

High-Temperature Permeability and Groundwater Chemistry of Some Nevada Test Site Tuffs

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Permeability measurements of samples of the Topopah Spring Member of the Paintbrush Tuff and the Bullfrog Member of the Crater Flat Tuff collected from the Nevada Test Site have been made at room temperature and in a temperature gradient. The room temperature permeabilities of the samples ranged from 0.8×10^{-18} to $64 \times 10^{-18} \text{ m}^2$ for the Topopah Spring Member and 0.5×10^{-18} to $8.4 \times 10^{-18} \text{ m}^2$ for the Bullfrog Member. These variable permeabilities probably reflect differences in crack and void configurations among the samples. The permeability of a given sample was only slightly affected by heating to maximum temperatures between 90°C and 250°C during experiments of up to 5 weeks' duration. The observed lack of permeability change is consistent with the hypothesis that the disposal of nuclear waste in tuff units in the unsaturated zone at the Nevada Test Site would not have a large effect on the permeability of the host rock. The fluids discharged from the tuff samples during the experiments were mostly dilute solutions of nearly neutral pH, whose compositions differed only slightly from the starting J13 groundwater composition. Waters of this type should be relatively noncorrosive to stainless steel waste canisters.

INTRODUCTION

The Nevada Test Site is one of the localities being considered for the underground disposal of nuclear waste. The area is directly underlain by several thousand feet of Cenozoic ash flow and bedded tuffs [Waters and Carroll, 1981]. A critical factor in developing a safe disposal scheme is to understand how the geologic materials at and around the potential disposal horizon would respond to the localized heating accompanying radioactive decay in the canisters.

This paper reports the results of a series of experiments that measure the permeability and groundwater chemistry of tuffaceous rocks subjected to a temperature gradient. This work was performed as a support study for the Nevada Nuclear Waste Storage Investigations (NNWSI) Project. Experiments were conducted on tuffs from two units that have been considered as possible disposal horizons: the Topopah Spring Member of the Paintbrush Tuff and the Bullfrog Member of the Crater Flat Tuff. A disposal site in Topopah Spring Member rocks would be in the unsaturated zone above the water table, whereas a Bullfrog Member disposal site would be below the water table. At the present time, the horizon under investigation is in rocks of the Topopah Spring Member; accordingly, most of the experiments of this study were conducted on Topopah Spring Member samples. Although the Topopah Spring Member results are therefore more pertinent, nevertheless the Bullfrog Member experiments provide useful information on the behavior of the surrounding tuff layers.

SAMPLE DESCRIPTIONS

The Bullfrog Member and Topopah Spring Member samples used in this study were collected from surface exposures of the specific units that are being considered for the repository. The Bullfrog Member rocks come from a moderately welded, vapor-phase altered ash flow layer that is devitrified but not zeolitized. Deformed, elongated pumice fragments and

numerous small voids occur in the matrix. The tuff in this layer is rich in phenocrysts, principally quartz, plagioclase, and potash feldspar, with minor amounts of biotite, hornblende, and some opaques. The groundmass contains considerable amounts of cristobalite and small amounts of illite, as indicated by X ray diffraction analysis. Patches of secondary calcite are found in some of the pumice fragments.

The Topopah Spring Member samples were obtained from a densely welded, devitrified layer that has not been zeolitized. These outcrop samples contain some elongated lithophysae up to several centimeters in length, which however, may not be present at the depth of the potential repository [Bish et al., 1984]. The Topopah Spring Member samples contain only a small number of quartz and feldspar phenocrysts, which occur principally in volcanic lithic fragments. Many highly flattened pumice fragments are visible in the groundmass. X ray diffraction analysis of the groundmass shows the presence of potash feldspar, cristobalite, and some quartz. The walls of the lithophysae are lined with quartz and calcite.

EXPERIMENTAL PROCEDURE

The experimental assembly is shown in Figure 1. A cylindrical sample of tuff, 7.62 cm in diameter and 8.89 cm long, was prepared with a 1.27-cm-diameter borehole. A coiled resistance heater placed within the borehole produced a temperature gradient between the center and outside of the rock. In most experiments, water flowed radially through the tuff from the higher temperature borehole to the lower temperature outer edge, in response to a small differential pore pressure gradient. However, the pore pressure inlet and outlet lines could also be reversed, causing fluid to flow from the outer edge of the cylinder to the borehole; this was done in one experiment. All exposed metal in the high-temperature borehole area was gold plated to prevent fluid contamination. Gold shims at the ends of the sample prevented fluid flow along the interface between the tuff and the fused silica cylinders that served as thermal insulators. The fused silica cylinders also are impermeable; thus water can flow only through the rock sample.

A thin, stainless steel mesh was wrapped around the outside of the sample to allow drainage of the pore fluids that had

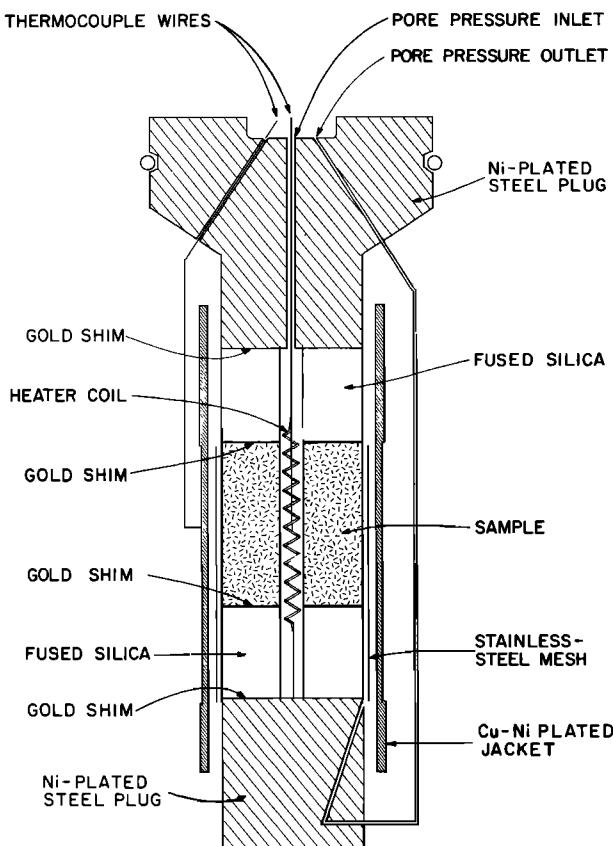


Fig. 1. Schematic sample assembly.

passed through the rock. In this way, the jacket for the sample assembly did not interfere with fluid flow, while still sealing the sample from the silicon oil that served as the confining pressure fluid. Pore pressure and hydrostatic confining pressure were held constant by a computer-controlled servo-mechanism.

The initial permeability of each tuff cylinder was measured at room temperature. Following that, fluid flow was halted while the sample was heated. Within approximately an hour a stable temperature gradient was established across the tuff cylinders, and flow was resumed. Deionized water was used as the pore fluid in the first experiment; the rest of the experiments were run using a natural groundwater collected from the J13 drillhole, which is located about 6 km southeast of the potential repository area. The main producing zone for the J13 well is in rocks of the Topopah Spring Member [Oversby, 1984]. The chemistry of this water is similar to that of groundwaters from the repository area [Bish et al., 1984, Tables 1 and 2], and the J13 groundwater is used as the reference water for laboratory experiments and geochemical modeling in the NNWSI Project [Oversby, 1984]. Three separate supplies of J13 water for the experiments were obtained at different times from Lawrence Livermore National Laboratory. Because of the natural variability of groundwater chemistry, the supplies differed slightly in composition, as shown in Table 1.

Samples of the pore fluids discharged from the tuff cylinders were collected at intervals during the experiments to determine any changes in water chemistry resulting from interaction with the heated tuffs. Fluid samples also were collected

during the initial, room temperature permeability experiments. An analytical technique for the determination of aluminum was developed only after completion of the Bullfrog Member experiments; because of this, the fluid sample treatment procedures varied slightly between the Bullfrog Member and the Topopah Spring Member experiments. For the Bullfrog experiments, the fluid sample size was 1.5 mL. Immediately upon collection, each sample was filtered through a 0.45- μm membrane filter, and a 0.25-mL aliquot was separated for silica analysis. Room temperature pH measurements were then made on the remaining sample. The fluids reserved for silica analysis were digested overnight in a 1 N NaOH solution and then analyzed by standard spectrophotometric techniques, using the molybdate blue method [American Society for Testing and Materials, 1974]. From the larger fluid sample, sodium, calcium, potassium, and magnesium concentrations were determined using atomic absorption techniques, and the total dissolved inorganic carbon content was determined with a carbon analyzer. Chloride, fluoride, sulfate, nitrate, and where present, nitrite and phosphate concentrations were determined using ion chromatography. All analyses were conducted soon after collection.

For the Topopah Spring Member experiments, the fluid sample size was increased to 2 mL. Following filtration and separation of the sample for silica analysis, a second, 1-mL aliquot was diluted to 5 mL with distilled water and acidified to a pH of about 2, using 10–15 μL of a 1:1 dilution of concentrated HCl. Room temperature pH measurements were made on the remaining fluid. The chemical analysis techniques were essentially the same as for the Bullfrog Member fluids, with the exception that the diluted and acidified sample was used for all cation analyses, including aluminum. The aluminum analyses were obtained using an atomic absorption graphite furnace technique that was developed by T. S. Presser of the U.S. Geological Survey to accommodate the small sample size. The aluminum values reported are a qualified total aluminum concentration, that is, filtered through a 0.45- μm membrane filter at 25°C. Details of the analytical procedure are presented by Moore et al. [1984a].

TABLE 1. Compositions of J13 Water Supplies Used in Different Experiments

| | A (B2, B3, and T1) | B (T2 and T3) | C (T4, T5, and T6) |
|------------------|--------------------------|---------------------|--------------------------|
| SiO ₂ | 61 | 57 | 60 |
| Na | 44 | 44 | 45 |
| K | 4.5 | 3.7 | 4.9 |
| Mg | 1.9 | 2.0 | 1.9 |
| Ca | 12 | 12 | 13 |
| HCO ₃ | 120* | 120 | 120 |
| SO ₄ | 17 | 19 | 19 |
| NO ₃ | 8.1 | 8.3 | 9.6 |
| F | 2.2 | 2.2 | 2.2 |
| Cl | 8.1 | 7.0 | 6.8 |
| HPO ₄ | | | 1.8 |
| pH (25°C) | 7.69 | 7.60 | 7.17 |
| Balance, % | -0.4 | -1.3 | +0.2 |

Concentrations are in milligrams per liter.

*Determined by both carbon analyzer and titration methods. Balance = [(cations – anions) – (cations + anions)/2] × 100.

TABLE 2. Summary of Experimental Conditions

| | Bullfrog Member | | | Topopah Spring Member | | | | | |
|--|-----------------|----------|----------|-----------------------|----------|----------|----------|---------------|---------------|
| | B1 | B2 | B3 | T1 | T2 | T3 | T4 | T5 | T6 |
| Borehole temperature, °C | 250 | 250 | 150 | 150 | 90 | 250 | 150 | 150 | 150 |
| Jacket temperature, °C | 68 | 73 | 48 | 50 | 36 | 83 | 43 | 44 | 45 |
| Confining pressure, MPa | 30 | 30 | 30 | 30 | 30 | 10 | 10 | 10 | 10 |
| Pore pressure, MPa | 10 | 10 | 10 | 10 | 10 | 3.4 → 1 | 1 | 1 | 1 |
| Differential pore pressure, MPa | 0.24 | 0.14 | 0.25 | 0.15 | 0.15 | 0 | 0.1 | 0.1 | 0.1 |
| Pore fluid | deionized water | J13(A) | J13(A) | J13(A) | J13(B) | J13(B) | J13(C) | J13(C) | J13(C) |
| Flow path (relative to bedding) | parallel | parallel | parallel | parallel | parallel | parallel | parallel | perpendicular | perpendicular |
| Flow direction (relative to high (H) and low (L) temperatures) | H → L | H → L | H → L | H → L | H → L | H → L | H → L | H → L | L → H |
| Duration, days | 12 | 21 | 37 | 20 | 17 | 21 | 10 | 14 | 17 |
| Room temperature permeability, $\text{m}^2 \times 10^{-18}$ | 2.4 | 8.5 | 0.5 | 3 | 64 | * | 5.2 | 10 | 0.85 |
| Final heated permeability, $\text{m}^2 \times 10^{-18}$ | 2.4 | 6 | 0.7 | 10 | 61 | * | 4.5 | 8 | 0.6 |
| Average daily flow, cm^3 | 65 | 100 | 14.5 | 99 | 125 | 17 | 43 | 68 | 4.75 |

*The sample contained a throughgoing fracture, so that permeability measurements at a reasonable flow rate could not be made.

EXPERIMENTS CONDUCTED

Three experiments were run using Bullfrog Member samples and six using Topopah Spring Member samples; the conditions are summarized in Table 2. Bullfrog Member experiments B1 and B2 were both run at a borehole temperature of 250°C, which is considered from modeling studies to be the upper limit of possible, although unanticipated, temperatures around the canisters of nuclear waste [Knauss *et al.*, 1985]. Deionized water was the pore fluid in B1, whereas the J13 groundwater was used in B2 and B3. The third Bullfrog Member experiment, B3, was run at 150°C borehole temperature to test the effects of a different heating temperature on permeability and pore fluid chemistry. Confining and pore pressures of 30 and 10 MPa, respectively, were used in these three experiments. The Bullfrog Member cylinders were cored such that flow was along the direction of bedding of the tuff, which simulated the lateral migration of fluids away from vertically emplaced canisters at the disposal site.

The six Topopah Spring Member experiments covered a wide range of possible temperature, pressure, and flow conditions. Since the potential Topopah Spring Member disposal site is in the unsaturated zone, heating accompanying radioactive decay in the canisters of nuclear waste will cause the pore waters to evaporate. The atmospheric boiling point of unconfined water is about 95°C at the elevation of the Nevada Test Site [Oversby, 1984]; water held by capillary forces in pores might remain liquid to temperatures of 140°–150°C [Knauss *et al.*, 1984]. To cover this range of maximum liquid water temperatures, experiments T1 and T2 were run at borehole temperatures of 150°C and 90°C, respectively. Experiment T3 was run at a 250°C borehole temperature to provide a comparison with Bullfrog Member experiments B1 and B2. Confining and pore pressures of T1, T2, and T3 were the same as in the Bullfrog Member experiments to allow a direct comparison of the two sets of results. In the course of experiment T2, flow was halted for intervals of 25, 50, and 100 hours

(Table 3), to determine the importance of fluid-tuff contact time on the water chemistry. The effect of flow rate on solution chemistry was investigated during experiment T3 by varying the flow rate over a range of 3 orders of magnitude (Table 3).

Experiments T4, T5, and T6 investigated different types of flow conditions, at a borehole temperature of 150°C and con-

TABLE 3. Changes in Experimental Conditions During Experiments T2, T3, and T4

| Experiment T2* | | |
|----------------------------|-----------------------------------|-----|
| Time, days into experiment | Duration, hours | |
| 3.84–5.92 | | 50 |
| 6.84–7.88 | | 25 |
| 9.73–13.9 | | 100 |
| Experiment T3† | | |
| Time, days | Flow Rate, cm^3/s | |
| 0–16.74 | 2×10^{-4} | |
| 16.76–17.00 | 2×10^{-3} | |
| 17.02–17.06 | 2×10^{-2} | |
| 17.08–17.73 | 2×10^{-4} | |
| 17.75–20.73 | 2×10^{-5} | |
| Experiment T4 | | |
| Time, days | Pore Pressure, MPa | |
| 0–7.80 | 3.3 | |
| 7.80–10.85 | 1 | |

*Fluid flow was halted during the time periods shown.

†Flow rates were varied as shown.

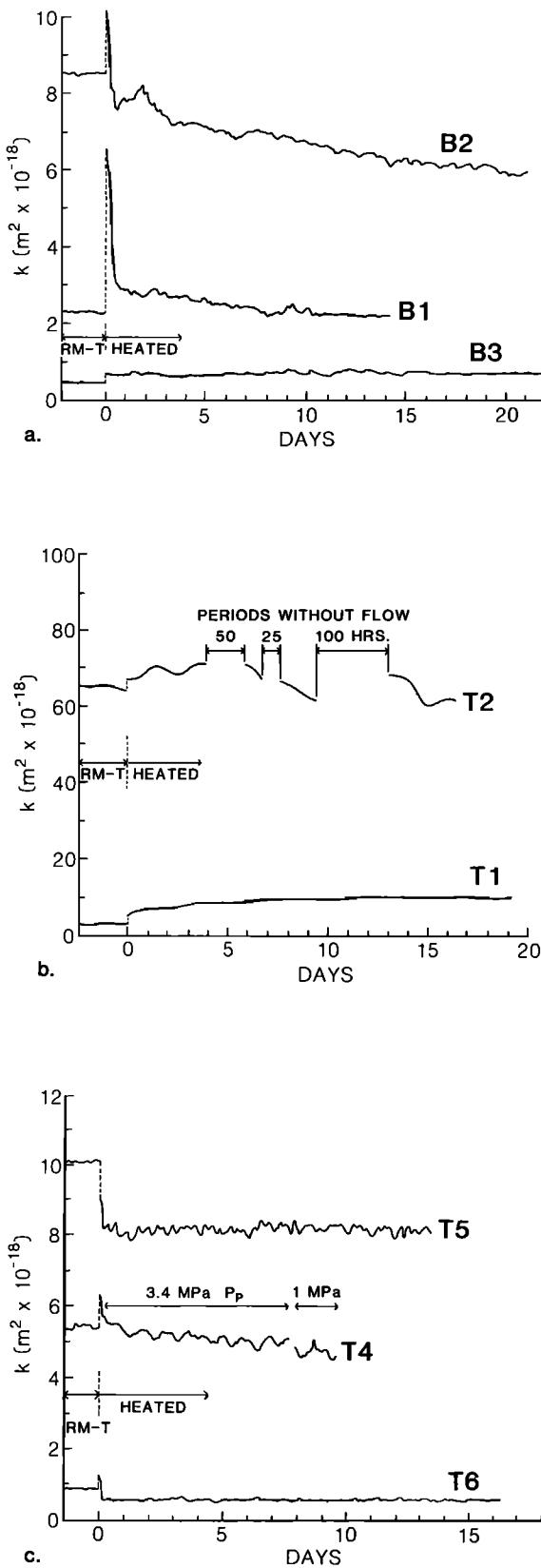


Fig. 2. Changes in permeability with time of (a) Bullfrog Member Tuff, and (b and c) Topopah Spring Member Tuff. The pore pressure of experiment T4 was reduced from 3.4 to 1 MPa after 8 days' flow, as indicated in Figure 2c.

fining pressure of 10 MPa. These temperature-pressure conditions were considered to approximate those expected at the disposal horizon. Experiment T4 served as a transition between the earlier Topopah Spring Member and Bullfrog Member experiments that were run at a 1:3 ratio of pore pressure to confining pressure and the later experiments that were run at a 1:10 ratio (Table 3). In T4 the pore fluid flowed parallel to the bedding direction, as it did in previous experiments. For T5 and T6, however, the tuff cylinders were cored with the bedding planes oriented perpendicular to the principal axis of the cylinder, so that some of the flow would be directed across rather than along the bedding. In T5 the fluid flowed from high to low temperatures, approximating the path of groundwater percolating downward from the heated disposal horizon. The flow direction was reversed for experiment T6; that is, groundwater flowed from the low-temperature outer edge of the sample to the high-temperature borehole. This flow direction simulated the movement of water from the earth's surface down to the disposal horizon in the tuff.

RESULTS

Permeability

The variations in permeability with time during the experiments were determined from measured changes in the mass flow rate over the constant pore pressure differential. The radial flow form of Darcy's law was solved for permeability and integrated over the radius from the borehole r_1 to the outer edge of the sample r_2 as follows:

$$k = \frac{Q_m}{2\pi l \Delta P} \int_{r_1}^{r_2} \frac{v(r)}{r} dr$$

In the equation, k is the permeability, Q_m the mass flow rate, l the length of the sample, and ΔP the fluid pressure gradient between the center and the outside of the sample; $v(r)$ is the dynamic viscosity of water, which is a function of temperature and therefore of radius in these experiments. The changes in $v(r)$ across the sample are taken into account in the computer program used to calculate permeability. The values of $v(r)$ used in the calculations were obtained from steam tables. The calculated permeabilities describe the bulk permeability properties of the rock cylinders.

The changes in permeability of the tuff cylinders with time are shown in Figure 2; in addition, the room temperature and final high-temperature permeabilities for each experiment are listed in Table 2. The starting, room temperature permeabilities of the Bullfrog Member samples varied between 0.5×10^{-18} and $8.5 \times 10^{-18} \text{ m}^2$ (Figure 2a), and the room temperature permeabilities of the Topopah Spring and Bullfrog Member cylinders ranged from 0.8×10^{-18} to $65 \times 10^{-18} \text{ m}^2$ (Figures 2b and 2c).

The tuff cylinders responded variably to heating. Samples B1, B2, T4, and T6 showed initial permeability increases followed by rapid decreases to values at or slightly below the room temperature values. The final measured permeabilities of these four experiments were 0–25% below the room temperature values. Decreasing the pore pressure from 3.5 to 1 MPa in T4 led to a slight overall permeability decrease (Figure 2c). Samples B3 and T1 showed slight increases in permeability with initial heating but no subsequent decreases. Instead, the permeability either remained at the higher value throughout

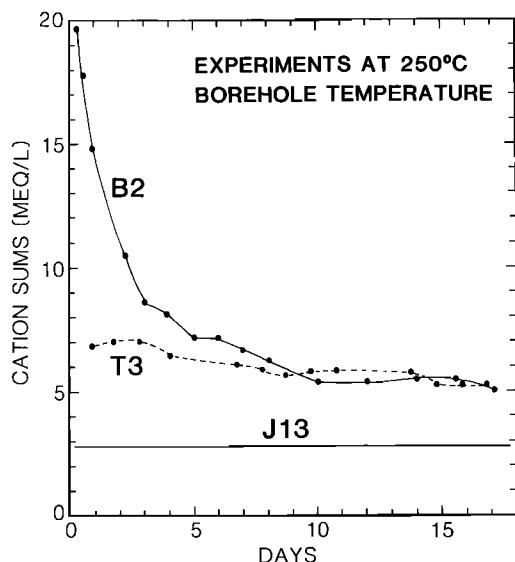


Fig. 3a

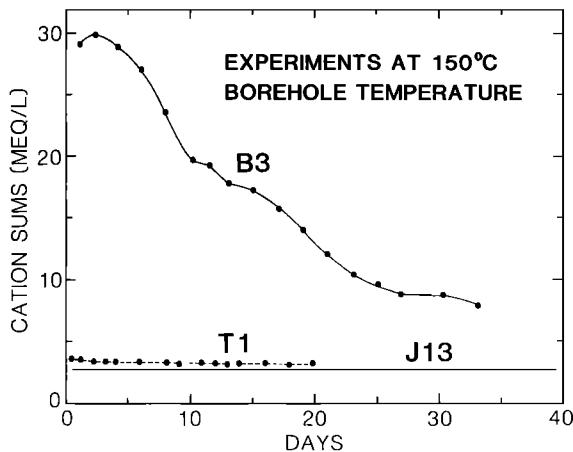


Fig. 3b

Fig. 3. Changes with time in the sum of cations (as an indication of total ionic concentrations) in the fluid samples collected during equivalent Topopah and Bullfrog experiments at (a) 250°C (B2 and T3) and (b) 150°C (B3 and T1) borehole temperature; data from Table 4.

the experiment, as in B3, or it increased at a slow rate for several days, as in T1. The tuff sample in experiment T5 showed an initial decrease rather than an increase with heating, followed by no further changes with time. The high-permeability sample T2 showed no overall changes as a result either of initial heating or of the various halts in fluid flow.

Fluid Chemistry

Selected results of the fluid chemical analyses for each experiment are presented in Table 4. Complete chemical data are available in *Byerlee et al. [1983]* and in *Moore et al. [1984a, b]*, and they are also used in Figures 3–5. The fluid compositions were analyzed with the SOLMNEQ computer program of *Kharaka and Barnes [1973]*, which computes the degree of saturation of a given solution with respect to many minerals as a function of temperature. The fluid compositions represent the state of the groundwater at its point of exit from

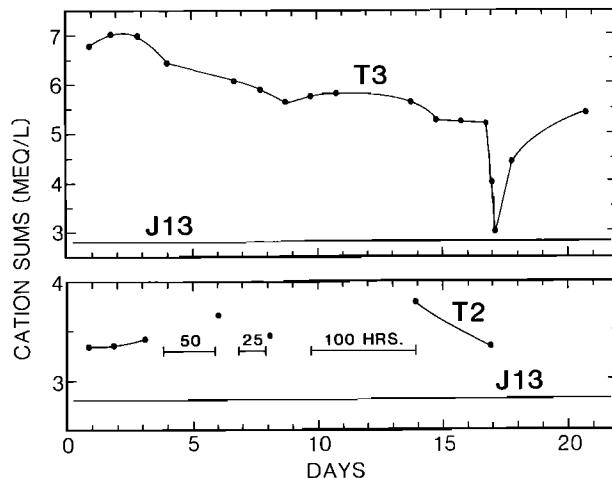


Fig. 4. Changes in cation sums (Table 4) with time of the fluid samples collected during Topopah experiments T2 and T3. (See Table 3 for changes in flow conditions during these experiments.)

the tuff. Therefore each fluid composition was analyzed with SOLMNEQ at the prevailing discharge temperature, which is the jacket temperature for all experiments except reverse-flow experiment T6. Values of ΔG , obtained from the SOLMNEQ calculations are presented in Table 5 for some of the possible low-temperature alteration minerals in tuff, such as silica phases, zeolites, clay minerals, and calcite. The specific mineral compositions used in the calculations are listed in *Kharaka and Barnes [1973]*. Positive values of ΔG , indicate that the solution is supersaturated with respect to the mineral considered; in Table 5, only the positive values of ΔG , are listed. The results give an indication of the minerals that potentially could precipitate from the fluids at the point of exit from the tuff samples. It should be noted that, because aluminum determinations were not made for the Bullfrog Member fluids, no ΔG , data are available for aluminosilicate minerals for those experiments. Therefore the lack of positive numbers for these minerals among the analyzed Bullfrog Member fluids in Table 5 does not necessarily indicate undersaturation.

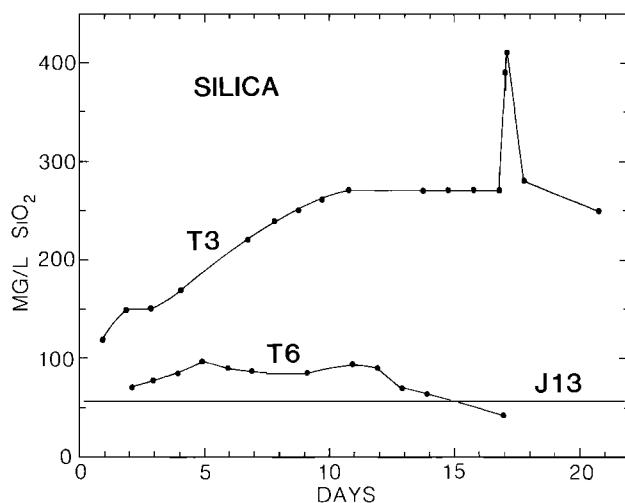


Fig. 5. Dissolved silica contents of the fluids collected during Topopah experiments T3 and T6. (See Table 3 for times that flow conditions were changed during experiment T3.)

TABLE 4. Selected Chemical Analyses of Fluids Collected During Experiments on the Bullfrog Member and Topopah Spring Member

| | <i>pH</i> | Days (25°C) | SiO ₂ * | Na | K | Mg | Ca | Al | HCO ₃ † | SO ₄ | NO ₂ | NO ₃ | HPO ₄ | F | Cl |
|----------------------|-----------|-------------|--------------------|-----|-----|-----|-----|------|--------------------|-----------------|-----------------|-----------------|------------------|-----|-----|
| <i>Experiment B1</i> | | | | | | | | | | | | | | | |
| Room temperature | 2.0 | 10.18 | NA | 860 | 16 | 0.8 | 7.6 | NA | 510 | 300 | | 530 | Tr | 3.4 | 390 |
| Room temperature | 3.0 | 10.33 | 160 | 460 | 9 | 0.2 | 1.6 | NA | 280 | 120 | | 200 | Tr | 2.0 | 140 |
| Heated | 0.2 | 10.12 | 380 | 690 | 19 | 0.2 | 1.5 | NA | 390 | 210 | | 310 | Tr | 5.3 | 240 |
| Heated | 1.2 | 10.34 | 700 | 590 | 14 | 0.2 | 0.5 | NA | 280 | 110 | | 180 | Tr | 6.0 | 110 |
| Heated | 8.2 | 9.72 | 370 | 230 | 7.1 | Tr | | NA | 280 | 15 | 5.9 | 15 | Tr | 1.4 | 20 |
| Heated | 13.9 | 9.70 | 300 | 150 | 4.4 | 0.1 | | NA | 190 | 3.6 | | 2.3 | Tr | 0.8 | 5.5 |
| <i>Experiment B2</i> | | | | | | | | | | | | | | | |
| Room temperature | 4.0 | 9.46 | 71 | 160 | 5.9 | 0.2 | 22 | NA | 270 | 97 | 2.7 | 5.7 | Tr | 3.3 | 13 |
| Heated | 0.3 | 8.87 | 160 | 400 | 22 | 0.2 | 34 | NA | 300 | 250 | | 160 | Tr | 8.8 | 110 |
| Heated | 2.3 | 9.14 | 230 | 220 | 14 | 0.1 | 11 | NA | 300 | 120 | 11 | 21 | Tr | 7.6 | 26 |
| Heated | 10.0 | 8.76 | 240 | 110 | 9.8 | 0.1 | 6 | NA | 210 | 35 | 4.2 | 1.0 | Tr | 4.0 | 9.6 |
| Heated | 21.2 | 8.53 | 230 | 90 | 9.7 | 0.1 | 9.4 | NA | 220 | 27 | 3.3 | | Tr | 3.3 | 8.7 |
| <i>Experiment B3</i> | | | | | | | | | | | | | | | |
| Room temperature | 1.0 | 9.85 | 150 | 390 | 4.4 | 0.1 | 1.2 | NA | 430 | 70 | 19 | 34 | 7.5 | 4.5 | 130 |
| Heated | 1.3 | 10.27 | 350 | 660 | 11 | 0.1 | 1.9 | NA | 570 | 89 | 32 | 40 | 16 | 7.5 | 180 |
| Heated | 6.0 | 10.58 | 730 | 620 | 5.6 | 0.1 | | NA | 370 | 54 | 13 | 29 | 6.9 | 7.0 | 88 |
| Heated | 21.0 | 10.24 | 410 | 270 | 3.6 | 0.1 | 2.5 | NA | 240 | 24 | 1.7 | 3.2 | 6.6 | 3.8 | 17 |
| Heated | 37.0 | 9.77 | 210 | 160 | 3.3 | | | NA | 220 | 18 | | 0.1 | 7.2 | 3.3 | 13 |
| <i>Experiment T1</i> | | | | | | | | | | | | | | | |
| Room temperature | | 7.55 | 42 | 42 | 27 | 1.8 | 27 | 0.23 | 180 | 25 | | | 4.7 | 2.1 | 13 |
| Heated | 0.1 | 7.52 | 86 | 46 | 31 | 1.1 | 17 | 0.16 | 170 | 22 | | 0.6 | 6.5 | 2.0 | 13 |
| Heated | 0.4 | 8.09 | 90 | 46 | 26 | 1.1 | 17 | 0.06 | 160 | 20 | | | 4.7 | 1.9 | 10 |
| Heated | 10.8 | 7.57 | 100 | 45 | 13 | 0.7 | 18 | 0.04 | 140 | 19 | 2.4 | 0.9 | 1.5 | 2.2 | 8.1 |
| Heated | 19.8 | 7.38 | 110 | 44 | 14 | 0.6 | 17 | 0.11 | 140 | 19 | 0.1 | | 2.6 | 2.2 | 8.9 |
| <i>Experiment T2</i> | | | | | | | | | | | | | | | |
| Room temperature | | 7.67 | 49 | 43 | 9.8 | 1.7 | 20 | 0.02 | 160 | 19 | | | 1.5 | 2.2 | 8.3 |
| Heated | 1.9 | 7.63 | 56 | 46 | 17 | 1.5 | 20 | 0.04 | 150 | 19 | | | 3.2 | 2.1 | 9.3 |
| Heated | 6.0 | 7.53 | 54 | NA | 16 | 1.9 | 25 | 0.03 | 170 | 21 | | | 0.7 | 2.2 | 9.9 |
| Heated | 8.0 | 7.65 | 55 | 43 | 14 | 1.6 | 22 | 0.10 | 160 | 20 | | | 1.7 | 2.1 | 9.7 |
| Heated | 14.0 | 7.32 | 54 | 45 | 15 | 1.8 | 26 | 0.07 | 180 | 21 | | | 0.4 | 2.0 | 9.7 |
| Heated | 16.9 | 7.71 | 57 | 45 | 9.6 | 1.5 | 20 | 0.06 | 160 | 19 | | | 0.7 | 2.2 | 8.3 |
| <i>Experiment T3</i> | | | | | | | | | | | | | | | |
| Room temperature | | 7.51 | 110 | 57 | 25 | 2.6 | 24 | 0.10 | 170 | 28 | | 6.4 | 2.9 | 3.0 | 22 |
| Heated | 0.9 | 7.19 | 120 | 68 | 54 | 3.2 | 44 | 0.03 | 240 | 35 | | 9.3 | 6.0 | 2.2 | 40 |
| Heated | 1.8 | 7.31 | 150 | 66 | 56 | 2.8 | 50 | 0.02 | 290 | 27 | | | 5.6 | 1.5 | 26 |
| Heated | 10.8 | 7.19 | 270 | 50 | 36 | 1.9 | 51 | 0.07 | 260 | 20 | | | 1.4 | 1.5 | 10 |
| Heated | 17.0 | 7.46 | 390 | 43 | 17 | 0.9 | 32 | 0.05 | 180 | 19 | | | 1.1 | 2.1 | 8.1 |
| Heated | 17.1 | 6.92 | 410 | 43 | 9.2 | 0.3 | 17 | 0.25 | 110 | 19 | | 1.3 | 0.7 | 2.3 | 7.6 |
| Heated | 17.7 | 7.27 | 280 | 47 | 29 | 1.1 | 31 | 0.08 | 190 | 20 | | 0.18 | 1.0 | 2.0 | 8.2 |
| Heated | 20.7 | 6.97 | 250 | 55 | 33 | 1.8 | 40 | 1.05 | 270 | 21 | | 0.6 | 1.3 | 1.4 | 8.9 |
| <i>Experiment T4</i> | | | | | | | | | | | | | | | |
| Room temperature | | 7.42 | 38 | 93 | 59 | 2.5 | 26 | 0.15 | 140 | 54 | 1.0 | 6.7 | 2.7 | 9.5 | 44 |
| Heated | 0.8 | 7.92 | 70 | 81 | 73 | 2.0 | 31 | 0.06 | 240 | 58 | 2.7 | 0.6 | 4.6 | 2.1 | 32 |
| Heated | 2.8 | 7.80 | 88 | 60 | 55 | 1.2 | 26 | 0.12 | 200 | 46 | | | 4.4 | 1.8 | 18 |
| Heated | 8.8 | 7.59 | 103 | 48 | 32 | 0.6 | 18 | 1.45 | 160 | 29 | | | 2.7 | 1.8 | 8.3 |
| <i>Experiment T5</i> | | | | | | | | | | | | | | | |
| Room temperature | | 7.38 | 32 | 70 | 45 | 0.8 | 10 | 0.07 | 170 | 20 | | 31 | 2.0 | 2.7 | 22 |
| Heated | 2.0 | 7.63 | 85 | 50 | 40 | 0.5 | 12 | 0.16 | 170 | 21 | | 0.7 | 2.5 | 2.6 | 13 |
| Heated | 5.0 | 7.59 | 85 | 50 | 30 | 0.4 | 15 | 0.17 | 140 | 21 | 2.2 | 1.1 | 3.0 | 2.8 | 11 |
| Heated | 7.0 | 7.52 | 86 | 49 | 33 | 0.4 | 16 | 0.10 | 160 | 20 | 0.2 | 0.3 | 2.9 | 2.2 | 11 |
| Heated | 14.0 | 7.30 | 93 | 46 | 17 | 0.4 | 15 | 0.11 | 150 | 19 | | 0.5 | 1.7 | 2.2 | 8.4 |
| <i>Experiment T6</i> | | | | | | | | | | | | | | | |
| Room temperature | | 7.49 | 51 | 48 | 7.9 | 2.1 | 13 | 0.04 | 140 | 19 | 0.1 | 6.0 | 2.2 | 2.7 | 10 |
| Heated | 2.1 | 7.73 | 70 | 62 | 90 | 0.4 | 13 | 0.03 | 190 | 31 | 13 | 2.7 | 3.3 | 12 | 26 |
| Heated | 3.9 | 7.67 | 84 | 65 | 120 | 0.3 | 14 | 0.08 | 280 | 40 | | 0.3 | 2.1 | 16 | 39 |
| Heated | 10.9 | 6.90 | 94 | 57 | 110 | 0.3 | 13 | 0.07 | 240 | 34 | | | 6.2 | 38 | |
| Heated | 16.9 | 6.84 | 42 | 49 | 82 | 0.1 | 5.0 | 0.03 | 190 | 29 | | | 0.9 | 21 | |

Values are in milligrams per liter. NA, not analyzed; Tr, trace.

*Total Si as SiO₂.

†Total inorganic C as HCO₃.

TABLE 5. Reaction States (ΔG_r , in kJ) of Selected Fluid Samples at the Discharge Temperature

| Experiment | Discharge Temperature | Time, Days | Adularia | Albite | Analcime | Calcite | Chlorite-Mg* | Gibbsite (c) | Illite | Montmorillonite-K | Quartz | α -Cristobalite |
|------------|-----------------------|------------|----------|--------|----------|---------|--------------|--------------|--------|-------------------|--------|------------------------|
| B1 | 68°C | 0.2 | n.d. | n.d. | n.d. | 3.5 | | n.d. | n.d. | n.d. | 4.0 | 0.8 |
| | | 8.2 | n.d. | n.d. | n.d. | | | n.d. | n.d. | n.d. | 5.6 | 2.4 |
| B2 | 73°C | 0.3 | n.d. | n.d. | n.d. | 7.5 | | n.d. | n.d. | n.d. | 4.8 | 1.7 |
| | | 21.2 | n.d. | n.d. | n.d. | 2.1 | | n.d. | n.d. | n.d. | 6.1 | 2.9 |
| B3 | 48°C | 1.3 | n.d. | n.d. | n.d. | 3.4 | | n.d. | n.d. | n.d. | 4.1 | 0.7 |
| | | 21.0 | n.d. | n.d. | n.d. | 3.9 | | n.d. | n.d. | n.d. | 4.7 | 1.4 |
| T1 | 50°C | 0.4 | 17.3 | 5.3 | | 2.1 | | | 26.2 | 24.1 | 4.9 | 1.5 |
| | | 19.8 | 19.2 | 8.8 | | | | 1.2 | 36.0 | 38.5 | 5.6 | 2.2 |
| T2 | 36°C | 1.9 | 16.6 | 5.5 | | | | 0.4 | 31.5 | 32.8 | 4.6 | 1.2 |
| | | 14.0 | 17.2 | 6.4 | | | | 3.3 | 36.0 | 38.7 | 4.6 | 1.1 |
| T3 | 83°C | 1.8 | 11.3 | | | 4.5 | | | 11.2 | 9.3 | 4.4 | 1.3 |
| | | 20.7 | 26.1 | 13.2 | | 1.2 | | 2.5 | 45.4 | 46.8 | 5.9 | 2.8 |
| T4 | 43°C | 0.8 | 20.4 | 7.2 | | 2.6 | | | 31.5 | 29.8 | 4.7 | 1.3 |
| | | 8.8 | 29.9 | 17.4 | 3.3 | | | | 10.1 | 57.1 | 60.1 | 5.8 |
| T5 | 44°C | 2.0 | 22.8 | 10.0 | | | | 2.1 | 39.2 | 40.2 | 5.2 | 1.8 |
| | | 14.0 | 20.3 | 9.4 | | | | 3.0 | 38.5 | 41.8 | 5.5 | 2.1 |
| T6 | 150°C | 2.1 | | | | 4.4 | 22.8 | | | | | |
| | | 3.9 | | | | 6.4 | 28.6 | | | | | |

Only positive values of ΔG_r , indicating supersaturation, are included in the table; n.d., no data, aluminum was not analyzed.

*Aluminum-free end-member.

DISCUSSION

Permeability

The results of the permeability experiments on the Bullfrog Member and Topopah Spring Member show that the room temperature permeabilities of these two tuff layers are quite variable. The Topopah Spring Member results indicate that the values are essentially independent of confining and pore pressure and of sample orientation. Instead, the range of starting permeabilities probably reflects sample-to-sample differences in the density, distribution, and configuration of cracks and pores. The initial effect of heating also 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. The proportional permeability change with heating is small compared with the range of room temperature permeabilities. Therefore heating did not affect the overall permeability of either tuff in these experiments.

The combination of heat and fluids also has little effect on the permeability of the tufts. In the time span of the experiments, almost no permeability changes were measured as heated groundwater flowed through the Bullfrog Member and Topopah Spring Member cylinders. The results for the Topopah Spring Member samples were independent of sample orientation, temperature, and the direction of fluid flow relative to temperature. The slight decrease in permeability accompanying the decrease in pore pressure in experiment T4 is consistent with a slightly greater degree of crack closure caused by the increase in effective pressure.

Fluid Chemistry

The first heated fluids collected during the Bullfrog Member experiments are characterized by considerably larger amounts of dissolved material and a much higher pH than the corresponding Topopah Spring Member fluids. However, these differences do not reflect mineralogical variations between the tufts but rather are due to the presence of readily leached evaporation deposits in the porous Bullfrog Member rocks [see also *Oversby and Knauss, 1983*]. The Topopah Spring Member samples contained only small amounts of these salts (e.g., room temperature T4 sample, Table 4). As seen in Table

4, this material was readily dissolved from the Bullfrog Member samples at room temperature, which supports the idea that its source was something much more soluble than the silicate materials in the tuff. In addition, the principal species in the room temperature and first-heated Bullfrog Member fluids—sodium, bicarbonate, silica, sulfate, chloride, and nitrate—are the same ones that predominate in the J13 groundwater. The nitrate in the salts must have been derived from evaporated groundwater, because it probably had an organic rather than a mineral source [*West and Skujins, 1978*]. By the end of the experiments, the soluble salts had been almost completely removed from the Bullfrog Member samples, as indicated by decreases in the concentrations of species such as chloride and sulfate to the levels of the starting water composition. In addition, both the total ionic concentrations (Figure 3) and the pH (Table 4) of the Bullfrog Member solutions decreased with time to values much closer to those of the corresponding Topopah Spring Member experiments.

The final Bullfrog Member fluids and all the Topopah Spring Member fluids collected during the experiments were somewhat enriched in total dissolved solids compared with the starting compositions; nevertheless, they were still very dilute solutions. The pore waters discharged from the Bullfrog Member cylinders principally contained sodium, bicarbonate, and silica, whereas the Topopah Spring Member fluids were enriched in potassium, calcium, bicarbonate, and silica. Changing the fluid pressure during experiment T4 had no effect on the composition of fluids discharged from the Topopah Spring Member cylinder. No obvious relationship was observed between solution concentrations and temperature for the Bullfrog Member experiments; however, the pore waters from the 250°C Topopah Spring Member experiment (T3) had higher overall concentrations than the waters from the 150°C and 90°C experiments (Table 4 and Figure 4).

The amount of material going into solution also depended upon the amount of time that the fluids were in contact with the tuff. During experiment T2, which was run at 90°C bore-hole temperature, the ionic concentrations in solution increased following each halt in fluid flow (Figure 4). The proportional increase was not high, probably due in part to the

low temperatures of the experiment; however, a direct relationship exists between the solution concentrations and the length of time that flow was halted. During experiment T3, an increase in the rate of fluid flow caused a significant decrease in the total ionic concentrations in solution (Figure 4). The flow rates were then reduced, and the concentrations increased to their original levels. The relatively high solution concentrations of reverse-flow experiment T6 (Table 4) may also be a function of reaction time, because the rate of fluid flow through this sample was 3–25 times lower than the rate for the other samples (Table 2).

The relationships between temperature and fluid composition and between reaction time and fluid composition illustrate some of the controls on the amount of material that comes into solution through fluid-tuff reactions. Some evidence also exists that material was being removed from solution through reaction with the tuff. For example, the magnesium concentrations of the fluids discharged from the heated Topopah Spring Member and Bullfrog Member samples were well below the starting J13 levels. Magnesium is readily incorporated from solution into alteration minerals such as chlorite and montmorillonite during rock-seawater interaction experiments at elevated temperatures [e.g., Hajash, 1975; Mottl and Holland, 1978; Seyfried and Bischoff, 1981]. Table 5 shows that several of the fluid samples had the potential to precipitate montmorillonite or chlorite at the point of discharge from the tuff, and Knauss *et al.* [1984] have observed abundant "illite/montmorillonite" clays forming on samples of Topopah Spring Member tuff that were reacted with J13 water at 150°C. Calcium also was removed from the J13 water that had passed through the Bullfrog Member cylinders. One explanation for the removal of calcium is the deposition of calcite (Table 5), which may also account for the loss of magnesium from solution [Knauss *et al.*, 1984]. Another possibility for calcium removal is its adsorption onto the surface of plagioclase phenocrysts; this reaction has been observed in a 150°C experiment reacting J13 water with a Bullfrog Member core sample [Knauss, 1984].

The concentrations of some species in the discharged fluids may be the net product of combined mineral dissolution and crystallization reactions. The dissolved silica concentrations measured during experiments T3 and T6 provide an example of such competing reactions (Figure 5). Increasing the rate of fluid flow during experiment T3 caused the concentration of silica in the discharged fluids to increase, which is the opposite trend to that followed by most of the ionic species in solution (Figure 4 and Table 4). The trend in ionic concentrations is consistent with the fact that less time was available for minerals to dissolve. The behavior for silica during experiment T3 (Figure 5) can be explained by the combined occurrence of a relatively rapid dissolution reaction (or reactions) and a relatively slow precipitation reaction(s). The silica dissolution reaction could better keep pace with the faster flow rates; as a result, large amounts of silica were still coming into solution at high flow rates but less silica was being removed, leading to a net increase in the silica contents. The rate of fluid flow during experiment T6 was the lowest of all nine experiments (Table 2), and by the end of this experiment, the silica concentrations in the discharged fluids were below the starting J13 levels. For this experiment, the increase in reaction time accompanying the slow flow rate allowed the silica precipitation reaction to proceed to a greater extent.

Comparison With Other Permeability Studies

The results of this study differ from those of similar experiments on granitic rocks, for which significant permeability

reductions were measured within a few days of heating to a borehole temperature of 250°C or 300°C [Morrow *et al.*, 1981; Moore *et al.*, 1983]. The permeability decreases in the granites were attributed to the formation of crack-filling mineral deposits, particularly silicate phases [Morrow *et al.*, 1981, Figures 5–6, p. 3006]. 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. Kranz and Blacic [1984] also measured permeability reductions and observed crack-filling, silica-rich precipitates in experiments conducted on sandstone and granite. Their samples were heated to a uniform temperature of 100°C, and the observed mineral deposition was attributed to local variations in pore pressure and strain energy.

The difference in permeability behavior between the tuff and granite samples may be caused by differences in the geometry of cracks and pores between the two rock types. The Bullfrog Member samples have a high porosity (approximately 26%; Blacic *et al.* [1982]) and large pore sizes (mostly equant-shaped voids). The Topopah Spring Member is somewhat less porous (approximately 9–12%; Blacic *et al.* [1982]) than the Bullfrog Member, but the Topopah Spring Member samples do contain some fractures. Material deposited in these large-aperture voids and fractures would have a minimal influence on permeability because the size of the flow path would not be significantly reduced. In contrast, the porosity of the granites (0.6–0.9%; Brace and Riley [1972, Table 1]) is more than an order of magnitude lower than that of the tuffs, and fluid flow in the granites is largely along narrow grain boundary and intragranular cracks that would be easily clogged by mineral deposits.

Another possible contribution to the lack of permeability change in the tuffs is that some of the reactions taking place during the tuff experiments involved changes in the composition of existing minerals rather than new mineral growth in cracks. An example would be the adsorption of calcium onto plagioclase crystals that was observed by Knauss [1984] during hydrothermal experiments on Bullfrog Member samples. In addition, minerals such as chlorite and montmorillonite show wide ranges of composition that are in part dependent on temperature. If the temperatures of the experiments differed from the temperature of initial crystallization of such minerals, some compositional modifications might occur.

SIGNIFICANCE TO NUCLEAR WASTE DISPOSAL

The potential nuclear waste disposal site in the Topopah Spring Member is in rock situated above the water table, and one of the desired characteristics of such a site is that any groundwater that does migrate downward to the disposal horizon should not be ponded around the canisters of nuclear waste. In experiments of up to 5 weeks' duration, samples of Bullfrog and Topopah Spring Member tuffs collected from the potential disposal area showed a general lack of permeability change. These results are not unfavorable to the hypothesis that the disposal of nuclear waste in such rocks will not significantly affect their permeability. However, it is difficult to extrapolate the short-term experimental results to the much longer times required for a safe nuclear waste disposal scheme. On the one hand, given a much longer time for fluid flow in a temperature gradient, even relatively large pores and cracks in the tuffs could eventually become filled with mineral deposits, thereby reducing permeability. On the other hand, the permeability experiments have modeled the worst case with respect to fluid flow in the tuffs. Because of the location of the potential disposal horizon in the unsaturated zone in an arid

climate, little groundwater will be available for reaction with the tuffs. Barring a major climatic change, crack-filling processes at the disposal site should proceed at a very low rate.

The fluid chemistry indicates that any groundwaters that do reach the canisters should not contain any materials that would be excessively corrosive to stainless steel canisters. All of the Topopah Spring Member fluid samples were dilute and nearly neutral in pH, including those from reverse-flow experiment T6 that were discharged from the high-temperature borehole. Because of the presence of some salt evaporation deposits, the initial Bullfrog Member fluid samples had a higher pH and larger amounts of dissolved material than the Topopah Spring Member pore waters. However, such surface evaporation deposits are not expected to occur at depth in the repository area [Knauss et al., 1984]. The Bullfrog Member and Topopah Spring Member fluids collected after removal of the surface salt deposits indicate that tuff layers surrounding the disposal horizon at depth also should have little effect on groundwater chemistry.

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