, indicating that reaction (1) and perhaps also (2) were reversed. This second type of behavior may have been caused by changes with time in solution parameters such as pH.

REFERENCES

Byerlee, J., Morrow, C., and Moore, D. (1983) Permeability and pore-fluid chemistry of the Bullfrog Tuff in a temperature gradient: Summary of Results. U.S. Geological Survey Open-File Report 83-475, 26 pp.

Hajash, A. (1975) Hydrothermal processes along mid-ocean ridges: an experimental investigation. Contributions to Mineralogy and Petrology 53, 205-226.

Kharaka, Y. K. and Barnes, I. (1973) SOLMNEQ: Solution-mineral equilibrium computations. NTIS, U.S. Department of Commerce, PB-215 899, 81 pp.

Knauss, K. G. (1984a) Hydrothermal interaction studies of Bullfrog Member tuff core wafers in J-13 water at 150°C: Quantitative analyses of aqueous and solid phases. Lawrence Livermore Laboratory, UCRL-53521, 24 pp.

Knauss, K. G. (1984b) Petrologic and geochemical characterization of the Topopah Spring Member of the Paintbrush Tuff: Outcrop samples used in waste package experiments. Lawrence Livermore Laboratory, UCRL-53558.

Knauss, K. G., Oversby, V. M., and Wolery, T.J. (1984) Post emplacement environment of waste packages. Materials Research Society Symposium Proceedings 26, 301-308.

Lichtner, P. C., and Helgeson, H. C. (1983) Numerical modeling of fluid flow with simultaneous chemical reaction in hydrothermal systems. Geological Society of America Abstracts with Programs 15, 627.

Moore, D. E., Morrow, C. A., and Byerlee, J. D. (1983) Chemical reactions accompanying fluid flow through granite held in a temperature gradient. Geochimica et Cosmochimica Acta 47, 445-453.

Moore, D. E., Morrow, C. A., and Byerlee, J. D. (1984) Changes in permeability and fluid chemistry of the Topopah Spring Member of the Paintbrush Tuff (Nevada Test Site) when held in a temperature gradient: Summary of results. U.S. Geological Survey Open-File Report 84-273, 33 pp.

Morrow, C., Lockner, D., Moore, D., and Byerlee, J. (1981) Permeability of granite in a temperature gradient. Journal of Geophysical Research 86, 3002-3008.

Morrow, C., Moore, D., and Byerlee, J. (1983) Permeability and pore-fluid chemistry of the Bullfrog Tuff in a temperature gradient. Proceedings 24th U.S. Symposium on Rock Mechanics, 819-828.

Morrow, C. A., Moore, D. E., and Byerlee, J. D. (1984) Permeability and pore-fluid chemistry of the Topopah Spring Member of the Paintbrush Tuff, Nevada Test Site, in a temperature gradient: Application to nuclear waste storage. Proceedings Materials Research Society Symposium, Scientific Basis for Nuclear Waste Management VII, vol. 26, 883-890.

Morrow, C. A., Moore, D. E., and Byerlee, J. D. (1985) Permeability changes in crystalline rocks due to temperature: effects of mineral assemblage. Proceedings Materials Research Society Symposium VIII, in press.

Mottl, M. J. and Holland, H. D. (1978) Chemical exchange during hydrothermal alteration of basalt by seawater -- I. Experimental results for major and minor components of seawater. Geochimica et Cosmochimica Acta 42, 1103-1117.

Oversby, V. M. and Knauss, K. G. (1983) Reaction of Bullfrog Tuff with J-13 well water at 90°C and 150°C. Lawrence Livermore Laboratory, UCRL-53442, 51 pp.

Seyfried, W. E., Jr. and Bischoff, J. L. (1981) Experimental seawater-basalt interaction at 300°C, 500 bars, chemical exchange, secondary mineral formation and implications for the transport of heavy metals. Geochimica et Cosmochimica Acta 45, 135-147.