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Reaction of Bullfrog Tuff with J-13 Well Water at 90°C and 150°C

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REACTION OF BULLFROG TUFF WITH J-13 WELL WATER
AT 90°C AND 150°C

ABSTRACT

A series of experiments were conducted to determine the nature and extent of reaction between the Bullfrog Member of the Crater Flat tuff and natural groundwater from well J-13 at the Nevada Test Site. The experiments were conducted on crushed tuff at 90°C and 150°C and on core wafer samples at 150°C. The results show the following: (1) Increasing the ratio of rock to water increases the rate of approach to steady-state concentrations in solution. (2) Surface outcrop samples of Bullfrog tuff contain a minor component of highly soluble material believed to be a residue from the evaporation of surface runoff water in the pores of the rock. This material can be removed by shaking the crushed rock with water at room temperature and subjecting it briefly to heat with fresh water. (3) Solution analyses for unfiltered samples that have reacted for short periods show higher concentrations of Al and Fe than do analyses for filtered samples; results for other elements are independent of filtration. This difference probably exists because of particulate matter in the solutions that dissolves when the samples are acidified prior to analysis. Agitation of samples during reaction produces sub-0.1 μ particles in the solutions. These particles dissolve when samples are acidified, resulting in abnormally high concentration values for some elements, such as Al and Fe. (4) Comparison of the results for crushed rock with those for core wafers shows that the method of sample preparation does not have a large effect on the results of rock-water interaction studies.

This paper presents the data for Al, B, Na, Li, K, Fe, Si, Ca, Mg, F, Cl, NO₃, and SO₄ concentrations in solution and for the pH of solutions. Additionally, it outlines the various experimental conditions used to determine the effects of different sample weights relative to solution volume, length of reaction time, presence and nature of highly soluble components, filtration of samples, agitation of samples during reaction, and method of sample preparation.

INTRODUCTION

This paper presents the results of a laboratory investigation begun in early 1982 of the interaction of Bullfrog tuff with natural groundwater from well J-13 located near Yucca Mountain at the southwest edge of the Nevada Test Site. We undertook the work reported to determine the expected changes in water chemistry in the near-field area of rock surrounding a high-level waste repository. Near-field rock is heated by the thermal output from the decay of radioactive waste and reacts with groundwater, causing changes in the water chemistry and alteration of minerals in the rock.

The Bullfrog Member of the Crater Flat tuff is one of four Yucca Mountain tuff units that were under consideration by the Nevada Nuclear Waste Storage Investigations (NNWSI) Project as a potential location for a mined geologic repository for high-level nuclear waste. Two of the units, the Topopah Spring Member of the Paintbrush tuff and the tuffaceous beds of the Calico Hills, are located above the water table in the unsaturated zone. The other units, the Bullfrog and Tram, are located below the water table. The NNWSI Project chose the Topopah Spring tuff as the reference repository horizon in mid-1982.

With the choice of the Topopah Spring tuff as the repository horizon, experimental work has been redirected to rock-water interaction testing of that unit. The results of the experiments herein described would have provided the postemplacement groundwater chemistry for the near-field region, had NNWSI chosen the Bullfrog unit. Instead, they will be used to aid in the development of the geochemical modeling code to be used in conjunction with near-field repository performance modeling.

We collected the water used in all rock-water interaction experiments from well J-13 in the southwest corner of Jackass Flats, near Forty-Mile Wash. J-13 supplies all facilities in Jackass Flats, e.g., E-MAD, as well as NNWSI activities at Yucca Mountain. The producing horizon in the well is a highly fractured interval within the Topopah Spring Member. We collected the water by pumping the well for several minutes, rinsing out a plastic-lined, 55-gal drum, and then filling the drum completely full. The water was neither filtered nor acidified at the collection point.

The proposed repository horizon within the Bullfrog Member of the Crater Flat was defined as an interval of welded, devitrified tuff equivalent to the 2340- to 2545-ft interval referenced to hole G-1. This definition was based on a correlation of the core logs, geophysical logs, mineralogy, and physical properties from drill holes G-1, G-2, UE25a-1, and UE25b-1. Although poorly exposed partial sections of the Bullfrog are shown in areas with existing geologic map coverage (Topopah Spring NW 15 quad), the outcrops were not suitable for precise location within the section. Eight and one-half miles northwest of Lathrop Wells, however, is an excellent section of Bullfrog tuff exposed on the extreme southwest spur of Yucca Mountain (nearest Bare Mountain and west of the Stromboli cinder cone) in an area currently unmapped on the Big Dune topographic sheet.

New data from exploratory drilling, mapping, and petrographic studies in the Bare Mountain-Crater Flat area show the correct stratigraphic relationships between the Crater Flat tuffs and the Belted Range tuffs. At this location, the emplacement temperature must have been somewhat higher than beneath Yucca Mountain, because a well-developed vitrophyre is present. This allows an unambiguous selection of a welded, devitrified interval equivalent to that proposed for the repository. Materials collected from this interval (spanning 20 to 30 ft of section) were collected and used to produce Batch A, Batch B, and core wafer material used in the rock-water interaction studies described in this paper. We trimmed the rock samples collected from the outcrop before using them in the experiments to remove any visible surface alteration products. Knauss (1983a) gives detailed characterization of these samples.

CRUSHED BULLFROG TUFF

EXPERIMENTAL PROCEDURES

Two sets of experiments were run on crushed Bullfrog tuff with J-13 water. In the first set, we used rock that was crushed to less than 100 mesh in a Spex Mill tungsten carbide vessel using tungsten carbide grinding balls. We discovered later that one of the grinding balls was made of stainless

steel. This crushed tuff material, referred to as Batch A, was found to be contaminated with small amounts of Cr, Ni, Co, and W. The highest level of contamination was 75 ppm for W.

In the second set of experiments, we used tuff that was crushed to less than 100 mesh with a plate grinder that has high purity alumina plates. This material is referred to as Batch B. Neutron activation analysis of Batch B tuff showed no evidence of contamination. A comparison of Batch A rock-water interaction test results at 150°C with those for Batch B indicates that the trace levels of metal contamination in the Batch A material did not affect the results.

In order to investigate the effect of the surface area (SA) of the samples relative to solution volume (V) on the reaction rate of the system, we designed for Batch A tuff a test matrix that uses five different sample weights and up to nine different lengths of contact time while keeping the volume of J-13 water and the temperature constant. The experiments were conducted in PTFE teflon containers housed in steel casings (Parr acid digestion bombs); each vessel is approximately 20 ml in volume. The outer casings were modified so that the bombs could be rolled slowly throughout the experiment, thus ensuring full contact of the rock powder with the liquid phase. The reaction temperature for the Batch A test matrix was 150°C. Sample weights and contact times used were 0.1 g and 0.2 g for 1, 2, 4, 8, 12, 16, 24, 32, and 48 days; 0.4 g for times up to 32 days; 0.8 g for times up to 16 days; and 1.2 g for times up to 8 days.

Before each experiment was started, the bombs were cleaned by washing, rinsing with high-purity water, filling with high-purity water, and placing in an oven at 150°C for at least 12 h. J-13 water control samples run in parallel with the rock-water tests indicate that this cleaning procedure was adequate.

At the start of each experiment, the appropriate amount of crushed rock was weighed into the cleaned teflon reaction vessel, 12 ml of J-13 water were added, the teflon lid was placed on the reaction vessel, and the teflon assembly was placed in the steel casing. The entire bomb assembly was then

laid horizontally onto the roller assembly in an oven that was maintained at 150°C throughout the experiment. On completion of the predetermined reaction time, the bomb assembly was removed from the oven, placed in an upright position, and allowed to cool in air until it could be easily opened. Cooling times were generally 1-2 h. This period allowed the finely powdered rock material to settle, leaving a relatively clear liquid phase.

After cooling, the bomb was opened, and the liquid phase was decanted into a centrifuge tube. The liquid sample was then centrifuged to bring down any suspended rock powder. The centrifuged liquid sample was decanted and divided into two portions. One portion was filtered through a 0.1 μ filter; the other was retained as an unfiltered sample. The pH of both samples, measured with narrow-range pH paper, was identical. Both samples were acidified with HNO_3 to make an approximately 0.1 N acid solution. Blank samples of J-13 water with no rock were treated identically. We analysed both filtered and unfiltered solutions by Inductively Coupled Plasma (ICP) spectrometry for Al, B, Fe, Si, Ca, K, and Na. (See "Results and Discussion" for crushed Bullfrog tuff.)

In the second set of experiments, we used Batch B tuff and two rock weight-exposure time matrices. The first was a partial duplication of the 150°C matrix to determine whether minor amounts of metal contamination introduced during the crushing of Batch A tuff had affected solution results. The second experimental matrix with Batch B tuff was run at 90°C to determine the effect of temperature on solution concentrations.

The experimental matrix for the 150°C Batch B test was run with sample weights of 0.1 g, 0.2 g, 0.4 g, and 0.8 g with exposure times of 1, 2, 4, 8, 12, and 16 days. We duplicated the procedure used with Batch A up to the point where the reaction solution was to be separated from the rock. Based on our experience with Batch A, we decided that analysis of unfiltered solutions for cations did not provide sufficient information over that gained from filtered sample results to justify continuation of both measurements. Consequently, for Batch B (both at 150°C and at 90°C) the entire solution was filtered through a 0.1 μ filter. The centrifuge step was omitted from the procedure since it was no longer necessary. Following filtration, the sample

was divided into two equal portions; one was retained for anion analysis by ion chromatography (IC); the other was acidified with HNO_3 and used for cation analysis by ICP spectrometry. No measurement of the pH was made on these samples.

During the experiment at 150°C , there were problems with the motor of the roller assembly; the rollers stopped on several occasions. We documented each interruption. Variations in solution results for samples where roller failure occurred are discussed in the next section, "Results and Discussion."

The test matrix for Batch B at 90°C was run with 0.1 g of rock contacted with J-13 water for periods of 1, 2, 4, 8, 16, 24, 32, 48, and 63 days. The 0.1-g samples were run in the static mode, with the Parr bomb standing upright on the floor of the oven. All other samples were rolled. For 0.2-g samples, contact times were the same as for 0.1 g, but the longest experiment was 48 days. Samples of 0.4 g had maximum run times of 24 days, and 0.8-g samples were run for up to 16 days.

The experimental procedure for Batch B at 90°C was identical to that for Batch B at 150°C , except that we measured the pH with a pH meter before the solutions were decanted from the teflon vessels. There were no problems with the roller assembly during the 90°C experiment.

The experiments conducted with Batch A tuff used J-13 water obtained from the well at a different time from that used with Batch B tuff. Minor differences between the chemistry of Batch A and B water exist because of natural variations expected from well water. Table 1 shows the analytical data for both batches of water, as well as the detection limits for the various elements. Measured values from the Lawrence Livermore National Laboratory (LLNL) and National Bureau of Standards (NBS) reference values for NBS SRM 1643A are also given. Differences between the two analyses of Batch B water indicate the reproducibility of the analytical method.

Cation analyses were made on an automated ICP spectrometer system. Details of the analytical method are described in Peck, et al. (1979). Anion measurements were made using a Dionex Model 2110i automated IC system coupled

Table 1. Detection limits, J-13 analyses, and standard sample results (all in ppm).

Element	Detection limit	J-13			SRM1643A	
		A	B-1	B-2	LLNL ^a	NBS ^b
Al	0.012	bd1 ^c	0.048	bd1	0.114	X ^d
B	0.012	0.140	0.122	0.118	bd1	X
Fe	0.003	bd1	0.016	bd1	0.082	0.088
Si	0.008	30.6	25.7	25.7	0.009	X
Ca	0.020	12.3	10.7	12.2	23.7	27
K	0.18	5.2	4.9	5.3	1.8	2
Mg	0.008	nm ^e	1.91	1.84	7.34	8
Na	0.028	47.9	37.0	45.0	8.76	9
Li	0.001	nm	0.05	nm	--	--
F	0.1	nm	nm	2.6	--	--
Cl	0.1	nm	nm	7.9	--	--
NO ₃	0.2	nm	nm	7.9	--	--
SO ₄	0.2	nm	nm	15.3	--	--

^a Measured values from Lawrence Livermore National Laboratory.

^b Reference values from National Bureau of Standards.

^c Below detection limits.

^d No NBS certified value.

^e Not measured.

with a computer for data acquisition and storage. Details of the procedure are identical to those in the Dionex Model 2110i manual dated February 15, 1982.

RESULTS AND DISCUSSION

The results of cation ICP analysis for the 150°C test matrix using Batch A Bullfrog tuff reacted with J-13 water are given in Tables 2 through 8. Table 9 shows the data for the pH of filtered solutions; the pH of unfiltered solutions was identical to that of filtered solutions within the precision of

Table 2. Sodium concentrations in ppm for crushed Bullfrog tuff A, 150°C rolled, in 12 ml of J-13 water. Initial J-13 Na = 47.9 ppm.

Duration of run (days)	Rock sample weight (g)									
	0.1		0.2		0.4		0.8		1.2	
	F ^a	U ^b	F	U	F	U	F	U	F	U
1	56.6	58.4	62.9	64.7	60.0	60.3	99.5	71.5	97.5	105
2	50.9	57.4	66.4	65.1	57.6	59.4	102	73.1	111	113
4	59.3	58.2	67.9	67.3	60.5	58.4	105	74.8	111	128
8	55.0	53.2	61.5	60.0	72.9	71.5	107	104	134	139
12	47.8	46.7	56.1	60.3	68.4	69.7	94.2	96.7	--	--
16	60.8	62.3	68.3	68.7	70.3	68.9	95.7	96.2	--	--
24	56.8	56.2	59.3	59.8	70.9	67.5	--	--	--	--
32	55.4	57.3	65.7	65.2	87.4	73.8	--	--	--	--
48	57.0	58.5	64.6	58.6	--	--	--	--	--	--

^a Filtered (0.1 μ filter).

^b Unfiltered.

Table 3. Boron concentrations in ppm for crushed Bullfrog tuff A, 150°C rolled, in 12 ml of J-13 water. Initial J-13 B = 0.14 ppm.

Duration of run (days)	Rock sample weight (g)									
	0.1		0.2		0.4		0.8		1.2	
	F ^a	U ^b	F	U	F	U	F	U	F	U
1	0.17	0.17	0.20	0.19	0.26	0.25	0.36	0.35	0.42	0.44
2	0.18	0.18	0.20	0.20	0.27	0.27	0.38	0.38	--	--
4	0.16	0.16	0.20	0.20	0.28	0.27	0.40	0.40	0.47	0.51
8	0.18	0.18	0.21	0.21	0.27	0.27	0.40	0.39	0.53	0.53
12	0.19	0.18	0.21	0.21	0.28	0.27	0.41	0.41	--	--
16	0.18	0.18	0.22	0.22	0.28	0.28	0.42	0.42	--	--
24	0.19	0.19	0.23	0.23	0.29	0.29	--	--	--	--
32	0.20	0.19	0.23	0.23	0.30	0.29	--	--	--	--
48	0.19	0.19	0.23	0.23	--	--	--	--	--	--

^a Filtered (0.1 μ filter).

^b Unfiltered.

Table 4. Potassium concentrations in ppm for crushed Bullfrog tuff A, 150°C rolled, in 12 ml of J-13 water. Initial J-13 K = 5.25 ppm.

Duration of run (days)	Rock sample weight (g)									
	0.1		0.2		0.4		0.8		1.2	
	F ^a	U ^b	F	U	F	U	F	U	F	U
1	9.61	10.7	11.9	12.7	10.5	10.6	11.3	11.6	13.9	21.1
2	8.19	9.15	11.4	11.6	9.08	9.53	10.7	10.9	11.3	13.8
4	8.63	8.81	9.92	12.1	8.19	8.23	7.99	8.47	16.0	36.8
8	7.72	7.33	8.64	8.26	8.53	8.41	7.46	8.49	8.10	12.6
12	6.19	5.88	7.61	8.08	7.07	7.49	5.12	6.82	--	--
16	7.04	7.01	6.93	6.96	6.12	6.22	4.73	6.37	--	--
24	6.06	5.82	5.54	5.57	4.44	4.41	--	--	--	--
32	6.24	6.70	6.26	6.13	6.12	6.57	--	--	--	--
48	6.24	6.28	5.88	6.21	--	--	--	--	--	--

^a Filtered (0.1 μ filter).

^b Unfiltered.

Table 5. Aluminum concentrations in ppm for crushed Bullfrog tuff A, 150°C rolled, in 12 ml of J-13 water. Initial J-13 Al < 0.008 ppm.

Duration of run (days)	Rock sample weight (g)									
	0.1		0.2		0.4		0.8		1.2	
	F ^a	U ^b	F	U	F	U	F	U	F	U
1	1.29	2.09	0.75	1.91	0.42	1.21	0.23	2.53	0.16	10.6
2	0.97	1.22	0.56	1.74	0.37	1.36	0.23	2.47	0.16	4.09
4	0.96	1.81	0.50	4.19	0.32	1.17	0.16	2.34	8.42	34.7
8	0.74	0.80	0.38	0.47	0.23	0.85	0.11	2.54	0.10	5.62
12	0.71	0.85	0.32	0.39	0.27	0.86	0.076	2.67	--	--
16	0.55	0.70	0.24	0.47	0.14	0.63	0.067	2.59	--	--
24	0.42	0.51	0.15	0.40	0.073	0.51	--	--	--	--
32	0.43	0.49	0.11	0.22	0.10	0.44	--	--	--	--
48	0.29	0.38	0.07	0.24	--	--	--	--	--	--

^a Filtered (0.1 μ filter).

^b Unfiltered.

Table 6. Iron concentrations in ppm for crushed Bullfrog tuff A, 150°C rolled, in 12 ml of J-13 water. Initial J-13 Fe < 0.002 ppm.

Duration of run (days)	Rock sample weight (g)									
	0.1		0.2		0.4		0.8		1.2	
	F ^a	U ^b	F	U	F	U	F	U	F	U
1	0.009	0.15	0.009	0.24	0.049	0.52	0.019	1.35	0.05	3.27
2	0.048	0.089	0.023	0.20	0.020	0.53	0.035	1.47	0.026	3.04
4	0.003	0.14	0.004	0.54	0.022	0.40	0.018	1.03	1.44	7.41
8	0.01	0.04	0.01	0.06	0.01	0.32	0.01	1.16	0.01	2.55
12	0.013	0.058	0.037	0.064	0.013	0.36	0.031	1.52	--	--
16	0.01	0.04	0.04	0.07	0.020	0.36	0.024	1.72	--	--
24	0.006	0.052	0.027	0.145	0.031	0.31	--	--	--	--
32	0.02	0.03	0.01	0.06	0.02	0.50	--	--	--	--
48	0.01	0.04	0.01	0.08	--	--	--	--	--	--

^a Filtered (0.1 μ filter).

^b Unfiltered.

Table 7. Silicon concentrations in ppm for crushed Bullfrog tuff A, 150°C rolled, in 12 ml of J-13 water. Initial J-13 Si = 30.6 ppm.

Duration of run (days)	Rock sample weight (g)									
	0.1		0.2		0.4		0.8		1.2	
	F ^a	U ^b	F	U	F	U	F	U	F	U
1	95.2	100	99.7	102	116	106	124	114	110	163
2	91.9	89.8	105	110	123	123	125	123	97.5	118
4	110	112	122	138	134	13	143	141	163	276
8	122	118	130	128	134	132	141	133	136	136
12	137	137	121	119	127	120	132	112	--	--
16	131	132	142	150	129	130	139	128	--	--
24	134	133	138	138	141	138	--	--	--	--
32	137	136	152	150	142	141	--	--	--	--
48	142	142	155	152	--	--	--	--	--	--

^a Filtered (0.1 μ filter).

^b Unfiltered.

Table 8. Calcium Concentrations in ppm for crushed Bullfrog tuff A, 150°C rolled, in 12 ml of J-13 water. Initial J-13 Ca = 12.3 ppm.

Duration of run (days)	Rock sample weight (g)									
	0.1		0.2		0.4		0.8		1.2	
	F ^a	U ^b	F	U	F	U	F	U	F	U
1	9.19	9.70	9.24	9.67	5.74	6.26	5.22	6.00	5.46	8.15
2	7.57	8.46	9.83	9.72	6.09	6.77	6.21	7.30	5.30	7.85
4	5.13	5.21	5.18	5.90	5.12	5.50	5.19	6.25	6.40	13.5
8	7.18	7.14	7.30	7.26	4.55	4.93	4.25	5.50	4.94	9.11
12	4.65	4.53	9.95	10.5	5.60	6.03	3.79	5.69	--	--
16	4.87	5.06	5.15	5.34	4.63	4.94	3.48	5.18	--	--
24	5.17	5.07	4.93	5.11	4.42	4.53	--	--	--	--
32	5.03	5.31	5.29	5.40	5.38	5.83	--	--	--	--
48	5.75	5.90	5.90	6.30	--	--	--	--	--	--

^a Filtered (0.1 μ filter).

^b Unfiltered.

Table 9. The pH of filtered solutions for crushed Bullfrog tuff A, 150°C rolled, in 12 ml of J-13 water.

Duration of run (days)	Rock sample weight (g)				
	0.1	0.2	0.4	0.8	1.2
1	7.0	7.0	7.0	7.4	7.5
2	6.5	6.5	6.5	7.0	6.8
4	7.0	7.0	7.2	7.2	7.5
8	7.0	7.0	7.5	8.0	7.5
12	7.4	6.8	7.0	8.1	--
16	8.0	8.0	8.5	9.0	--
24	8.0	8.0	8.5	--	--
32	7.5	8.5	8.5	--	--
48	8.5	8.5	--	--	--

the measurement (± 0.2 pH units). Table 10 gives the data for blank samples of J-13 water with no rock, carried through the procedure in parallel with the rock-water samples.

Examination of Tables 2 through 8 shows that there is no systematic difference between analytical results on filtered and unfiltered solutions for Na, B, K (except possibly the 1.2-g samples), Si (for samples less than 1.2 g),

Table 10. J-13 water blanks, 150°C rolled, run in conjunction with crushed Bullfrog tuff A matrix (concentrations in ppm).

Duration of run (days)	B		Na		Ca		Al	
	F ^a	U ^b	F	U	F	U	F	U
1	0.13	0.14	50.7	50.4	7.90	7.90	bd1 ^c	bd1
2	--	--	46.3	44.1	3.20	3.02	0.02	0.01
4	0.14	0.13	53.6	54.5	2.98	3.34	bd1	bd1
12	0.14	0.13	39.9	40.7	1.90	3.24	0.02	0.05
24	0.15	0.15	45.9	46.3	2.22	2.03	0.08	0.10
48	0.15	0.15	51.2	51.3	1.60	1.62	bd1	bd1

Duration of run (days)	Fe		Si		K		pH
	F ^a	U ^b	F	U	F	U	F
1	0.004	bd1 ^c	28.0	28.5	5.91	5.50	7.0
2	0.027	bd1	26.8	25.8	4.77	4.53	6.5
4	0.008	bd1	27.7	27.5	6.14	6.11	7.0
12	0.009	0.02	27.5	28.0	4.61	4.88	7.4
24	0.042	0.006	27.5	26.5	4.90	4.82	8.0
48	bd1	bd1	28.2	28.3	5.96	5.9	7.0

^a Filtered (0.1 μ filter).

^b Unfiltered.

^c Below detection limits.

and Ca (for samples less than 0.8 g). Elements that show consistent differences between filtered and unfiltered solutions are Al, Fe, the 0.8- and 1.2-g Ca results, and the 1.2-g Si results. The behavior of Al as a function of time and SA/V suggests that there are differences between filtered and unfiltered results because of suspended colloidal material that slowly coagulates and precipitates. When samples are acidified, the suspended material can dissolve. Analyses of these solutions then show apparently high concentrations of elements that were in colloidal suspension prior to acidification. Figure 1 shows the behavior of Al as a function of time and plots results for 0.1-g rock samples for both filtered and unfiltered solutions. At times greater than 24 days, the results on filtered and unfiltered samples are identical, indicating that particulate material in runs conducted for longer times has completely been removed from suspension.

High concentrations of Al, Si, and Fe found in the filtered portion of the 1.2-g sample that reacted for 4 days suggest that either the filter membrane used for this sample was defective, allowing particulate matter larger than 0.1μ to pass through the filter, or sub- 0.1μ particulate matter was present in that sample. Samples that contained a large amount of solid matter relative to liquid were difficult to filter. It is possible that some concentrations of Al, Fe, Si, K, and Ca for filtered portions of the 0.8- and 1.2-g samples were somewhat high because of slight damage to the filter membranes during filtration.

Two elements (Na and B) showed solution concentrations that were strongly dependent on the ratio of rock to water but not on contact time. This behavior, illustrated in Fig. 2, suggested the presence of a highly soluble phase that was completely removed from the rock in the early stages of the

Figure 1. Bullfrog Batch A, Al concentration as a function of reaction time (filtered and unfiltered solution; 12 ml of J-13; 0.1-g tuff; 150°C; initial Al $\leq$ 0.008 ppm).

Figure 2. Bullfrog Batch A, Na concentration as a function of reaction time and sample weight (filtered solutions; 12 ml of J-13; 150°C; initial Na = 47.9 ppm). Here, Na concentrations depend strongly on the rock-water ratio and not on contact time.

reaction. Subsequent experiments discussed at the end of this section confirmed the presence of the soluble phase.

Potassium concentrations (Table 4) increased in the early stages of reaction and then slowly decreased to near the starting value. The initial increase occurs because of the highly soluble component; the slow decrease probably reflects equilibration of the solutions with the alkali feldspar in the rock samples.

Data for Si (Table 7) are plotted in Fig. 3. The main source of Si is the dissolution of quartz and cristobalite from the Bullfrog tuff. Dissolution of both of these minerals is kinetically controlled, as indicated in Fig. 3 by the initial rapid rise in concentration from 30 ppm to near 100 ppm during the first day of reaction, followed by a gradual increase. All samples show Si concentrations that exceed the solubility of cristobalite at 150°C (122 ppm, Walther and Helgeson, 1977). The high concentration of Si in solution may exist because of a small amount of residual glassy phase in these samples, or because of alteration of the surface of the samples during crushing. The short-term solubility of silica seems to be controlled by the most soluble SiO_2 polymorph present. Thus, the solutions are supersaturated with respect to quartz and cristobalite, even though these minerals are the major SiO_2 phases in the rock. On longer time scales, the solubility of silica should be controlled by quartz.

Data for Ca (Table 8) are plotted in Fig. 4. Calcium concentrations in solution decrease fairly rapidly from the initial J-13 concentration of 12 ppm

Figure 3. Bullfrog Batch A, Si concentration as a function of reaction time and sample weight (filtered solutions; 12 ml of J-13; 150°C; initial Si = 30.6 ppm). The main source of Si is the dissolution of quartz and cristobalite, which is kinetically controlled.

Figure 4. Bullfrog Batch A, Ca concentration as a function of reaction time (filtered solutions; 12 ml of J-13; 150°C; initial Ca = 12.3 ppm). When Ca is removed from solution precipitation is slow.

to values between 3.5 and 5.5 ppm. Post-test characterization of core wafer experiments (discussed in "Bullfrog Tuff Core Wafer Experiments") shows that Ca was removed from solution onto the surface of plagioclase phenocrysts in the rock (Knauss, 1983b). There is little difference between concentrations for filtered and unfiltered solutions, which suggests that the removal of Ca from solution is not accompanied by a significant formation of suspended particulate matter.

Data for the pH (Table 9) are plotted in Fig. 5. The increase in the pH of solutions from the initial J-13 value of 7 follows the increase in Si concentration in the solutions.

Data for the J-13 water blank samples run at 150°C without rock (Table 10) show that B, K, Na, Al, and Fe remain at their original concentrations, while Si shows a slight decrease in concentration. The largest effect of heating J-13 water at 150°C is a decrease in Ca concentration. This occurs most likely because of the precipitation of calcite at the higher temperature.

Fluctuations in concentration data for Na, B, K, and Si indicate the accuracy of the ICP measurements on a day-to-day basis. The comparison of filtered vs unfiltered data for the same exposure time shows that the precision of the measurements on any given day is far better than the day-to-day reproducibility for K and Na.

We ran the experiment with Batch B tuff to resolve two issues: (1) did the small amount of contamination introduced during sample crushing affect the solution results, and (2) were the solution results from two separate, but closely related, outcrop samples in reasonable agreement with each other. Because of the limited objectives of this experiment, the matrix included contact times only up to 16 days. Experience with Batch A tuff showed that samples of 1.2 g of rock in 12 ml of water were extremely difficult to handle. Consequently, the maximum sample size used was 0.8 g in 12 ml of water.

Figure 5. Bullfrog Batch A, pH as a function of reaction time (12 ml of J-13; crushed tuff; 150°C).

During the running of this test matrix, the motor driving the roller mechanism broke down on several occasions. Samples that were in the oven and not being rolled for more than 75% of the run were labeled "complete roller failure." Complete roller failure occurred only with the 4-day samples; the rolling mechanism stopped at some point within the first day of these 4-day samples. Samples labeled "partial roller failure" experienced a static phase during the run, but were rolled the majority of the run time.

The J-13 water used for the Batch B tuff experiment came from a different collection barrel than that used for Batch A tuff. The natural variability of J-13 water produces small differences in the solution chemistry of these two water samples. Thus, initial J-13 values for Batch B tuff experiments were slightly different from those for Batch A. Tables 11 through 23 give the average of the values for the two analyses of Batch B water (Table 1). Tables 11 through 19 present solution data for cations, and Tables 20 through 23, for anions. Below is a discussion on the comparison of results for Batch A and B cations, and information gained as a result of the unplanned disruption of agitation by rolling.

Sodium concentrations (Table 11) are virtually identical for Batch A and Batch B samples, taking into consideration the small difference in Na

Table 11. Sodium concentrations in ppm for crushed Bullfrog tuff B, 150°C rolled, in 12 ml of J-13 water. Initial J-13 Na = 41 ppm.

Duration of run (days)	Rock sample weight (g)				
	0.1	0.2	0.4	0.8	Blank
1	48.0	56.4	71.4	110	38.5
2	43.1	50.6	62.0	97.6	39.7
4	46.2 ^a	50.2 ^a	64.8 ^a	112	--
8	45.8 ^b	53.8 ^b	62.6	113	--
12	50.7 ^b	49.9	63.4	109	40.5
16	49.1 ^b	48.9	66.3	107	--

^a Complete roller failure.

^b Partial roller failure.

Table 12. Lithium concentrations in ppm for crushed Bullfrog tuff B, 150°C rolled, in 12 ml of J-13 water. Initial J-13 Li = 0.05 ppm.

Duration of run (days)	Rock sample weight (g)				Blank
	0.1	0.2	0.4	0.8	
1	0.041	0.047	0.052	--	0.040
2	0.041	0.045	0.050	0.059	--
4	0.044 ^a	0.044 ^a	0.051 ^a	--	0.042
8	0.042 ^b	0.047 ^b	--	--	--
12	0.048 ^b	--	--	--	0.043
16	0.045 ^b	--	--	--	--

^a = Complete roller failure.

^b = Partial roller failure.

Table 13. Boron concentrations in ppm for crushed Bullfrog tuff B, 150°C rolled, in 12 ml of J-13 water. Initial J-13 B = 0.12 ppm.

Duration of run (days)	Rock sample weight (g)				Blank
	0.1	0.2	0.4	0.8	
1	0.27	0.43	0.75	--	0.114
2	0.27	0.45	0.73	1.37	--
4	0.40 ^a	0.47 ^a	0.80 ^a	1.44	0.13
8	0.29 ^b	0.47 ^b	0.78	1.45	--
12	0.36 ^b	0.46	0.80	1.45	0.13
16	0.34 ^b	0.47	0.82	1.40	--

^a Complete roller failure.

^b Partial roller failure.

Table 14. Potassium concentrations in ppm for crushed Bullfrog tuff B, 150°C rolled, in 12 ml of J-13 water. Initial J-13 K = 5.1 ppm.

Duration of run (days)	Rock sample weight (g)				Blank
	0.1	0.2	0.4	0.8	
1	10.6	23.5	15.8	--	5.55
2	7.17	8.71	9.34	10.1	--
4	7.91 ^a	8.14 ^a	9.28 ^a	9.67	5.65
8	6.79 ^b	7.64 ^b	7.61	9.18	--
12	7.77 ^b	6.87	7.71	7.84	5.83
16	7.19 ^b	6.56	7.16	7.29	--

^a Complete roller failure.

^b Partial roller failure.

Table 15. Aluminum concentrations in ppm for crushed Bullfrog tuff B, 150°C rolled, in 12 ml of J-13 water. Initial J-13 Al = 0.05 ppm.

Duration of run (days)	Rock sample weight (g)				Blank
	0.1	0.2	0.4	0.8	
1	1.08	0.78	0.53	--	0.26
2	1.13	0.77	0.73	0.34	--
4	1.33 ^a	1.03 ^a	0.88 ^a	0.40	<0.008
8	0.89 ^b	0.79 ^b	0.51	0.56	--
12	0.98 ^b	0.45	0.34	0.34	0.05
16	0.84 ^b	0.41	0.29	0.24	--

^a Complete roller failure.

^b Partial roller failure.

Table 16. Iron concentrations in ppm for crushed Bullfrog tuff B, 150°C rolled, in 12 ml of J-13 water. Initial J-13 Fe = 0.016 ppm.

Duration of run (days)	Rock sample weight (g)				
	0.1	0.2	0.4	0.8	Blank
1	0.045	0.062	0.088	--	0.005
2	0.103	0.110	0.264	0.152	--
4	0.011 ^a	0.022 ^a	0.036 ^a	0.201	0.003
8	0.017 ^b	0.029 ^b	0.196	0.343	--
12	0.013 ^b	0.072	0.118	0.206	<0.003
16	0.020 ^b	0.074	0.120	0.146	--

^a Complete roller failure.

^b Partial roller failure.

Table 17. Silicon concentrations in ppm for crushed Bullfrog tuff B, 150°C rolled, in 12 ml of J-13 water. Initial J-13 Si = 25.7 ppm.

Duration of run (days)	Rock sample weight (g)				
	0.1	0.2	0.4	0.8	Blank
1	63.5	72.5	81.8	--	21.1
2	68.6	73.5	85.0	95.0	--
4	76.0 ^a	81.6 ^a	96.6 ^a	105	22.2
8	87.3 ^b	93.5 ^b	99.8	107	--
12	94.1 ^b	95.2	100	110	23.3
16	103 ^b	97.0	109	108	--

^a Complete roller failure.

^b Partial roller failure.

Table 18. Calcium concentrations in ppm for crushed Bullfrog tuff B, 150°C rolled, in 12 ml of J-13 water. Initial J-13 CA = 11.4 ppm.

Duration of run (days)	Rock sample weight (g)				
	0.1	0.2	0.4	0.8	Blank
1	6.73	7.33	7.14	--	5.59
2	6.68	7.54	7.60	6.57	--
4	4.60 ^a	4.57 ^a	3.33 ^a	5.58	2.57
8	3.86 ^b	4.36 ^b	6.95	6.56	--
12	5.53 ^b	5.46	6.13	4.50	3.65
16	3.43 ^b	5.50	4.92	4.97	--

^a Complete roller failure.

^b Partial roller failure.

Table 19. Magnesium concentrations in ppm for crushed Bullfrog tuff B, 150°C rolled, in 12 ml of J-13 water. Initial J-13 Mg = 1.88 ppm.

Duration of run (days)	Rock sample weight (g)				
	0.1	0.2	0.4	0.8	Blank
1	0.18	0.22	0.21	--	0.115
2	0.16	0.14	0.20	0.13	--
4	0.072 ^a	0.070 ^a	0.071 ^a	0.142	0.124
8	0.059 ^b	0.066 ^b	0.156	0.206	--
12	0.065 ^b	0.095	0.098	0.116	0.092
16	0.047 ^b	0.085	0.096	0.093	--

^a Complete roller failure.

^b Partial roller failure.

Table 20. Fluoride concentrations in ppm for crushed Bullfrog tuff B, 150°C rolled, in 12 ml of J-13 water. Initial J-13 F = 2.6 ppm.

Duration of run (days)	Rock sample weight (g)				Blank
	0.1	0.2	0.4	0.8	
1	1.0	2.1	3.4	3.4	1.7
2	2.1	2.1	2.6	3.2	--
4	2.3 ^a	2.4 ^a	3.0 ^a	3.8	2.0
8	2.1 ^b	2.1 ^b	3.2	3.9	--
12	2.5 ^b	3.0	3.3	3.9	2.5
16	2.6 ^b	2.9	3.5	4.0	--

^a Complete roller failure.

^b Partial roller failure.

Table 21. Chloride concentrations in ppm for crushed Bullfrog tuff B, 150°C rolled, in 12 ml of J-13 water. Initial J-13 Cl = 7.9 ppm.

Duration of run (days)	Rock sample weight (g)				Blank
	0.1	0.2	0.4	0.8	
1	14.4	12.7	15.6	28.4	5.8
2	7.5	8.2	10.2	14.4	--
4	8.1 ^a	8.4 ^a	11.0 ^a	19.8	6.1
8	7.5 ^b	8.2 ^b	10.9	19.4	--
12	8.1 ^b	10.0	12.8	22.0	7.1
16	8.2 ^b	9.2	12.0	20.5	--

^a Complete roller failure.

^b Partial roller failure.

Table 22. Nitrate concentrations in ppm for crushed Bullfrog tuff B, 150°C rolled, in 12 ml of J-13 water. Initial J-13 NO_3 = 7.9 ppm.

Duration of run (days)	Rock sample weight (g)				
	0.1	0.2	0.4	0.8	Blank
1	9.1	12.3	15.8	25.0	6.1
2	8.8	10.8	15.2	24.2	--
4	8.9 ^a	10.8 ^a	16.4 ^a	27.6	6.2
8	8.8 ^b	11.0 ^b	16.2	27.3	--
12	8.8 ^b	11.8	18.0	27.0	6.6
16	9.5 ^b	11.7	17.9	27.2	--

^a Complete roller failure.

^b Partial roller failure.

Table 23. Sulfate concentrations in ppm for crushed Bullfrog tuff B, 150°C rolled, in 12 ml of J-13 water. Initial J-13 SO_4 = 15.3 ppm.

Duration of run (days)	Rock sample weight (g)				
	0.1	0.2	0.4	0.8	Blank
1	18.9	26.6	34.6	54.8	13.1
2	17.6	22.1	33.0	52.7	--
4	19.4 ^a	22.6 ^a	38.2 ^a	59.4	13.7
8	18.4 ^b	22.7 ^b	34.7	59.6	--
12	19.8 ^b	26.5	37.0	58.2	14.1
16	20.2 ^b	24.6	38.7	59.3	--

^a Complete roller failure.

^b Partial roller failure.

concentration in the J-13 water used. A comparison of samples that experienced roller failure with those rolled throughout the run shows no effect of roller failure on Na; the presence of a highly soluble Na component is again clearly indicated. There was no effect on Na in the J-13 water blank samples heated at 150°C.

Data for Li (Table 12) are close to the initial J-13 value for all samples but with a slight indication of a highly soluble component.

Boron results (Table 13) show clear evidence of a highly soluble component, more in Batch B than in Batch A. This contrasts with the Na soluble component, which was similar in both batches of tuff. Blank samples show no change in J-13 B concentrations because of heating. There is also no indication of differences between rolled and unrolled samples.

Data for K (Table 14) show a sharply higher concentration for Batch B than for Batch A for 1-day exposure, indicating a larger component of highly soluble K in Batch B material. Concentration levels in the remaining samples are very similar in both batches, showing a slow removal of "excess" K from solution. Roller failure had no effect on K concentrations.

Aluminum concentrations (Table 15) show trends similar to those seen in Batch A material, with an initial, sharp rise in Al, followed by a slow decrease. The rate of decrease for Batch B is slower than for Batch A, the reason for which is not known. Samples affected by roller failure show abnormally high Al in relation to their neighbors in the matrix. The high Al concentration in the blank sample for 1-day exposure suggests contamination of that sample, either from an incompletely cleaned reaction vessel or from filtration and handling of the liquid sample.

Data for Fe (Table 16) show major differences between Batch B and Batch A, with the results for the former being consistently higher for samples that were rolled throughout the exposure time. Samples that experienced a static phase during exposure have low Fe concentrations, similar to Batch A. This suggests that the Fe in Batch B solutions is colloidal and is stabilized in suspension by the rolling action.

Silicon concentrations (Table 17) for Batch B are slightly below the solubility of cristobalite at 150°C and are uniformly lower than for Batch A; the difference is approximately 30 to 40 ppm and does not depend on exposure time. This supports the inferred presence of a small amount of glassy material in Batch A tuff that dissolves much more rapidly than the main SiO_2 minerals. The core wafer results for Si (discussed in "Bullfrog Tuff Core Wafer Experiments") are more similar to Batch A Si concentrations. Trace glass in the samples may be undevitrified residual glass, or it may have been introduced by either the vigorous crushing method used on Batch A tuff or the polishing of one surface of the core wafers. Silicon concentrations for blank samples show a slight lowering of Si as a result of heating the J-13 water.

Calcium concentrations (Table 18) show the same values as for Batch A, except that the initial precipitation for Batch B low-weight samples is faster than for Batch A. Failure of the roller mechanism resulted in lower Ca in solution than would be expected by comparison with neighboring samples. Blank samples show that Ca in J-13 water is much less soluble at 150°C than at room temperature (approximately 22°C).

Magnesium (Table 19) has very low solubility in J-13 water at 150°C, as shown by the blank samples and by the rock-water tests. Lack of agitation caused by roller failure increased the rate of removal of Mg from solution.

Data for anions (Tables 20 through 23) show a linear dependence on sample weight and, with the exception of Cl, no dependence of concentration on reaction time. Again, this is evidence for the existence of highly soluble material in the rock. Chloride concentrations increase sharply on the first day of exposure and then decrease to steady-state values that are higher than values for J-13 water and depend on sample weight. An examination of the anion data for 0.4- and 0.8-g samples shows the following estimates for the amounts in solution resulting from the soluble phase in ppm in 12 ml. Chloride estimates are based on day-1 data only; estimates for other anions are based on an average of all data.

	<u>0.4 g</u>	<u>0.8 g</u>
F	0.5	1.0
Cl	7	20
NO ₃	8	18
SO ₄	21	42

We devised an experiment to test for the existence of the inferred soluble salts and to evaluate the estimates of their abundance inferred from the long-term data. Samples of both Batch A and Batch B tuff weighing 0.4 and 0.8 g were used. Each sample was weighed into a clean teflon vessel to which 12 ml of J-13 water were added. The vessel was capped and shaken by hand for 2 min at room temperature. We let the rock powder settle for 1 h, then we decanted the liquid phase. The liquid sample was treated following the Batch B filtration and subsequent steps. Fresh J-13 water was added a second time to the rock remaining in the teflon vessel, and the sample was reacted in the static mode overnight at 150°C (day 1). This liquid was decanted, filtered and treated as for Batch B samples. Fresh J-13 water was added a third time to the rock, and the reaction was carried out for 3 days in the rolled mode (days 1-4). Following reaction, the liquid was decanted, filtered and analyzed. Fresh J-13 water was added to the remaining rock, and the 3-day rolled reaction step was repeated.

Table 24 gives results of cation analyses from this experiment, and Table 25, the anion analyses. Day 0 represents the room temperature shake data. Table 24 shows that there are two readily soluble components. The component removed at room temperature consisted of Al and Fe in erratic amounts, minor B, substantial amounts of K and Na, and some Ca in Batch B. A second component of soluble material was removed during the first heat treatment. It contained the major B release and amounts of K and Na similar to the room temperature soluble fraction. Again, dissolution was accompanied by a sharp rise in the pH. The first 3-day heat treatment showed minor release of soluble B and K but no further Na release. The pH of these samples was substantially lower than those containing readily soluble material. The second 3-day reaction showed no release of readily soluble material.

Table 24. Cation data in ppm for soluble component search experiment.

Day ^a	Weight (g)	Batch	Al	B	Si	Fe	Ca	K	Mg	Na	pH
		J-13	0.05	0.12	25.7	0.02	11.4	5.1	1.9	41	7.1
0	0.4	A ^b	0.90	0.11	22.5	0.29	10.4	9.6	1.3	45	7.9
0	0.8	A	1.69	0.13	24.3	0.54	11.5	12.6	1.3	54	8.0
0	0.4	B	0.14	0.22	21.2	0.06	12.9	7.2	1.2	53	8.2
0	0.8	B	3.8	0.35	27.9	1.57	15.0	10.6	1.6	68	8.5
1	0.4	A	1.30	0.17	80.6	0.32	8.3	10.5	0.5	48	8.3
1	0.8	A	1.33	0.23	93.2	0.42	7.6	12.8	0.4	58	8.4
1	0.4	B	1.06	0.52	77.1	0.20	8.9	9.4	0.3	52	8.3
1	0.8	B	0.87	0.95	91.9	0.12	7.3	11.1	0.2	65	8.4
1-4	0.4	A	0.86	0.12	83.9	0.14	9.9	7.3	0.2	40	7.9
1-4	0.8	A	2.74	0.14	98.3	1.00	10.2	8.8	0.6	42	8.1
1-4	0.4	B	0.64	0.16	83.8	0.09	10.4	6.2	0.2	39	7.9
1-4	0.8	B	1.04	0.17	93.1	0.37	8.9	7.3	0.3	42	8.0
4-7	0.4	A	0.81	0.11	84.3	0.03	6.5	5.0	0.1	35	8.0
4-7	0.8	A	0.61	0.12	93.1	0.02	6.8	6.6	0.1	39	7.9
4-7	0.4	B	0.75	0.12	89.1	0.07	7.7	5.6	0.2	36	7.9
4-7	0.8	B	0.67	0.12	91.6	0.10	8.2	6.0	0.2	38	7.8

^a Day 1 is first overnight heat treatment; day 1-4 is first 3-day heat treatment; day 4-7 is second 3-day heat treatment.

^b This is the room temperature shake sample (day 0), using 0.4 g of Batch A tuff.

Data for anions in Table 25 parallel those for cations, with the major release of soluble material occurring during the room temperature shaking step. No anion concentrations in excess of J-13 values were found in either of the 3-day exposures, as shown in Fig. 6, where data for F, Cl, and SO₄ are depicted graphically. Below is the total measured anion release of readily soluble material (in ppm) for Batch B. These data were obtained from the total of day-0 and day-1 release.

	0.4 g	0.8 g
F	.7*	4.0
Cl	1.9	6.6
NO ₃	6.8	14.4
SO ₄	19	39

* Day-1 release was estimated to be zero, since the measured value was less than the J-13 value.

Table 25. Anion Data in ppm for soluble component search experiment.

Day ^a	Weight (g)	Batch	F	Cl	NO ₃	SO ₄
		J-13	2.6	7.9	7.9	15.3
0	0.4	A ^b	3.4	7.7	8.9	23.6
0	0.8	A	3.5	8.4	11.1	30.3
0	0.4	B	3.3	9.0	12.0	30.6
0	0.8	B	6.1	11.4	16.2	46.1
1	0.4	A	2.2	7.5	7.4	16.5
1	0.8	A	2.8	7.7	8.2	17.7
1	0.4	B	2.3	8.7	10.6	18.9
1	0.8	B	3.1	10.8	14.0	23.5
1-4	0.4	A	2.5	7.2	6.6	15.3
1-4	0.8	A	1.9	6.8	6.4	14.9
1-4	0.4	B	2.3	6.8	6.9	13.9
1-4	0.8	B	2.5	7.7	7.2	15.2
4-7	0.4	A	2.5	7.9	7.2	15.8
4-7	0.8	A	2.7	8.2	7.4	15.9
4-7	0.4	B	2.0	6.8	6.8	14.4
4-7	0.8	B	1.8	6.3	5.7	13.4

^a Day 1 is first overnight heat treatment; day 1-4 is first 3-day heat treatment; day 4-7 is second 3-day heat treatment.

^b This is the room temperature shake sample (day 0), using 0.4 g of Batch A tuff.

Figure 6. Removal of readily soluble material from crushed tuff (RTS = room temperature shake sample).

The measured values are in excellent agreement with predictions for NO_3 and SO_4 for both sample weights, and for F at 0.4 g. The high F release from the 0.8-g sample may occur because of the presence of a trace mineral containing F. Measurements of Cl release are low compared to predictions, probably owing to back-reaction onto the rock material.

The readily soluble material found in these experiments is attributed to caliche deposits in the pores of the rock. Air-drilled samples of Topopah Spring tuff obtained from a horizontal borehole at Fran Ridge do not contain readily soluble material (Knauss and Oversby, work in progress), while surface outcrop samples of Topopah Spring tuff do (Oversby, 1983). Future work with surface outcrop samples will include the room temperature shaking and overnight cooking steps as pretreatment for rock-water interaction studies.

Tables 26 through 33 present results of cation analyses for the 90°C test matrix. Data for the pH are in Table 34. Anion data are in Tables 35 through 38.

Sodium concentrations at 90°C (Table 26) are only slightly lower than those for 150°C samples. Most or all of the Na can be attributed to the caliche material. One sample, the 0.2-g, 2-day exposure, was accidentally diluted by about a factor of 2. Tabulated data were corrected back to the original 12 ml volume. This dilution did not affect Na results but may have affected K, Al, Fe, and Ca data.

Boron concentrations in solution after reaction at 90°C (Table 27) are only slightly lower than those found for 150°C runs. Again, the presence of highly soluble caliche material probably accounts for the presence of B. Dilution of the 0.2-g, 2-day sample does not seem to have altered the B in solution.

Potassium concentrations in solution after reaction at 90°C (Table 28) are slightly higher than those for 150°C runs, except for 1-day exposure times. Again, the data suggest that a highly soluble K component goes into solution within the first day of reaction, producing a solution that is supersaturated with respect to K. Potassium then slowly reacts with the rock,

Table 26. Sodium concentrations in ppm for crushed Bullfrog tuff, 90°C in 12 ml of J-13 water; 0.1 g static, remainder rolled. Initial J-13 Na = 41 ppm.

Duration of run (days)	Rock sample weight (g)				Blank
	0.1	0.2	0.4	0.8	
1	41.9	45.4	61.1	88.4	--
2	38.1	43.9 ^a	65.4	92.5	38.4
4	41.4	44.2	58.8	74.6	--
8	42.2	49.3	59.3	91.1	34.8
16	44.6	46.1	59.0	92.2	32.6
24	41.9	50.2	61.1	--	--
32	43.9	47.8	--	--	32.8
48	41.9	44.0	--	--	--
63	37.8	--	--	--	--

^a Sample diluted.

Table 27. Boron concentrations in ppm for crushed Bullfrog tuff, 90°C in 12 ml of J-13 water; 0.1 g static, remainder rolled. Initial J-13 B = 0.12 ppm.

Duration of run (days)	Rock sample weight (g)				Blank
	0.1	0.2	0.4	0.8	
1	0.267	0.371	0.663	1.13	--
2	0.243	0.355 ^a	0.717	1.27	0.126
4	0.271	0.390	0.651	1.23	--
8	0.267	0.409	0.719	1.35	0.120
16	0.304	0.420	0.744	1.37	0.113
24	0.280	0.436	0.751	--	--
32	0.287	0.443	--	--	0.112
48	0.288	0.425	--	--	--
63	0.276	--	--	--	--

^a Sample diluted.

Table 28. Potassium concentrations in ppm for crushed Bullfrog tuff, 90°C in 12 ml of J-13 water; 0.1 g static, remainder rolled. Initial J-13 K = 5.1 ppm.

Duration of run (days)	Rock sample weight (g)				
	0.1	0.2	0.4	0.8	Blank
1	7.21	7.81	10.8	14.6	--
2	6.24	8.88 ^a	11.4	11.8	4.87
4	6.72	7.89	12.4	12.3	--
8	6.74	8.96	10.3	11.0	4.71
16	6.90	7.96	10.3	11.0	4.70
24	6.84	8.14	10.5	--	--
32	6.63	8.79	--	--	4.64
48	6.55	7.10	--	--	--
63	5.89	--	--	--	--

^a Sample diluted.

Table 29. Aluminum concentrations in ppm for crushed Bullfrog tuff, 90°C in 12 ml of J-13 water; 0.1 g static, remainder rolled. Initial J-13 Al = 0.05 ppm.

Duration of run (days)	Rock sample weight (g)				
	0.1	0.2	0.4	0.8	Blank
1	0.365	0.297	0.504	6.39	--
2	0.393	0.857 ^a	0.885	0.555	< 0.012
4	0.439	0.332	4.13	1.01	--
8	0.383	0.500	0.927	1.57	0.01
16	0.529	0.540	2.51	0.951	0.066
24	0.461	0.383	4.36	--	--
32	0.556	4.87	--	--	0.055
48	0.521	1.23	--	--	--
63	0.887	--	--	--	--

^a Sample diluted.

Table 30. Iron concentrations in ppm for crushed Bullfrog tuff, 90°C in 12 ml of J-13 water; 0.1 g static, remainder rolled. Initial J-13 Fe = 0.016 ppm.

Duration of run (days)	Rock sample weight (g)				Blank
	0.1	0.2	0.4	0.8	
1	0.067	0.030	0.103	2.34	--
2	0.018	4.80 ^a	0.202	0.178	0.012
4	0.060	0.041	1.14	0.336	--
8	0.015	0.087	0.278	0.621	0.002
16	0.032	0.123	1.06	0.408	0.013
24	0.015	0.107	2.02	--	--
32	0.036	2.00	--	--	0.014
48	0.022	0.455	--	--	--
63	0.150	--	--	--	--

^a Sample diluted.

Table 31. Silicon concentrations in ppm for crushed Bullfrog tuff, 90°C in 12 ml of J-13 water; 0.1 g static, remainder rolled. Initial J-13 Si = 25.7 ppm.

Duration of run (days)	Rock sample weight (g)				Blank
	0.1	0.2	0.4	0.8	
1	31.3	34.0	42.4	55.9	--
2	31.4	34.3 ^a	45.7	51.5	25.0
4	33.7	36.1	48.7	51.7	--
8	34.6	39.1	47.4	55.5	23.3
16	39.0	41.6	51.8	57.3	22.8
24	37.4	41.7	54.0	--	--
32	39.4	50.9	--	--	21.7
48	40.5	45.0	--	--	--
63	40.9	--	--	--	--

^a Sample diluted.

Table 32. Calcium concentrations in ppm for crushed Bullfrog tuff, 90°C in 12 ml of J-13 water; 0.1 g static, remainder rolled. Initial J-13 Ca = 11.4 ppm.

Duration of run (days)	Rock sample weight (g)				
	0.1	0.2	0.4	0.8	Blank
1	7.71	8.19	7.67	10.6	--
2	6.69	9.43 ^a	8.27	6.29	9.91
4	7.07	7.61	8.80	6.38	--
8	5.95	7.71	6.85	5.78	8.79
16	4.98	6.75	7.77	5.77	8.53
24	3.32	6.45	9.56	--	--
32	3.01	7.70	--	--	3.75
48	2.42	4.93	--	--	--
63	2.11	--	--	--	--

^a Sample diluted.

Table 33. Magnesium concentrations in ppm for crushed Bullfrog tuff, 90°C in 12 ml of J-13 water; 0.1 g static, remainder rolled. Initial J-13 Mg = 1.88 ppm.

Duration of run (days)	Rock sample weight (g)				
	0.1	0.2	0.4	0.8	Blank
1	0.847	0.548	0.382	1.06	--
2	0.545	0.571 ^a	0.386	0.232	1.62
4	0.445	0.361	0.620	0.263	--
8	0.243	0.296	0.287	0.339	1.44
16	0.196	0.236	0.604	0.267	1.24
24	0.120	0.185	0.982	--	--
32	0.111	1.02	--	--	0.397
48	0.066	0.317	--	--	--
63	0.113	--	--	--	--

^a Sample diluted.

Table 34. The pH for crushed Bullfrog tuff, 90°C in 12 ml of J-13 water; 0.1 g static, remainder rolled. Initial J-13 pH = 7.1.

Duration of run (days)	Rock sample weight (g)				
	0.1	0.2	0.4	0.8	Blank
4	--	8.27	8.45	8.53	--
8	--	8.26	8.48	8.74	8.45
16	--	8.48	8.58	8.65	8.54
24	8.57	8.64	8.72	--	--
32	8.68	8.70	--	--	8.47
48	8.84	8.89	--	--	--
63	9.00	--	--	--	--

Table 35. Fluoride concentrations in ppm for crushed Bullfrog tuff, 90°C in 12 ml of J-13 water; all samples rolled. Initial J-13 F = 2.6 ppm.

Duration of run (days)	Rock sample weight (g)			
	0.2	0.4	0.8	Blank
1	2.2	2.5	2.9	--
2	2.0	2.8	3.4	2.3
4	2.3	2.6	3.2	--
8	2.4	2.7	3.3	2.1
16	2.4	2.6	3.3	2.0
24	2.4	2.6	--	--
32	2.4	--	--	2.1
48	2.3	--	--	--

Table 36. Chloride concentrations in ppm for crushed Bullfrog tuff, 90°C in 12 ml of J-13 water; all samples rolled. Initial J-13 Cl = 7.9 ppm.

Duration of run (days)	Rock sample weight (g)			Blank
	0.2	0.4	0.8	
1	8.1	10.8	14.3	--
2	9.4	11.2	15.5	7.0
4	8.2	10.2	15.0	--
8	8.9	11.3	15.2	7.0
16	8.8	11.1	15.0	6.5
24	9.0	10.9	--	--
32	9.0	--	--	7.0
48	8.5	--	--	--

Table 37. Nitrate concentrations in ppm for crushed Bullfrog tuff, 90°C in 12 ml of J-13 water; all samples rolled. Initial J-13 NO₃ = 7.9 ppm.

Duration of run (days)	Rock sample weight (g)			Blank
	0.2	0.4	0.8	
1	11.7	17.8	27.0	--
2	11.0	20	32	8.7
4	12.2	18	31	--
8	14.0	20.5	32	7.5
16	14.0	21	32	7.5
24	13.7	19.0	--	--
32	13.2	--	--	7.7
48	13.5	--	--	--

Table 38. Sulfate concentrations in ppm for crushed Bullfrog tuff, 90°C in 12 ml of J-13 water; all samples rolled. Initial J-13 SO_4 = 15.3 ppm.

Duration of run (days)	Rock sample weight (g)			Blank
	0.2	0.4	0.8	
1	27	41	54	--
2	28	42	61	19
4	28	39	58	--
8	30	41	60	18
16	29	41	59	17
24	29	43	--	--
32	29	--	--	17
48	28	--	--	--

causing a gradual decrease in solution concentrations of K. This back-reaction seems to be slower at 90°C than at 150°C. Measured K for the diluted sample is slightly higher than that for neighboring 0.2-g samples in the matrix; however, the difference is not large enough to allow an unambiguous interpretation to be made.

Aluminum concentrations (Table 29) for samples reacted in the static mode (0.1-g samples) show a fairly consistent pattern of gradual increase for longer reaction times; the slow dissolution of feldspars could be the reason. Data for rolled samples are erratic, with no pattern. This suggests that rolling the samples causes particulate matter smaller than $0.1\ \mu$ to become suspended in the liquid phase. Some, but not necessarily all, of this particulate Al could dissolve when samples are acidified with HNO_3 . All samples that gave high Al concentrations were refiltered. Subsequent ICP analyses confirmed that the high Al was truly in solution at the time of the original analyses. Table 39 shows a comparison of data for the high Al samples as originally analyzed and for refiltered samples. In all cases, the Al concentrations increased with storage time; this strongly supports the

Table 39. Comparison of ICP results for original (I) and refiltered (II) solutions from 90°C test matrix, ppm.

Weight (g)	Time (days)	Al		Fe		Si		B	
		I	II	I	II	I	II	I	II
0.2	32	4.9	7.0	2.00	2.25	50.9	55.2	0.44	0.43
0.2	48	1.2	2.2	0.46	0.58	45.0	46.7	0.42	0.41
0.4	4 ^a	4.1	7.8	1.14	1.51	48.7	55.8	0.65	0.64
0.4	16	2.5	4.2	1.06	1.26	51.8	53.7	0.74	0.70
0.4	24 ^a	4.4	8.4	2.02	3.02	54.0	62.4	0.75	0.74
0.8	1 ^a	6.4	10.3	2.34	2.91	55.9	63.4	1.13	1.10
0.8	8 ^a	1.6	3.4	0.62	0.84	55.5	60.0	1.35	1.32

Weight (g)	Time (days)	Mg		K		Na		Ca	
		I	II	I	II	I	II	I	II
0.2	32	1.02	1.11	8.8	11.4	47.8	58.3	7.7	9.0
0.2	48	0.32	0.41	7.1	8.9	44.0	53.9	4.9	5.9
0.4	4 ^a	0.62	0.72	12.4	14.3	58.8	64.6	8.8	9.5
0.4	16	0.60	0.67	10.3	12.2	59.0	67.4	7.8	8.7
0.4	24 ^a	0.98	1.33	10.5	13.6	61.1	73.8	9.6	11.4
0.8	1 ^a	1.06	1.22	14.6	17.9	88.4	91.2	10.6	11.9
0.8	8 ^a	0.34	0.42	11.0	14.4	91.1	96.8	5.8	7.0

^a Original analysis 12/21/82; others 1/14/83. All reanalyses 2/14/83.

thesis that sub-0.1 μ particles remain in solution and slowly dissolve in the dilute HNO_3 solution. Concentrations of all other elements except B were also higher in the refiltered samples, a fact that supports the presence of sub-0.1 μ mineral particles held in suspension. These particles subsequently dissolved in the acidified solutions.

Data for Fe (Table 30) closely resemble those for Al. Again, the suggestion is that sub- $0.1\ \mu$ particulate material is present in some of the rolled samples but not in those reacted in the static mode. The increase in Fe content for acidified samples, which are allowed to stand for 4-7 wk (Table 39), supports this interpretation.

Results for Si (Table 31) show that dissolution of silica is slower for the static samples than for the rolled samples. The increase in Si found for acidified samples that were allowed to stand (Table 39) suggests that dissolution may be faster if agitation produces sub- $0.1\ \mu$ particulate material. Note that Si is highest in the original samples for those samples that had high Fe and Al; Si increases with time for acidified samples (Table 39). The 90°C exposure times were not long enough to produce steady-state concentrations for Si.

Calcium data (Table 32) at 90°C show the same slow precipitation trend observed at 150°C . The removal of Ca from solution is fastest for the samples that were not rolled, again suggesting that agitation of the samples stabilizes supersaturation. The diluted sample has a slightly higher Ca concentration than its matrix neighbors, indicating that some sub- $0.1\ \mu$ particulate matter may have dissolved upon dilution of the sample. Acidified samples that were allowed to age (Table 39) also showed increases in Ca.

Magnesium concentrations (Table 33) are substantially higher at 90°C than at 150°C . Samples with high Al also show high Mg, again suggesting the presence of sub- $0.1\ \mu$ particulate material. Reanalysis of these samples (Table 39) showed a slight increase in Mg with time.

The pH of solutions after reaction at 90°C is between 8.3 and 9.0 and shows no correlation with Si concentration (Table 34). This is in contrast to the 150°C results, where the pH and Si show a positive correlation.

Anion data (Tables 35 through 38) show evidence for the highly soluble material, the presence of which was established by the results given in Table 25. Since the same split of Batch B material was used for all experiments, the soluble component should be the same for 90°C as 150°C . This is confirmed

for F and SO_4 , while NO_3 at 90°C is marginally higher than at 150°C and Cl is somewhat lower. The differences may result from slight heterogeneity in the abundance of the soluble caliche material, or from minor differences in anion-mineral reactions at the two temperatures.

BULLFROG TUFF CORE WAFER EXPERIMENTS

To complement the hydrothermal rock-water interaction experiments using crushed Bullfrog tuff and J-13 water, we decided to conduct analogous experiments using solid core wafers to accomplish the following:

- Confirm water chemistry changes resulting from accelerated tests with crushed tuff.
- Determine water chemistry changes occurring solely because of surface area and sample preparation effects.
- Determine changes in the chemistry of primary phases.
- Determine the distribution and chemistry of secondary phases.
- Determine the geochemical/thermomechanical properties of hydrothermally altered rock.

The first two items are discussed in this report. The last three items are covered in a separate report summarizing the Bullfrog tuff (Tcfb) core wafer, solid phase analyses (Knauss, 1983b). The outcrop material used in all NNWSI experimental work conducted at LLNL has been well characterized and is described in detail by Knauss (1983a).

EXPERIMENTAL PROCEDURES

The core wafers were prepared by slicing a 1-in. OD core removed from the center of a slabbed block of tuff. Each slice was 0.1 in. thick and was cut with an Isomet saw using a 0.012-in. thick, low concentration, diamond blade lubricated with a water plus water soluble oil mixture. Both sides of each wafer were then ground with $20\ \mu$ aluminum oxide. Finally, one side was polished optically flat with $0.3\ \mu$ diamond paste.

We used the following steps in the core wafer experiment:

- Characterize the starting materials.
- React polished core wafer with J-13 water in teflon-lined autoclaves at 150°C.
- Vary number of wafers and reaction time.
- Analyze filtered, acidified solutions for cations.
- Analyze filtered, unacidified solutions for anions.
- Measure the pH electrochemically on unfiltered, unacidified solutions.
- Determine the weight change in core wafers.
- Characterize the solid phases (primary and secondary) by Scanning Electron Microscope (SEM) and Electron Microprobe analyses.

The crushed tuff used in previously described experiments have the following surface areas:

Batch A	Batch B
5.06 m ² /g (Ar BET)	3.80 ± .03 m ² /g (Ar BET)
6.25 m ² /g (N ₂ BET)	4.79 m ² /g (N ₂ BET)

The core wafers have surface areas of $3.63 \pm .18$ m²/g (Ar BET), which suggests that Bullfrog tuff material either has relatively high, interconnected porosity or is highly fractured.

The wafers were supported in such a manner as to expose all surfaces to the solution. Either one or two wafers were run in 80 g of J-13 water, resulting in surface area/volume (SA/V) ratios of either 1100 or 2200 cm⁻¹. This falls well within the SA/V range spanned by the crushed tuff experiments.

The teflon-lined autoclaves were cleaned prior to use by rinsing with deionized water, filling and cooking the bombs for 2 days at 150°C, and then rinsing again. An experiment was conducted to determine the loss of aqueous species to the teflon liners during quenching and the extent to which this material might be removed from the container wall. (See "Results and Discussion" for the core wafer experiments.)

After placing the preweighed core wafers in the sample holder, the J-13 water was weighed in; the entire teflon liner was weighed to monitor potential fluid loss. The bomb was then sealed and placed in an oven maintained at 150°C. Samples were taken at 1-, 2-, 3-, 4-, 6-, and 8-wk intervals. At the end of an experiment, the bomb was removed from the oven and opened as soon as it was cool enough to handle. The teflon liner was weighed and then opened, and the wafer immediately removed. An unfiltered sample was then quickly taken for electrochemical pH measurement using an HNU combination glass electrode. The pH was recorded at 1-min intervals for 5 min. Two 10-ml samples were then taken and filtered through 0.1 μ polycarbonate (Nuclepore) filters into acid-washed (and thoroughly rinsed) plastic tubes. The cation analysis sample was acidified with 50 λ of Ultrex HNO_3 and the pH checked with narrow-range paper. If the pH was higher than 1.0, additional HNO_3 was added. The thoroughly rinsed core wafers were dried in a dessicator and reweighed. An aliquot of J-13 water was analyzed to determine the composition of the starting fluid.

RESULTS AND DISCUSSION

For the following discussion note the sample code given here:

<u>Time (wk)</u>	<u>1 wafer</u>	<u>2 wafers</u>
1	CW1	
2	CW2	
3	CW3	CW7
4	CW4	CW8
6		CW9
8	CW5, CW6	CW10

Table 40 gives the results of the ICP cation analyses, as well as the experimental conditions with respect to mass, surface area, and time. Table 41 gives the IC anion analyses.

The ICP data for Al, K, Ca, Mg, Na, B, and Si have been plotted as a function of time in Figs. 7 through 13, respectively. The numerical symbols plotted refer to the number of wafers used in that experiment and hence

Table 40. ICP results for Bullfrog core wafers.

Sample number	Mass (g)	SA (m ²)	Time (days)	Concentration (ppm)							pH
				Al	Si	Ca	K	Mg	Na	B	
1	2.269	8.232	7.04	0.405	125	3.45	9.00	0.028	51.0	0.234	--
2	2.403	8.718	14.03	0.365	134	2.96	8.69	0.013	50.6	0.226	--
3	2.600	9.432	20.93	0.350	139	2.79	8.50	0.331	53.1	0.258	--
4	2.376	8.618	28.02	0.296	137	3.78	7.77	0.018	50.2	0.353	--
5	2.543	9.225	53.96	0.268	147	2.68	6.15	0.012	48.6	0.250	7.72
6	2.391	8.673	54.97	0.293	146	2.75	5.61	0.021	47.5	0.268	8.07
7	4.951	17.96	20.98	0.204	136	4.57	10.0	0.046	58.9	0.484	--
8	4.840	17.56	28.02	0.210	142	2.95	9.12	0.020	62.6	0.392	--
9	4.515	16.38	39.96	0.232	149	1.98	6.62	0.014	54.2	0.379	8.34
10	4.777	17.33	54.99	0.225	144	2.92	6.47	0.025	54.8	0.344	7.61
J-13	0	0	--	0	30.0	11.5	5.47	1.73	45.2	0.120	--

Table 41. IC results for Bullfrog core wafers.

Sample number	Concentration, mg/L (ppm)					
	Flouride	Chloride	Nitrite	Nitrate	Sulfate	C ₂ O ₄ ²⁻
PRB ^a	<0.1	0.7	<0.1	0.2	0.05	<0.1
CW1	3.0	8.4	<0.1	10.1	20.3	3
CW2	2.9	7.8	0.9	10.0	20.0	1
CW3	3.1	7.8	1.2	10.0	20.0	2
CW4	3.3	8.2	1.1	10.7	22	<0.1
CW5	4.1	8.0	1.5	10.5	21	2
CW6	3.7	7.7	0.9	10.0	21	<0.1
CW7	3.8	7.8	1.3	11.0	21	3.5
CW8	nm ^b	nm	1.2	10	20	5
CW9	4.0	7.8	1.2	10.5	21	5
CW10	4.2	7.9	0.7	11.0	21	<0.1

^a Prerun blank.^b Not measured.

Figure 7. Bullfrog core wafer, Al concentration as a function of reaction time.

Figure 8. Bullfrog core wafer, K concentration as a function of reaction time.

Figure 9. Bullfrog core wafer, Ca concentration as a function of reaction time.

Figure 10. Bullfrog core wafer, Mg concentration as a function of reaction time.

Figure 11. Bullfrog core wafer, Na concentration as a function of reaction time.

Figure 12. Bullfrog core wafer, B concentration as a function of reaction time.

Figure 13. Bullfrog core wafer, Si concentration as a function of reaction time.

distinguish two classes by surface area. The symbol "3" represents the initial J-13 composition. The solution chemistry shows the following trends:

- Al and K concentrations increase over the first week and then decrease, K very regularly and Al somewhat irregularly and showing a weak SA/V effect.
- Ca and Mg concentration levels drop over the first week and then remain essentially constant; Mg is almost completely removed from solution.
- Na and B concentrations increase over the first week and then remain fairly constant; both show a positive SA/V effect.
- Si concentrations increase sharply over the first week and then seem to be essentially constant.

The positive SA/V effect observed for Na and B is further evidence for the surface soluble salts shown to be present in the anion data. Some of this component may have been removed during the slicing and polishing of the core wafers. The samples collected were in outcrop exposed within an arroyo. The presence of evaporite minerals in these core wafers is not surprising. Whether they are present in significant quantities at depth below Yucca mountain is presently unknown, but is considered to be unlikely.

The weight losses experienced by the wafers, the nature and distribution of secondary phases produced, and the alteration of primary phases resulting from reaction with J-13 water are documented by Knauss (1983b).

The changes in aqueous chemistry with time observed here for the intact core wafers agree well with those observed for crushed material. This validates the use of crushed material to increase SA/V and hence accelerate testing. This work with intact material also allows the solid phase characterization referred to above.

An experiment was conducted to determine the loss of aqueous species to the teflon liner of Parr bombs during quenching and the extent to which this material might be removed from the container wall. Three experiments in this series were run for 2 mo at 150°C using J-13 water. CW5 and CW6 each had one wafer, while CW10 had two wafers. After sampling CW5, the liner was emptied, filled with deionized water, and cooked at 150°C for 2 days (CW5-PRB-F); this is normal cleaning procedure. After sampling CW6 and CW10, the liners were emptied, filled with 0.1 N HCl, and cooked at 90°C for 2 days. Both filtered (CW6-PRB-F, CW10-PRB-F) and unfiltered samples (CW6-PRB-U, CW10-PRB-U) were taken. A J-13 blank was also run. The results are summarized in Table 42.

Table 42. Results of the teflon cleaning procedure test.

Sample number	Concentration (ppm)							
	Al	Cu	Fe	Si	Ca	K	Mg	Na
DL ^a	0.012	0.004	0.002	0.004	0.020	0.180	0.008	0.028
J-13	0.048	0.002	0.016	25.7	10.7	4.89	1.91	37.0
CW5 ^b	0.268	0.002	--	147	2.68	6.15	0.012	48.6
CW5-PRB-F	0.039	0.010	0.001	0.386	0.093	0.348	0.209	0.306
CW6 ^b	0.293	0.001	0.002	146	2.75	5.61	0.021	47.5
CW6-PRB-F	0.213	0.059	0.116	0.627	0.531	0.587	0.370	0.819
CW6-PRB-U	0.102	0.050	0.112	0.769	0.377	0.478	0.366	0.500
CW10 ^c	0.225	0.001	0.003	144	2.92	6.47	0.025	54.8
CW10-PRB-F	0.085	0.060	0.125	0.308	0.160	0.569	0.099	0.641
CW10-PRB-U	0.062	0.045	0.120	0.486	0.069	0.345	0.091	0.422

^a DL is the ICP detection limit, which approximates the blank for the Millipore Water used in PRB.

^b One core wafer.

^c Two core wafers.

Experiments CW5 and CW6 both resulted in very similar water chemistry, thereby allowing a comparison of the efficiency with which deionized water and dilute acid remove material from teflon liners following an experiment. The liners released significantly more Al, Cu, Fe, Ca, K, and Na to the acid than to the deionized water. This is not a problem, assuming the experimental conditions remain neutral to alkaline and the amounts of material remain small. Note that for Na and Si, the experimental solutions contain concentrations orders of magnitude higher than those produced by leaching the liners. For elements K and Ca, the J-13 starting solutions are from 10 to 50 times higher than the leach. For Mg, Fe, Cu, and Al, however, the concentrations produced in the acid leach are comparable or even higher than those of the rock-water interaction solutions described above. The Cu measured in the acid leaches may have come from the teflon itself, since none of the rock-water interaction results produced significant Cu in solution. No element was present in the acid leach solutions at greater than 1 ppm, and the total difference between acid leach and deionized water leach summed over all cations was 2 ppm total cations. This represents approximately 3% of the J-13 cation concentration. The only cases where ambiguity from water rather than acid cleaning of teflon might be present in results would be for Mg, Fe, and Al at concentration levels below 0.2 ppm.

SUMMARY AND CONCLUSIONS

Two separate batches of crushed Bullfrog tuff were reacted with J-13 well water at 150°C. The sample that was crushed by a more vigorous grinding (Batch A) had higher Si in solution following reaction than the sample that was pulverized using a flat plate grinder (Batch B). Polished core wafers reacted at 150°C produced Si concentrations closer to those found with Batch A. It is possible that the sample preparation method for Batch A and the polishing of the core wafers produced a small amount of glassy material that dissolved at a rate faster than the matrix minerals. Silicon concentrations found with Batch A and the core wafer experiments exceeded the solubility of cristobalite at 150°C, while results for Batch B were slightly below cristobalite solubility limits.

Comparison of results for different weights of crushed rock in a fixed volume of water as a function of reaction time shows that for kinetically controlled processes, such as dissolution of SiO_2 , the larger sample weights approach steady state more rapidly than the smaller sample weights for equivalent particle size range. Surface area measurements by BET showed that the surface area accessible to gas was similar for samples crushed to less than 100 mesh and for core wafer slices of rock. This shows that the porosity in the rock is highly interconnected and explains the rapidity with which core wafer samples reached pseudo steady-state concentrations in comparison to crushed rock samples.

All of the Bullfrog tuff material used in these experiments was collected from surface outcrops. The rock contains variable amounts of highly soluble Na, Ca, and K salts, much of which can be removed by shaking the crushed rock with water at room temperature. The water cooled slicing and polishing associated with making core wafers removed most, but not all, of this highly soluble material. Part of the increase in the pH found for solutions of J-13 water reacted with crushed rock appears to be due to the highly soluble component. Reacted core wafers, which had little of the soluble material present during reaction, had a lower pH than reacted crushed tuff, which contained relatively large amounts of the highly soluble material.

Filtration of liquid samples from 150°C runs for run times of 16 days or less removed particles that contained Al and Fe. It is inferred that these particles were colloidal and were in the process of coagulation and precipitation. Runs of 24 days or longer at 150°C showed no significant differences between filtered and unfiltered samples.

Experiments at 90°C showed evidence of sub- $0.1\ \mu$ particles in some samples. These particles dissolved in the acid added prior to ICP analysis, which produced erratic results for Al and Fe analyses. Refiltration and analysis of samples having abnormally high Al showed that dissolution of the particles continued for some time after the original analysis. Erratic results were found only for those samples that had been agitated by rolling during reaction.

The general trends in water chemistry found in this work follow. These trends take into account the presence of highly soluble material.

- Silicon concentration over the time period of these experiments is controlled by the most soluble SiO_2 phase rather than by the least soluble phase.
- Calcium and Mg concentrations in solution are lowered as a result of reaction with the rock.
- Aluminum and Fe concentrations show an initial increase followed by a gradual decrease with time. Final concentrations for Al were higher at 90°C than at 150°C .
- The highly soluble material, which is probably the result of evaporation of surface water in rock pores, consists of Na, Ca, and K salts. A soluble phase containing B is also present.
- Release of soluble material causes a substantial increase in the pH. The relatively high pH observed for Batch B crushed material is probably largely due to the soluble material rather than to the major phase reactions.
- Solution compositions resulting from reaction of solid core wafers with J-13 water are consistent with those obtained with crushed tuff.
- The only source of F, Cl, NO_3 , and SO_4 found in these experiments was the highly soluble material. No anions in solution seem to have come from the unaltered tuff minerals.

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