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Hydrothermal Interaction of Solid Wafers of Topopah Spring Tuff with J-13 Water at 90 and 150°C Using Dickson-Type, Gold-Bag Rocking Autoclaves: Long-Term Experiments

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Abstract

The Nevada Nuclear Waste Storage Investigations Project conducted long-term experiments to study the hydrothermal interaction of rock and water representative of a potential high-level waste repository at Yucca Mountain, Nevada. The results of these experiments complement those obtained previously in short-term experiments at similar and higher temperatures. These long-term experiments also help in assessing the effects of kinetic inhibition in the precipitation of secondary minerals at the lower temperatures and allow a more complete determination of the approach of the fluid toward a steady-state composition. Considered collectively, the results of both the short- and long-term experiments provide information useful in defining the near-field repository environment during and shortly after the thermal period caused by the emplacement of nuclear waste.

These long-term experiments were conducted using solid polished wafers cut from drillcore samples of Topopah Spring tuff. A natural ground water was used as the reacting fluid. Analytical techniques for determining the composition of fluids and solids were similar to those used in previous short-term experiments. All experiments were run in Dickson-type, gold-bag rocking autoclaves that were periodically sampled under *in situ* conditions. Two long-term (304-day) experiments were run at temperatures of 90 and 150°C and 50-bar pressure.

Introduction

The Nevada Waste Storage Investigations (NNWSI) Project is studying the suitability of the Topopah Spring Member of the Paintbrush Tuff (Tpt) as a potential site for a high-level waste (HLW) repository at Yucca Mountain. Before an appropriate waste package can be designed for this repository in tuff, however, it is necessary that the near-field environment surrounding the waste package be understood.

To investigate rock/water interactions and the resulting fluid and rock compositions expected to be encountered in this environment, we ran a series of experiments. This series, which included short-term runs with both crushed tuff and solid wafers of tuff, lasted from 60 to 80 days (Knauss et al., 1984, 1985a,b). The conditions for the short-term experiments covered the estimated range of anticipated (90 and 150°C) and unanticipated but possible (250°C) temperatures for waste disposal in a tuff environment. However, the experiments were done under saturated conditions, with higher fluid-to-solid ratios than anticipated and run at pressures sufficient (at least 50 bars) to ensure the presence of only liquid water at all temperatures.

From the results of the short-term experiments at lower temperatures (90 and 150°C), particularly the experiments run with solid wafers of tuff, it is clear that the aqueous phase had not achieved a steady-state composition by the end of two months of reaction. Even the dominant constituent of the aqueous cations, silicon (Si), continued to increase slowly at the end of runs with solid wafers of tuff. Geochemical modeling calculations using the reaction progress code EQ3/6 (Delany, 1985) run at 150°C suggest that up to six months may be required for the solution composition to approach a steady-state condition in experiments run with wafers of tuff.

The modeling calculations also suggest that clinoptilolite would be the dominant run product and control the Si concentration in solution at a steady-state value at 150°C. However, at the end of the short-term runs, detailed analyses of the reacted wafer show that run products are relatively rare and are dominated by clays. Because the version (3230b) of the EQ6 code that was used considers precipitation to be an instantaneous process that occurs immediately upon reaching saturation with a given mineral, failure to detect the predicted assemblage of reaction products may simply reflect a kinetic inhibition of the precipitation process for one or more of the secondary minerals. In this case, we might expect the assemblage of run products to be dominated by those minerals that possess the most rapid precipitation kinetics [a consequence of the Ostwald step rule (Dibble and Tiller, 1981)], rather than by the ones predicted by equilibrium thermodynamic constraints.

Both of the preceding arguments illustrate the importance of making longer term runs at the lower temperatures used in previous experiments. Such experiments are described in this report.

For the long term hydrothermal interaction experiments, solid polished wafers of tuff were taken from drillcore USW G-1 at a depth equivalent to the depth of the potential repository beneath Yucca Mountain. The advantages of using solid wafers of tuff were described by Knauss et al. (1985b). A natural water taken from a nearby well (J-13) that produces water largely from the Tpt was used as the reacting fluid. The experiments were at 90 and 150°C and 50-bar pressure for 304 days.

Dickson-type, gold-bag rocking autoclaves were used for both the short- and long-term hydrothermal interaction experiments (Seyfried et al., 1979). These vessels are designed to allow repeated fluid sampling at *in situ* conditions without perturbing the experiment (Walther and Orville, 1983).

This report presents the results of analyses of fluid samples taken during the course of the tuff/wafer reaction, as well as post-test analyses of the reacted wafer and any secondary minerals observed. The analytical techniques used are identical to those used in the short-term experiments (Knauss et al, 1985a,b).

Starting Materials

The NNWSI Project uses a natural ground water from well J-13 on Jackass Flat at the Nevada Test Site as the reference water for waste package experimental work. The method by which this water is collected and used has been described by Knauss et al. (1985a). The average of many analyses of this water used in waste package experiments was given by Delany (1985). An analysis of the J-13 water used in a particular experiment was made at the start of that experiment. This value is represented as "day 0" in all fluid composition data tables and plots.

The rock used in waste package experiments is a densely welded, devitrified ashflow tuff (Tpt). This tuff was taken from 1232 ft below the surface, in drillhole USW G-1; it has been characterized in detail in previous reports (Knauss et al., 1985a,b).

The preparation of the solid polished wafers of tuff was described in detail by Knauss and Beiriger (1984a). Scanning electron microscope (SEM) observations of representative unreacted wafers that have been subjected to a thorough ultrasonic wash show their surfaces to be largely devoid of the adhering ultrafine material or polishing compound (alumina) that might be expected to result from the cutting and grinding operations. This treatment should preclude the "ultrafine" effect seen when untreated, crushed rock is reacted hydrothermally (Holdren and Berner, 1979; Petrovich, 1981; Knauss and Wolery, 1986). Circumstantial evidence that this ultrafine effect is not seen in experiments with polished wafers comes from two sources. Primak (1981) noted that the stressed surface layer produced by grinding vitreous silica is removed by fine polishing. Furthermore, previous short-term experiments run with crushed, unwashed Tpt clearly show an initial ultrafine effect, while short-term experiments run with polished wafers of Tpt show no such effect (Knauss et al., 1985a,b)

Experimental Techniques

All experiments are carried out in Dickson-type, gold-bag rocking autoclaves. These are high-pressure vessels with an inner, flexible gold bag (containing the reacting solids and fluid) that collapses as sample fluid is withdrawn. To maintain constant pressure, additional distilled water is injected into the surrounding autoclave (Seyfried et al., 1979). The gold bag has a volume of approximately 230 ml, which allows many samples to be taken from the same solution without quenching the run. This bag is sealed by a titanium (Ti) collar and titanium head containing a gold filter, which prevents solids from being removed when fluid is withdrawn from the cell. The fluid sample passes through a gold capillary tube contained within a stainless exit tube, goes past a titanium needle-valve assembly, and is bled through a teflon nipple into a plastic syringe. In this way, the solution is exposed to only gold and titanium during the experiment and to teflon and plastic upon sampling.

The entire pressure vessel is contained within a large furnace heated by an electrical resistance heater. The whole assembly (pressure vessel plus furnace) can be rocked constantly througn 180 deg, at a rate of 6 cycles per minute, on a rack holding two furnaces. The autoclave is pressurized with distilled water, and the pressure is monitored with gauges mounted on each furnace. The temperature of the furnace is controlled by means of digital proportionating temperature controllers and is monitored continuously. Chromel-alumel thermocouples and digital thermometers accurate to ±1°C are used to measure the internal temperature of the pressure vessel.

The autoclaves were modified recently to allow continuous monitoring during rocking of the furnace control thermocouple and the vessel temperature and pressure. This was accomplished by running all thermocouple and transducer cables through a flexible metal conduit. The modifications also allowed all signals to be fed into a data logging system that produced a continuous digital record of all system parameters. Thus, experiment failure caused by cable and power-cord fatigue should be greatly reduced.

The Ti head in the reaction cell was also modified slightly to hold the solid polished wafers run in these experiments. The Ti gland nut that holds the gold filter was threaded to accept a small Ti bolt. The polished wafer, with a small hole drilled in its center, was sandwiched between two washers cut from gold mesh, and the Ti bolt was used to suspend the wafer beneath the Ti head of the reaction cell. In this way, the wafer was exposed to the solution and afforded a convenient surface upon which secondary minerals resulting from the hydrothermal interaction could grow.

The experiments described here ran for 304 days. Unlike the crushed-tuff experiments, during which the rocking motion was halted only during sampling (Knauss et al., 1985a), the wafer experiments were rocked only a few hours each day. This limited rocking was a compromise between two extremes: the continuous rocking required to maintain complete solution/solid contact in experiments with crushed tuff, and the no-rocking permitted in experiments with solid monoliths suspended in such a way as to maintain solution/solid contact. If a wafer were to break during the run and fall to the bottom of the gold bag, periodic rocking would maintain solution/solid contact while mitigating the destructive effects of continuous rocking on the rack's electrical and mechanical components.

Fluid samples were drawn from the gold bag through the titanium valve and injected into a preweighed plastic disposable syringe. First, however, approximately 1 ml of fluid was drawn off and discarded to bleed any stagnant solution from the gold capillary tube. Aliquots of fluid were then drawn slowly to avoid flashing and were used for the analyses described in detail below. Pressure was maintained with a Sprague pump during the sampling procedure. For the long-term experiments, samples were taken at 8, 15, 30, 60, 121, 241, 303, and 304 days after starting. At the conclusion of each run, the furnace power was switched off, and the pressure vessel was disassembled as soon as practical (approximately 10 to 15 hours, depending on the run temperature). The fluid sample taken as the gold bag was being loaded was designated "day 0." The sample taken at day 303 was the last sample taken at run conditions of temperature and pressure. The sample taken at day 304 was a sample of the quenched fluid taken immediately after the gold bag was opened.

Immediately upon sampling, the fluid samples were analyzed for carbonate alkalinity (by means of infrared CO_2 analysis) and pH. A complete suite of cations and anions was measured in both diluted and full-strength samples, using techniques and sample-handling procedures described in detail by Knauss et al. (1985b).

At the completion of each run, the solid polished wafers were removed from the Ti and gold reaction cells and gently rinsed in distilled water. Then, they were air dried to constant weight in a desiccator.

The primary analytical tool for post-test solid-phase analysis was the scanning electron microscope/electron microprobe (SEM/EMP). The SEM/EMP approach, outlined in a previous report (Knauss and Beiriger, 1984a), involves both a low-magnification scan of the entire wafer to locate phenocrysts and matrix areas for subsequent wavelength dispersive spectrometry (WDS) analyses and a high-magnification scan of the entire wafer to locate run products that might be growing on the surface of the wafer. The analytical conditions used for the post-run WDS analyses of phenocrysts and matrix were identical to those used in the pre test analyses (Knauss, 1984). The secondary minerals found in these particular experiments were characterized compositionally using energy-dispersive spectrometry (EDS) only. The EDS spectra were plotted, and a semiquantitative analysis (SSQ) was performed on the basis of these spectra. When secondary minerals were sufficiently large and plentiful to be recovered from the surface of the wafer, other analytical techniques [x-ray diffraction (XRD), infrared spectroscopy (IR), etc.] were also used for characterization.

Experimental Results

DB13 Experiment (150°C)

The drillcore sample Tpt G-1 1232 was reacted with J-13 water at 150°C and 50 bars for 303 days in experiment DB13. The complete cation and anion analyses of fluid samples collected during this experiment are given in Table 1. The fluid composition, plotted as a function of time, is shown in Fig. 1. Also included are analyses of the starting fluid and the quench sample taken at the conclusion of the run.

Table 1. Cation analyses,[a] anion analyses, and pH in fluid samples taken during experiment DB13 in which a polished wafer of Tpt G-1 1232 was heated with J-13 water at 150°C and 50 bars for 303 days.[g]

	Fluid composition (ppm)											pH
Sample	Al	Si	Ca	K	Mg	Na	HCO_3[d]	F	Cl	NO_3	SO_4	(25°C)
DB13-0	0.017[b]	28.0	14.0	6.0	2.05[b]	47.0	105[e]	2.2	7.1	9.1	18.6	7.68
DB13-8	1.05	70.0	7.0	7.0	0.085[b]	52.0	107[e]	2.5	7.2	10.0	19.6	6.81
DB13-15	1.00	86.5	7.5	6.5	0.077[b]	48.2[b]	—[f]	2.5	7.6	10.1	19.3	6.94
DB13-30	0.665[b]	122.5	7.5	6.5	0.056[b]	47.9[b]	101	2.5	7.3	9.9	19.3	6.87
DB13-60	—[c]	142.0	7.0	5.0	0.115	52.5	110	2.4	7.0	9.3	18.4	6.65
DB13-121	0.779[b]	135.5	7.1	5.0	0.045[b]	49.6[b]	118	2.3	7.3	10.7	18.7	7.25
DB13-241	0.53	146.4	6.1	4.6	0.11	50.8	133	2.0	7.2	10.1	17.5	7.20
DB13-303	0.58	142.6	6.6	4.7	0.029[b]	49.8[b]	134	2.2	7.7	9.6	20.7	6.97
DB13-304	0.46	141.6	14.9	4.1	0.092[b]	50.7[b]	118	2.2	7.5	9.1	20.7	6.14

[a] Monochrometer unit.

[b] Polychrometer unit.

[c] Not detected in 10-fold diluted sample, no fullstrength.

[d] IR CO_2 analyses.

[e] IC HCO_3 analyses.

[f] No analysis.

[g] Sample number designation is DB XX-YY, where XX is run number and YY is elapsed time at run temperature in days. The samples with YY = 0 are described in the text and are the unreacted J-13 water actually used in the experiment.

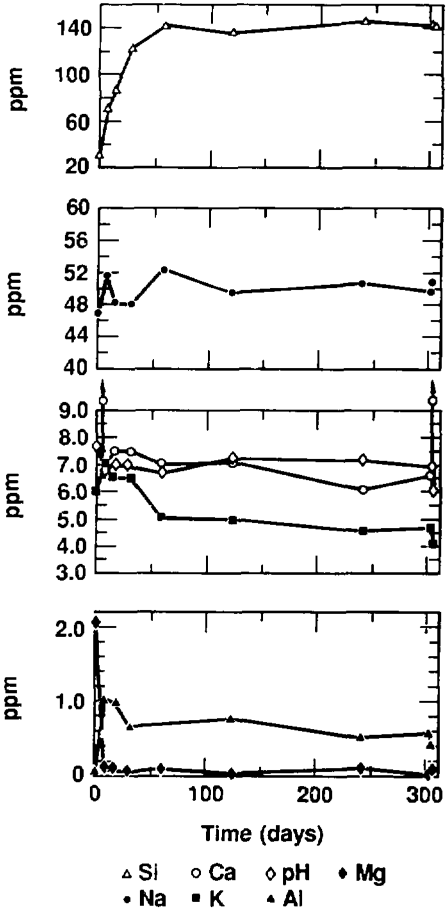

Figure 1. Fluid composition (ppm) vs time (days) for J-13 water reacted with a solid polished wafer of drillcore sample Tpt G-1 1232 at 150°C for 304 days in experiment DB13. Note that the starting Ca concentration (14.0 ppm) and the Ca concentration of the quench sample at the conclusion of the run (14.9 ppm) have not been plotted.

The reaction of tuff with ground water at 150°C resulted in significant changes in the composition of the fluid phase over the course of the 10-month experiment. Within the first 60 days, the Si in the fluid reached a steady-state concentration of 140 ppm, and this concentration was maintained throughout the remainder of the run. Aluminum (Al) concentration reached a maximum of about 1 ppm over the first two weeks and then decreased within 30 days to a concentration of about 0.6 ppm, which was maintained during the following nine months. The magnesium (Mg) concentration dropped immediately and was maintained at 0.1 ppm or less. Similarly, the calcium (Ca) concentration dropped to about 7 ppm immediately and remained between 6 and 7 ppm throughout the run, although a brief rise to 7.5 ppm occurred during the few weeks following the initial sampling.The potassium (K) concentration rose during the first week to 7.0 ppm and then decreased over the next two months to about 5.0 ppm, a concentration that was maintained throughout the rest of the run. The solution pH (as represented by the quench pH) decreased initially to about 6.8 and remained below 7 for the first two months. After four months of reaction, the pH had increased to about 7 and remained at about this value for the rest of the experiment. Within the uncertainty (approximately ±5%) in the sodium (Na) analyses, the Na concentration was unchanged after almost a year of reaction. The anions were similarly unchanged during the reaction. The concentrations of Ca, K, and Al in the quench sample taken at the end of the run suggest that some retrograde reactions took place between the fluid phase and the solids. Calcium was released from the solid phase, while K and Al were removed from the fluid phase.

The results of post-test SEM/EMP analyses of primary phases on the wafer from experiment DB13 are given in Table 2. Analyses of phenocrysts of alkali feldspar, plagioclase, quartz, magnetite, and biotite, as well as analyses of the matrix, are included. It should be remembered that the matrix consisted of a fine-grained (micron-scale) assemblage of quartz, cristobalite, and alkali feldspar and that the oxide totals, therefore, may not equal 100%. The calculated end-member feldspar compositions (Ab-Or-An) are represented in the ternary diagram shown as Fig. 2. Note that the plagioclase ranges from An_{11} to An_{28}, with a median value of about An_{17}. The potassium feldspar compositions range from Or_{36} to Or_{72}, with a median value of about Or_{60}. The analyzed ratio (FeO/FeO + MgO + MnO) × 100 of the biotite ranges from 62 to 73. These bulk compositions are similar to those of the starting material (Warren et al., 1984; Knauss et al., 1985b). The total wafer weight loss is 0.0413 g, or 1.81% of the original wafer weight.

Table 2. Results of post-test SEM/EMP analyses of primary phases on the wafer from experiment DB13 for feldspar, biotite, magnetite, matrix, and quartz.

Sample	Si	Al	Na	K	Ca	Ba	Mg	Ti	Fe	Mn	Sum
Feldspar wt% oxides											
35	66.12	19.36	4.59	10.35	0.37	0.00	0.00	0.06	0.18	0.00	101.03
36	65.78	19.62	4.42	10.51	0.33	0.00	0.00	0.16	0.18	0.02	101.02
37	65.81	19.77	4.32	10.36	0.34	0.04	0.00	0.04	0.16	0.00	100.84
38	66.73	19.83	4.38	10.47	0.29	0.06	0.00	0.08	0.17	0.04	102.05
39	66.35	19.69	4.84	10.73	0.30	0.04	0.00	0.10	0.19	0.00	102.24
40	65.70	19.30	4.29	10.45	0.32	0.09	0.00	0.10	0.09	0.00	100.34
42	66.40	19.97	4.35	10.52	0.27	0.05	0.00	0.03	0.15	0.00	101.74
43	65.68	19.35	4.49	10.52	0.30	0.09	0.00	0.06	0.15	0.00	100.64
44	65.76	18.74	4.36	10.80	0.33	0.00	0.00	0.05	0.13	0.00	100.17
45	66.23	19.01	6.15	7.74	0.37	0.15	0.01	0.00	0.14	0.02	99.82
46	65.51	19.71	5.10	9.24	0.25	0.21	0.00	0.03	0.08	0.00	100.13
47	66.12	19.70	5.28	9.07	0.32	0.18	0.00	0.00	1.07	0.03	101.77
48	66.51	19.17	7.19	6.11	0.49	0.13	0.00	0.03	0.07	0.06	99.76
49	67.14	19.29	5.52	8.53	0.36	0.18	0.00	0.04	0.11	0.03	101.20
50	67.35	20.20	6.92	6.32	0.46	0.11	0.03	0.06	0.18	0.00	101.63
52	66.94	19.82	5.63	8.35	0.35	0.13	0.00	0.00	0.12	0.03	101.37
54	65.56	19.46	4.29	10.80	0.20	0.27	0.03	0.04	0.12	0.02	100.79
55	66.25	19.05	4.49	10.65	0.21	0.36	0.00	0.10	0.14	0.00	101.25
56	66.53	19.98	4.75	9.88	0.33	0.29	0.00	0.02	0.11	0.00	101.89
57	65.92	19.62	4.29	10.91	0.30	0.26	0.00	0.06	0.12	0.00	101.48
58	65.54	19.65	5.74	8.45	0.38	0.20	0.00	0.04	0.11	0.00	100.11
59	65.35	19.48	4.96	9.52	0.27	0.16	0.00	0.05	0.14	0.00	99.93
60	64.58	19.16	5.05	9.40	0.34	0.27	0.02	0.01	0.10	0.41	99.34
61	65.85	19.37	4.87	9.58	0.33	0.06	0.00	0.07	0.13	0.00	100.26
62	64.90	19.27	4.48	10.19	0.28	0.18	0.01	0.00	0.14	0.02	99.47
63	65.35	19.18	4.19	10.49	0.32	0.31	0.02	0.00	0.12	0.00	99.98
64	64.68	19.28	4.25	10.56	0.31	0.27	0.01	0.06	0.12	0.00	99.54
65	64.00	19.15	5.50	8.45	0.36	0.16	0.00	0.04	0.15	0.03	97.84
66	65.05	19.42	6.47	6.68	0.44	0.24	0.00	0.00	0.14	0.02	98.46
67	64.82	19.26	4.47	10.17	0.32	0.06	0.00	0.04	0.16	0.04	99.34
68	65.68	19.36	5.83	7.70	0.51	0.10	0.00	0.00	0.19	0.00	99.46
69	65.67	19.23	4.67	9.65	0.32	0.10	0.00	0.05	0.13	0.00	99.82
70	64.70	19.44	4.61	10.13	0.29	0.13	0.02	0.03	0.19	0.02	99.56
71	64.70	18.98	4.46	10.00	0.34	0.12	0.00	0.03	0.18	0.00	98.81
72	64.84	19.43	4.70	9.72	0.35	0.13	0.00	0.00	0.11	0.00	99.28
73	65.10	19.33	4.40	10.26	0.39	0.20	0.00	0.00	0.13	0.00	99.81
74	65.47	19.43	4.52	9.92	0.33	0.22	0.00	0.08	0.16	0.00	100.13
75	65.26	19.14	3.74	11.66	0.14	0.03	0.00	0.00	0.05	0.04	100.06
76	65.25	19.31	3.99	10.69	0.14	0.00	0.00	0.00	0.07	0.00	99.45
77	65.96	19.33	3.43	12.00	0.08	0.08	0.00	0.00	0.11	0.00	109.99
78	65.12	19.42	3.75	11.16	0.17	0.11	0.00	0.00	0.06	0.49	100.28
79	65.29	19.23	3.58	11.42	0.10	0.00	0.00	0.00	0.03	0.02	99.67
80	63.43	19.06	4.34	11.35	0.21	0.00	0.00	0.03	0.02	0.00	98.44
81	65.97	18.95	4.33	10.55	0.13	0.16	0.00	0.08	0.04	0.05	100.26
82	65.21	19.08	4.88	9.40	0.14	0.00	0.00	0.05	0.04	0.00	98.80
83	66.12	18.96	4.11	10.86	0.12	0.00	0.02	0.05	0.11	0.00	100.35
84	65.84	19.92	5.10	9.22	0.48	0.00	0.00	0.06	0.09	0.00	100.71
85	64.87	19.30	4.18	10.79	0.35	0.00	0.00	0.00	0.08	0.00	99.57
86	66.59	19.58	4.40	10.35	0.37	0.06	0.00	0.00	0.10	0.00	101.45
87	66.51	19.36	3.90	11.06	0.23	0.21	0.09	0.00	0.13	0.02	101.51

Table 2. (Continued.)

Sample	Si	Al	Na	K	Ca	Ba	Mg	Ti	Fe	Mn	Sum
Feldspar wt% oxides (continued)											
88	66.26	19.67	3.88	11.47	0.18	0.00	0.00	0.00	0.12	0.00	101.58
89	65.73	19.46	4.25	10.49	0.19	0.02	0.00	0.00	0.13	0.00	100.27
90	64.87	18.97	3.90	11.06	0.12	0.11	0.00	0.00	0.14	0.02	99.19
91	64.24	18.79	3.20	11.90	0.07	0.07	0.00	0.00	0.13	0.00	98.40
92	65.56	18.96	3.37	12.02	0.10	0.07	0.00	0.00	0.07	0.05	100.20
93	64.08	19.43	3.66	11.71	0.19	0.00	0.00	0.00	0.07	0.00	99.14
94	66.23	18.38	3.24	12.00	0.06	0.00	0.00	0.00	0.10	0.02	100.03
95	65.62	23.03	8.71	1.03	3.47	0.05	0.02	0.01	0.13	0.05	102.12
96	65.01	23.00	8.90	1.07	3.53	0.00	0.00	0.00	0.18	0.03	101.72
97	64.93	23.20	8.79	1.34	3.71	0.02	0.02	0.04	0.10	0.07	102.22
98	64.90	23.36	8.60	1.32	3.58	0.02	0.02	0.00	0.11	0.04	101.95
99	64.50	23.25	8.81	1.04	3.70	0.00	0.00	0.00	0.14	0.03	101.47
100	62.90	23.90	8.55	0.97	4.20	0.07	0.02	0.03	0.16	0.06	100.86
101	63.05	24.45	8.25	0.93	4.85	0.00	0.02	0.07	0.16	0.05	101.83
104	65.19	23.22	8.58	1.31	3.53	0.07	0.01	0.10	0.13	0.06	102.20
106	66.01	21.43	9.37	1.45	2.26	0.00	0.00	0.00	0.13	0.02	100.67
107	65.05	21.49	9.28	1.41	2.48	0.00	0.00	0.00	0.18	0.00	99.89
108	66.36	22.12	9.21	1.25	2.36	0.00	0.00	0.00	0.18	0.02	101.50
109	66.65	21.99	9.32	1.13	2.39	0.00	0.00	0.00	0.16	0.00	101.64
110	62.11	23.68	8.34	0.74	4.98	0.32	0.00	0.04	0.14	0.03	100.38
112	61.45	25.34	7.86	0.66	5.79	0.27	0.00	0.08	0.17	0.03	101.65
113	61.47	24.80	7.88	0.71	5.73	0.00	0.02	0.00	0.09	0.05	100.75
114	62.60	23.60	8.48	0.84	4.78	0.17	0.01	0.03	0.14	0.05	100.70
116	61.17	25.42	7.87	0.67	5.86	0.07	0.01	0.00	0.18	0.00	101.25
117	61.36	25.23	8.13	0.71	5.61	0.14	0.00	0.01	0.10	0.03	101.32
118	61.78	25.27	8.07	0.58	5.68	0.09	0.00	0.00	0.15	0.03	101.65
122	65.94	22.47	9.74	1.12	2.47	0.22	0.00	0.00	0.15	0.00	102.11
123	65.72	22.88	9.66	1.27	2.54	0.11	0.00	0.00	0.16	0.00	102.34
125	63.45	23.21	9.12	1.06	3.61	0.00	0.00	0.10	0.14	0.00	100.69
127	65.17	23.34	9.04	1.35	3.22	0.07	0.00	0.09	0.17	0.00	102.45
129	64.93	23.33	9.73	0.70	3.22	0.12	0.00	0.08	0.23	0.00	102.34
130	63.82	23.66	8.87	0.86	3.89	0.03	0.00	0.02	0.19	0.06	101.40
131	64.03	23.79	8.71	1.15	3.94	0.02	0.00	0.39	0.16	0.03	102.22
132	63.48	24.42	8.59	1.18	4.01	0.05	0.00	0.05	0.16	0.05	101.99
133	64.42	24.04	8.53	1.09	4.07	0.00	0.00	0.05	0.15	0.03	102.38
134	64.52	23.76	8.74	1.07	3.76	0.00	0.00	0.02	0.19	0.09	102.15
135	64.98	23.21	8.82	1.29	3.56	0.13	0.02	0.00	0.15	0.05	102.21
137	63.52	23.76	8.81	1.13	3.64	0.13	0.00	0.00	0.15	0.07	101.21
138	62.85	23.99	8.83	1.30	3.72	0.13	0.00	0.00	0.17	0.02	101.01
139	63.57	23.66	9.10	1.31	3.65	0.04	0.01	0.00	0.15	0.03	101.52
140	64.99	23.45	8.80	1.31	3.61	0.00	0.00	0.06	0.17	0.05	102.44
142	64.59	23.79	8.92	1.08	3.77	0.00	0.00	0.09	0.15	0.04	102.43
176	67.48	19.71	4.57	9.71	0.29	0.15	0.00	0.04	0.15	0.04	102.14
179	66.94	19.91	4.19	10.22	0.26	0.00	0.00	0.00	0.17	0.03	101.72
Mean	65.06	20.93	6.15	6.72	1.61	0.10	00.0	0.03	0.14	0.03	100.78
Std	1.37	2.14	2.15	4.50	1.85	0.09	0.01	0.05	0.10	0.07	1.13
Biotite wt% oxides											
145	37.43	13.70	0.63	8.88	0.07	0.00	10.51	4.69	19.83	0.72	96.46
146	36.85	13.25	0.54	8.60	0.11	0.12	9.96	4.15	22.64	0.78	97.00

Table 2. (Continued.)

Sample	Si	Al	Na	K	Ca	Ba	Mg	Ti	Fe	Mn	Sum
Biotite wt% oxides (continued)											
147	35.33	12.62	0.52	8.41	0.07	0.00	9.65	4.03	25.96	0.70	97.29
148	36.14	12.96	0.50	8.62	0.06	0.00	9.67	4.18	24.35	0.81	97.29
149	34.52	12.51	0.45	8.23	0.08	0.00	8.85	4.26	26.44	0.73	96.09
151	35.64	13.15	0.52	8.76	0.06	0.11	9.77	4.09	22.46	0.72	95.30
153	38.04	13.62	0.57	8.83	0.05	0.10	10.83	4.23	19.81	0.72	96.80
154	38.03	13.77	0.61	8.92	0.06	0.18	11.22	4.36	19.11	0.73	96.99
155	36.20	13.24	0.54	8.86	0.06	0.03	10.27	4.25	22.82	0.74	97.01
Mean	36.46	13.20	0.54	8.68	0.07	0.06	10.08	4.25	22.60	0.74	96.69
Std	1.22	0.45	0.06	0.24	0.02	0.07	0.71	0.19	2.66	0.03	0.65
Magnetite wt% oxides											
11	0.17	1.34	0.05	0.03	0.08	0.03	0.04	13.05	77.77	0.87	93.43
12	0.23	0.80	0.00	0.02	0.16	0.07	0.02	2.96	86.21	1.39	91.86
13	0.14	0.69	0.00	0.02	0.40	0.11	0.00	3.04	88.01	0.98	93.39
14	0.19	0.52	0.00	0.00	0.04	0.11	0.03	7.51	82.30	0.77	91.47
15	0.68	0.86	0.00	0.00	0.13	0.00	0.15	3.80	86.54	1.10	93.26
21	0.48	1.80	0.03	0.03	0.04	0.14	0.13	5.22	83.07	1.39	92.33
22	0.22	1.75	0.00	0.00	0.06	0.08	0.00	5.00	82.81	1.21	91.13
23	0.33	1.59	0.00	0.02	0.04	0.04	0.00	5.14	83.21	1.15	91.52
24	0.50	1.83	0.00	0.04	0.05	0.00	0.00	4.18	85.17	1.10	92.87
25	0.44	2.41	0.00	0.06	0.02	0.00	0.00	3.95	83.23	1.04	91.15
29	0.42	1.32	0.04	0.06	0.04	0.00	0.02	15.51	74.57	2.04	94.02
Mean	0.35	1.36	0.01	0.03	0.10	0.05	0.04	6.31	82.99	1.19	92.40
Std	0.17	0.59	0.02	0.02	0.11	0.05	0.05	4.17	3.89	0.34	1.03
Matrix wt% oxides											
173	78.70	11.64	2.36	6.06	0.16	0.00	0.00	0.11	0.31	0.03	99.37
174	76.26	12.91	2.89	6.40	0.21	0.00	0.12	0.15	0.78	0.05	99.77
175	89.00	7.49	1.88	3.44	0.17	0.00	0.02	0.15	0.33	0.02	102.50
Quartz wt% oxides											
156	98.35	0.34	0.00	0.01	0.00	0.04	0.02	0.00	0.07	0.00	98.83
157	99.16	0.25	0.00	0.00	0.00	0.07	0.00	0.09	0.00	0.03	99.60
158	99.63	0.27	0.00	0.00	0.01	0.00	0.00	0.09	0.04	0.00	100.04
159	99.85	0.67	0.02	0.01	0.00	0.13	0.00	0.05	0.11	0.05	100.89
160	99.99	0.29	0.00	0.03	0.02	0.00	0.00	0.02	0.05	0.01	100.89
161	97.97	0.51	0.02	0.02	0.00	0.00	0.00	0.11	0.08	0.07	98.78
162	99.99	0.55	0.02	0.00	0.01	0.08	0.00	0.12	0.08	0.02	101.09
163	98.03	0.45	0.00	0.03	0.00	0.05	0.00	0.14	0.06	0.05	98.81
164	99.99	0.27	0.00	0.02	0.00	0.00	0.00	0.10	0.04	0.07	100.76
165	99.61	0.27	0.00	0.02	0.00	0.18	0.00	0.02	0.10	0.03	100.23

Few secondary minerals were produced by the hydrothermal alteration of the tuff at 150°C following more than 300 days of interaction. The dominant run product was a hydrated Ca-aluminosilicate, most probably the zeolite dachiardite. An attempt was made to pluck one of the crystal aggregates from the surface of the wafer for XRD identification using single-crystal camera techniques, but it was unsuccessful because the run products were simply too small and

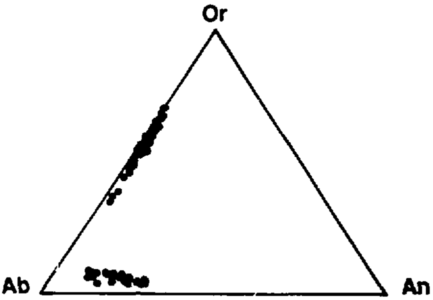

Figure 2. Post-test composition of coexisting feldspars (mole %) plotted in the ternary albite (Ab)-anorthite (An)-orthoclase (Or) following experiment DB13, in which a polished wafer of Tpt B-1 1232 was reacted with J-13 water at 150°C for 304 days.

too rare. Thus, the identity of the run products may only be inferred from EDS spectra and morphology, although in this case the evidence is fairly strong.

As can be seen in Fig. 3, the only secondary mineral produced in experiment DB13 (150°C for 304 days) looks identical to the dominant secondary mineral (dachiardite) produced in experiment DB9 (250°C for 64 days) (see Knauss and Beiriger, 1984b; Knauss et al., 1985b). It displays the same forms and characteristic faces. Moreover, as seen in the collected EDS spectra shown in Fig. 4 and the semiquantitative analyses based on these spectra (Table 3), the composition is essentially the same. A careful examination of the wafer's surface showed that only a few crystal clusters of zeolite had formed and that the surface was otherwise devoid of the poorly crystalline material (clays) found on wafers that were reacted for shorter time periods at 150°C.

DB12 Experiment (90°C)

Experiment DB12 was identical to experiment DB13 except that the run temperature was 90°C instead of 150°C. The results of the fluid analyses taken at 90°C are given in Table 4, and the results are plotted vs time in Fig. 5.

It is apparent that the solution composition had not reached any sort of steady state even after 304 days of interaction with the rock at this low temperature. The Si concentration continued to increase throughout the experiment and, in the last sample collected, was still slightly below cristobalite solubility (50 ppm) (Fournier and Rowe, 1962). Within the limits of uncertainty, the Na concentration was relatively unchanged and the Ca, following a slight increase during the first 60 days, returned to about the starting concentration and remained at that level throughout the experiment. Notably, the Ca was unchanged in the quench (day 304) sample, which differed from the DB13 results for Ca during the quench of the vessel. There was a detectable decrease in the Mg concentration and pH during the experiment, with the most rapid change occurring in the first week. The K concentration showed the same initial spike over the first few samples; this was followed by a decrease, as seen at the higher temperature, although the K then slowly increased throughout the rest of the 90°C experiment. The marked decrease in K was again seen in the quench sample, suggesting a retrograde reaction with the solid. The Al concentration at 90°C did not display a prominent spike over the first few samples but did increase during the run and then decrease slightly. There was no indication in the quench Al concentration of retrograde interactions. Within the measurement uncertainty, the anion concentrations were relatively constant throughout the run and were similar to the initial J-13 water concentrations.

The results of the post-test SEM/EMP analyses of primary phases on the wafer from experiment DB12 are given in Table 5. Analyses of phenocrysts of alkali feldspar, plagioclase, quartz, and magnetite, as well as analyses of the matrix, are included. The calculated and member feldspar compositions (Ab-Or-An) are represented in the ternary diagram shown as Fig. 6. Note that the plagioclase ranges from An_{14} to An_{24}, with the median value being about An_{18}, and that the potassium feldspar compositions range from Or_{34} to

Table 3. Semi-quantitative analyses based on EDS spectra of dachiardite produced in experiments DB13 (150°C for 304 days) and DB9 (250°C for 64 days).

Oxide	DB13 (150°C)	DB9 (250°C)
Na_2O	0.000	0.000
K_2O	0.000	0.008
CaO	0.074	0.058
MgO	0.000	0.000
Al_2O_3	0.092	0.102
SiO_2	0.832	0.830

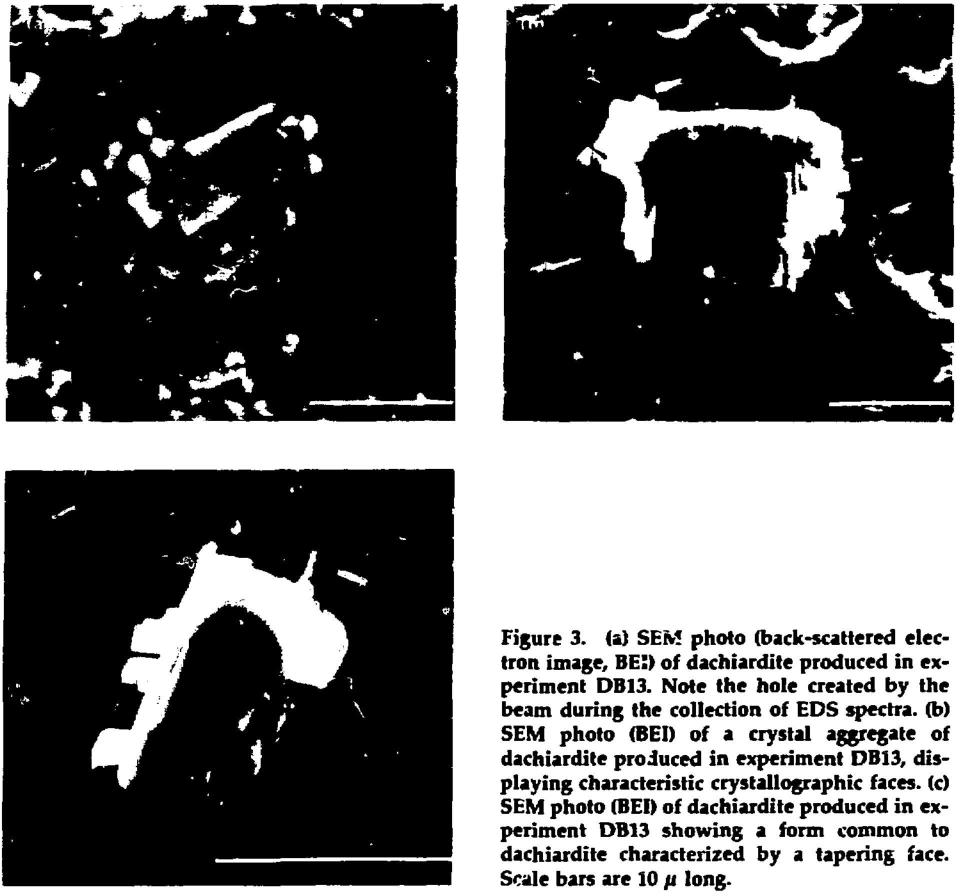

Figure 3. (a) SEM photo (back-scattered electron image, BEI) of dachiardite produced in experiment DB13. Note the hole created by the beam during the collection of EDS spectra. (b) SEM photo (BEI) of a crystal aggregate of dachiardite produced in experiment DB13, displaying characteristic crystallographic faces. (c) SEM photo (BEI) of dachiardite produced in experiment DB13 showing a form common to dachiardite characterized by a tapering face. Scale bars are 10 μ long.

Or_{67}, with a median value of about Or_{60}. Although a few biotite phenocrysts were present on wafer DB12, none of these was amenable to analysis because they were extensively altered to oxides. The post-test-measured bulk compositions were similar to those of the unreacted wafer. The total wafer weight loss was 0.0039 g, or 0.17% of the original wafer weight.

No secondary minerals were observed on wafer DB12 during the post-test SEM examination and EMP analyses. In fact, the only evidence that the wafer itself had been altered was the highlighting of twin lamellae on a few of the alkali feldspar phenocrysts. At 90°C, the rates of reaction were slow and the extent of reaction minor, even after more than 300 days of interaction.

Discussion

The long-term experiments reported here were prompted by the results of a series of short-term hydrothermal rock/water interaction experiments we carried out previously (Oversby, 1984a,b and 1985; Knauss and Beiriger, 1984a; Knauss et al., 1985a). In those experiments we

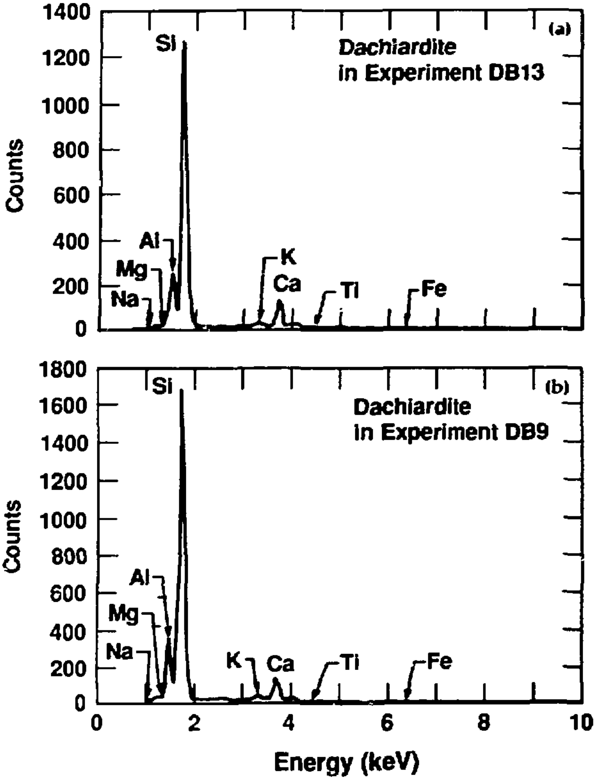

Figure 4. (a) EDS spectra collected on a dachiardite crystal produced in experiment DB13. (b) EDS spectra collected on a dachiardite crystal produced in experiment DB9.

Table 4. Cation analyses,[a] anion analyses, and pH in fluid samples taken during experiment DB12 in which a polished wafer of Tpt G-1 1232 was heated with J-13 water at 90°C and 50 bars for 303 days.

	Fluid composition (ppm)											pH
Sample	Al	Si	Ca	K	Mg	Na	HCO_3[c]	F	Cl	NO_3	SO_4	(25°C)
DB12-0	0.006[b]	31.0	14.0	5.0	2.05	49.5	104[d]	2.1	6.8	8.6	17.6	7.68
DB12-8	0.056[b]	31.5	14.5	6.0	1.60	46.5	129[d]	2.4	7.1	9.2	19.7	7.39
DB12-15	0.066[b]	31.5	14.0	6.5	1.60	51.0	—[e]	2.5	7.4	9.0	19.5	7.50
DB12-30	0.076[b]	33.0	15.0	6.5	1.60	46.7[b]	147	2.5	7.1	9.8	19.2	7.25
DB12-60	0.046[b]	41.0	15.5	5.5	1.65	52.5	117	2.4	7.0	9.6	18.5	7.14
DB12-121	0.036[b]	41.3[b]	13.8	5.5	1.30[b]	50.5	128	2.2	7.2	8.4	18.6	7.26
DB12-241	0.19	45.8	13.4	6.0	1.36	46.5	144	2.0	6.9	10.5	18.5	7.12
DB12-303	0.21	47.4	13.9	6.6	1.23	46.9	124	2.2	7.5	8.6	20.8	7.19
DB12-304	0.20[b]	47.2	13.9	5.0	1.31	43.9	112	2.2	7.4	9.1	20.6	6.57

[a] Monochrometer unit.

[b] Polychrometer unit.

[c] IR CO_2 analyses.

[d] IC HCO_3 analyses.

[e] No analysis.

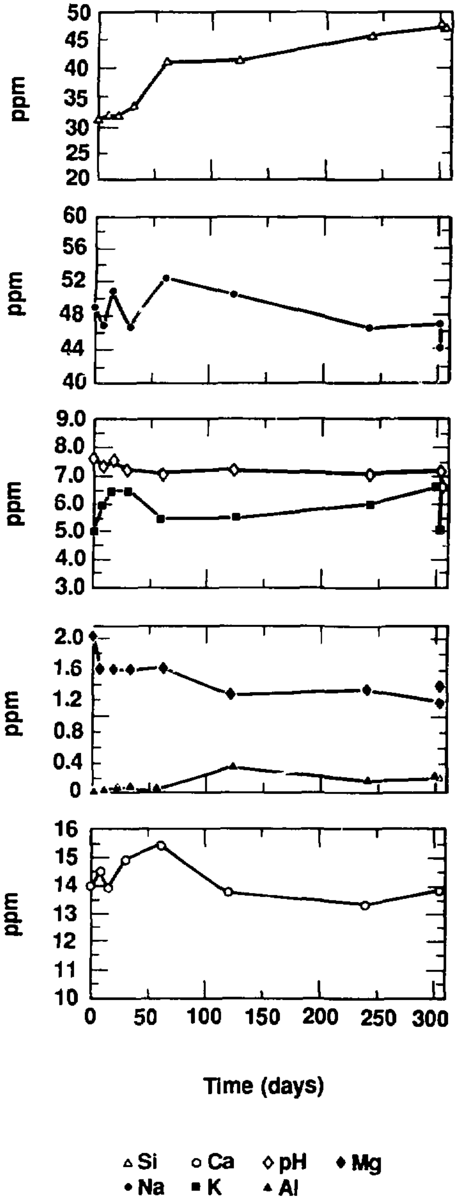

Figure 5. Fluid composition (ppm) vs time (days) for J-13 water reacted with a solid polished wafer of drillcore sample Tpt G-1 1232 at 90°C for 304 days in experiment DB12.

studied the composition of fluid that might be available to contact, corrode, and mobilize (or immobilize) radionuclides contained in a waste package emplaced in a potential repository at Yucca Mountain, Nevada. Early short-term experiments were conducted in Teflon-lined vessels at low temperatures (150°C or less) and used both crushed tuff and solid wafers of tuff (e.g., Oversby, 1984a,b and 1985; Knauss and Beiriger, 1984a). Subsequent short-term experiments were run in Dickson-type, gold-bag rocking autoclaves using either crushed tuff (Knauss et al., 1985a) or solid wafers of tuff (Knauss et al., 1985b). None of these experiments ran for more than a few months, and, from the results obtained, it is clear that a steady state was not reached for the concentration of all dissolved constituents. Also, without experiments of longer duration, it would not be possible to determine if the acceleration of reaction rates by increasing surface area produced a solution whose composition was the same as one that evolved more slowly in experiments with lower surface-area/volume ratios.

Attempts to model some of the short-term rocking autoclave experiments with solid wafers of tuff (Delany, 1985) were fairly successful in reproducing the evolving aqueous phase composition, but the predicted product phases did not always match exactly those phases observed in post-test examinations of the wafer surface. Because the version of the reaction progress code used did not account for precipitation kinetics, the possibility existed that a kinetic inhibition of the precipitation delayed the appearance of the missing product phases and that longer experiments would be required to observe them. These and other concerns prompted the long-term experiments that are the subject of this report.

To address these concerns, we compared the compositions of fluids produced in the long-term rocking autoclave experiments with those produced in the short-term rocking autoclave experiments using both crushed tuff and solid wafers of tuff. The results for the elements Si, Na, Ca, Mg, K, and Al and for pH are plotted vs absolute time in Fig. 7 for the experiments at 150°C and in Fig. 8 for those at 90°C. The concentrations are plotted vs absolute time because they do not scale in any consistent way to a surface-area/volume-normalized reaction parameter. The crushed tuff experiments, however, do have a BET surface-area/volume ratio that is about 10 to 15 times higher than that of the solid wafer experiments (the mass ratio difference is approximately three to four times higher for the crushed tuff-vs-wafer experiments). The crushed

Table 5. Results of post-test SEM/EMP analyses of primary phases on the wafer from experiment DB12 for feldspar, magnetite, quartz, and matrix.

Sample	Si	Al	Na	K	Ca	Ba	Mg	Ti	Fe	Mn	Sum
Feldspar wt% oxides											
1	65.10	19.76	4.83	9.56	0.33	0.00	0.00	0.00	0.10	0.00	99.68
3	65.13	19.73	4.15	10.36	0.19	0.16	0.00	0.00	0.10	0.00	99.82
4	65.76	19.96	4.22	10.41	0.23	0.21	0.00	0.08	0.11	0.00	100.98
5	65.89	19.69	4.27	10.20	0.21	0.22	0.00	0.00	0.12	0.00	100.60
6	64.83	19.70	4.51	10.22	0.23	0.00	0.00	0.07	0.16	0.05	99.77
7	66.46	19.69	4.22	10.37	0.21	0.00	0.00	0.00	0.08	0.05	101.08
8	66.16	19.81	5.03	9.40	0.23	0.10	0.00	0.00	0.14	0.02	100.89
9	65.45	19.74	4.59	9.81	0.25	0.11	0.00	0.00	0.13	0.02	100.10
10	65.58	19.95	4.56	9.75	0.21	0.05	0.00	0.06	0.13	0.03	100.32
11	65.02	19.47	4.47	10.15	0.24	0.05	0.00	0.00	0.00	0.03	99.43
12	65.47	19.91	4.30	10.43	0.22	0.23	0.00	0.00	0.00	0.00	100.56
13	65.20	19.48	4.55	10.12	0.26	0.07	0.00	0.00	0.00	0.03	99.71
14	65.57	19.72	4.36	10.47	0.23	0.20	0.00	0.00	0.00	0.03	100.58
15	66.45	19.63	4.40	10.26	0.26	0.12	0.00	0.00	0.00	0.04	101.16
16	65.52	19.86	5.02	10.29	0.22	0.07	0.00	0.00	0.06	0.02	101.06
17	66.03	20.05	4.36	10.36	0.22	0.00	0.00	0.06	0.08	0.00	101.16
18	66.43	20.33	4.42	10.31	0.23	0.00	0.00	0.06	0.08	0.05	101.91
19	65.84	20.05	4.51	10.35	0.27	0.18	0.29	0.00	0.08	0.00	101.57
20	65.42	19.87	4.36	10.43	0.27	0.10	0.00	0.03	0.14	0.24	100.86
21	65.57	19.77	4.26	10.59	0.23	0.02	0.00	0.00	0.11	0.00	100.55
22	65.74	20.00	4.36	10.25	0.25	0.08	0.00	0.00	0.12	0.00	100.84
23	65.12	19.52	4.08	10.54	0.17	0.00	0.00	0.06	0.06	0.06	99.61
24	65.56	19.73	4.44	10.64	0.18	0.00	0.00	0.00	0.11	0.02	100.68
25	64.82	20.11	4.49	10.51	0.18	0.07	0.00	0.00	0.08	0.00	100.26
26	65.70	19.53	4.26	10.42	0.16	0.00	0.00	0.00	0.05	0.00	100.12
27	65.93	19.73	4.33	10.29	0.18	0.10	0.00	0.04	0.10	0.04	100.74
28	66.53	19.93	4.36	10.49	0.21	0.14	0.00	0.04	0.08	0.03	101.81
29	66.44	19.91	5.04	10.39	0.20	0.15	0.00	0.01	0.09	0.00	102.23
30	66.06	20.01	4.38	10.41	0.24	0.07	0.00	0.00	0.73	0.02	101.92
31	65.97	19.85	[illegible]	10.19	0.24	0.07	0.00	0.00	0.08	0.00	100.62
32	66.17	19.30	4.33	10.58	0.20	0.05	0.00	0.02	0.09	0.00	100.74
33	65.92	19.15	4.19	10.49	0.16	0.19	0.00	0.08	0.14	0.00	100.32
34	65.82	19.56	4.54	10.33	0.17	0.07	0.00	0.07	0.10	0.00	100.66
35	64.69	20.03	4.24	10.08	0.19	1.35	0.00	0.15	0.14	0.00	100.87
36	64.66	20.58	4.31	9.79	0.21	1.54	0.00	0.03	0.10	0.00	101.22
37	65.63	20.28	4.18	9.72	0.20	1.12	0.00	0.08	0.07	0.00	101.28
38	64.86	20.29	4.03	10.26	0.20	1.62	0.00	0.00	0.00	0.00	101.26
39	64.69	20.19	4.37	9.68	0.27	1.39	0.00	0.00	0.06	0.00	100.65
40	65.14	20.23	4.40	9.84	0.25	1.41	0.00	0.00	0.07	0.00	101.34
41	65.30	19.72	4.44	9.59	0.18	1.07	0.00	0.00	0.07	0.00	100.37
42	64.87	20.07	4.15	10.27	0.18	0.95	0.00	0.00	0.03	0.00	100.52
43	65.70	20.04	4.64	9.48	0.19	0.73	0.00	0.00	0.06	0.00	100.84
44	65.79	20.37	4.43	9.84	0.21	1.24	0.00	0.00	0.08	0.03	101.99
45	66.15	19.45	4.09	10.31	0.09	0.00	0.00	0.00	0.03	0.00	100.12
46	66.38	19.58	3.98	11.04	0.09	0.00	0.00	0.07	0.05	0.00	101.19
47	67.26	19.66	3.66	11.26	0.08	0.01	0.00	0.00	0.02	0.00	101.95
48	67.27	19.54	3.88	10.43	0.11	0.00	0.00	0.00	0.05	0.02	101.30
49	67.58	19.00	4.25	9.84	0.08	0.00	0.00	0.04	0.06	0.04	100.89
52	67.02	19.52	4.17	10.53	0.06	0.05	0.00	0.02	0.07	0.00	101.44
53	66.43	19.50	5.10	9.11	0.09	0.00	0.00	0.00	0.08	0.04	100.35

Table 5. (Continued.)

Sample	Si	Al	Na	K	Ca	Ba	Mg	Ti	Fe	Mn	Sum
Feldspar wt% oxides (continued)											
54	66.58	19.60	4.24	10.01	0.10	0.00	0.00	0.07	0.08	0.00	100.68
55	67.34	19.71	3.80	11.05	0.03	0.00	0.00	0.00	0.11	0.00	102.04
56	66.84	19.86	4.07	10.40	0.19	0.03	0.00	0.07	0.14	0.15	101.75
57	65.87	20.14	6.08	7.60	0.52	0.00	0.00	0.00	0.17	0.00	100.38
58	67.03	19.17	4.91	8.89	0.17	0.00	0.04	0.04	0.23	0.00	100.48
59	66.67	18.92	4.13	9.73	0.05	0.00	0.00	0.03	0.10	0.00	99.63
60	66.74	19.22	4.48	10.07	0.07	0.00	0.00	0.00	0.07	0.00	100.65
61	67.44	19.21	4.56	9.64	0.10	0.09	0.00	0.02	0.04	0.00	101.10
62	66.55	19.80	4.32	9.84	0.13	0.04	0.00	0.07	0.05	0.00	100.80
63	66.75	19.43	4.88	9.11	0.18	0.00	0.00	0.02	0.05	0.00	100.42
64	66.67	19.54	4.27	9.94	0.11	0.00	0.00	0.00	0.07	0.02	100.71
65	66.43	19.07	4.28	10.11	0.14	0.10	0.00	0.09	0.08	0.05	100.35
66	65.64	19.83	6.42	6.65	0.63	0.00	0.00	0.10	0.13	0.00	99.40
67	66.73	19.49	4.21	10.29	0.14	0.03	0.00	0.00	0.32	0.00	101.21
68	66.50	19.41	4.42	10.61	0.11	0.09	0.00	0.01	0.12	0.00	101.27
69	66.53	19.34	3.54	11.06	0.10	0.04	0.00	0.00	0.15	0.00	100.76
70	66.89	19.65	4.50	9.83	0.11	0.16	0.00	0.04	0.15	0.03	101.36
71	65.52	19.16	4.05	9.91	0.13	0.14	0.00	0.00	0.23	0.01	99.15
72	66.75	19.07	4.89	9.11	0.27	0.00	0.00	0.08	0.32	0.00	100.49
73	66.58	19.32	5.06	9.07	0.29	0.00	0.00	0.05	0.22	0.05	100.64
74	66.24	19.62	4.81	9.20	0.35	0.00	0.00	0.02	0.17	0.02	100.43
75	67.40	18.54	3.79	10.15	0.09	0.00	0.00	0.07	0.14	0.07	100.25
76	66.37	19.04	4.37	9.84	0.18	0.00	0.00	0.06	0.11	0.03	100.00
77	65.98	19.05	4.40	9.87	0.09	0.03	0.00	0.00	0.14	0.00	99.56
78	65.67	19.79	5.20	8.85	0.29	0.08	0.00	0.00	0.09	0.00	99.97
79	66.45	19.67	5.04	9.31	0.29	0.16	0.00	0.00	0.04	0.00	100.94
80	66.05	20.23	4.92	9.51	0.35	0.06	0.00	0.00	0.06	0.00	101.18
81	66.31	19.32	4.17	10.64	0.06	0.09	0.00	0.00	0.08	0.00	100.67
82	65.42	19.76	5.11	9.24	0.36	0.00	0.00	0.09	0.06	0.00	100.04
83	66.86	19.98	4.54	10.34	0.17	0.00	0.00	0.05	0.09	0.00	102.03
84	65.99	20.09	4.77	9.51	0.39	0.00	0.02	0.07	0.10	0.00	100.94
85	67.01	18.94	3.71	10.60	0.04	0.00	0.00	0.00	0.13	0.00	100.43
86	66.80	19.25	4.39	10.33	0.09	0.00	0.00	0.03	0.05	0.02	100.96
87	65.87	19.15	4.82	9.64	0.21	0.20	0.00	0.00	0.08	0.00	99.97
88	66.44	19.76	4.63	9.94	0.18	0.21	0.00	0.00	0.12	0.00	101.28
126	63.63	23.26	8.95	0.92	3.55	0.67	0.00	0.02	0.17	0.00	101.17
127	63.22	23.80	8.71	1.15	3.91	0.10	0.00	0.04	0.24	0.00	101.17
128	63.44	23.57	8.75	0.92	3.79	0.05	0.00	0.00	0.21	0.00	100.73
129	63.64	23.47	8.79	1.14	3.69	0.10	0.00	0.04	0.18	0.04	101.09
130	63.48	23.73	8.78	0.92	4.01	0.10	0.00	0.00	0.20	0.00	101.22
131	63.79	23.42	8.80	1.16	3.58	0.11	0.03	0.04	0.13	0.02	101.08
132	63.42	23.27	8.60	1.26	3.60	0.00	0.03	0.05	0.15	0.00	100.38
133	63.66	23.64	8.90	1.09	3.49	0.06	0.02	0.06	0.13	0.00	101.05
134	62.78	23.72	8.64	0.89	4.24	0.00	0.03	0.00	0.43	0.03	100.76
135	62.83	24.36	8.48	0.89	4.49	0.00	0.20	0.06	0.13	0.00	101.44
136	63.60	23.06	8.92	1.23	3.31	0.15	0.00	0.09	0.14	0.00	100.50
137	61.74	24.93	8.58	0.72	4.77	0.07	0.00	0.09	0.17	0.00	101.07
138	62.71	24.29	8.35	0.97	4.21	0.07	0.00	0.01	0.28	0.00	100.89
139	62.43	24.70	8.51	0.87	4.56	0.12	0.14	0.09	0.15	0.00	101.57
140	62.51	24.38	8.19	1.11	4.34	0.12	0.00	0.04	0.06	0.00	100.75
141	64.01	23.56	9.12	1.10	3.48	0.20	0.00	0.04	0.18	0.00	101.69

Table 5. (Continued.)

Sample	Si	Al	Na	K	Ca	Ba	Mg	Ti	Fe	Mn	Sum
Feldspar wt% oxides (continued)											
142	64.57	23.43	8.83	1.20	3.57	0.14	0.00	0.00	0.17	0.00	101.91
143	64.00	23.24	9.21	0.94	3.51	0.07	0.00	0.04	0.18	0.00	101.19
144	64.65	23.67	9.16	0.79	3.60	0.22	0.00	0.06	0.17	0.00	102.32
145	64.70	23.31	8.86	1.33	3.30	0.05	0.38	0.01	0.11	0.00	102.05
146	63.95	23.72	9.12	1.04	3.37	0.03	0.00	0.00	0.16	0.02	101.41
147	64.26	23.91	8.86	0.96	4.05	0.00	0.00	0.00	0.16	0.00	102.20
148	64.60	23.94	9.21	0.72	3.65	0.06	0.00	0.03	0.25	0.00	102.46
149	63.67	23.48	9.15	0.82	3.61	0.04	0.00	0.00	0.19	0.05	101.01
150	63.71	23.84	9.07	1.10	3.71	0.14	0.00	0.03	0.20	0.01	101.81
151	63.50	23.34	9.13	1.18	3.68	0.00	0.00	0.01	0.17	0.00	101.01
152	64.17	23.58	9.18	0.87	3.46	0.06	0.00	0.03	0.14	0.01	101.50
153	64.16	23.55	9.28	0.80	3.40	0.00	0.00	0.06	0.17	0.02	101.44
154	63.74	23.83	8.82	1.05	3.67	0.11	0.00	0.06	0.17	0.02	101.47
155	63.53	23.56	8.66	1.15	3.66	0.00	0.39	0.04	0.13	0.07	101.19
156	63.35	23.54	8.72	1.17	3.65	0.00	0.00	0.02	0.16	0.03	100.64
157	63.65	23.99	8.94	1.20	3.89	0.00	0.00	0.01	0.13	0.04	101.85
158	64.36	23.34	8.70	1.18	3.62	0.00	0.00	0.06	0.14	0.05	101.45
159	64.22	23.74	8.61	1.13	3.65	0.06	0.00	0.07	0.12	0.03	101.63
160	63.57	23.45	8.87	1.27	3.85	0.00	0.00	0.03	0.15	0.06	101.25
161	64.52	23.53	8.82	1.19	3.76	0.00	0.26	0.03	0.19	0.02	102.32
162	64.22	23.75	9.05	1.18	3.67	0.06	0.00	0.00	0.17	0.03	102.13
163	63.74	23.86	8.63	1.24	3.68	0.04	0.00	0.00	0.14	0.03	101.36
164	63.94	23.64	8.99	1.18	3.63	0.11	0.39	0.03	0.14	0.03	102.08
165	64.70	23.20	9.06	1.43	2.97	0.00	0.00	0.00	0.15	0.00	101.51
166	63.60	23.49	8.94	1.16	3.59	0.07	0.00	0.00	0.17	0.04	101.06
167	63.10	24.63	8.64	1.04	4.04	0.09	0.02	0.00	0.13	0.00	101.69
168	63.46	23.86	8.68	0.97	3.97	0.07	0.00	0.00	0.15	0.00	101.16
170	63.96	23.25	8.97	1.25	3.56	0.25	0.00	0.00	0.14	0.06	101.44
171	64.24	23.63	8.76	1.25	3.65	0.00	0.00	0.00	0.18	0.02	101.73
172	63.63	23.88	8.82	1.12	3.76	0.16	0.01	0.00	0.12	0.05	101.55
173	64.03	23.41	8.97	1.22	3.52	0.00	0.00	0.00	0.19	0.04	101.38
Mean	65.37	21.00	5.98	6.82	1.44	0.16	0.02	0.03	0.14	0.02	100.97
Std	1.79	2.12	2.15	4.30	1.71	0.33	0.07	0.04	0.13	0.03	0.69
Magnetite wt% oxides											
89	0.19	0.51	0.06	0.03	0.05	0.15	0.12	18.14	66.95	0.88	87.08
91	0.22	0.26	0.11	0.02	0.03	0.00	0.12	3.88	83.47	1.64	89.75
92	0.19	0.29	0.05	0.03	0.04	0.01	0.08	4.85	82.28	1.11	88.93
93	0.20	0.17	0.04	0.01	0.06	0.00	0.08	6.85	79.01	1.40	87.82
94	0.59	0.54	0.00	0.05	0.35	0.05	0.23	0.94	76.94	6.72	86.41
95	0.20	0.49	0.00	0.04	0.02	0.07	0.19	0.89	76.97	7.03	85.90
97	0.23	0.52	0.06	0.06	0.04	0.17	0.17	3.65	75.24	7.45	87.54
98	0.08	0.84	0.00	0.06	0.02	0.18	0.00	3.00	80.05	4.05	88.28
99	0.00	0.85	0.07	0.00	0.00	0.00	0.00	3.06	82.03	3.97	89.98
100	0.31	0.82	0.04	0.02	0.25	0.02	0.03	3.55	80.38	3.98	89.40
101	0.00	0.91	0.04	0.00	0.00	0.12	0.00	7.73	76.65	3.96	89.41
102	0.00	1.32	0.06	0.00	0.00	0.00	0.07	3.80	80.02	4.01	89.28
103	0.00	0.84	0.03	0.00	0.00	0.00	0.07	2.59	80.18	4.37	88.07

Table 5. (Continued.)

Sample	Si	Al	Na	K	Ca	Ba	Mg	Ti	Fe	Mn	Sum
Magnetite wt% oxides (continued)											
104	0.18	1.04	0.00	0.00	0.00	0.07	0.00	3.59	81.24	1.48	87.60
105	0.22	0.86	0.00	0.00	0.03	0.00	0.00	1.56	84.50	1.69	88.86
106	0.13	0.75	0.00	0.02	0.04	0.00	0.00	1.08	83.47	1.82	87.31
107	0.10	0.84	0.00	0.01	0.00	0.00	0.00	1.82	84.14	1.34	88.25
108	0.07	1.31	0.00	0.00	0.04	0.07	0.00	2.93	82.75	1.20	88.37
109	0.13	0.94	0.00	0.00	0.00	0.03	0.00	0.81	85.21	0.74	87.86
110	0.12	1.12	0.00	0.00	0.00	0.04	0.00	0.71	85.17	0.68	87.90
111	0.13	0.90	0.04	0.00	0.06	0.00	0.00	0.98	84.07	0.88	87.06
112	0.09	1.10	0.00	0.00	0.02	0.00	0.08	1.89	83.61	1.22	88.01
Mean	0.15	0.79	0.02	0.02	0.05	0.04	0.06	3.56	80.65	2.80	88.14
Std	0.13	0.32	0.03	0.02	0.09	0.06	0.07	3.76	4.24	2.16	1.06
Quartz wt% oxides											
173	64.03	23.41	8.97	1.22	3.52	0.00	0.00	0.00	0.19	0.04	101.38
174	99.16	0.21	0.06	0.02	0.03	0.05	0.00	0.05	0.03	0.02	99.63
175	98.35	0.21	0.08	0.04	0.03	0.10	0.00	0.08	0.03	0.04	98.96
176	99.23	0.03	0.00	0.02	0.02	0.08	0.00	0.08	0.00	0.05	99.51
177	98.17	0.25	0.07	0.02	0.00	0.00	0.00	0.08	0.00	0.02	98.61
178	97.74	0.21	0.12	0.03	0.02	0.10	0.00	0.02	0.00	0.03	98.27
179	99.12	0.25	0.12	0.02	0.03	0.11	0.00	0.00	0.00	0.04	99.69
180	98.19	0.29	0.10	0.02	0.04	0.06	0.00	0.00	0.00	0.02	98.72
181	98.73	0.26	0.09	0.00	0.02	0.03	0.00	0.00	0.04	0.00	99.17
182	98.20	0.30	0.12	0.01	0.03	0.09	0.06	0.03	0.30	0.00	98.84
183	98.16	0.21	0.08	0.02	0.00	0.08	0.00	0.06	0.00	0.01	98.62
Mean	55.20	15.66	4.45	5.05	1.07	0.14	0.02	3.58	13.01	0.49	98.68
Std	27.98	8.98	3.12	4.69	1.57	0.35	0.07	11.67	27.63	1.31	4.78
Matrix wt% oxides											
184	76.15	13.42	3.45	5.81	0.20	0.00	0.17	0.04	0.64	0.06	99.94
185	80.38	11.99	3.12	4.65	0.25	0.00	0.00	0.11	0.41	0.00	100.91
186	75.86	14.15	3.41	6.30	0.19	0.09	0.10	0.31	1.33	0.11	101.85
187	81.40	11.01	4.44	1.22	0.91	0.00	0.03	0.16	1.41	0.04	100.62
188	74.69	14.70	3.35	7.18	0.13	0.03	0.00	0.03	0.25	0.03	100.39
189	76.05	13.58	2.73	6.91	0.18	0.00	0.08	0.02	0.90	0.06	100.51
190	81.28	11.40	4.83	0.68	1.16	0.02	0.01	0.12	0.58	0.02	100.10
191	77.00	13.03	5.27	1.87	1.06	0.00	0.10	0.05	0.78	0.00	99.16
192	80.04	10.47	4.06	1.53	0.84	0.00	0.09	0.06	1.21	0.06	98.36
193	78.30	11.90	2.73	5.84	0.18	0.09	0.02	0.05	0.27	0.14	99.52

tuff was also dry sieved only and undoubtedly contained adhering ultrafines (Holdren and Berner, 1979; Petrovich, 1981; Knauss and Wolery, 1986), while the wafers were largely devoid of such material.

At 150°C the concentration of Si, the dominant cation, clearly shows the effects of the accelerated reaction rates used in the crushed tuff experiments. Within the first two weeks of the crushed tuff experiment, the Si reached the same steady-state concentration (140 ppm) eventually reached by the long-term wafer experiment, whereas the short-term wafer experiment was still increasing in Si at the conclusion of the run. This concentration is very similar in the modeling results obtained by Delany (1985) in a long-term, open-system calculation, a point considered at greater length later in this discussion. The comparison between experiments for the element Na is not so clear cut. The short-term crushed tuff

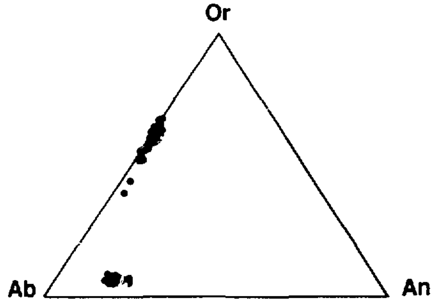

Figure 6. Post-test composition of coexisting feldspars (mole%) plotted in the ternary albite (AB)-anorthite (An)-orthoclase (Or) following experiment DB12, in which a polished wafer of Tpt G-1 1232 was reacted with J-13 water at 90°C for 304 days.

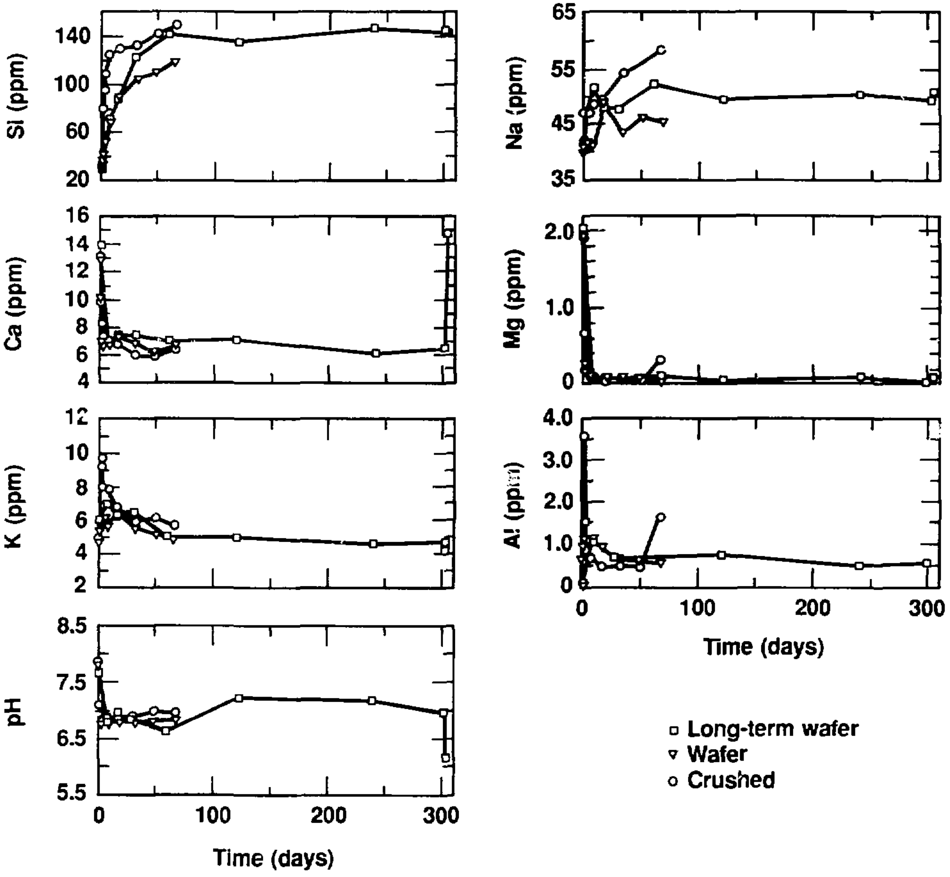

Figure 7. Fluid composition (ppm) vs time (days) for J-13 water reacted with drillcore sample Tpt G-1 1232 at 150°C in short-term experiments with crushed tuff and a solid wafer of tuff and in a long-term experiment with a solid wafer of tuff.

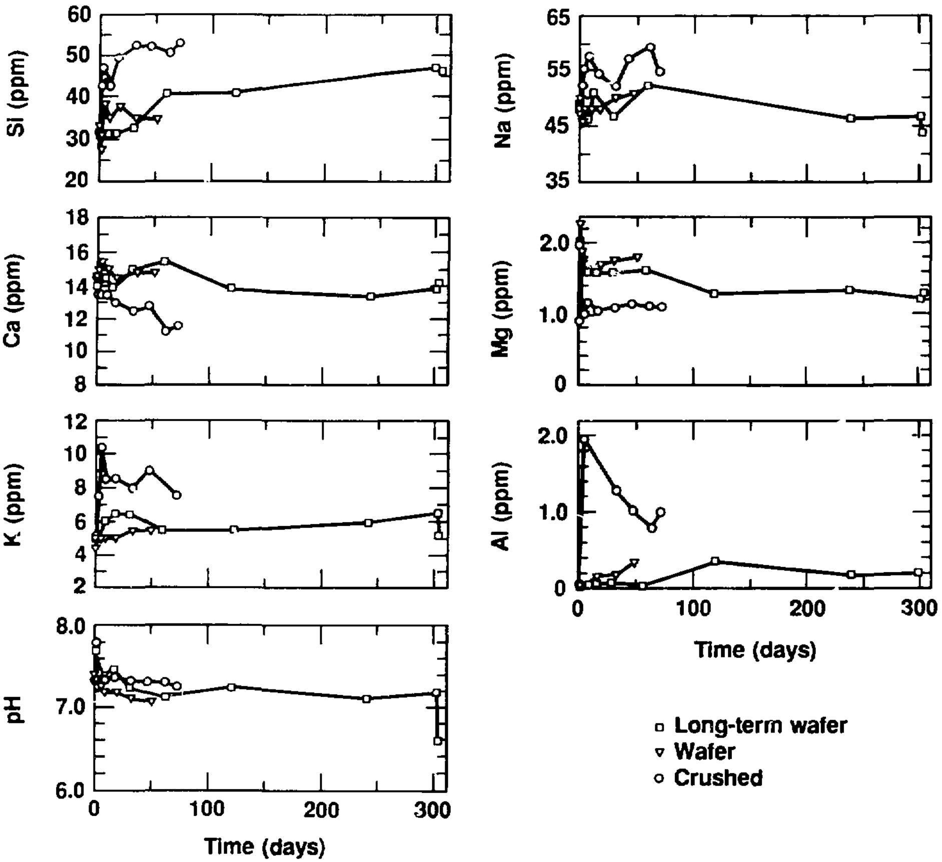

Figure 8. Fluid composition (ppm) vs time (days) for J-13 water reacted with drillcore sample Tpt G-1 1232 at 90°C in short-term experiments with crushed tuff and a solid wafer of tuff and in a long-term experiment with a solid wafer of tuff.

experiment clearly shows Na continuing to rise at the end of the run, while the short-term wafer experiment shows no such continuous increase. The long-term wafer Na concentration is relatively constant after the first few months and is about midway (50 ± 5 ppm) between the other experiments. The trends for Ca and Mg are quite consistent for all three experiments; within the first week or less, they showed an immediate drop to about the same concentration: 6 or 7 ppm for Ca and 0.1 ppm or less for Mg. Unfortunately, no quench sample was taken in the short-term experiments, but the retrograde behavior seen for Ca in the long-term experiment has been observed in other experiments run at 150°C with compositionally equivalent glassy tuff (Knauss, 1986). The trends for K and Al are also very consistent in all three experiments, although the initial pulse in concentration for both elements is accentuated in the crushed tuff experiment. Both elements reached their steady-state concentrations (ignoring the final Al measurement made in the crushed tuff experiment) within two months or less: 4 or 5 ppm for K and about 0.5 ppm for Al.

The quench (25°C) pH also shows a consistent initial drop of almost one log unit in all three experiments, but the long-term results suggest that the pH will then rise on the order of 0.5 log units to a value close to 7.0. The result is a calculated *in situ* (150°C) pH that is mildly alkaline.

The reaction rates at 90°C are so slow that they accentuate the effects produced by surface-area/volume differences between experiments. It is also apparent, even after almost a year of interaction, that the rock/water system has not achieved a steady-state composition. The Si results illustrate both points. In the crushed tuff experiment, for example, the Si concentration rises (somewhat erratically but distinctly more quickly than in the wafer experiments) to a relatively constant value that is slightly higher than the concentration that would be controlled by cristobalite solubility (50 ppm). In the long-term wafer experiment, the Si shows a slow, steady rise toward a similar concentration, but it continues to rise at the conclusion of the run. The Na concentrations in all three experiments are scattered (with only a few exceptions) about a value of 50 ± 5 ppm. The results for Ca and Mg also illustrate the effects of surface-area/volume differences between the experiments. The crushed tuff experiment shows much more pronounced decreases in both the Ca and Mg concentrations than in either the short- or long-term wafer experiments. The concentration of Ca in the long-term wafer experiment remains very close to the initial J-13 water value while that in the crushed tuff experiment drops about 2 or 3 ppm. The concentration of Mg drops rapidly to a steady value of about 1.0 ppm in the crushed tuff experiment and decreases slowly throughout the run for the long-term wafer experiment, eventually reaching 1.2 ppm by the end of the run. The initial spike in the concentrations of both K and Al is seen in the crushed tuff experiment, followed by more or less continuous decreases in concentration for the remainder of the two-month run. In the short-term wafer experiment, no spike is seen for either K or Al and only a slow increase is apparent. In the long-term wafer experiment, the K spike is greatly diminished in size and is spread out over the first month. This spike is followed by a gradual rise to a concentration (7 ppm) that is very similar to the K concentration reached after two months in the crushed tuff experiment. In the long-term wafer experiment, the Al spike is not seen; rather, the concentration rises to about 0.2 ppm and remains at about that level after the first four months. The trends in pH are more consistent, with an initial drop of 0.3 or 0.4 log units followed by a fairly constant quench pH of about 7.2. Again, the result is a calculated *in situ* pH that is only mildly alkaline and relatively less alkaline than that at 150°C.

As mentioned earlier, the modeling calculations made at 150°C for short-term experiments (Delany, 1985) could accurately mimic the evolving fluid composition (with a few minor exceptions) observed in actual experiments, but the predicted product phases differed slightly from those actually observed. The modeled experiments contained Ca-smectite, cristobalite, and Ca-zeolite. Early in the model run, the calcite was briefly supersaturated; as the run progressed, however, it became undersaturated. In the actual experiment, the secondary phases were dominated by clay-like phases and rare gibbsite (or boehmite) and cristobalite. No zeolites were formed in the actual experiment, and all run products were poorly crystalline. However, given more time, the actual experiment might have produced zeolites, if they were kinetically inhibited from precipitating.

Model calculations of a similar system (the only difference being a fixed CO_2 fugacity of $10^{-3.5}$ and a run time of 100 years) show that the system reached steady state at approximately 180 days. The modeled Si concentration was maintained at 146 ppm, which was controlled by the concentrations of Na, K, Ca, and Al in solution together with the presence of clinoptilolite. These modeled results for a long-term run are very similar to observations made in the long-term (304-day) wafer experiment at 150°C. The steady-state Si concentration in the actual experiment was 140 ± 5 ppm, and the dominant secondary mineral observed was a Ca-bearing, Si-rich zeolite that was inferred to be dachiardite. These results are in remarkably good agreement and confirm that there is, in fact, a kinetic inhibition in the precipitation of zeolite. They also support Delany's (1985) suggestion that, given additional data on the thermodynamic and kinetic properties of clays and zeolites and improved solid solution models, one should be able to model the dissolution of tuff accurately using data obtained from relatively short-term laboratory experiments.

Current short-term experiments being conducted in the gold-bag, rocking autoclaves are investigating the alteration of compositionally equivalent glassy Tpt tuff taken from a stratigraphic position directly below the potential repository horizon. Preliminary results (Knauss, 1986) confirm the field observations of Levy (1984) that hydrothermal alteration of the originally glassy tuff results in the formation of the zeolite clinoptilolite. However, the reproducible zeolitization of the devitrified repository rock to produce dachiardite as the dominant secondary mineral (Knauss et al., 1984b, 1985b) underscores the importance of the nature of the starting rock mineralogy and crystallinity (not just composition) in controlling solution composition and, hence, secondary mineralogy. Natural analogues must be selected with caution and cannot entirely replace experiments run with the actual rock and water being investigated.

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