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EXPERIMENTAL INVESTIGATION OF SODIUM  
BENTONITE STABILITY IN HANFORD BASALT

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Basalt Waste Isolation Project

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## EXPERIMENTAL INVESTIGATION OF SODIUM BENTONITE STABILITY IN HANFORD BASALT

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## ABSTRACT

Sodium bentonite is a candidate material for the waste package backfill component in a repository in basalt at the Hanford Site. Preliminary hydrothermal experiments have been conducted under near-field geochemical conditions expected to occur in the reference repository location in the Grande Ronde Basalt. Experiments have been conducted in the basalt/groundwater, bentonite/groundwater, and basalt/bentonite/groundwater systems. The experiments have been conducted at 300°C using a simulated Grande Ronde groundwater, reference Umtanum basalt, and sodium bentonite. Key data generated by the experiments include experimental solution analyses as a function of time and preliminary solids analysis by scanning transmission electron microscopy and X-ray diffraction. Solution trends of the major aqueous species were similar in the three systems and are characterized by: (1) the gradual reduction of the pH value from ~9.75 to a steady-state value of ~6, (2) an initial rapid increase followed by a gradual decrease in silica concentration, and (3) a slight or negligible increase in sodium, sulfate, and chloride concentrations. In the bentonite/groundwater experiment, small amounts (<1%) of an albite reaction product were observed. Conversely, the formation of illite, a common bentonite alteration product, was not observed. These results indicate that sodium bentonite will remain sufficiently stable at 300°C under hydrothermal conditions in basalt to permit its use as a backfill material.

## INTRODUCTION

The Basalt Waste Isolation Project is developing a multiple barrier waste package to contain high-level nuclear waste as part of an overall system (i.e., waste package, repository sealing system, and host rock) designed to isolate the waste in a repository located in basalt beneath the Hanford Site. The three basic components of the waste package are the waste form, the canister, and the backfill. An extensive testing program is under way to determine the chemical, physical, and mechanical properties of potential canister and backfill materials; the ultimate goal of which is to recommend specific materials for use in the waste package.

As part of this overall program, the suitability of bentonite as a waste package backfill material is being investigated. Sodium bentonite is a favorable material because it is well known for its low permeability when compacted [1] and capacity for swelling (i.e., self-healing) within a confined volume [2]. These properties are especially important because the primary function of the waste package backfill component in basalt is to minimize mass transport between the waste package and the host rock. Minimization of groundwater transport has the effect of reducing canister corrosion and waste form leaching. Consequently, a low-permeability medium such as dense bentonite is required. However,

unless sodium bentonite can be shown to be chemically stable in the reference repository environment under expected hydrothermal conditions, it cannot be considered a viable waste package backfill material. Therefore, preliminary hydrothermal experiments have been completed under near-field geochemical conditions expected to occur in a repository constructed in basalt. Analyses of solution and solid samples are reported below and based on the data, conclusions are drawn concerning the stability of sodium bentonite in a basalt environment.

#### STARTING MATERIALS AND MATERIALS PREPARATION

Realistic experiments required the use of basalt materials and synthetic groundwaters that closely approximate near-field repository host rock and groundwater. Therefore, a basalt reference material (RUE-1), collected from a surface outcropping of the Umtanum flow (a candidate repository horizon) was chosen. Prior to the experiments, monolithic fragments were crushed to a small size (-115 to +250 mesh) to facilitate hydrothermal reaction; fracture mineralization was removed from RUE-1 because secondary mineralization at the surface and at depth will differ somewhat in phase composition and volume percentage.

As a result of the crushing procedure, very fine particles coated the surfaces of the mineral grains. These particles can strongly influence the chemical reactions that occur; therefore, a procedure for removing the fines was developed. The crushed basalt grains were washed three times in an ultrasonic bath with ultrapure water. The final washwater was analyzed by the inductively coupled plasma spectrometer technique to assure that all fines have been removed. Observation of the cleaned grains by scanning electron microscopy indicated that ~99% of the fines had been removed. A bulk chemical analysis of the RUE-1 and the deep core basalt is given in Table I.

TABLE I

Comparison of repository level Umtanum basalt compositions for a repository elevation and a surface outcrop reference sample (RUE-1)

<u>Oxides</u>	<u>Repository elevation basalt</u>	<u>Surface outcrop basalt</u>
SiO <sub>2</sub>	54.9	55.29
TiO <sub>2</sub>	2.17	2.12
Al <sub>2</sub> O <sub>3</sub>	14.3	13.47
FeO <sup>b</sup>	13.1	13.09
MnO	0.22	0.22
MgO	3.48	3.78
CaO	7.30	7.12
Na <sub>2</sub> O	2.66	2.99
K <sub>2</sub> O	1.48	1.60
P <sub>2</sub> O <sub>5</sub>	0.35	0.35
Total	99.96	100.32

<sup>a</sup>X-ray fluorescence analysis by Temple University

<sup>b</sup>Total Fe as FeO

Baroid National West Bentonite (-400 mesh) was used in all experiments. It is a typical Wyoming bentonite, consisting of about 85% sodium montmorillonite. The bentonite was not pretreated prior to the experiments and was used as received. In addition to the montmorillonite, small amounts of quartz, feldspar, cristobalite, illite, and calcite or gypsum were present in the starting material.

A simulated groundwater composition has been determined from field analyses and a procedure for synthesizing it has been developed. The initial groundwater composition is listed in Table II under the zero time column. It is characterized by a high percentage of sodium, silica, chloride, and fluoride. The solution is poor in carbonate species and has a high pH (~9.75).

TABLE II

Change of solution composition with time for bentonite and synthetic groundwater at 300°C, 300 bars; initial water:rock = 10:1, one month

Concentration (mg/L)	Time (hr)						
	0	1	4	23	162	329	616
Si	33.9	624.9	610.0	598.5	550.6	536.2	524.0
Na	357.2	296.2	289.4	291.5	278.4	265.1	263.9
Al	0.09	8.79	7.68	7.75	4.61	3.34	2.63
K	4.09	7.25	6.90	7.14	7.04	7.45	8.33
Ca	2.96	2.58	4.36	3.46	2.13	2.18	1.97
Mg	0.32	0.13	0.14	0.13	0.10	0.10	0.10
Fe	0.009	0.14	0.10	0.09	0.14	0.13	0.09
B	0.33	4.38	4.33	4.47	4.42	4.42	4.39
SO <sub>4</sub> <sup>2-</sup>	163.		87.0	90	100	110	115
F <sup>-</sup>	32.0		14.0	9.0	5.5	3.8	3.4
Cl <sup>-</sup>	290		403.0	350	355	360	375
S <sup>2-</sup>							5.3
pH	9.76	5.69	5.75	5.69	5.54	5.35	5.34

Zero hour solution sample = starting synthetic groundwater

#### EXPERIMENTAL PROCEDURE AND MATERIALS ANALYSIS

Experiments were run in a Dickson-type, rocking autoclave in which basalt powder and/or bentonite (15 g) and synthetic groundwater (150 mL) were placed in a 250-mL gold bag that was then placed in an internally heated pressure vessel. The autoclave was then brought to temperature and pressure over a period of ~5 hr. Small amounts of solution (5-mL increments) were drawn from the gold bag solution composition as a function of time. Cation analyses were obtained by inductively coupled plasma spectrometry (ARL Model 34000). Anions were primarily characterized by ion chromatography (Dionex System 14). Certain anions, such as sulfide, were determined with ion-selective electrodes. After solutions were removed from the autoclave and allowed to cool to room temperature, pH measurements of solution samples were taken with an Orion Model 901 ion analyzer and a Corning semi-micro combination electrode. Solids characterization included scanning electron microscopy, scanning transmission electron microscopy, and X-ray diffraction.

At the completion of experimental run, the gold bag assemblage and surrounding pressure vessel were removed from the internally heated furnace and cooled by a running stream of water ( $\sim 10$  min) over the exterior of the bag.

### EXPERIMENTAL RESULTS

The bentonite/groundwater experiment was completed at  $300^{\circ}\text{C}$  and 300 bars pressure with an initial water to rock ratio of 10:1. The run duration was 616 hr. The solution data are listed in Table II, some of which are presented in Figures 1 through 3. The concentration of silica increased from 33.9 to 625 mg/L in the first hour and then slowly decreased to 524 mg/L. Sodium concentration decreased about 12% from 1. to 616 hr, varying 296 to 264 mg/L. The aluminum content increased from 0.09 to 8.79 mg/L in the first hour and then steadily decreased to a final concentration of 2.63 mg/L. Potassium content gradually increased in content from 4.09 mg/L initially to a final concentration of 8.33 mg/L. Fluoride showed a steady decrease in concentration from 32 to 3.4 mg/L, and chloride content showed a slight increase in content from 290 to 375 mg/L. The sulfate content decreased from 163 to 87.0 mg/L after the first 4 hr and then slowly increased to a final value of 115 mg/L. A sulfide odor was detected in all the solution samples. The pH dropped rapidly from an initial value of 9.76 to 5.69 in the first hour and remained relatively stable thereafter.

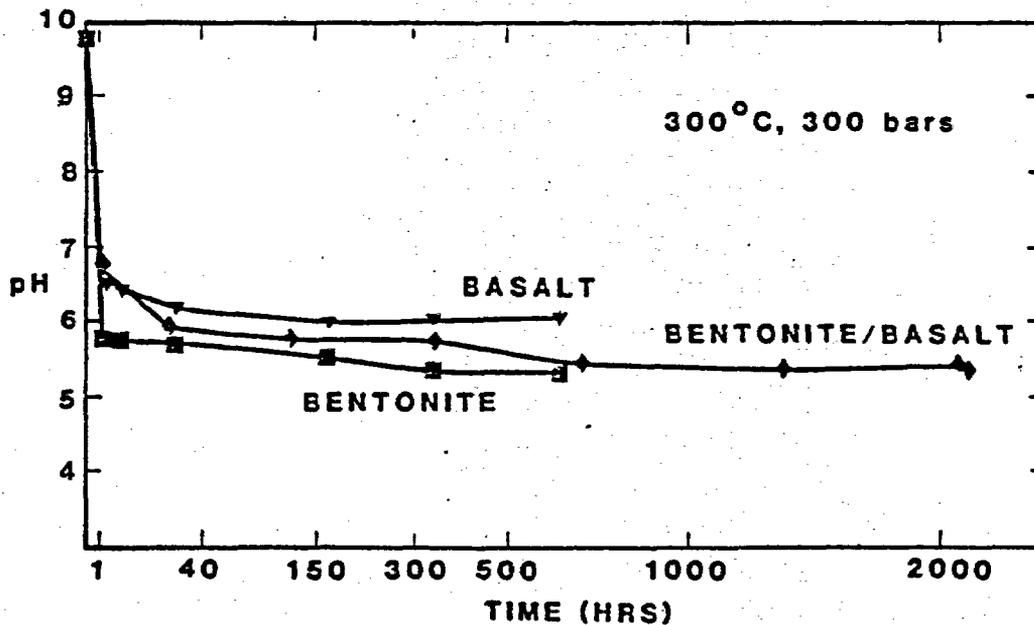


Figure 1. Change in pH in backfill/groundwater experiments.

Solid run products were analyzed by scanning transmission electron microscopy and scanning electron microscopy analysis. Electron diffraction patterns of clay from the unreacted starting bentonite showed that the d-spacings corresponded to typical montmorillonite. The energy dispersive system spectra indicated mostly aluminum and silica with minor amounts of sodium, calcium, and iron. Although the reacted bentonite underwent a reduction in mean grain size from  $\sim 10$  to  $< 5$   $\mu\text{m}$ , the energy dispersive system spectra indicated that the montmorillonite had essentially the same composition as the reacted material. Grain size reduction probably represents mechanical breakup of the grains as a

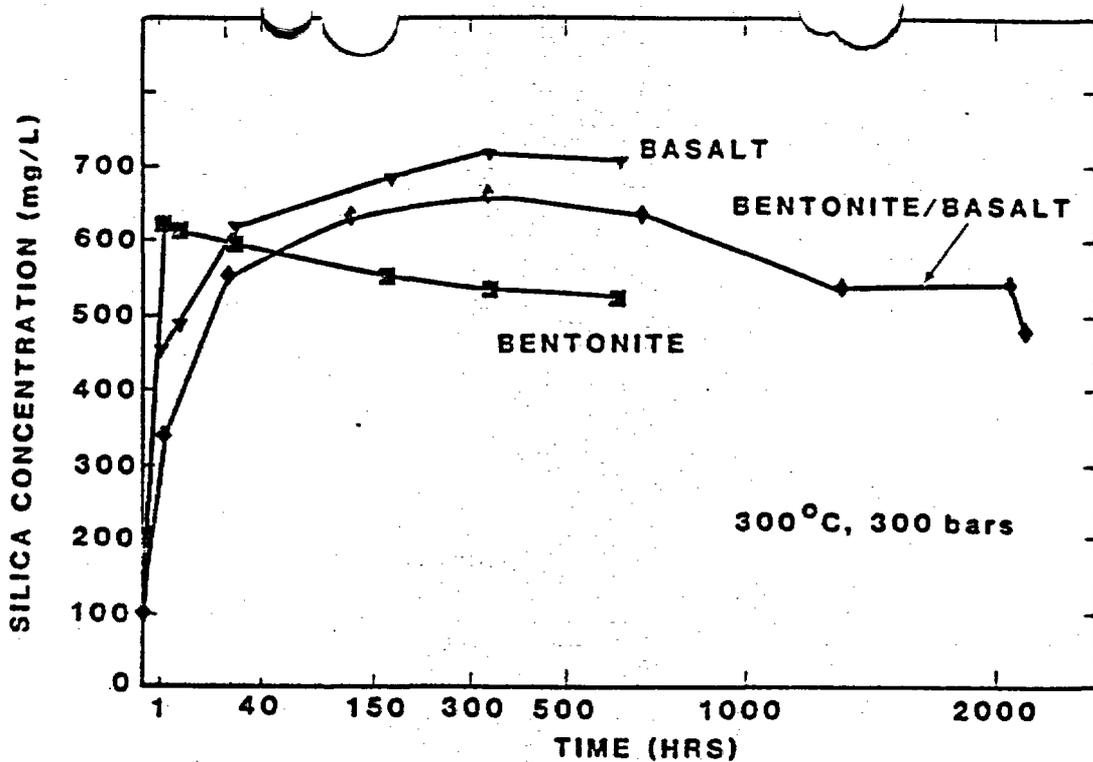


Figure 2. Change in silica concentration in backfill/groundwater experiments

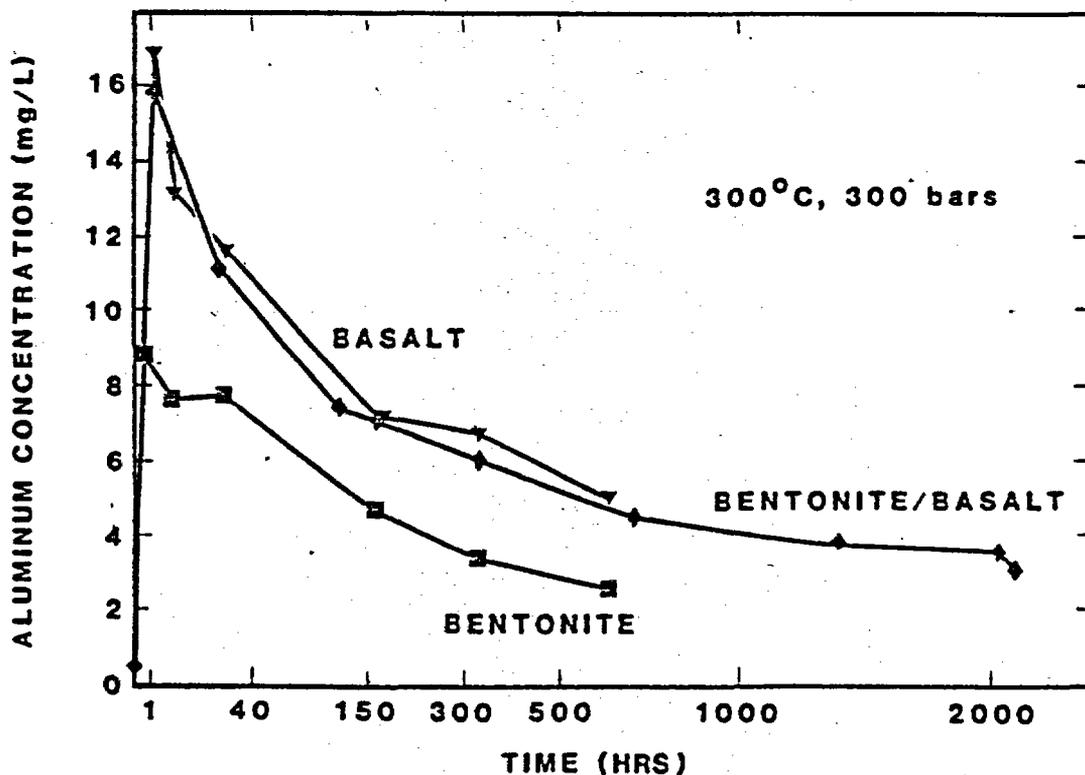


Figure 3. Change in aluminum concentration in backfill/groundwater experiments.

result of sample agitation during the experiment.

In addition to the bentonite, other phases were also identified, including nontronite, quartz, amorphous silica, paragonite, and albite. Albite appears to

be a reaction product because it was not observed in the starting materials. Albite occurs as tiny crystals that vary in size from 10 nm wide by 100 nm long up to 200 nm wide by 2,000 nm long. These crystals were only visible at high magnifications in the scanning transmission electron microscope. The composite chemical analysis from several crystals corresponds to the formula of  $\text{Na}_{0.80}\text{Al}_{1.06}\text{Si}_3\text{Ca}_{0.06}\text{O}_8.05$ . The silica phase is present as extremely tiny spheres (~100 Å in diameter) and chains of spheres. Despite the prevalence of these spheres, it was not possible to observe a diffraction pattern, which indicates that they are amorphous. The nature of their shape and size indicates that they are forming after the run is brought down from pressure and temperature. In addition to the silica, one crystal of paragonite was discovered, which was either formed during hydrothermal reaction or was present in the original material. A larger fraction of material will have to be examined in the scanning transmission electron microscope if the question of origin is to be resolved.

Realizing that the presence of basalt will influence the solution composition and chemical reactions occurring in the system, experiments have been run in the basalt/groundwater and basalt/bentonite/groundwater systems to determine more accurately the effect of the basalt environment on bentonite stability. Of particular interest was the additional contribution of potassium to the solution from basalt/groundwater interaction, which may enhance the alteration of sodium bentonite to illite.

Solution analyses from basalt/groundwater and basalt/bentonite/groundwater experiments completed at 300°C, 300 bars are listed in Tables III and IV, some of which are shown in Figures 1 through 3.

TABLE III

Solution data for Umtanum basalt (RUE-2) + synthetic groundwater, 300°C, 300 bars. Initial water:rock = 10:1. Mesh size = -115+250, 1 month

Concentration (mg/L)	Time (hr)						
	0	1	4	20	41	139	356
Si	34.4	370.4	440.7	553.3	613.4	678.8	704.2
Na	363.3	269.9	267.1	267.1	269.8	276.7	289.1
Al	<0.075	23.61	18.32	13.37	10.65	8.34	7.4
K	4.05	104.6	114.4	110.4	105.9	92.8	76.1
Ca	2.94	1.25	9.69	0.89	0.64	0.39	1.48
Mg	0.32	<0.10	0.19	<0.10	<0.10	<0.10	<0.10
Fe	0.006	0.06	0.06	0.05	0.04	0.04	0.23
$\text{SO}_4^{2-}$	172	165	170	160	170	170	175
$\text{F}^-$	33	29.5	31.5	34	39	40	41.5
$\text{Cl}^-$	278	305	315	295	320	320	325
pH	9.86	6.71	6.44	6.24	6.13	5.96	6.01

Zero hour solution sample = starting synthetic groundwater

The following solution compositional trends were observed in both the bentonite/groundwater and the basalt-bearing experimental systems: (1) a large initial increase in silica and aluminum concentration followed by a gradual decline with time, (2) a rapid decrease in the pH from an initial value of ~9.76 to a steady-state value of ~5.5 to 6.5, and (3) the detection of sulfide gas in the experimental solution samples. Solution behavior from the experimental systems containing basalt differed slightly from that of the bentonite/groundwater system with the other major species. In the basalt-containing systems, sodium, chloride, and sulfate showed no significant changes in concentration; whereas in the bentonite/groundwater system, real decreases in sodium, sulfate, and

Fluoride content and an increase in chloride content were observed with time. Also, potassium showed an increase followed by a decrease in concentration in the basalt-containing systems but no change in concentration in the bentonite/groundwater system.

TABLE IV

Umtanum basalt (RUE-2) + bentonite + synthetic Grande Ronde groundwater, 300°C 300 bars; initial water:solids = 10:1; basalt:bentonite = 1:1; basalt mesh size = -115+250, 3 months

Concentration (mg/L)	Time (hr)							
	0	1	20	118	334	672	1337	2130
Si	34	333	551	632	661	632	537	479
Na	375	361	314	295	290	302	238	213
Al	<0.08	15.9	11.1	7.4	6.0	4.5	3.6	3.0
K	4.00	27.2	37.4	36.9	29.0	24.9	18.1	14.8
Ca	3.01	2.60	1.59	1.68	1.92	2.35	1.12	0.78
Mg	0.31	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.1
Fe	<0.006	0.13	0.05	0.04	0.04	0.08	0.03	0.05
B	0.27	1.35	2.49	2.45	2.54	2.89	2.60	2.48
SO <sub>4</sub> <sup>2-</sup>	168		150	170	170	180	90	50
F <sup>-4</sup>	30		21.5	16	10	7	6.5	5.5
Cl <sup>-</sup>	276		320	320	320	350	345	285
pH (25°C)	9.78	6.67	5.94	5.79	5.78	5.42	5.38	5.35

Zero hour solution sample = starting synthetic groundwater

#### DISCUSSION

The large concentrations of silica found in reacted solutions from the bentonite/groundwater experiment have several possible sources. According to the Baroid analysis, several weight percent of quartz and cristobalite are present in the bentonite. Another possible source of aqueous silica is dissolution of the tetrahedral layers in montmorillonite. Using experimentally derived equilibrium expressions [3], the estimated solubilities of  $\beta$ -cristobalite and  $\alpha$ -cristobalite are 642 and 492 mg/L is consistent, with cristobalite being the silica solubility-controlling phase in the system. It is possible, however, that longer experimental runs may show further reduction of silica in solution.

The apparent alteration of montmorillonite to albite may explain, at least partially, the decrease in sodium and aluminum solution. However, the extent of the decrease in sodium and aluminum concentration due to the precipitation cannot be determined because the percentage of alteration is not known. Another possible decrease in aluminum concentration could be caused by the precipitation of illite. However, the gradual increase in potassium content in solution with time argues against the precipitation of illite.

The behavior of the sulfate species is difficult to resolve. One possible explanation for the initial drop in concentration is that sulfate is being reduced. During the sampling procedure, reduced sulfate degasses as hydrogen sulfide, so that measured sulfate concentration is decreased. The results of two additional short-term, exploratory, cold-seal experiments appear to support the premise that sulfate reduction is occurring. In one experiment, bentonite and synthetic groundwater were reacted at 300°C, 300 bars pressure at a 15:1 water:rock ratio for 3 days. A strong sulfide odor was detected after opening the capsule. In a second experiment, bentonite and de-ionized water were reacted at 300°C, 300 bars pressure at a 10:1 water:rock ratio for 3 days. No

sulfide odor was detected at the second run. These indicate that sulfur species did not dissolve significantly into solution and that the sulfate initially present in the groundwater was being reduced during the experiment. If so, then the reducing conditions were rapidly established in the bentonite/groundwater system. More experimental work is required before the observed sulfate behavior can be fully resolved.

Preliminary solids analysis shows that alteration products in the basalt-bearing systems include quartz, smectite, illite, and mordenite. The combination of solution and solids data suggests that the primary reaction in the basalt/groundwater and basalt/bentonite/groundwater systems is the dissolution of basalt glass followed by the precipitation of a pure silica phase (i.e., cristobalite and/or quartz) and smectite, illite, and mordenite. The zeolite phase (mordenite) is the most abundant reaction product in the basalt/bentonite/groundwater system. In contrast to the bentonite/groundwater system, no albite reaction product was observed. The increase and decrease of silica in solution marks a dissolution of basalt glass followed by the precipitation of the pure silica phase. The increase and decrease of aluminum and potassium as well as the decrease in magnesium and iron concentrations suggest that precipitation of mordenite, illite, and iron-magnesium-rich smectites has occurred. This hypothesis is further supported by the existence of these phases in the fracture mineralization of the host rock. An additional reaction which probably occurred was the alteration of smectite (either sodium bentonite or iron, magnesium smectite) to illite following the exchange of sodium, magnesium, or iron for potassium. However, the alteration of sodium bentonite to illite has not yet been observed and it is unlikely that major alteration has occurred.

## CONCLUSIONS

The experimental data discussed above indicate that montmorillonite will remain sufficiently stable at 300°C under hydrothermal conditions to permit its use as a backfill material. Limited experimental data in the literature which might be applicable to the basalt geochemical environment also suggest that sodium montmorillonite is stable at 300°C. Other experiments involving hydrothermally reacted montmorillonites at high temperatures [4] show that saturated montmorillonite did not react to mixed-layer clay in a potassium-free system at 300°C for 1 month. However, noticeable reaction did occur at 400°C in a 17-day run where the reaction products rectorite (mixed-layer paragonite and montmorillonite), albite, kaolinite, and quartz were observed. More experiments and longer run times are required to determine the behavior of sodium bentonite under site-specific geochemical conditions. In particular, the validity of the albite alteration and the degree of alteration must be addressed in future experiments.

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