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Reaction of the Topopah Spring Tuff with J-13 Well Water at 90°C and 150°

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REACTION OF THE TOPOPAH SPRING TUFF WITH J-13 WELL WATER AT 90°C and 150°C

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ABSTRACT

The Nevada Nuclear Waste Storage Investigations (NNWSI) Project is examining the suitability of the Topopah Spring Member of the Paintbrush Tuff for potential development as a high level nuclear waste repository. As part of the NNWSI Project, the Lawrence Livermore National Laboratory is responsible for the design and testing of waste packages suitable for use.in the Topopah Spring tuff at Yucca Mountain. Definition of the physical and chemical environment of the waste package is part of that task. This report describes a series of hydrothermal experiments using crushed tuff from the Topopah Spring Member and natural groundwater from Well J-13. The purpose of these experiments is to define the changes in water chemistry that would result from temperature changes caused by emplacement of high level nuclear waste in a repository in the Topopah Spring tuff.

Experiments were conducted at 90 and at 150*C in Teflon-lined reaction vessels. Results are given for four rock to water ratios at 90°C and for reaction times up to 72 days. Data for 150°C cover reaction times up to 64 days and four rock to water ratios. The composition of evaporite deposits contained in the pores of surface outcrop rock material used in these experiments is determined and for two of the data sets rock material was pretreated to remove this "caliche"-type material.

The main conclusion that can be drawn from this work is that-changes in the water chemistry due to heating of the rock-water system can be expected to be very minor. There is no significant source of anions (F^-, C^-, F^-, C^+) $NO_3^$, or $SO_L^{\mathbb{F}}$) in the rock; solution anion compositions after reaction of pretreated rock with J-13 water differ very little from the starting compositions. The major changes in cations are an increase in silica to approximately the level of cristobalite solubility, supersaturation of aluminum followed by slow precipitation, and fairly rapid precipitation of Ca and Mg due to the retrograde solubility of calcite.

INTRODUCTION

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Lawrence Livermore National Laboratory is developing designs for high level nuclear waste packages as part of the Nevada Nuclear Waste Storage Investigations Project (NNWSI). The potential repository site under study by the NNWSI Project is located at Yucca Mountain, Nye County, Nevada; the reference repository horizon is in the Topopah Spring Member of the Paintbrush Tuff. At the proposed repository level the tuff is densely welded and devitrified. The rock consists predominantly of a fine-grained intergrown assemblage of quartz, cristobalite, and alkali. feldspar, with a small proportion of phenocrysts. Phenocryst minerals are alkali feldspar, plagioclase, biotite, and quartz.

Performance objectives for high level nuclear waste packages, as given in lOCFR Part 60, require prediction of the corrosion performance of metals for times up to 1000 years, and of the performance of waste forms for times up to 10,000 years. Successful prediction of performance for these long time periods requires a thorough understanding of the physical and chemical environmental conditions to which the packages will be subjected. Definition of the waste package environment involves detailed description of the preemplacement (ambient) conditions at the proposed repository horizon and determination of the changes that will result after emplacement of waste packages.

There are three major causes of change due to construction of a high level waste repository. The first is the physical changes in the rock unit due to mining of the rock. The second cause of potential environmental change is the radiation field associated with the waste. The third cause of change in the environment is the thermal power of the waste. The thermal output of the waste will heat the surroundings, causing physical and chemical changes in the repository rock and water systems. This report addresses the chemical changes due to heating of repository rock with representative groundwater.

Experiments were conducted using Topopah Spring tuff collected from Fran Ridge, several miles east of Yucca Mountain, and water from well J-13. The location of Yucca Mountain, Fran Ridge, and J-13 are shown in Fig. 1. At the location of J-13, the elevation is lower than at Yucca Mountain, and the Topopah Spring tuff (Tpt) lies below the water table. The Tpt is the major producing horizon for J-13; thus, the water chemistry is probably close to

Figure 1. Map showing the location of Yucca Mountain, Fran Ridge, and well J-13. The outcrop locality for rock samples used in this work is marked Tpt-FR. Tcfb-TS is the outcrop locality for Bullfrog tuff samples. Other localities marked are drill holes.

that which will prevail in the Tpt at Yucca Mountain. At Yucca Mountain, the Tpt lies well above the water table in the unsaturated zone. Samples of water from the Tpt in the unsaturated setting have not yet been obtained, but collection of samples is planned as part of the exploratory shaft testing program. Until samples of water are available from the unsaturated repository horizon, the water from well J-13 has been adopted as a reference water chemistry for NNWSI experimental work.

The expected environmental conditions in the unsaturated zone limit the temperature at which liquid water will exist. For the expected case with no substantial sealing of fractures and pores in the host rock, the local atmospheric boiling point of unconfined water is approximately 95°C. Water contained in pores is held by capillary forces; this water might have a somewhat higher effective boiling point. To bracket the expected temperature range, and to provide data for geochemical modeling studies, temperatures of 90 and 150°C were selected for the hydrothermal experiments.

The experiments described in this report used crushed rock and Teflon-lined reaction vessels. The techniques used required quenching of solutions prior to separation of the rock and water after reaction. Other experiments are in progress that use gold-bag rocking autoclaves, which allow sampling at temperature. Experiments are also in progress or recently completed that use core wafer Tpt tuff, both from outcrop samples and from drill cores. The core wafer experiments allow identification of alteration products formed in the rock and identification of secondary phases formed by precipitation from solution. Results from these experiments will be the subject of separate reports.

EXPERIMENTAL PROCEDURE

WATER PROCUREMENT AND STORAGE

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The water used in these experiments was obtained from well J-13 at the Nevada Test Site. The location of the well is shown in Fig. 1. . A clean plastic-lined 55-gallon drum was rinsed and then filled directly from the well head. The drum was shipped from NTS to LLNL and stored on a loading dock outside Building 281. When water was needed for experiments, a sample from

the drum was siphoned into a one gallon polyethylene bottle. This bottle was used as the main laboratory supply and was refilled from the drum as needed. For easier handling a portion of the water was transferred from the one gallon container into a small plastic squeeze bottle. Both plastic bottles were stored in a closed cupboard when not in use. Storage under dark conditions is necessary to prevent the growth of algae in the water.

ROCK SAMPLE PREPARATION

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Rock samples used in these experiments were collected from an outcrop located at Fran Ridge. The location is shown in Fig. 1; a detailed description of the locality is given by Knauss (1984). Rock samples were shipped from NTS to LLNL where they were trimmed to remove external weathered material, slabbed, and cut into pieces small enough to feed into a small ceramic plate jaw crusher. Details of the rock preparation are given by Knauss (1984).

Preparation for these experiments involved crushing of the small rock pieces using a small ceramic plate jaw crusher to reduce the rock to particle sizes suitable for further crushing in a plate grinder. The plates are made of high purity alumina. Previous experience indicated that this method of crushing introduced less contamination than use of ball mill crushing (Oversby and Knauss, 1983). Following crushing in the plate grinder, the rock powder was sieved through 60 and 100 mesh screens on a mechanical sieve shaker. All material passed the 60 mesh screen (250 micrometer opening size) and of the total of 945 g, 659 g passed through the 100 mesh screen (150 micrometer).

The rock powder was homogenized in a drum mixer for 24 hours and then split using a mechanical splitter. Of the first splits, one was labeled A-1 $(470 \t{g})$ and retained for future use; the second portion was split again. One split (235 g) was retained and labeled $A-2$; the other portion was further split to give two samples of crushed rock weighing 115 g each. These splits were labeled A-3 and A-4. All experiments described in this report used material from split A-4. The surface area of the rock powder measured on split A-2 using BET Ar gas adsorption was 1.15 \pm 0.29 m²/g (Knauss, 1984). Before a sample of rock was taken for use in the experiments, the storage bottle was shaken by hand to homogenize the powder.

PARR BOMB CLEANING PROCEDURE

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All experiments were conducted in Teflon capsules encased in metal containers. Standard Parr Acid Digestion Bombs (model numbers 4745 and 4748) were used. Cleaning of Teflon with acid can result in adsorption of acid into the Teflon and this can lead to release of acid from the capsules during hydrothermal experiments conducted in neutral solutions. When the Teflon capsules are free of surface contamination, water will drain freely from the capsule without appearing to wet the surface. All capsules used in these experiments were either new or had only been used previously in similar rock-water experiments. Absence of surface contamination was confirmed by rinsing the capsules thoroughly with deionized water.

Rinsed capsules were cleaned prior to use by the following procedure:

- (1) Rinse Teflon liner with deionized water three times.
- (2) Rinse Teflon liner with Millipore water.
- (3) Fill Teflon liner 902 full with Millipore water.
- (4) Assemble liner into outer casing and place in Blue M oven at temperature greater than or equal to temperature at which test matrix will be conducted. Leave in oven for two days.
- (5) Remove assembly from oven, cool, disassemble and discard water.
- (6) Repeat steps 3 and 4.
- (7) Remove assembly from oven, cool, disassemble, measure pH of water. Discard water. If pH of water is greater than or equal to 5.0, proceed to start of rock-water test. If pH is less than 5.0, repeat steps 6 and 7 until pH greater than or equal to 5.0 is achieved.

This procedure has been checked by analysis of solutions from water cleaning and from acid cleaning. Results showed that this procedure is adequate so long as similar materials are used in the Teflon capsules during the hydrothermal experiments (Oversby and Knauss, 1983). If the type of materials being tested is changed, a cleaning with dilute HCI is recommended, followed by the cleaning procedure given above.

PRETREATMENT OF ROCK POWDER TO REMOVE READILY SOLUBLE MATERIAL

Previous experience has shown that surface outcrop samples obtained from near Yucca Mountain contain readily soluble material (Oversby and Knauss, 1983). This soluble material appears to be a type of caliche deposit and is not present in material that is protected by a significant amount of overlying rock (Oversby, 1983). The soluble material can be easily removed by shaking the rock powder in water for 2 minutes, allowing the powder to settle, and decanting the solution. A further step of cooking overnight with fresh J-13 water ensures that removal of the soluble material is substantially complete. Pretreatment to remove soluble salts was used for experiments at 90°C and for the rolled experiments at 150 $^{\circ}$ C; rock used in the static experiments at 150 $^{\circ}$ C was not pretreated.

The detailed procedure for pretreatment is

- (1) Weigh rock sample into cleaned Teflon capsule.
- (2) Weigh J-13 water into Teflon capsule; 12 g for small capsule, 48 g for large capsule.
- (3) Close Teflon capsule and shake by hand for 2 minutes.
- (4) Allow sample to settle for approximately one hour; shorter settling times tend to leave fines in suspension.
- (5) Open capsule and decant liquid through 40 filter paper. Filter the solution through 0.1 micron filter. Divide filtered sample into three portions for analysis:
	- a. Anion portion stored in plastic tube;
	- b. Alkalinity portion stored in small glass tube;
	- c. Cation portion add 2 drops of 50% HNO₃ per six mls of solution and store in plastic tube. Securely cover all sample tubes.
- (6) Weigh fresh J-13 water into capsule containing rinsed rock.
- (7) Close capsule, place in outer container, and place assembly into Blue M oven at matrix temperature. Record temperature. Leave assembly in oven overnight. Record start time.
- (8) Remove sample from oven. Record time. Cool in air to temperature where bomb can be opened without difficulty.
- (9) Repeat step 5.

ROCK-WATER TEST MATRIX PROCEDURE

This procedure is written assuming that the pretreatment step was not done. If the pretreatment was applied, this procedure would be started at step 2.

- (1) Weigh rock sample into cleaned Teflon capsule.
- (2) Weigh J-13 water into capsule.
- (3) Close capsule, place in outer container, and place in Blue M oven at required temperature. Record time and temperature.
- (4) Leave at temperature in oven for desired time; periodically check and record temperature.
- (5) At the end of the predetermined reaction interval remove sample assembly from oven and record time and temperature.
- (6) Open bomb as soon as it is cool enough to handle (approximately 50-C), allow contents to cool to room temperature and measure pH with meter calibrated with standard solutions of pH 7 and 10. Following pH measurement, filter solution through 40 filter paper. Collect rock sample on filter paper and leave to dry in air.
- (7) Filter the solution from step 6 through a 0.1 micron filter. Split the sample as described under step 5 of the pretreatment procedure.
- (8) Collect any remaining solids from the Teflon cup onto the filter paper by rinsing the cup with deionized water. After all solids are on the filter paper, cover the paper with-a Kimwipe and allow solids to dry at room temperature. Transfer solids when dry- to a small storage bottle and store as archive sample.
- (9) Submit solution samples for analysis as soon as practicable after collection.

Variations are made to this procedure during the course of some experiments. Those variations will be described in the section on Results and Discussion.

ANALYTICAL METHODS

Cation analyses were performed using an automated inductively-coupled plasma (ICP) spectrometer system. Details of the system are given in Peck .et al. (1979). The ICP system operated in a fixed channel mode giving

simultaneous analysis for 28 elements. The instrument is calibrated with standard solutions, and the calibrations are checked by the operator during a series of analyses by using a "check standard" that is run as an unknown. Samples of J-13 water are regularly submitted along with hydrothermal test solutions; these samples are given identification numbers that make them appear to the ICP operator to be part of the hydrothermal test set. On two occasions sets of multiple J-13 blanks were run on the same day. Data for J-13 control samples are given in Table 1.*

The set of six control blank samples of J-13 that were run on 3/7/84 and the set of four control blank samples that were run on 2/15/84 were each labeled as a related data set, and as such were run consecutively. Agreement among the measured values is excellent for all elements in the 3/7/84 set and for all except Al, Fe, and Na in the $2/15/84$ set. The standard deviation for these samples is lower for all elements except aluminum than that found for samples run on different days.

The rock-water interaction tests described in this report were run on a schedule such that within each experimental matrix all samples that had the same exposure time were run in the same ICP sample set. Thus, for purposes of comparison of results, the standard deviation found for the 2/15/84 and 3/7/84 J-13 samples gives the best indication of the precision of the cation analyses. For samples with different reaction duration, the standard deviation found-for all J-13 cation analyses should be used as the indicator of analytical precision.

Anion analyses were performed using a Dionex Model 2110i Ion Chromatograph with a "fast run" AS4 separator column and an anion fiber suppressor. Detection limits are 0.1 ppm for Cl^- and F^- , and 0.2 ppm for NO_3^- and SO_L^+ . Alkalinity measurements were made using a Technicon Autoanalyzer, an automated version of the standard total alkalinity titration. This method measures the sum of the OH, HCO_{3} , CO_{3} , and any other titratable anions (such as $H_3SiO_4^T$) in solutions. For the pH range and Si concentrations of samples resulting from these experiments the contribution of silica species to alkalinity may become significant for $pH \geq 8.5$.

^{*} Tables appear together and are collected in the section following References.

Data for J-13 analyses used as control blank samples are given in Table 2. For these analyses there is no correlation between standard deviation and whether the samples were run consecutively on the same day or on different days except for a slight trend in the sulfate results. One set of data, run on 8/30/83, gives values that are systematically low for all elements. The reason for this apparent bias in the data is thought to be due to the samples having been run by an inexperienced operator. Data from experimental runs reported in this paper that were also analyzed on 8/30/83 are reported in parentheses to indicate that the results may be biased toward low values.

RESULTS AND DISCUSSION

COMPOSITION OF THE CALICHE COMPONENT

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Rock samples for two of the experimental matrices described in this report were pretreated to remove the readily soluble caliche material as described in the pretreatment procedure. The 90°C test matrix used large capacity Parr bombs with 48 ml of J-13 water and rock sample weights of 0.4, 0.8, 1.6, and 3.2 g. Table 3 gives data for the anion composition of the room temperature rinse solutions and Table 4 the data for the overnight cooked rinse. Sample identification numbers are the run duration in days for the sample following pretreatment and the sample weight in grams. Data given in parentheses in Tables 3 and 4 were run by an inexperienced operator and may be slightly biased toward low values (see section on analytical method for details). Suspect analyses were not used in obtaining averages for the data.

There is no indication of fluoride or carbonate in the caliche component; in fact the concentration of these species in the rinse solutions is slightly lower than the J-13 values indicating a small amount of sorption onto the rock. Chloride, nitrate, and sulfate increase systematically with increasing rock to water ratio. This relationship can be seen clearly in Fig. 2 where the averages for Cl⁻, NO₃, and SO_{$_L$} from Table 3 are plotted against sample weight. The data for a given sample weight show only slight variations in the amount of caliche component, with the exception of the sample labeled 1-3.2. This sample is among the group of suspect analyses and appears to be a

Figure 2. Concentrations of anions in pretreatment room temperature rinse solutions (Table 3) plotted as a function of sample weight.

mislabeled result. Data for the cooked rinse solutions show a small amount of caliche component. This may be caused by incomplete removal of the room temperature rinse solution during the decanting operation.

Two experimental matrices were conducted at 150-C; for one of these, the rock was pretreated to remove caliche material. In this case, small Parr bombs were used, so the experiment was scaled down by a factor of four with respect to both water volume and rock weight. This provides equivalent rock to water ratios for the 0.2 g-12 ml data to the 0.8 g-48 ml data. Data for room temperature rinse solutions are given in Table 5 and for cooked rinse solutions in Table 6. Again, the caliche component is quite consistent in composition and is almost completely removed by the room temperature rinse. Comparison of the average data for 0.2 g-12 ml in Table 5 with the 0.8 g-48 ml data in Table 3, and the other equivalent weight-volume sets, shows that the agreement with respect to the average caliche component between the two experiments is excellent.

Data for cation concentrations in the room temperature rinse solutions for the 90°C pretreatment are given in Table 7 and for the cooked rinse solutions in Table 8. The major cation components in the caliche material are clearly calcium, potassium, and sodium, with perhaps a very small amount of boron. Data for aluminum are somewhat erratic; silicon decreases slightly, indicating minor sorption onto the rock from the J-13 water. The cation component shows the same consistency in composition as was found for the anion component of the caliche. The cation data for sample 1-3.2 are similar to those for other 3.2 g samples. This suggests that the low anion results given in Table 3 for that sample represent a mislabeled sample, and the data should be disregarded.

Cation data for the room temperature pretreatment solutions for the small Parr bomb 150°C runs are given in Table 9, and data for the cooked rinse solutions are in Table 10. Again, the composition of the caliche component is very uniform, and the comparison of data for comparable sample weight - water volume pairs between Tables 9 and 7 shows excellent agreement.

TEST MATRIX RESULTS AT 150°C

The first test matrix was run at 150° C in large capacity Parr bombs. The rock material was not pretreated to remove the caliche component. All runs used 48 ml of J-13 water; rock sample weights used were 0.4, 0.8, 1.6, or 3.2 g. Run durations were 1, 2, 4, 8, 16, 24, 32, 48, or 64 days. Blanks, which consisted of J-13 water without rock, were run for 2, 8, 16, and 32 days. The large Parr bombs are too heavy for use with a roller device in the oven, so the tests were run in a static mode with the bombs placed upright. To avoid caking of the rock powder on the bottom of the Teflon capsule, each bomb was shaken by hand several times a day on Monday, Wednesday, and Friday during the reaction interval. This procedure will be referred to as "static-agitated" to distinguish it from a strictly static mode of operation.

Tables 11 through 16 give data for anions, alkalinity, and pH of the solutions at the conclusion of the reaction time. Data for fluoride in the J-13 blanks (Table 11) show a regular increase with reaction time. The only source of fluoride in the blanks is from the Teflon capsules themselves, since there is no rock in the system. Fluoride concentrations in the sample runs are similar to those in the blanks; there is no indication of fluoride being

contributed to the system by the rock, or of the precipitation of fluoride from solution onto the rock.

Data for the anions chloride, nitrate, and sulfate clearly show the presence of the caliche component. There is no systematic trend in the concentration data for a given sample as a function of reaction time; therefore, the data for each sample weight have been averaged. Tables 12 through 14 also give the average composition of the room temperature rinse pretreatment solutions from the 90C experimental matrix (Table 3). This value is the caliche component plus the contribution due to J-13. The additional caliche component removed during the overnight cooking at 90°C (measured value from Table 4 minus J-13 value) is also given. The total caliche component estimated by adding the Table 3 and Table 4 minus J-13 contributions is less in all cases than the measured values for these samples. However, the differences between measured anions and the estimate of the caliche contribution are fairly small and show the same trends as the caliche component data. This strongly suggests that the increases in anion concentrations seen in these runs are due to caliche material present in slightly greater amounts than was found for the rock samples used in the other two matrices.

Alkalinity data (Table 15) show a systematic decrease as reaction time increases. There is no trend in the data as a function of sample weight. Part of the decrease in alkalinity is due to the precipitation of $(Ca, Mg)CO₃$; however, there also appears to be a loss of alkalinity due to uptake of $CO₂$ by the Teflon reaction vessels (Knauss et al., 1983).

Data for pH (Table 16) show a slight tendency for increase as a function of reaction time; however, there is considerable scatter in the data and the trend is not clear. The pH of the blank samples of J-13 remained essentially constant for heating times up to 32 days.

Tables 17 through 24 contain data for cations from the 150'C static-agitated experiments. Interpretation of results for Ca, K, and Na will be complicated by the presence of the caliche component in the solutions. Aluminum (Table 17) rises rapidly, reaching maximum concentration within one day of reaction, and then slowly decreases as reaction time increases. Concentrations are highest in the solutions where rock to water ratio is lowest. The behavior of aluminum may be modeled by rapid dissolution of feldspar, resulting in supersaturation of aluminum in solution, followed by slow precipitation of gibbsite (Knauss et al., 1983).

The caliche component cation data (Tables 7 through 10) showed no evidence for boron in the readily soluble material. Data for boron (Table 18) in this set of experiments, however, show the pattern of increase in concentration as a function of sample weight that is independent of reaction time. That behavior is the signature of readily soluble material. The reason for the presence of boron in these samples and not in those used for the other two matrices is not understood, given that the same homogenized batch of rock powder was used in all cases.

Iron is present at very low levels in J-13 water. Reaction of the water with Topopah Spring tuff at 150°C produces only very slight increases in iron (Table 19).

Silicon (Table 20) shows an initial rapid rise in concentration followed by a slower approach to steady state values. Solubility of silicon is controlled by cristobalite in the Topopah Spring tuff plus J-13 system, at least for the longest reaction times yet observed (Knauss et al., 1983). For short reaction times the effect of rock to water ratio is clearly seen; increasing the available surface area for dissolution to occur results in a more rapid approach to steady state concentrations.

Calcium data (Table 21) show a pattern that is partly due to the presence of caliche material and partly due to the precipitation of calcite from solution. The contribution of caliche-derived calcium may be estimated by using the data from Table 7. These data are Ca concentrations due to J-13 plus caliche, and are given in Table 21 on the line marked 0 days. If we assume that this estimate is approximately correct, we can conclude that the amount of Ca precipitated rapidly (during first day of reaction) from these solutions depends on the initial concentration of Ca in solution. Further reaction indicates a slow approach to lower steady state concentrations. The final steady state value may be dependent on rock to water ratio in this case, particularly if the presence of the caliche material has influenced the nature of the early precipitated phases. For example, the 1.6 g sample appears to have precipitated 14.4 μ g/ml of Ca as calcite while the 3.2 g sample has precipitated 18 μ g/ml of Ca. This will lead to differences in the HCO₃ concentrations of those two solutions and will cause the final Ca concentration in.equilibrium with solid calcite to be different in the two systems.

The difference in alkalinity (Table 15) for these two samples supports the assumption that the Ca was precipitated as calcite. Calcium data for J-13 control samples also show evidence of calcite precipitation.

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Data for potassium (Table 22) show no trend as a function of reaction time; the only trend is an increase in concentration that correlates directly with rock to water ratio. In all cases, the amount of potassium is higher than that found from the caliche component data in Table 7. The difference may be partly due to a somewhat higher proportion of caliche material in these samples; however, some of the difference is probably due to rapid dissolution of a small amount of alkali feldspar as indicated from the aluminum data. Potassium in the J-13 blanks remains constant, indicating that no potassiumbearing phase precipitates on heating J-13 water alone.

Magnesium (Table 23) decreases very rapidly to low levels in solution in all cases. The phase precipitated has been identified as magnesium rich calcite, where the Mg is enriched in the cores of the calcite crystals (Knauss et al., 1983).

Data for sodium (Table 24) show a clear dependence on sample weight as well as a slight trend to increase in concentration as a function of reaction time. Concentrations obtained from the caliche component alone in J-13 water (from Table 7) are shown for comparison. Trends in the data suggest that the sodium increase is due partly to a higher caliche component contribution than that given by Table 7 combined with slow dissolution of alkali feldspar.

The second set of experiments run at 150°C were conducted in small Teflon capsules. The exterior of the Parr bombs had been modified so that the bombs could be laid sideways on rollers inside the oven. The roller mechanism functioned without interruption during the experiment, providing a gentle agitation of the rock powder and solution. The rock powder was pretreated using the room temperature and overnight cooked rinse steps described in the section on experimental procedures. Solution chemistry data for the pretreatment solutions are given in Tables 5, 6, 9, and 10.

Some of the Parr bombs used in these experiments were being used for the first time. It was necessary to repeat steps 6 and 7 of the cleaning procedure twice to achieve a pH greater than 5.0 in the cleaning solution. The bombs were leak tested by cooking for two days at 150°C with a weighed amount of water; weights of capsules plus water before and after the two days at temperature showed that less than $1\tilde{z}$ of the water had been lost.

During this set of experiments the pH of solutions was measured before filtration and again after filtration. The purpose of this procedure was to determine whether the filtration step caused sufficient uptake of atmospheric $CO₂$ to alter the pH. The data for both sets of pH measurements are given in Table 25. The pH measured after filtration is always lower than that measured before filtration, indicating that $CO₂$ uptake during filtration is sufficient to alter the pH. The average difference between the two measurements is 0.38 ± 0.20 pH units.

The pH of J-13 blank solutions increases as a function of time spent at the reaction temperature. This change in pH is contrary to the expected drop in pH resulting from calcite precipitation. The rise in pH is attributed to loss of $CO₂$ from solution into the Teflon. The pH of solutions from experiments run in gold-bag rocking autoclaves stays near neutral (Knauss et al., 1983). Data for alkalinity of J-13 blanks at the end of the reaction period (Table 26) show a substantial loss of alkalinity, far greater than can be accounted for by precipitation of magnesium and calcium as carbonates. This supports the interpretation that the pH drop is due to $CO₂$ loss to the Teflon capsules.

Fluoride concentrations (Table 27) at the end of the reaction period are essentially identical to the J-13 values. There is little or no indication of fluoride loss from the Teflon into the J-13 blank samples, indicating that the cleaning procedure was adequate in this case to remove any mobile fluoride prior to start of the experimental matrix.

Data for chloride (Table 28) concentrations are in all cases indistinguishable from the J-13 chloride concentration. There is no increase in chloride concentration of the water due solely to reaction with the rock at 150°C. Nitrate concentrations (Table 29) are slightly lower following reaction with the rock. This may be due to a slight uptake of $NO₂$ by the Teflon since it is most unlikely that a nitrate-bearing phase would precipitate. The sulfate data (Table 30) are also slightly lower than the J-13 sulfate concentration. This may be due to ${50}^{\circ}$ uptake by the Teflon or to precipitation of a small amount of a sulfate-bearing phase. The J-13 blank samples show chloride, nitrate, and sulfate concentrations similar to those of the rock-water reaction solutions.

Aluminum concentrations (Table 31 and Fig. 3) increase rapidly to values between 1.6 and 2.7 ppm, the largest increases being for the smallest rock

Figure 3. Aluminum solution concentrations plotted as a function of reaction time at 150° C.

sample weights. The slow precipitation, observed previously in the static-agitated experiments, is een, but the final Al concentrations for a given rock to water ratio and reaction time are greater for the rolled experiments. This suggests that supersaturation is partially stabilized by the constant agitation present in the rolled experiments.

Boron concentrations (Table 32) are generally similar to J-13 values, except for the 0.4 g-48 day sample. The rest of the data for this sample are normal; the reason for the high boron result is not known, but is more likely to be an analytical artifact than a real result.

Iron concentrations (Table 33) are only slightly higher than the J-13 value. This is due partly to the limited amount of iron present in the rock for reaction, but mainly due to the oxidizing conditions in the reaction system and the low solubility of iron under those conditions.

Silicon (Table 34 and Fig. 4) increases rapidly at first and then more slowly in its approach to the solubility of cristobalite (122 ppm Si at 150'C,

Figure 4. Silicon solution concentrations plotted as a function of reaction time at 150° C.

Walther and Helgeson, 1977). Comparison with the results for the static-agitated 150°C experiments (Table 20) shows that for a given sample weight to water volume ratio, the concentration of Si in the rolled experiment is lower than that for the static test. The presence of the caliche component in solution in the static experiments may have influenced the reaction rate and Si concentration at a given reaction time.

Calcium concentrations in solution (Table 35) drop rapidly from the J-13 value of 12.5 ppm and continue to decrease slowly until a concentration of approximately 3 ppm is reached. Calcium in the J-13 blank is lower than that for the rock-water solutions, indicating that some calcium must be added to solution by the rock during reaction. Magnesium (Table 36) follows the behavior of calcium but is nearly completely removed from solution.

Potassium (Table 37) shows an initial increase that is proportional to rock sample weight, suggesting that some residual readily soluble material

might have been present; however, the anion data given previously do not support this suggestion. After the first day of reaction, potassium concentrations remain essentially constant with time.

Data for sodium (Table 38) show solution concentrations that are uniformly lower than that of J-13 water. This suggests that sodium may be reacting with a phase present in the rock, probably the alkali feldspar. If sodium from solution is exchanging with potassium in the alkali feldspar, an explanation for the decrease in Na accompanied by the increase in K is provided.

TEST MATRIX RESULTS AT 90°C

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The test matrix at 90°C was run in the static-agitated mode in large Parr bombs. All except 3 of the Teflon capsules used in these experiments had been used previously in the 150°C static-agitated runs. The rock samples were pretreated as described in the section on experimental procedure to remove the readily soluble salt component. Solution compositions from the pretreatment steps are given in Tables 3, 4, 7, and 8. The pH measurements for the 90'C samples were made following filtration and splitting of the sample; the anion sample was used for pH determination.

Data for anion concentrations are given in Tables 39 through 42. The samples for 1 and 24 days of reaction were run by an inexperienced operator and may be biased toward low values; see discussion of analytical methods for further details. The suspect data are shown in parentheses in Tables 39 through 42 and were not used in determining the average concentrations shown in those tables.

Fluoride concentrations (Table 39) are essentially identical to J-13 fluoride. There is no indication of any fluoride being contributed to the solutions from the Teflon, in contrast to the results found when these reaction vessels were used at 150° C (Table 11). Chloride concentrations (Table 40) are also essentially identical to the J-13 value, although there is a slight indication of an increase in chloride as a function of sample weight. Nitrate concentrations (Table 41) are also very close to the J-13 value, with samples for low rock weights being slightly below J-13 and high rock weights being slightly above. Sulfate concentrations (Table 42) are approximately 1 ppm below the J-13 value.

Alkalinity data (Table 43) show a sharp decrease after one day of reaction, followed by a slight tendency to further decrease for the 0.4 and 0.8 g samples. The 90°C samples have higher alkalinity than those at 150° C, which is consistent with less calcite precipitation at the lower temperature.

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The pH data given in Table 44 were measured on samples after filtration. As such, the measured values are probably systematically low. A comparison of pH measurements before and after filtration, discussed in the previous section, indicated that the bias is 0.38 ± 0.20 pH units for solutions with pH of approximately 9. Thus, the pH for the 90°C solutions following reaction but before filtration was probably between 8.5 and 9. There is no trend in the pH data as a function of sample weight, and only a slight indication of increase as a function of reaction time.

Aluminum concentrations (Table 45 and Fig. 5) rise to approximately 0.5 ppm during the first day of reaction. The 0.4 and 0.8 g samples then show

Figure 5. Aluminum solution concentrations plotted as a function of reaction time at 90'C.

a slow further increase, reaching concentrations of 0.89 ppm for the 0.4 g sample and 0.74 ppm for the 0.8 g sample after 72 days. The 1.6 g samples show no trend in aluminum concentration as a function of reaction time, while the 3.2 g samples show a yery slow decrease. The inverse correlation of final aluminum concentration with sample weight is the same trend that was observed for the 150°C data (Table 31). At the higher temperature, supersaturation was achieved during the first day of reaction and data for all sample weights showed slow precipitation. At 90°C the systems with low rock to water ratios appear to be continuing to supersaturate, even after 72 days of reaction.

Boron concentrations (Table 46) are virtually identical to the J-13 concentration, with only a slight hint of increase as a function of sample weight and reaction time. Iron concentrations (Table 47) are very low and indistinguishable from J-13 iron concentration.

Data for silicon (Table 48) show a slow increase in concentration as a function of reaction time. The data are plotted in Fig. 6 as a function of

Figure 6. Silicon solution concentrations plotted as a function of reaction time at 90° C.

reaction time and in Fig. 7 as a function of the scaled reaction time. The scaled reaction time adjusts for the differences in rock surface area to solution volume ratio and is proportional to rock surface area divided by solution volume (SA/V) multiplied by reaction time, i.e., $(SA/V) \cdot (t)$. Since for these samples the surface area of the sample is directly proportional to the sample weight the scaled reaction time used was $(wt/V)*(t)*(48/3.2)$. The factor 48/3.2 normalizes the data to the SA/V for the largest rock to water ratio. As can be seen in Fig. 7, there is a definite dependence of dissolution rate on SA/V, indicating that these solutions did not reach steady state values.

Calcium data (Table 49) are rather scattered, but show a general tendency toward lower concentrations as a function of reaction time. There is also a correlation between sample weight and final Ca concentration; the reason for this correlation is not presently understood. The trends in the magnesium data (Table 50) are much smoother and indicate an initial fairly rapid

Figure 7. Silicon concentrations at 90°C plotted as a function of a normalized reaction parameter. See text for details.

decrease in Mg over the first few days of reaction followed by slow precipitation of magnesium throughout the reaction period.

Potassium concentrations (Table 51) show no trend as a function of reaction time but do show a slight positive correlation with sample weight. The averages for each sample weight are virtually identical to those for the comparable sample weight in the 150°C data in Table 37. This suggests that the potassium may be contributed by total dissolution of a trace phase.

Data for sodium (Table 52) are somewhat scattered and show no clear trends with either sample weight or reaction time. The range of observations brackets the J-13 concentration and generally measurements are within ±5 ppm of the J-13 value.

COMPARISON WITH BULLFROG TUFF RESULTS

The Bullfrog Member of the Crater Flat Tuff is a rock unit that lies below the water table at Yucca Mountain. The mineralogy and chemistry of the Bullfrog tuff are similar-to those of the Topopah Spring tuff, except that the proportion of phenocrysts in the Bullfrog is substantially larger.

Prior to selection of the Topopah Spring tuff as the reference repository horizon at Yucca Mountain, NNWSI had considered several other rock units, including the Bullfrog tuff. Experiments were conducted by Oversby and Knauss (1983) to determine the changes in water chemistry resulting from reaction of J-13 water with Bullfrog tuff at 90 and 150'C. The rock samples used were collected from an outcrop northwest of Lathrop Wells. The rock material was not treated to remove evaporite material prior to reaction; however, some experiments were done to determine the composition of the evaporite component.

Two batches of rock were used in the Bullfrog experiments. Table 53 shows the composition of caliche-type material removed from 0.8 g of each batch into 12 ml of J-13 water by shaking at room temperature for two minutes. The data are from Oversby and Knauss (1983) and were adjusted by subtraction of the J-13 concentrations for each species. The data from Tables 5 and 9 for the average pretreatment at room temperature of 0.8 g of Topopah Spring tuff in 12 ml J-13 water were used to obtain the results listed in the column labeled Topopah Spring.

The two batches of Bullfrog tuff came from the same outcrop locality and were collected at the same time. Batch B material contained approximately

three times the amount of caliche material per gram of rock; however, the composition of the caliche is very similar between the two batches. In contrast, the Topopah Spring tuff from Fran Ridge contains far more caliche material than either of the Bullfrog samples, and shows marked differences in composition of the soluble component. The source of the caliche material is runoff water that collects in pores of the rock and later evaporates, leaving behind any solids originally dissolved in the water. Thus, the caliche material at a given locality is indicative of the local runoff water chemistry, and it is not surprising that there are large differences in composition between the two outcrop localities compared in Table 53.

The surface area of the Bullfrog tuff is much higher than that of the Topopah Spring tuff collected at Fran Ridge. Core wafers of Bullfrog tuff had surface areas of 3.6 m^2/g , Batch A crushed tuff had 5 to 6 m^2/g , and Batch B had 3.8 to 4.8 m^2/g (Oversby and Knauss, 1983). Because of the higher rock surface area to solution volume in the Bullfrog experiments compared to those using an equivalent rock weight to solution volume of Topopah Spring tuff, the silicon concentration in solution for a given reaction time is much higher in the Bullfrog experiments.

Data for sodium and boron in the experiments using unpretreated crushed Bullfrog tuff were dominated by the caliche component. Data for Na and B from core wafer experiments are closer to the results obtained on pretreated Topopah Spring tuff (Oversby and Knauss, 1983). The preparation of the core wafers involves cutting and polishing in the presence of water, which effectively removes most of the caliche material from the wafers.

Aluminum concentrations showed the same pattern of supersaturation followed by precipitation; however, the concentrations were lower in all the 150C experiments than the comparable Topopah Spring samples. Data for aluminum at 90°C for Bullfrog samples was erratic, in contrast to the very consistent nature of the Topopah Spring 90°C data. The erratic behavior may have been due to the large amount of aluminum in the caliche material in the Bullfrog (Oversby and Knauss, 1983).

The results for potassium, calcium, and magnesium in the two sets of experiments are very similar, especially if allowance is made for the small amount of potassium in the caliche component. This is to be expected, given the mineralogical similarity of the two rocks.

ESTIMATION OF STEADY-STATE WATER CHEMISTRY

None of the experiments reported in this paper reached steady-state solution concentrations. The matrix permeability of the Topopah Spring tuff is low and the downward infiltration rate of water at Yucca Mountain is also low. This suggests that water flow through the rock matrix material at the repository level would be slow enough to achieve steady-state solution compositions at the appropriate temperatures. Long term experiments using J-13 water and Topopah Spring tuff are in progress in Teflon-lined reaction vessels and in gold bag rocking autoclaves to determine the steady-state chemistry. Pending completion of those experiments, the data given above will be used together with the solubility of cristobalite to predict the steady-state solution compositions.

Table 54 gives the estimated water chemistry at steady-state for the system Topopah Spring tuff plus J-13 water. Data given in the sections on results showed that the only source of anions to change the water chemistry came from the caliche component, and not from the rock itself. Experiments using rock from drill cores have established that there is no caliche material associated with the Topopah Spring tuff where it lies below the region affected by surface runoff (Oversby, 1983). Thus, the estimates for anions are simply the original J-13 values, with a slight lowering in the case of sulfate to allow for some precipitation.

Boron, iron, and sodium concentrations are not expected to change as the result of hydrothermal reaction of the Topopah Spring tuff and J-13 water. Potassium increases slightly, and appears to be essentially independent of temperature. Aluminum concentrations will increase with temperature, while calcium and magnesium concentrations will decrease. Silicon concentrations have been set at the cristobalite solubility level (Walther and Helgeson, 1977) for each temperature. Quartz is present in the rock and may control Si solubility in the very long term; however, data obtained to date indicate that silica precipitation is very slow, and the kinetics of quartz formation may be too slow to control the solubility.

CONCLUSIONS

Reaction of the Topopah Spring Member of the Paintbrush Tuff with J-13 well water, a groundwater obtained from a locality at which the Topopah Spring tuff is an aquifer, shows that changes in water chemistry due to heating the rock and water to temperatures up to 150°C are limited to minor effects in all cases except silicon. Silicon concentrations increase due to dissolution of cristobalite and are expected to reach 122 ppm at 150° C at steady-state.

Surface outcrop samples used in these experiments contained a substantial amount of easily removed evaporite deposits on the rock surface. This type of material is not expected to be encountered at depth under Yucca Mountain (Oversby, 1983) and should be removed prior to use of the rock in experiments where the evaporite material might affect the results. A relatively simple pretreatment procedure is effective in removing the evaporite salts.

Anion data show that there is no detectable source of anions in the rock at temperatures up to 150°C.

The pH of solutions in these experiments increased as a result of reaction. Data from comparable experiments conducted in gold-bag rocking autoclaves do not show such an increase (Knauss et al., 1983). The increase in pH observed here is attributed to uptake of $CO₂$ by the Teflon reaction vessels. Alkalinity determinations for these experiments are expected to underestimate the alkalinity of the rock-water system for this reason.

Changes in concentration occurred for aluminum, potassium, magnesium, and calcium as a result of reaction. Magnesium and calcium decrease due to the precipitation of $(Ca, Mg)CO₃$ (Knauss et al., 1983). Aluminum increases to form a supersaturated condition followed by slow precipitation. The solubility of aluminum in this system appears to be controlled by gibbsite (Knauss et al., 1983). Potassium increases from 5 to 9 ppm, probably due to dissolution of alkali feldspar. There was no significant difference in potassium concentration as a function of temperature.

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The success of these experiments is the result of the contributions of many individuals. Thanks to the care and effort of Jan Brown we made

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effective use of laboratory time and space, and had no instances where experiments had to be rerun. She successfully conducted two of the experimental matrices simultaneously and coordinated delivery of samples to the analytical laboratories. Cation analyses were performed by A. Langhorst, ion chromatography by S. Sanders and J. Harrar, and alkalinity by R. Swanziger. Their careful measurements and attention to detail is greatly appreciated. Rock crushing, matrix execution, and pH measurements were done by Jan Brown. Without her efforts this work would not have been accomplished. T. Wolery provided the calculations of cristobalite solubility.

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Summary of all control blanks (ppm)								
Date	${\bf A}1$	В	Fe	Si	Ca	$\bf K$	Mg	Na
7/19/83	0.009	0.121	0.009	27.0	11.9	5.46	1.88	43.4
8/4/83	0.003		0.002	26.2	13.5	5.19	2.07	44.9
9/13/83	0.001	0.120	0.002	27.0	12.8	4.54	1.91	43.3
10/24/83	0.013	0.125	0.008	26.9	13.3	4.89	1.93	43.6
12/6/83	0.012		0.004	27.5	12.5	5.09		45.5
3/7/84	0.009		0.004	27.8	10.5	5.67	1.86	43.3
Av 2/15/84	0.040		0.015	26.2	12.2	4.73	1.90	41.2
Av3/7/84	0.011		0.004	27.0	13.0	5.51	1.92	43.4
Average	0.012	0.122	0.006	27.0	12.5	5.14	1.92	43.6
Std. Dev.	0.011	0.002	0.004	0.52	0.90	0.37	0.063	1.19

Table 1. Data for ICP analyses of J-13 water.

Six control blanks on J-13 run on 3/7/84

Four control blanks run on 2/15/84

Summary of all control blanks.			Alkalinity				
Date	F^-	$c1$ ⁻	NO_3	SO_{4}^{E}	meq/1	ppm , $RCO3$	Date
8/30/83	1.8	5.3	6.4	13.4	2.29	140	7/27/83
9/30/83	2.3	6.8	9.3	19.8	2.13	130	8/5/83
Av 3/26/84	2.4	7.1	9.2	18.5	2.16	132	5/2/83
Av3/14/84	2.3	6.6	9.0	18.1	2.19	134	Average
Average	2.2	6.5	8.5	17.5	0.07	4.2	Std. Dev.
Std. Dev.	0.23	0.69	1.20	2.42			
ReAver.	2.3	6.8	9.2	18.8			
NewStdDev	0.05	0.21	0.12	0.73			

Table 2. Data for anion analyses by IC (ppm) and alkalinity for J-13 control blanks.

Six control blanks on J-13 run on 3/26/84

Table 3. Anion concentrations (ppm) in room temperature rinsing solutions of Tpt plus 48 ml of J-13 water (pretreatment for 90^oC run).

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Table 3. (Continued).

a Sample identification numbers are the run duration in days for the sample following pretreatment and the sample weight in grams.

b Data in parentheses may be slightly biased toward low values and were not used in obtaining averages.

Table 4. Anion concentrations (ppm) in solutions from pre-rinsed Tpt tuf heated at 90°C with 48 ml of J-13 water for 1 day

Table 4. (Continued).

a Sample identification numbers are the run duration in days for the sample following pretreatment and the sample weight in grams.

^D Data in parentheses may be slightly biased toward low values and were not used in obtaining averages.

 c nd = analysis not done.

Table 5. Anion concentrations (ppm) in room-temperature 12-m1 rinsing solutions of Tpt plus J-13 water (pretreatment for 150°C run).

a Sample identification numbers are the run duration in days for the sample following pretreatment and the sample weight in grams.

Table 6. Anion concentrations (ppm) in at 150°C with 12 ml of J-13 water for 1 solutions from pre-rinsed Tpt heated

a Sample identification numbers are the run duration in days for the sample following pretreatment and the sample weight in grams.

Table 7. Cation concentrations (ppm) in room temperature rinse solutions of Tpt plus 48 ml of J-13 water (pretreatment for 90°C run).

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Table 7. (Continued).

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^a Sample identification numbers are the run duration for the sample in days following pretreatment and the sample weight in grams.

Table 8. heated at Cation concentrations (ppm) in solutions from pre-rinsed Tpt tuff 90°C with 48 ml of J-13 water for 1 day.

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a Sample identification numbers are the run duration for the sample in days following pretreatment and the sample weight in grams.

Table 9. Cation concentrations (ppm) in room-temperature 12 ml rinsin solutions of Tpt plus J-13 water (pretreatment for 150°C run)

a Sample identification numbers are the run duration for the sample in days following pretreatment and the sample weight in grams.

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Table 10. Cation concentrations (ppm) in solutions from pre-rinsed Tpt heated at 150°C with 12 ml of J-13 water for 1 day.

^a Sample identification numbers are the run duration for the sample in days following pretreatment and the sample weight in grams.

Table 11. Fluoride concentration Topopah Spring tuff with 48 ml of J-13 fluoride concentration = 2.3 (ppm) in solutions from reaction at 150°C of J-13 water in static-agitated mode. Initial ppm.

Table 12. Chloride concentration (ppm) in solutions from reaction at 150°C of Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 chloride concentration *-* 6.8 ppm.

(ppm) in solutions from reaction at 150°C of Table 13. Nitrate concentrations Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 nitrate concentrations = 9.2 ppm. \sim \sim

Table 14. Sulfate concentrations (ppm) in solutions from reaction at 150°C of Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 sulfate concentration is 18.8 ppm. $\ddot{}$

Table 15. Alkalinity of solutions from reaction at 150°C of Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode.

Alkalinity (meg/1)

Alkalinity, as HCO₃ (ppm)

Table 16. pH of solutions from reaction at 150°C of Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial pH of J-13 water is 7.6.

Table 17. Aluminum concentration (ppm) in solutions from reaction at 150°C of Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 aluminum concentration is 0.012 ppm.

Table 18. Boron concentration (ppm) in solutions from reaction at 150°C of Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 boron concentration is 0.122 ppm.

Table 19. Iron concentration (ppm) in solutions from reaction at 150'C of Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 iron concentration is 0.006 ppm.

Table 20. Silicon concentration (ppm) in solutions from reaction at 150 $^{\circ}$ C of Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 silicon concentration is 27.0 ppm.

Table 21. Calcium concentration (ppm) in solutions from reaction at 150°C of Topopah Spring tuff with 48 ml of J-13 water in static-agitated-mode. Initial J-13 calcium concentration is 12.5 ppm.

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Table 22. Potassium concentration (ppm) in solutions from reaction at 150°C of Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 potassium concentration is 5.1 ppm.

Table 23. Magnesium concentration (ppm) in solutions from reaction at 150°C of Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 magnesium concentration is 1.92 ppm.

Table 24. Sodium concentration (ppm) in solutions from reaction at 150°C of Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 sodium concentration is 43.6 ppm.

Table 25. pH of solutions from reaction at 150°C of pretreated Topopah Spring tuff with 12 ml of J-13 water in rolled reaction mode. Initial pH of J-1 water is 7.6.

 \overline{a} Unfiltered.

b Filtered.

c Blank was run 45 days.

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Table 26. Alkalinity of solutions from reaction at 150°C of pretreated Topopah Spring tuff with 12 ml of J-13 water in rolled reaction mode.

Alkalinity (meq/l). Initial J-13 alkalinity is 2.19 meq/l.

Alkalinity, as HCO_3 (ppm). Initial J-13 alkalinity is 134 ppm HCO_3 .

a Blank was run 45 days.

Table 27. Fluoride concentration (ppm) in solutions from reaction at 150°C of pretreated Topopah Spring tuff with 12 ml of J-13 water in rolled reaction mode. Initial J-13 fluoride concentration is 2.3 ppm. ä,

a Blank was run 45 days.

Table 28. Chloride concentration (ppm) in solutions from reaction at 150°C of pretreated Topopah Spring tuff with 12 ml of J-13 water in rolled reaction mode. Initial J-13 chloride concentration is 6.8 ppm.

a Blank was run 45 days.

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Table 29. Nitrate concentration (ppm) in solutions from reaction at 150°C of pretreated Topopah Spring tuff with 12 ml of J-13 water in rolled reaction mode. Initial J-13 nitrate concentration is 9.2 ppm.

a Blank was run 45 days.

Table 30. Sulfate concentration (ppm) in solutions from reaction at 150°C of pretreated Topopah Spring tuff with 12 ml of J-13 water in rolled reaction mode. Initial J-13 sulfate concentration is 18.8 ppm.

a Blank was run 45 days.

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Table 31. Aluminum concentration (ppm) in solutions from reaction at 150°C of pretreated Topopah Spring tuff with 12 ml of J-13 water in rolled reaction mode. Initial J-13 aluminum concentration is 0.012 ppm.

a Blank run was 45 days.

Table 32. Boron concentration (ppm) in solutions from reaction at 150'C of pretreated Topopah Spring tuff with 12 ml of J-13 water in rolled reaction mode. Initial J-13 boron concentration is 0.122 ppm.

Table 33. Iron concentration (ppm) in solutions from reaction at 150°C of pretreated Topopah Spring tuff with 12 ml of J-13 water in rolled reaction mode. Initial J-13 iron concentration is 0.006 ppm.

a Blank run was 45 days.

Table 34. Silicon concentration (ppm) in solutions from reaction at 150°C of pretreated Topopah Spring tuff with 12 ml of J-13 water in rolled reaction mode. Initial J-13 silicon concentration is 27.0 ppm.

Table 35. Calcium concentration (ppm) in solutions from reaction at 150°C of pretreated Topopah Spring tuff with 12 ml of J-13 water in rolled reaction mode. Initial J-13 calcium concentration is 12.5 ppm.

a Blank run was 45 days.

Table 36. Magnesium concentration (ppm) in solutions from reaction at 150°C of pretreated Topopah Spring tuff with 12 ml of J-13 water in rolled reaction mode. Initial J-13 magnesium concentration is 1.92 ppm.

Table 37. Potassium concentration (ppm) in solutions from reaction at 150°C of pretreated Topopah Spring tuff with 12 ml of J-13 water in rolled reaction mode. Initial J-13 potassium concentration is 5.1 ppm.

a Blank run was 45 days.

Table 38. Sodium concentration (ppm) in solutions from reaction at 150°C of pretreated Topopah Spring tuff with 12 ml of J-13 water in rolled reaction mode. Initial J-13 sodium concentration is 44 ppm.

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Table 39. Fluoride concentration (ppm) in solutions from reaction at 90°C of pretreated Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 fluoride concentration is 2.3 ppm.

a Excluding parenthetical data.

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Table 40. Chloride concentration (ppm) in solutions from reaction at 90°C of pretreated Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 chloride concentration is 6.8 ppm.

a Excluding parenthetical data.

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Table 41. Nitrate concentration (ppm) in pretreated Topopah Spring tuff with 48 ml mode. Initial J-13 nitrate concentration solutions from reaction at 90°C of of J-13 water in static-agitated is 9.2 ppm.

a Excluding parenthetical data.

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Table 42. Sulfate concentration (ppm) in pretreated Topopah Spring tuff with 48 ml mode. Initial J-13 sulfate concentration solutions from reaction at 90°C of of J-13 water in static-agitated is 18.8 ppm.

a Excluding parenthetical data.

a

Table 43. Alkalinity of solutions from reaction at 90°C of Topopah Spring tuff with 48 ml of J-13 water in the static-agitated mode. Initial J-13 alkalinity is 2.19 meq/l (134 ppm HC03).

Table 44. pH of solutions from reaction at 90C of pretreated Topopah Spring tuff with 48 ml of J-13 water in the static-agitated mode. Initial pH of J-13 water is 7.6.

Table 45. Aluminum concentration (ppm) in solutions from reaction at 90 $^{\circ}$ C of pretreated Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 aluminum concentration is 0.012 ppm.

Run duration (days)	Sample weight (g)				
	0.4	0.8	1.6	3.2	Blank
$\mathbf{1}$	0.476	0.530	0.558	0.508	
3	0.566	0.561	0.532	0.451	0.008
6	0.613	0.634	0.576	0.478	
12	0.669	0.654	0.576	0.479	\triangle 008
\bullet 24	0.660	0.649	0.550	0.455	
36	0.742	0.694	0.568	0.449	0.008
48	0.752	0.686	0.473	0.385	
60	0.709	0.693	0.537	0.392	0.008
72	0.887	0.741	0.526	0.388	

Table 46. Boron concentration (ppm) in solutions from reaction at 90°C of pretreated Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 boron concentration is 0.122 ppm.

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Table 47. Iron concentration (ppm) in solutions from reaction at 90 $^{\circ}$ C of pretreated Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 iron concentration is 0.006 ppm.

Table 48. Silicon concentration (ppm) in solutions from reaction at 90°C of pretreated Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 silicon concentration is 27.0 ppm.

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Table 49. Calcium concentration (ppm) in solutions from reaction at 90°C of pretreated Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 calcium concentration is 12.5 ppm.

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Table 50. Magnesium concentration (ppm) in solutions from reaction at 90°C of pretreated Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 magnesium concentration is 1.92 ppm.

Table 51. Potassium concentration (ppm) in solutions from reaction at 90°C of pretreated Topopah Spring tuff with 48 ml of J-13 water in static-agitated mode. Initial J-13 potassium concentration is 5.1 ppm.

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Table 52. Sodium concentration (ppm) in solutions from pretreated Topopah Spring tuff with 48 ml of J-13 water mode. Initial J-13 sodium concentration is 43.6 ppm. reaction at 90°C of in static-agitated

> Table 53. Comparison of caliche material removed from 0.8 g of Batch A and Batch B Bullfrog tuff to that removed from Topopah Spring tuff. Units are ppm per ml of rinse solution.

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Table 54. Estimate of steady-state wate chemistry for the system Topopah Sprin tuff $+$ J-13 water

 \overline{a} in \overline{b}

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