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Rock-Brine Chemical Interactions

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Research Project 653-2

Final Report, February 1982

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ABSTRACT

This report presents the results of experimental interaction of powdered volcanic rock with aqueous solutions at temperatures from 200 to 400°C, 500 to 1000 bars fluid pressure, with reaction durations of approximately 30 days under controlled laboratory conditions. The aim of this research is to develop data on the kinetics and equilibria of rock solution interactions that will provide insight into the complex geochemical processes attending geothermal reservoir development, stimulation, and reinjection. The research was done in the Stanford Hydrothermal Lab using gold cell equipment of the Dickson design. This equipment inverts the solution rock mixture several times a minute to ensure thorough mixing. Solution samples were periodically withdrawn without interruption of the experimental conditions. The data from these experiments suggests a path dependent series of reactions by which geothermal fluids might evolve from meteoric or magmatic sources.

EPRI PERSPECTIVE

PROJECT DESCRIPTION

This final report for RP653-2 describes a series of laboratory experiments that measured rock-brine interactions of the type expected in geothermal reservoirs. Powdered volcanic rocks (basalt, rhyolite, and andesite) were reacted with "geothermal fluids" (water and NaCl solutions) at temperatures from 200 to 400°C and pressures of 500 to 1000 bars. The reaction was done in inert gold pressure vessels that were inverted several times a minute to promote good mixing and rapid reactions. Solution could be withdrawn from the vessels without interrupting the experiment, making it possible to track the course of the reactions with time. The results of these experiments were analyzed in terms of changes in solution and mineral chemistries.

PROJECT OBJECTIVES

The goals of this project were:

- To evaluate the changes in solution chemistry and mineral assemblages from rock-brine interaction
- To correlate these changes with solution chemistry and formation of secondary minerals at hydrothermal sites

PROJECT RESULTS

The experimental work led to results that increase our knowledge of rock-brine interactions, especially in terms of reaction kinetics. In most of the experiments, results were kinetically controlled; the rock-brine mixture kept changing through the course of the experiment and did not reach equilibrium. The results of this work may be useful for the interpretation of fluid chemistry data of hot dry rock projects. However, it is difficult to correlate these results with the solution and mineral chemistry of geothermal reservoirs because the rocks and fluid in a reservoir have generally been in contact with each other long enough to reach equilibrium.

Some of the experimental results can be correlated with geothermal situations as described below:

- Sodium and calcium ratios quickly reach equilibrium values in solution even when the bulk material is not yet at equilibrium. This could be explained if ion exchange equilibria occur more rapidly than other equilibria, which is quite likely. This could also explain the success of the Na-K-Ca geothermometer, since Na-K-Ca ratios will be at equilibrium at a given temperature even if there is not complete equilibrium of rock and fluid at that temperature. Therefore, these ratios would be an accurate reflection of the temperature of a geothermal fluid in the reservoir.
- Silica solution values could not be used for prediction of the temperature of solution because silica was capable of reaching high levels of supersaturation in the fluid with a very slow return to equilibrium saturation values. This behavior reflects the difficulties of scale control of silica-containing fluids in geothermal systems. High degrees of supersaturation and slow precipitation of silica is common in these systems. In the experiments done in this study, silica supersaturation remained high even in solutions that should form metal silicates (not silica) at equilibrium. This shows that it would not be effective to change the metal content of a geothermal fluid in order to promote precipitation of silica as silicate.

The experimental results on trace elements, mineral alteration, and pH changes are clearly kinetically controlled. Therefore, it is difficult to relate these experimental results to real geothermal situations. It is interesting, however, that increased chloride content of the fluid leads to increased trace metal dissolution from the rocks. This is certainly due to chloride's ability to stabilize metals in solution by the formation of complex ions.

In conclusion, the results of these experiments increase the understanding of the kinetics of rock-water and rock-brine interaction. Further, the Na-Ca results help to explain the effectiveness of Na-K-Ca geothermometers, and the silica results show the difficulties of fluid constituent manipulation as a way of increasing or controlling silica precipitation.

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SUMMARY

INTRODUCTION AND METHODOLOGY

Geothermal reservoirs commonly occur in permeable volcanic rock horizons such as porous tuffs or fractured basalts. This research supplies basic experimental data analogous to the natural process of hydrothermal alteration of these volcanic rock types and solution composition under geothermal conditions. The report summarizes the results of these experiments.

The reactions were chosen to encompass a wide range of starting solution compositions (0, 2, 10 and 20% NaCl), and volcanic rock types (rhyolite, andesite and basalt) in the temperature range found in many geothermal systems (200-400°C). The experiments were done at high pressure (500 bars) in a rock-brine apparatus from which periodic samples could be withdrawn to track the results of the experiment. This apparatus allowed full mixing of the rock and brine, and fluid withdrawal without pressure or temperature change of the experiment.

The results of these experiments are summarized below:

1. Total dissolved material in solution increased with increased time, glassiness of the rock, ionic strength of the initial solution, temperature and lower water to rock ratio.
2. Some components (Al, Mg, Ca) showed solution concentration peaks early in most experiments, others rose slowly to broad maxima (SiO₂ and K), others increased steadily (Fe, B, Li).
3. Solution pH showed initial decreases, and subsequent increases. Steady state pH values were progressively lower at higher ionic strengths. They were lower in solution reacted with basalt compared to rhyolite at the same salinity and temperature.
4. In many solutions, SiO₂ reached supersaturation levels, but in only one experiment did a pure SiO₂ phase (cristobalite) precipitate.
5. Some experiments showed significant decreases in K and SiO₂ concentration after 190 hours, which indicated the precipitation of K-Na zeolite at molar K/Na ratios greater than 0.111.

6. Significant levels of several trace elements were produced in the experiments. Trace element concentrations increased with increasing NaCl content of the brine. Many natural hydrothermal systems tend to contain trace elements at lower levels, so it is believed that the trace element dissolution rates observed in this work are kinetic rather than equilibrium effects.
7. Major secondary solid phases produced by the 300°C rhyolite experiment were Na feldspar and zeolites. Smectite was the most common secondary phase of the basalt and andesite experiment. At 200°C, little alteration of the solid phase was produced, reflecting slower growth kinetics at this temperature.
8. Calculated activity ratios of alkali and alkaline earths in solution imply that these activities are controlled by rapid ion-exchange reactions at 300°C. These activity ratios have near-equilibrium values even though bulk equilibrium is not believed to have been established within the reaction cell. This finding may help interpret geothermometry based on these ionic ratios.

Section 1

INTRODUCTION

HYDROLOGIC SYSTEMS

Rocks in the earth's crust have interacted with aqueous solutions in diverse ways over times of millions of years, at a wide range of temperatures and pressures; huge volumes of crystal rocks have rearranged, both in bulk composition and mineralogy. Cool surface rocks have been affected by meteoric waters that penetrate to deeper hot zones. Actively flowing waters have been encountered in bore holes of geothermal systems as deep as 12,000 feet, and geological arguments support penetration to as deep as 18,000 feet. The range of temperature and pressure implied is from 25 to 500°C and 1-600 atmospheres.

Solutions encountered in geothermal systems range in salinity from very dilute solutions of meteoric origin (100-1000 ppm) to concentrated brines of up to 300,000 ppm total dissolved solids. The nature of the fluids reflect the geologic history of the rock units. Young marine sedimentary rocks contain relatively unmodified seawater; young continental rocks tend to have dilute waters except where they are associated with evaporative salt deposits, from which much soluble matter can be leached. As rocks become more and more deeply buried and are subjected to increasing temperatures and pressures, processes take place such as lithification, expulsion of fluids, and chemical interaction with pore solutions. The large range in rock compositions and salt concentrations of solutions reflect variations in host rocks, local mineralogy, residence times of the fluids, and the chemical and pressure conditions. Igneous activity leads to the injection of masses of liquid silicate into various levels of the crust; many geologists believe that the magma contains dissolved H_2O which is released during the end stages of crystallization. Water of magmatic origin would subsequently rise in the crust transporting heat and dissolved constituents. The fluids may react with preexisting rocks, altering existing minerals and in some cases forming ore deposits. Magmatic waters often mix with fluids of other origins; geochemical evidences suggest that the waters of geothermal systems have become so diluted with other kinds of water that any existing magmatic waters in them cannot be detected by the methods currently available.

AIM OF RESEARCH

The aim of this research is to provide data on the kinetics and equilibria of rock-solution interactions at temperature-pressure-compositional conditions relevant to geothermal processes. Data obtained from these experiments may help in predicting changes in the physical and chemical properties of a geothermal reservoir during reservoir development, stimulation, and reinjection. We feel that the data obtained from these experiments can also aid in relating hot spring and bore-hole compositions to variables such as subsurface temperatures, reservoir rock types, and fluid residence time. Our observations remain at a qualitative level. However, with continued experimental and computational work, a rigorous model of the geochemistry of geothermal reservoirs may yet be developed.

PREVIOUS EXPERIMENTAL STUDIES

Aside from a few early specialized reconnaissance studies, the first systematic work was done by Ellis and his group at the Chemistry Division of Division of Scientific and Industrial Research, New Zealand during the 1960's (1,2,3,4). As part of the efforts to exploit geothermal systems for power, the New Zealand government recognized the need for knowledge of mineral reactions with aqueous solutions. Subsequent research in New Zealand proved to be of great importance to exploration and development of geothermal power, not only in New Zealand but elsewhere.

The rocks of the New Zealand geothermal fields are dominantly rhyolitic ash units that overlie sedimentary sandstones and shales. Experiments were done on a variety of rock types, mostly rhyolites and sandstones, to determine changes in both solution composition and mineralogy during the progressive alteration of these rocks. The group was interested in whether the compositions of natural fluids in the New Zealand geothermal systems could be accounted for by rock-water reactions. In addition, it was of great interest to measure chemical parameters, such as silica content, which could be useful in estimating underground temperatures, reservoir characteristics, sources of fluids and residence times.

The New Zealand group (1,2,3,4) reacted coarsely powdered rocks with aqueous solutions (H_2O and NaCl solutions) at temperatures from 150 to $600^{\circ}C$ at elevated pressures and a range of reaction times. They analyzed the solutions for major components (Na, K, Ca, Mg, SiO_2) and minor constituents (Li, Rb, Cs, Cl, F, B, SO_4 , NH_3 , As). They found that the solutions approached steady state compositions with regard to most components in a few days. The chemical characteristics

of the solutions were similar to those of hot springs and bore-hole fluids, demonstrating for the first time that compositions of natural fluids could be accounted for by rock-fluid interactions. They found that some elements, such as Cl, B, N, and F, were almost quantitatively extracted from the rocks in a few days; they were considered to have been present in the rocks in easily soluble forms, on mineral surfaces and in microfissures. Although they believed they had not achieved equilibrium between the rocks and solution, they concluded that the solution compositions were controlled by reactions with individual minerals and by exchange reactions. Cl ions were demonstrated to play a large role in extracting some of the heavy elements from rocks.

Bischoff and Dickson (5,6) did the first dynamic rock-solution reaction in the Dickson Hydrothermal Laboratory at Stanford University. They reacted powdered basalt with seawater at 200°C and 500 bars for seven months, by use of small-angle rocking Teflon-cell Dickson hydrothermal equipment. This equipment permitted sampling at regular intervals without disturbance of the temperature and pressure conditions. The solutions were analysed for major and minor constituents. The data were applied to problems concerning the reaction of basalt with seawater at mid-ocean ridges and the possible role of the reaction in the formation of metallic deposits, the geochemical balance of the oceans, and alteration of rocks. They showed that basalt altered to secondary phases which are found in cored sea-floor basalts. It was possible to account for much of the Fe and Mn sea-bottom sediments as their extraction from basalt by hot circulating seawaters. The Mg and K deficit and the H^+ surplus of seawater could also be explained by cycling of seawater through shallow crust. This original study of Bischoff and Dickson stimulated additional interest in the overall problem of how the ocean attained its present composition. The balance between the supply from the continents in run-off waters and the extraction processes in the ocean is not wholly understood. For the first time, an experimental basis was presented to support a possible role of seawater interaction with the underlying basalts of the ocean basins. This and other work has led to an evaluation of the rate at which seawater circulates through the basalt crust, with the surprising result that all the waters of all the oceans pass through the underlying basalts in a time as short as 7 million years. In essence, the oceans are merely temporary storage ponds, constantly in a state of flux, with some H_2O returned to the continents through evaporation and rainfall, and the rest cycled through underlying crustal basalts and returning in modified form to the oceans. This study was followed by a paper by Seyfried, Bischoff and Dickson (7).

Nearly simultaneously with the work of Bischoff and Dickson, other work using different approaches was going on. Mottl et al. (8), Mottl (9) and Hajash (10,11) reacted basalt powders with seawater from 200⁰ to 500⁰C in sealed gold tubes for times up to one year. They extended knowledge of the reaction to a broader range of temperatures, but in general their conclusions were similar to those of Bischoff and Dickson. They noted drops in pH, increased solubilities of several transition metals (Fe, Cu, Zn, Mn) and production of alteration minerals found in nature. Seyfried (12) did extensive work on the basalt-seawater reaction for his Ph.D. dissertation, which considerably expanded the knowledge of the effects of temperature, crystallinity and rock-to-solution ratios. Ewers (13) reacted sedimentary rock powders in sealed silica-glass tubes with aqueous solutions at elevated temperatures for several days and he reported that enough leaching of Sb, As, Se and S had taken place for the reaction to account for the heavy element concentrations of New Zealand geothermal fluids. Dibble and Dickson (14) reacted granite with aqueous solutions at temperatures up to 250⁰C by circulating water methods and by use of the Dickson Teflon-cell equipment. They found that Li was easily solubilized from the interior portions of pieces of granite 4 inches in diameter. The common presence of Li in geothermal fluids and other types of ground waters could be explained by the kinds of extraction revealed in the experiments. A set of papers from the Stanford group, Dickson, Seyfried, Mottl and Bischoff, have appeared recently (15,16,17,18,19,20).

EXPERIMENTAL APPROACHES

Rock-solution reactions at elevated temperatures and pressures have been done by four approaches, each of which has advantages and disadvantages, as discussed below.

Most experimental work has been done by the static closed-tube method, which consists of holding the rock-solution mixtures in inert metal sealed tubes (commonly gold) in pressure vessels kept at the desired elevated temperatures (10,11,13). After a lapse of time, which in some cases may amount to a year, the pressure vessel is rapidly cooled (quenched), opened, and the experimental mixtures are recovered. The solution is separated from the solid, and both are examined. Generally, very little solution is present, making precise analyses difficult or impossible; in such experiments, attention is focused on the mineralogical and chemical changes of the solid phases. Much data has been acquired by static closed-tube methods of interest primarily in mineral stability studies and metamorphic rock genesis. The static, quench closed-tube method suffers from

several effects: the reaction rate may be controlled by diffusion in solution, which is quite slow in static systems; little information is forthcoming on the compositions of reacted solutions because of the small volumes of the tubes; uncertainties exist as to the extent to which the solutions back-react with solid phases during the quench; and, even at best, the experiments give information valid only for the reaction time chosen, making analysis of time-dependent processes (kinetics) tedious or impractical.

A second approach is to hold the rock powder and solution in a metallic pressure vessel from which samples can be withdrawn from time to time. Much of the extensive and valuable work done in New Zealand was by this method. It should be considered a modified static method, useful in preliminary and pioneering studies, but again subject to several difficulties. The lack of dynamic agitation of rock with solution leads to slow reactions and dominance of surface effects. The minerals react only partially, activity calculations show that the solutions fall far short of attaining equilibrium compositions. Much of the work has been with equipment lacking internal filters, leading to uncertainties as to whether particulate matter might have been suspended in the samples of solution. An insurmountable difficulty is that it is not possible to avoid interaction of the metal of the pressure vessel with solution, which may set the oxygen fugacity by the metal metal-oxide couples, which in turn affects the pH of the solution. Particularly bothersome is the extraction of trace elements from the pressure vessel walls.

A third approach is another modified static method, the flow-by or flow-through methods (21). Rocks are held in pressure vessels, and aqueous solutions are permitted to flow around and through the rocks at controlled rates. Sampling of solution is done at regular time intervals, providing time-dependent process information. The rocks can be examined at the close of experiments and the changes in mineralogy, permeability and porosity measured. Fluids can be cycled through the rocks repeatedly and the effects observed. This approach has some valuable features: although the times of the experiments fall far short of times needed for equilibrium, knowledge is gained of the initial effects taking place when solutions penetrate rocks. Particularly valuable are the results of flow-through experiments on jacketed rock cores which yield data on permeability behavior at high temperatures (22) performed at the Los Alamos Scientific Laboratory, New Mexico. Problems with the flow-through method stem from the reactivity of the metallic vessels, the slowness of the reaction, and the relative complexity of the equipment.

A fourth approach is used in the Hydrothermal Laboratory of the Geology Department of Stanford University. Specialized equipment, originally developed to study the solubility of metallic sulfides in corrosive aqueous solutions, has proved particularly appropriate to the study of the kinetics of rock-solution reactions. An inert container, made of teflon or gold, is suspended in a steel pressure vessel. The solid and liquid are held in the cell, permitted to react at the desired temperature and pressure while being continually mixed. The mixing is promoted by a rocking device which turns the pressure vessel-furnace assembly upside down and back several times per minute. The inner cell communicates to the outside by means of a capillary stainless steel tube, lined with Teflon or gold, which is connected to a special non-contaminating valve block developed for the purpose. Samples of solution are withdrawn from the inner cell at regular intervals of time by opening the valve, creating a slight pressure drop in the line which forces fluid through a filter at the top of the cell and out into the capillary tube into a sample-catching device (commonly a hypodermic syringe). The pressure is kept essentially constant during sampling by pumping fluid into the volume surrounding the cell at the same rate that the inner cell is being depleted.

The advantages of using the Dickson hydrothermal equipment over other kinds of equipment are several. The reaction is done in an inert (gold, teflon) environment in large volume cells (150-300 ml). Sampling can be done at desired time intervals without disturbance of the temperature and pressure conditions, permitting solution compositions to be measured during the reactions. Reaction rates are greatly increased over static approaches because of the active mixing of solids and solutions, and it is common to attain steady states in solution compositions in about 30 days rather than the years required for some static situations. The advantages collectively viewed, provide an order of magnitude improvement over other methods.

The disadvantages of the equipment are that, although conceptually simple in design, its construction and use requires time and experience that only a few laboratories have been willing or able to allocate. The equipment is expensive, but not exceptionally so when compared to other high-temperature and high-pressure laboratory equipment. Each experiment consumes about 30 days on the average, with considerable preparation and follow-through required. No direct information can be gained on the changes in the solid phases during the reaction; the solids in the cell at the close of an experiment are examined, and the sequence of mineralogical and chemical changes that took place earlier must be deduced by correlating the mineralogical features with the chemical behavior of the solutions.

Section 2

PRESENT WORK

EXPERIMENTAL MATERIALS

Three types of rocks were used in the experiments: fine grained crystalline basalt; glassy microcrystalline andesite; and rhyolite glass. Volcanic rocks were chosen for these experiments for several reasons: 1) volcanic rocks because of either their fine grain nature or their glassiness react more rapidly than their coarse grain plutonic rock equivalents, 2) most geothermal areas are associated with volcanic events. Often high permeability silicic ash beds or fractured basalts provide aquifers in which high temperature geothermal fluids and gases are found.

The basalt was from a cinder cone in the Clear Lake volcanic area in northcentral California, just east of the south end of Clear Lake, approximately 30 miles northeast of The Geysers geothermal area. The chemical compositions of the basalt and of the other two rocks are listed in Table 2-1. Compared to average basalt the rock used in this experiment is somewhat high in K_2O and SiO_2 and relatively low in CaO (23). Petrographically, the basalt consists of large (2-10 mm) plagioclase and clinopyroxene phenocrysts in a fine-grained groundmass of slightly preferred oriented plagioclase microlites and nearly opaque solids.

The andesite, provided by Dr. Y. Seki of Saitama University, Japan, is the Japan andesite standard rock, JA-1, collected by the Japan Geologic survey from the Hakone volcanic field in southeastern Honshu, south of Mt. Fuji. This rock consists of plagioclase and augite phenocrysts in a groundmass of finer plagioclase, pyroxene, quartz and opaque minerals. The Hakone caldera and the surrounding region have been described by Kuno (24) and Oki (25).

The rhyolite, provided by Dr. J.J. Rytuba of the U.S.G.S., is from the chilled margin of an intrusive in the McDermitt caldera in north central Nevada (26). The rock is almost entirely glass, with sparse sanidine and quartz phenocrysts. The rock contains unusually high total Fe compared to most rhyolites.

Table 2-1

CHEMICAL COMPOSITION OF STARTING ROCKS IN WT %

	McDermitt Rhyolite	Clear Lake Basalt	Japan Andesite
SiO ₂	68.9	58.8	63.61
TiO ₂	0.37	1.29	0.95
Al ₂ O ₃	11.9	18.63	15.41
Fe ₂ O ₃	3.6		2.41
FeO	1.1	6.80	4.42
MgO	0.20	5.1	1.59
CaO	0.40	9.1	5.64
Na ₂ O	3.6	2.6	3.91
K ₂ O	5.2	1.45	0.84
H ₂ O ⁺	3.9	N.A.	0.43
H ₂ O ⁻	0.1	N.A.	0.24
P ₂ O ₅	0.02	0.37	0.16
MnO	0.072	0.12	0.17
Total	99.36	104.2	99.78

Figure 2-1. Schematic diagram of gold cell apparatus (Dickson equipment).

In preparation for the experiments, all rocks were ground in an agate mortar and sieved. The $<100\text{ }\mu\text{m}$ fraction of the basalt and rhyolite and the $<50\text{ }\mu\text{m}$ fraction of the andesite were set aside for the experiments. Four solution types were used: distilled water, and 0.1, 2, 10, and 20 wt% NaCl solutions.

Procedures

Temperatures were 200, 300 and 400°C , and fluid pressures were 500 or 1000 bars.

The experimental gold cell hydrothermal equipment is similar in design to the Teflon cell equipment described by Dickson et al. (27) and the gold-cell equipment of Rytuba and Dickson (28). Some gold cells were equipped with titanium caps of the type described by Seyfried et al., (29). The gold cells, of approximately 200 cc maximum volume, are held within a stainless steel pressure vessel (Figure 2-1).

Each pressure vessel is held in a furnace mounted in a rack which rocks the furnace through 180 degrees five to six times per minute. The rocking aids in keeping the rock particles mixed with solution, thereby greatly increasing the reaction rates.

A gold filter at the top of the sample cell and at the lower end of the sampling tube retains particles larger than about $0.5\text{ }\mu\text{m}$. Solutions with drawn through the gold filter pass through a gold capillary tube inside a stainless steel exit tube, which connects to a special sampling valve at the other end. The valve is a Dickson-Gordon valve, which consists of a high-pressure valve block with a corrosion-free titanium needle and seat, specially designed in our laboratory. The fluid contacts only titanium and gold during the experiments. We have not detected any contamination during the use of the gold-cell, valve-block assembly.

Sampling is done with negligible disturbance of pressure and temperature conditions of the experiment. Liquid samples are withdrawn through the valve block into a weighed plastic syringe. Constant fluid pressure is maintained by regulated pumping of H_2O into the pressure volume external to the gold cell as samples of solution are being withdrawn. Some samples were filtered through $0.2\text{ }\mu\text{m}$ filters immediately following their withdrawal from the sample cell.

Analytical Methods

The sampling tube was flushed of stagnant solution by withdrawing about 1 ml (flush) immediately before sampling. Samples of approximately 5 ml, taken at time intervals of increasing spacing, were divided into separate portions for analyses of major elements, trace elements, (see below) and for pH determination. Samples analysed for major elements were diluted immediately and acidified with ultrapure HNO_3 . Samples examined for trace elements were acidified with one drop of concentrated HNO_3 and stored in an air-tight plastic vial. Room temperature pH was measured on a third aliquot. Major constituents (Ca, Na, K, Mg, Fe and SiO_2) were determined by atomic absorption methods, using standards in an appropriate NaCl matrix. Standard deviation of this method averaged $\pm 3\%$.

Trace elements (including Ag, Al, As, Au, B, Ba, Co, Cu, Hg, Li, Mn, Ni, Sb, Sn, Tl) were determined by special spark emission spectrographic methods developed by Dr. A. S. Radtke in the emission spectrograph facility of the Branch of Analytical Laboratories, U.S. Geological Survey, Menlo Park, California. One gm of solution was dried on 150 mg of spectrographically pure graphite overnight at 110°C . Pure NaCl was added to bring the total non-carbon solid weight to 75 mg, which produced 225 mg of charge, with a standard graphite-to-solid ratio of 2. A master standard for the elements was prepared following the same procedure. The graphite-NaCl mixture had two analytical advantages: 1) the reduced mutual adsorption effects of the different elements, prevented by the essentially constant matrix, making possible the use of one polycomponent standard; and 2) even and controllable volatilization of the carbon-salt charge. The charge was subdivided and analysed for two groups of elements, as follows:

Refractory Elements. Duplicate 30 mg charges in graphite electrodes, burned under an atmosphere of argon and oxygen (30%) for 75 seconds, with the spectral lines recorded on an Eastman Kodak emulsion plate Type III-o (made especially for the U.S.G.S.)

Volatile Elements Duplicate 45 mg charges in graphite electrodes, burned under pure argon atmosphere for 75 seconds, with spectral lines recorded on Eastman Kodak emulsion plates type SWR (made especially for the U.S.G.S.).

Chloride was determined in the diluted samples by the use of a halide sensing specific ion electrode (E&K Scientific), with a standard deviation of 3-5%.

The pH values were determined with an Orion combination electrode, at room temperature immediately after the sample was taken. Standard deviation was ± 0.1 pH units.

Changes in Solid Phases. Most solids, retrieved from the reaction cell at the termination of experiments, were exceedingly fine and mud-like, in a non-lithified condition. Solids of some experiments, particularly the rhyolite-NaCl-300°C, became almost totally lithified into solid kernels. Particles of reacted and fresh rock tend to become cemented by alteration minerals.

The solids were washed, dried, and examined by X-ray diffractometry, optical and scanning electron microscopy (SEM). The SEM was equipped with an energy dispersive X-ray analyzer (EDAX), which permitted semi-quantitative chemical analyses of the phases.

Section 3

EXPERIMENTAL RESULTS

SOLUTION COMPOSITIONS

Tables 3-1 to 3-17 summarize the composition of solutions during the experiments. Most experiments had durations of about 720 hours (30 days). All solutions were analyzed for major elements (those present in rocks at levels above 0.2%): Si, Fe, Mg, Ca, Na, and K. Minor and trace elements were also determined; the exact number depended on the levels that appeared in solution. Sought were: Ag, Al, As, Au, B, Ba, Cr, Cu, Fe, Hg, La, Li, Mg, Mn, Pb, Sb, Sc, Sr, Ti, Tl, and W.

The total dissolved material in solution varied with time, crystallinity of the rock, the solution-to-rock ratio, the ionic strength of the solution, and temperature. All other factors held equal, total dissolved material increased with glassiness of the rock, low solution to rock ratios, high ionic strengths, and high temperature. Some components showed their highest concentrations early in the experiment; others rose slowly to broad maxima; and others continuously increased in concentration. Commonly, the pH values dropped early in the experiments, then gradually increased thereafter. Most major components came to near steady-state levels within about 200 hours, but the minor constituents showed highly variable behavior.

In none of the experiments did the solids attain stable equilibria with solutions. The solutions showed variations in compositions which reflected a complicated sequence of changes in solid phases. Glassy rocks are particularly reactive and break down rapidly to extremely fine, near-amorphous hydrated silicate solids which tend to coarsen, recrystallize, and transform to more stable minerals. Some elements are freed to solution rapidly in relatively large amounts during the first stages of glass breakdown, when the solutions develop an initially more acid condition, and when the solubilities of the solids are high. With the passage of time, the solids coarsen and solubilities drop; with the nucleation of more stable phases, solubilities also drop. The amounts of the different components that appeared in solution reflected changing pH and concentration of H_2S , SO_2 , CO_3 , Cl and F, which act as precipitants or as complex ion-formers.

A useful check is the extent to which a charge balance exists among positively and negatively charged ions in the analyzed solutions. Most higher concentration solutions showed acceptable balances, but low concentration solutions showed some departures from balance, which possibly reflects analytical errors or the presence in solution of unanalyzed constituents, such as Br^- , F_3^- , HCO_3^- or S^{-2} . H_2S was detected by odor in several solutions of the basalt-andesite experiments, but was below our detection limits of <1 ppm for H_2S .

The results of the various experiments have been broken down into individual sections based on initial solution salinity (distilled water, 0.1%, 2%, 10% and 20% NaCl). Experiments using the different rock types and at different temperatures are discussed within these major sections.

Reaction with H_2O . Distilled H_2O was reacted with McDermitt rhyolite at 200° and 300°C , and with Clear Lake basalt at 300°C . These reactions were aimed at modeling the reaction of dilute solutions, which are analogous to meteoric waters commonly found in natural systems. The data indicate the nature and levels of elements that can be extracted from rocks by simple H_2O analogues of geothermal fluids, and the kinds of mineralogical readjustments to low ionic strength fluids. Some early experiments of Ellis and Mahon (1,2) used distilled H_2O in static (non-agitated) systems.

Results of the pure H_2O experiments are plotted on Figures 3-1, and 3-2 and are found in Tables 3-1, 3-2, and 3-3. Figure 2 shows the concentration of major solutes for the McDermitt - 300° experiment plotted versus time. Data for both filtered ($0.25\ \mu\text{m}$) and unfiltered data were included on this figure. Rapidly varying solution concentrations resulted from the quick and intense breakdown of the glass, which led to early anomalously high concentrations of SiO_2 , K, and Na. The initial increases in concentration were accompanied by a concomitant increase in solution pH values, caused in part by reactions that maintain charge balances as cations are solubilized from the rock.

Other studies have shown that the solubility of silica is independent of solution pH between pH 4 to 8 (see Stumm and Morgan, 1970). The metastably high SiO_2 concentrations of the initially clear samples causes amorphous SiO_2 to precipitate in the sampling syringe, necessitating special procedures to redissolve the SiO_2 for analysis. As the experiments proceed, the solids coarsen, recrystallize, or transform to new phases, and solution cations migrate back to the solid

Table 3-1

CONCENTRATION OF DISSOLVED SPECIES DURING THE INTERACTION OF RHYOLITE AND
H₂O AT 300°C, 500 BARS

Sample (Hrs.)	pH	Cl	SiO ₂	Na	K	Ca	Mg	Fe	Mn	Ti	Ba	B	Cu	Pb
1 (0)	8.48	--	1873	64.5	23	<0.5	0.1	--	0.04	0.25	0.2	0.17	0.17	0.04
2 (1)	6.49	--	--	47.8	3.0	<0.5	1.9	0.6	0.04	0.17	0.19	0.71	0.065	0.031
3 (22)	6.22	--	--	57.7	4.7	<0.5	7.0	0.9	1.2	<0.17	--	<0.1	0.175	0.076
4 (144)	8.5	--	9346	64.5	239	<0.5	2.1	48	3.1	<0.3	0.59	<0.1	0.41	0.14
5 (168)	7.22	--	898	39.1	103	<0.5	0.8	31	--	0.26	0.76	<0.1	0.31	0.19
6 (264)	7.63	--	1965	324	136	<0.5	0.5	41	1.8	3.6	1.52	<0.1	0.32	0.17
7 (348)	6.38	--	--	357	137	<0.5	1.3	71	2.7	5.5	0.69	<0.1	0.32	0.24
7 filter (348)	6.38	--	1996	365	125	<0.5	0.2	34	1.2	1.7	0.69	0.13	0.11	0.135
8 (576)	8.05	--	--	351	111	<0.5	0.6	32	0.4	0.56	0.66	0.10	0.10	0.08
8 filter (576)	8.05	--	1933	449	70	<0.5	0.1	8	0.2	1.55	0.65	0.18	0.05	0.05
9 (836)	8.11	--	--	377	47	<0.5	0.1	0.5	0.06	0.09	<0.08	0.09	0.03	0.015
9 filter (836)	8.11	--	1497	381	48	<0.5	0.1	0.5	0.02	0.08	0.11	0.05	0.02	0.017

(--) Not analyzed or below detection

Table 3-2

CONCENTRATION OF DISSOLVED SPECIES DURING THE INTERACTION OF BASALT AND
H₂O AT 300°C, 500 BARS

Sample (Hrs.)	pH	Cl	SiO ₂	Na	K	Ca	Mg	Fe	Al	Mn	Ti	Ni	Ba	Au	B	As	Pb
1 (0)	5.83	<20	681	46.8	24	0.25	0.97	<0.1	>7.5	0.19	0.40	0.52	<0.37	.002	0.57	0.56	0.072
2 (1)	5.75	<20	1367	77.9	41	0.77	1.68	<0.1	>7.5	1.9	2.2	0.30	0.37	0.004	0.86	0.68	0.082
3 (18)	6.45	20	2233	152	79	2.77	10.3	29	>7.5	0.74	10.7	0.46	1.2	0.10	2.28	0.78	0.088
4 (43)	5.15	20	2066	122	127	1.99	11.8	33	>7.5	0.53	8.8	0.29	0.96	0.35	2.47	3.8	0.09
5 (82)	6.17	20	2154	130	181	1.82	15.4	41	>7.5	0.49	10.1	0.52	1.0	0.71	3.49	3.9	0.13
6 (186)	5.12	20	2062	166	118	2.44	29.0	62	>7.5	0.77	8.8	0.49	0.8	0.011	5.67	0.81	0.13
6 filter (186)	5.12	20	1829	91	12.9	--	0.75	<0.1	>3.8	0.18	0.37	0.74	<0.37	0.004	0.88	0.51	0.089
7 (377)	5.49	20	2265	187	121	2.42	50	105	>7.5	0.59	5.9	0.39	0.61	0.006	>5.93	0.88	0.096
7 filter (377)	5.49	20	1897	97	4.9	--	1.0	<0.1	>3.8	<0.18	<0.37	1.2	<0.37	.006	1.11	0.96	0.87
8 (473)	6.25	20	1818	160	105	2.39	61	123	>7.5	0.59	6.3	1.4	0.54	0.007	>5.93	2.9	0.13
8 filter (473)	6.25	20	918	69	3.1	--	0.9	<0.1	3.8	0.18	<0.37	0.26	<0.37	0.003	0.77	0.38	0.11

(--) Not analyzed or below detection

Figure 3-1 Concentrations of major elements during the interaction of rhyolite-H₂O at 300°C.

Table 3-3

CONCENTRATION OF DISSOLVED SPECIES DURING THE INTERACTION OF
RHYOLITE-H₂O AT 300°C, 500 BARS

Sample (Hrs.)	pH	Cl	SiO ₂	Na	K	Ca	Mg	Fe
1 (0)	7.55	20	650	45	27.1	<0.4	0.56	<0.1
1 filter (0)	7.55	45	819	85	31.5	<0.4	0.71	<0.1
2 (24)	7.15	<20	4080	145	275	29	31.2	51.5
2 filter (24)	7.15	43	880	78	13.1	<0.4	0.3	<0.1
3 filter (73)	7.3	20	950	91	17.7	<0.4	0.43	<0.1
4 (313)	8.25	<20	2930	136	159	27	26	63.2
4 filter (313)	8.25	20	870	100	23	0.4	0.3	0.1
5 filter (577)	8.45	20	970	107	33	<0.4	<0.3	<0.1

Figure 3-2. Concentrations of trace elements during the interaction of rhyolite-H₂O at 300°C, 500 bars.

phases; pH increases as H^+ is consumed. At the stage at which pH began to increase, the behavior of Na, K, SiO_2 in dilute solutions resembled their behaviors in higher salinity solutions. However, other cations such as Al, Fe, Mg, Mn, and Ti, (Figure 4) behaved differently, and showed increases from low initial concentrations. Concentrations in some solutions filtered through 0.25 μm filters within 3 minutes of sampling are distinctly lower, indicating that some cations have been absorbed on, or incorporated in, rapidly nucleated silica particles that grew to $>0.25 \mu m$ or larger in the time between sampling and weighing. Concentrations of the minor elements began to drop by 806 hours, when a silica phase (cristobalite) had begun to precipitate and an approximation to equilibrium of solution with Na-K silicates had been attained. The absolute levels of these components except for SiO_2 are similar to those of many geothermal fluid and to experimental values of Ellis and Mahon (1).

The Clear Lake basalt reaction at $300^\circ C$ with distilled water (Figure 3-3) was similar to the McDermitt rhyolite reaction, except that the basalt reacted more slowly, and no large initial maxima were encountered. Solution concentrations were anomalously high, especially in unfiltered solutions; as with the rhyolite-reacted solutions, 0.25 μm -filtered solutions were lower in many components, implying that homogeneous condensation of large (filterable) near-colloidal particles had happened during brief stands.

The $200^\circ C$ experiment on the McDermitt rhyolite (distilled water) resembled the $300^\circ C$ experiment. The $200^\circ C$ experiment was terminated after 577 hours because of plugging of the gold capillary tube by precipitated solids.

Possibly the high concentrations found in unfiltered solutions reflect the presence of colloidal-like molecular particles that passed the internal gold filter. Experiments on the homogeneous nucleation of silica from solution by Rothbaum and Rohde (30) showed that dissolved silica gradually forms increasingly large soluble aggregates, eventually forming filterable megascopic particles. In our experiments, the anomalously highly concentrated SiO_2 forms polymeric aggregates that are initially small enough to pass through the internal gold filter. Rapid polymerization at room temperature eventually produces particles retained by the 0.25 μm filter. The homogeneous nuclear development of polymeric groups in solution probably is a precursor to the nucleation of solid phases.

Figure 3-3. Concentrations of major elements during the interaction of basalt-H₂O at 300°C, 500 bars.

The different elements in the glass show various modes of reaction with solution. Silica is preferentially removed from glass surfaces, leaving SiO_2 -depleted layers that are enriched in the other components. The silica rapidly forms highly stable soluble compounds, presumably H_4SiO_4 hydrates or higher polymeric aggregates, which are known to be sluggish in nucleating solid forms of silica or crystalline silicate minerals. Other elements, such as Al, rise momentarily to metastably high levels. Other studies at low temperatures (31) demonstrated that low solubility, Al-rich solid phases such as $\text{Al}(\text{OH})_3$, precipitate from solutions metastably high in Al in a few minutes. The Al in solution thereafter is controlled at low levels by properties of an Al-containing solid phase. The SiO_2 -depleted surface, which became relatively enriched in important silicate mineral-forming elements such as Na, K, Ca, Mg, Fe and Al, and absorbed H_2O , eventually serve as sites for nucleating the kinetically favored, more rapidly forming silicates, such as montmorillonite. The solution levels of elements in the solid phases become controlled by properties of initially formed, commonly metastable, solid phases. The absolute concentrations would adjust to equilibrium values with the passage of time and the appearance of the equilibrium assemblage of solid phases.

The levels of elements extracted from rhyolite and basalt by pure H_2O (except for SiO_2) are similar to levels in meteoric waters that have reacted with volcanic rocks in geothermal systems.

Reaction with 0.1% NaCl. Clear Lake basalt powder was reacted with 0.1% NaCl solution at 200°C , 500 bars (Table 3-4); and with Japan andesite powder at 200°C , 500 bars, 300°C , 500 bars, and 400°C at 1,000 bars (Tables 3-5 to 3-8). The reactions were aimed at modeling dilute chloride water interactions that have happened in many geothermal systems, such as Wairakai, N.Z. (32). The presence of NaCl in the solutions prevented experimental difficulties encountered with distilled water.

Figures 3-4, 3-5 present plots of the data for the 300° and the 400°C andesite reactions as a function of time. The solutions reacted quickly with andesite, and near steady-state concentrations were attained within a few days. Small decreases in pH occurred early in the 300°C experiment, followed by steady increases in pH to values above neutrality (pH 5.5) at 300°C .

Table 3-4

CONCENTRATION OF DISSOLVED SPECIES DURING THE
INTERACTION OF BASALT AND 0.1 % NaCl
AT 200°C, 500 BARS

Sample (Hrs.)	pH	Cl	SiO ₂	Na	K	Ca	Mg	Fe
1 (0)	6.95	500	131	387	41	<0.4	<0.3	<0.1
2 (24)	8.22	529	471	384	107	<0.4	<0.3	<0.1
3 (69)	8.3	494	573	382	115	<0.4	<0.3	<0.1
3 filter (69)	8.3	494	572	382	115	<0.4	<0.3	<0.1
4 (216)	8.3	545	713	364	118	<0.4	<0.3	<0.1
5 (882)	8.25	540	901	371	143	<0.4	<0.3	<0.1

Table 3-5

CONCENTRATION OF DISSOLVED SPECIES DURING THE
INTERACTION OF ANDESITE AND 0.1 % NaCl
AT 200° C, 10/1 SOLUTION TO ROCK RATIO

Sample (Hrs.)	pH	Cl	SiO ₂	Na	K	Ca	Mg	Fe
1 (0)	5.90	571	<20	412	4.63	9.27	0.6	<0.1
2 (24)	5.50	564	479	401	12.6	4.21	0.4	<0.1
3 (116)	6.62	630	585	385	15.4	4.88	0.2	<0.1
4 (329)	6.90	583	592	417	17.7	4.98	0.2	<0.1
5 (740)	7.10	608	635	437	21.6	—	0.1	<0.1

(—) Not analyzed

Table 3-6

CONCENTRATION OF DISSOLVED SPECIES DURING THE
INTERACTION OF ANDESITE AND 0.1 % NaCl
AT 200° C, 50/1 SOLUTION TO ROCK RATIO

Sample (Hrs.)	pH	Cl	SiO ₂	Na	K	Ca	Mg	Fe
1 (0)	5.80	480	255	356	6.18	3.76	0.19	<0.1
2 (29)	6.15	494	474	363	8.47	2.78	0.20	<0.1
3 (248)	6.35	521	603	360	10.9	2.86	0.2	<0.1
4 (416)	6.40	510	644	360	11.9	2.86	0.01	<0.1
5 (705)	6.50	486	629	348	11.9	3.05	<0.01	<0.1
6 (1036)	6.45	483	648	356	16.5	3.15	<0.01	<0.1
7 (1375)	6.39	482	652	346	16.5	2.55	<0.01	<0.1

Table 3-7

CONCENTRATION OF DISSOLVED SPECIES DURING THE
INTERACTION OF ANDESITE AND 0.1 % NaCl
AT 300° C, 10/1 SOLUTION TO ROCK RATIO

Sample (Hrs.)	pH	Cl	SiO ₂	Na	K	Ca	Mg	Fe	Ni	Al	As	B	Pb
1 (0)	5.7	627	791	404	18.3	16.1	<0.05	1.0	0.28	2.4	0.57	0.70	0.043
2 (24)	6.2	563	1367	384	42	14.1	<0.05	1.3	0.52	1.3	0.79	0.40	0.037
3 (72)	5.2	545	1204	379	61	15.1	<0.05	1.1	0.47	1.3	0.89	0.50	0.12
4 (168)	5.8	545	1281	385	75	7.0	<0.05	0.88	0.40	0.95	1.2	0.58	0.42
5 (336)	6.33	540	1267	376	75	10.1	<0.05	0.90	0.37	1.0	0.84	0.65	0.027
6 (528)	6.42	501	1224	376	77	1.5	<0.05	0.81	0.35	1.0	0.95	0.61	0.24
7 (859)	6.60	561	1215	385	81	0.15	<0.05	0.82	0.16	2.2	1.0	0.68	0.030
8 (2032)	7.05	566	882	379	85	—	0.24	0.96	0.33	2.4	1.87	0.63	0.038

(—) Not analyzed

Figure 3-4. Concentrations of major elements during the interaction of andesite and 0.1% NaCl at 300°C, 500 bars.

Potassium rapidly increased in concentration at the start of the reaction, and subsequently showed slight increases, reflecting sluggish changes in the properties of the solids. Sodium dropped slightly initially, indicating that rapid ion exchange or surface absorption had taken place, but leveled to steady-states in one day. Calcium, however, showed an immediate jump to 16 ppm, and subsequently steadily decreased. This behavior of Ca probably reflects initial ion exchange of Ca by Na, followed by slow incorporation of Ca in the reaction products (smectite). SiO_2 increased sharply to meta- stably high, nearly constant values that were much lower than was found in reacted distilled water of other experiments.

Figure 3-5 shows that the reaction of andesite at 400°C is quite similar to the 300°C experiment. The pH values pass through a maximum at about 7 days and drop to a steady state of 6.3. Both Na and K develop steady state values within the first day. Ca did not show the initially high input; only 0.13 ppm was found in the first sample. SiO_2 rose to a maximum in one day and subsequently fell rapidly to a near steady-state concentration.

To summarize, reactions of 0.1% NaCl solutions are rapid, and steady-state concentrations are readily attained. The concentrations of Na, K, Ca and Mg are controlled by ion exchange reactions and mineral properties. SiO_2 concentrations remain higher than the solubilities of any crystalline silica phase, even in the presence of myriads of quartz crystals. The sluggishness of the adjustment of the silica in solution is well illustrated. The pH values hover about neutrality to slightly alkaline, but they remain less alkaline than pH values of reacted pure water, showing that NaCl significantly affects room temperature pH.

Reactions with 2% NaCl. Tables 3-9, 3-10, 3-11, and 3-12 present data on the reaction of basalt and rhyolite with 2% NaCl solutions at 300° and at 200°C . The choice of the 2% NaCl concentration an attempt to model higher concentration solutions found in some geothermal systems, such as Heber, which contain 1 to 3% total dissolved salts. The 2% NaCl concentration is not far from the total dissolved salt content of seawater, which is important in geothermal systems of Japan and Iceland.

Figure 3-6 presents plots of the data from the 300° -rhyolite-2% NaCl experiment as a function of time. The pH values dropped to minima at about 20 hours and increased afterward to steady state values near 6.5. Initially, Na dropped and K increased. After 100 hours, Na increased. K passed through a maximum after 200

Figure 3-5. Concentration of major elements during the interaction of andesite and 0.1% NaCl at 400°C, 500 bars.

Table 3-8

CONCENTRATION OF DISSOLVED SPECIES DURING THE
INTERACTION OF ANDESITE AND 0.1 % NaCl
AT 400°C, 10/1 SOLUTION TO ROCK RATIO

Sample (Hrs.)	pH	Cl	SiO ₂	Na	K	Ca	Mg	Fe
1 (0)	5.0	618	1924	418	70.6	0.13	<0.1	<0.1
2 (27)	6.10	694	2205	389	126	<0.05	<0.1	<0.1
3 (75)	6.50	661	1927	403	152	<0.05	0.13	<0.1
4 (170)	6.60	606	1767	389	153	<0.05	<0.1	<0.1
5 (311)	6.31	620	1757	385	147	<0.05	0.11	<0.1
6 (532)	6.24	588	1852	390	154	<0.05	<0.1	<0.1

Table 3-9

CONCENTRATION OF DISSOLVED SPECIES DURING THE
INTERACTION OF RHYOLITE AND 2% NaCl
AT 200° C, 500 BARS

Sample (Hrs.)	pH	Cl*	SiO ₂	Na	K	Ca	Mg	Fe
1 (0)	6.65	11.4	209	7021	259	60.3	7.35	<0.1
2 (48)	4.94	11.8	758	7073	1515	86.7	5.85	<0.1
3 (168)	5.32	11.6	889	6608	2033	89.1	2.51	<0.1
4 (384)	5.45	11.6	905	6508	2140	86.4	1.28	<0.1
5 (1221)	5.90	11.6	938	6200	2094	81.1	0.87	<0.1
6 (2013)	5.60	11.2	954	6278	2127	74.8	0.61	<0.1
7 (2469)	5.62	10.1	899	6193	2102	72.4	0.60	0.1

Table 3-10

CONCENTRATION OF DISSOLVED SPECIES DURING THE
INTERACTION OF BASALT AND 2% NaCl
AT 200° C, 500 BARS

Sample (Hrs.)	pH	Cl*	SiO ₂	Na	K	Ca	Mg	Fe
1 (0)	6.65	11.7	165	7145	379	43.6	1.9	<0.1
2 (24)	6.15	11.7	504	6979	940	73.9	<0.3	<0.1
3 (72)	5.90	11.5	540	6985	1009	77.4	<0.3	<0.1
4 (308)	6.19	11.6	648	7117	1213	82	<0.3	<0.1
5 (672)	6.25	11.6	730	7134	1279	83	<0.3	<0.1
6 (1152)	6.27	11.2	782	7050	1284	80	<0.3	<0.1

*Concentration in parts per thousand

Table 3-11

CONCENTRATIONS OF DISSOLVED SPECIES DURING THE INTERACTION OF RHYOLITE AND
2% NaCl AT 300°C, 500 BARS

Sample (Hrs.)	pH	Cl*	SiO ₂	Na	K	Ca	Mg	Fe	Al	Mn	B	Au	Ni	As	Pb	Cr	Sr	Tl	Li
1 (0)	5.85	13.27	955	7147	1384	33.5	<0.4	1.36	>5.0	<0.1	0.66	<0.005	0.06	0.26	0.95	0.030	0.13	0.025	<2.5
2 (1)	5.67	13.33	1154	6598	2090	14.2	<0.4	0.25	>5.0	<0.1	0.73	0.012	0.05	0.30	0.055	0.026	0.07	0.027	<2.5
3 (19)	5.52	10.00	1410	6712	2524	9.0	<0.4	0.25	>2.5	<0.1	0.15	<0.005	0.12	0.75	0.033	0.023	0.06	0.032	<2.5
4 (47)	5.54	11.10	1512	6526	2616	8.6	<0.4	0.71	>2.5	<0.1	1.3	0.039	0.12	0.66	0.036	0.024	0.06	0.026	4.1
5 (92)	5.62	11.34	1621	6494	2736	7.9	<0.4	0.4	>2.5	<0.1	2.3	0.23	0.06	0.61	0.035	0.022	0.06	0.025	4.6
6 (188)	5.90	10.97	1640	6870	2780	8.3	<0.4	0.35	>2.5	<0.1	2.4	<0.005	0.05	1.2	0.037	0.029	0.07	0.026	4.9
7 (428)	6.2	13.74	1412	6881	2122	8.0	<0.4	0.34	0.88	0.10	3.2	<0.005	0.05	1.9	0.029	0.024	0.07	0.025	4.8
8 (836)	6.5	11.87	1374	7315	1684	7.8	<0.4	0.26	1.6	<0.12	6	<0.005	<0.06	2.3	0.043	0.028	0.06	<0.03	4.7

*Concentration in parts per thousand

Table 3-12

CONCENTRATIONS OF DISSOLVED SPECIES DURING THE INTERACTION OF BASALT AND
2% NaCl AT 300°C, 500 BARS

Sample (Hrs.)	pH	Cl*	SiO ₂	Na	K	Ca	Mg	Fe	Al	Mn	Ba	As	Tl	B	Pb	Li
1 (0)	5.87	10.26	584	7596	361	22.7	<0.4	0.45	2.8	<0.18	0.31	<0.37	<0.037	<0.37	0.047	<3.7
2 (1)	5.5	9.67	--	6926	--	--	<0.4	1.0	3.0	<0.18	0.39	<0.37	<0.037	0.51	0.45	<3.7
3 (21)	5.17	10.22	1576	7100	1605	12.9	<0.4	1.1	1.7	0.18	0.73	0.43	0.038	1.6	0.054	<3.5
4 (50)	5.04	10.04	1666	7134	1597	12.5	<0.4	1.9	1.9	0.20	0.76	0.39	0.037	2.3	0.058	3.6
5 (98)	4.96	9.41	1659	7116	1553	12.5	<0.4	--	1.2	0.18	0.79	0.40	<0.037	2.4	0.081	3.7
6 (194)	4.95	9.80	1787	7140	1503	11.7	<0.4	1.4	1.1	0.18	0.74	--	0.044	4.1	0.08	3.7
7 (410)	5.10	9.83	1665	7133	1191	28.7	<0.4	1.6	0.46	0.18	--	1.1	0.05	<5.9	0.06	3.7
8 (842)	5.52	9.96	1461	7345	1138	60	<0.4	1.2	0.47	0.45	0.63	0.95	0.037	<5.9	0.065	3.8

(--) Not analyzed

*Concentration in parts per thousand

Figure 3-6. Concentrations of major elements during the interaction of rhyolite-2% NaCl at 300°C, 500 bars.

hours. Ca jumped to 34 ppm at first sampling, but decreased to a steady value of about 8 ppm within 20 hours. Mg remained below detection (0.4 ppm). SiO_2 rose to a broad maximum in 188 hours, and eventually dropped to a concentration slightly lower than the amorphous silica solubility. Chloride decreased from the initial value, 12,100 ppm, to about 11,000 ppm at 188 hours, and remained relatively steady thereafter.

Figure 3-7 presents data on the reaction of basalt with 2% NaCl under the same conditions (300°C, 500 bars). The basalt reaction is nearly identical to the rhyolite reaction except that Ca, Fe and Al were present at measureable levels. Fe was nearly constant, and Al decreased continuously. The pH showed a minimum that was higher than the pH minimum for the rhyolite reaction.

Reactions of 2% NaCl at 300°C were characterized by (1) broad minima in pH, (2) initially, rapidly increased K and SiO_2 followed by abrupt decreases to steady state levels, and (3) measurable trace metal concentrations. Reactions of 2% NaCl solutions at 200°C showed lower SiO_2 concentrations; slightly lower pH values for the rhyolite, and slightly higher pH values for basalt; and decreasing Na concentrations. K and Ca concentrations rose more slowly to steady values at 200°C as compared to the 300°C experiments.

Reactions with 10% and 20% NaCl solutions. Tables 3-13, 3-14, 3-15 and 3-16 present data on the reactions of 10% and 20% NaCl solutions at 300°C with rhyolite and basalt. The high concentrations were selected to model concentrated solutions of a type found in several areas, including the Salton Sea geothermal system (33). These solutions, which may contain as much as 30% total dissolved salts, characteristically have unusually high concentrations of such elements as lead, zinc, copper and silver (34). Our aim was to determine experimentally the kinds of mineral assemblages and solution types that form under such high salinity conditions.

The general trends of the reactions of the 10% and 20% NaCl solutions are nearly identical for both the rhyolite and basalt. Differences in absolute levels, however, were observed that depended on types of solution and rocks. The reactions of 10% NaCl are discussed in detail below as examples.

Figure 3-8 shows plots of the data on the reaction of rhyolite with 10% NaCl. A striking feature is the high K concentration found in the initial sample, 9280 ppm, showing the rapidity with which Na displaces K from the rocks. The

Figure 3-7. Concentrations of major elements during the interaction of basalt and 2% NaCl at 300°C, 500 bars.

Table 3-13

CONCENTRATIONS OF DISSOLVED SPECIES DURING THE INTERACTION OF RHYOLITE AND
10% NaCl AT 300°C, 500 BARS

Sample (Hrs.)	pH	Cl*	SiO ₂	Na*	K	Ca	Mg	Fe	Al	Mn	B	Au	Ni	As	Pb	Cr	Sr	Sb	Tl
1 (0)	2.45	61.0	1357	33.3	9280	173	5	4.3	4.6	21	1.2	0.078	1.2	0.86	5.6	0.061	0.63	<0.23	0.36
2 (1)	5.15	60.3	1693	33.2	5140	108	1.5	1.4	4.4	3.3	0.9	0.021	0.1	0.56	0.94	0.037	0.37	<0.22	0.37
3 (19)	5.35	61.5	—	—	—	—	1.8	2.1	3.8	27	1.2	0.11	0.4	0.75	1.9	0.044	0.44	<0.22	0.65
4 (47)	5.4	61.3	1491	32.2	6590	174	1.4	2.9	4.0	21	2.0	0.09	0.3	0.84	2.0	0.05	0.53	<0.26	0.66
5 (185)	5.2	61.1	1545	34.5	6730	174	<0.7	1.5	1.3	12	3.7	0.074	0.1	1.5	2.3	0.025	0.38	0.4	—
6 (238)	5.2	59.8	1319	34.0	5940	178	<0.7	1.8	0.74	9	5	0.059	0.09	2.3	2.8	0.044	0.32	0.65	0.45
7 (408)	5.3	61.6	1327	33.3	6130	182	<0.7	2.1	0.72	9	10	0.061	0.18	5.2	2.9	0.031	0.28	0.73	0.48
8 (644)	5.47	60.8	1301	32.9	5290	177	<0.7	1.9	1.3	12	10	0.058	0.26	5.0	4.0	0.019	0.29	0.91	0.55
9 (839)	5.31	61.2	1273	32.8	5860	173	<0.7	2.5	1.1	15	10	0.10	0.16	8.5	4.3	0.045	0.39	1.4	0.79
9 filter (839)	5.31	63.3	1239	33.0	5470	177	<0.7	—	—	—	—	—	—	—	—	—	—	—	—

(—) Not analyzed

*Concentration in parts per thousand

Table 3-14

CONCENTRATIONS OF DISSOLVED SPECIES DURING THE INTERACTION OF BASALT AND
10 % NaCl AT 300°C, 500 BARS

Sample (Hrs.)	pH	Cl*	SiO ₂	Na*	K	Ca	Mg	Fe	Al	Mn	Ba	B	Au	Bi	Tl
1 (0)	5.5	57.8	485	35.2	767	7.1	0.4	2.5	2.7	0.29	1.71	0.45	0.004	0.45	0.04
2 (1)	5.32	58.8	1183	37.4	1603	100.4	0.4	4.4	2.9	0.72	2.4	0.45	0.004	0.46	0.045
3 (22)	4.62	58.	1422	36.3	2538	143	2.86	13.3	1.4	1.64	2.9	0.85	0.03	0.95	0.08
4 (43)	3.5	59.2	1566	37.7	2832	171	5.32	20	1.1	3.0	4.2	1.25	0.59	1.7	0.08
5 (90)	4.3	58.8	1663	36.6	2882	207	3.83	26	0.87	2.6	3.6	—	—	—	—
6 (187)	4.45	58.3	1716	35.4	2850	200	4.3	22	0.63	2.8	3.4	1.24	0.09	1.9	0.14
7 (419)	3.9	57.8	1780	36.15	2949	226	3.26	20	0.37	2.8	3.8	4.06	0.08	1.4	0.08
8 (609)	4.43	58.1	1825	34.9	3033	247	1.93	17	0.38	2.5	3.1	—	0.09	1.4	0.07
9 (823)	4.73	58.2	1762	35.3	3103	294	1.0	8	0.1	2.0	3.3	6.04	0.06	0.6	0.09

(—) Not analyzed

*Concentration in parts per thousand

Figure 3-8. Concentrations of major elements during the interaction of rhyolite and 10% NaCl at 300°C, 500 bars.

initial high K value gave way to a minimum at 1 hour, possibly reflecting the nucleation of a K-containing solid phase. Beyond 1 hour, K went through another maximum at about 100 hours, falling to a steady-state level at around 200 hours. SiO_2 rose to a maximum at 185 hours, and fell thereafter to steady state values less than the solubility of amorphous silica. Na and Cl remained essentially constant. Mg jumped to 5 ppm and dropped rapidly below 0.7 ppm, the detection limit. Ca had reached a steady value by the time of first sampling. The pH at first sampling was quite low, 2.45, but it rose rapidly to a steady value, 5.3, at room conditions, which would be near neutral at 300°C . Minor elements were freed to solution in high quantities.

In summary, rocks react rapidly with 10 and 20% NaCl, forming alteration products and stable solution compositions. Silica concentrations remained high; in time, SiO_2 -consuming solid phase reactions would cause SiO_2 to drop to the saturation level required by the minerals. Minor and trace elements are extracted efficiently in amounts sufficiently high to account for composition of natural brines.

Trace Elements

Natural solutions have trace element compositions influenced by rock-water interactions, but in ways that are not clear. The trace element compositions of the experimental solutions were determined to find whether they could be related to factors such as rock types, temperature, solution types, and reaction times. The experimental data potentially provide a basis for the interpretation of natural fluid compositions. However, analytical difficulties prevented completion of the analyses of all solutions. The fragmentary data on hand gives a hint that compositions do relate in a systematic way to the factors mentioned above.

Rhyolite- 300°C - H_2O . The trace element contents of initially pure H_2O reacted with rhyolite at 3/1 solution to rock ratio (S/R=3) at 300°C during 836 hours are given in Table 3-1 and Figure 3-2. The elements Ti, Ba, B, Cu, and Pb, enter solution in significant quantities, at ppm levels initially, and pass through maxima at about 300 hours to decline to ppb levels by 800 hours. The trace element concentrations have recorded the effects of complex solid and solution phase events. As discussed previously, rhyolite breaks down rapidly and extensively in reaction with H_2O to form exceedingly fine-grained, nearly amorphous solids, while the solution takes on unusually high levels of major

constituents, especially SiO_2 . After the initial reaction a slow adjustment takes place. Solid phases coarsen and recrystallize, and new solids appear. The solution, which is generally acidic initially, tends to fluctuate somewhat in pH before steadying down to approach presumably the equilibrium pH. The trace elements freed early in the reaction tend to redistribute between the solution and solid phases according to the nature of the dissolved species and their modes of interaction with the solids.

Rhyolite-300°C-2% NaCl. Table 3-11 and Figure 3-9 present data on the trace element levels (B, Au, Ni, As, Pb, Cr, Sr, Tl, Li) in 2% NaCl solutions reacted with rhyolite (3/1 S/R) at 300°C during 836 hours. Greater amounts of trace elements were solubilized than in the H_2O experiments. Fe and Mn showed early decreases to near steady levels. Au was below detection (<0.005 ppm) except for two samples at 47 and 92 hours. The NaCl solutions contained or generated complexing agents which drastically modified the behavior of the trace elements.

Rhyolite-300°C-10% NaCl. Table 3-13 and Figure 3-10 present trace element data on 10% NaCl solutions reacted with rhyolite at S/R of 3 at 300°C during 839 hours. Trace elements appeared at higher levels than with the 2% NaCl, and they mostly showed steady increases throughout the experiment. Significant levels of elements found in many ore deposits and geothermal systems entered solution, such as Au, Cu, Sb, Pb, As and Mn.

Basalt-300°C- H_2O . Table 3-2 presents levels of Ba, As, Ti, B, Pb, and Ni in pure H_2O solutions produced by the reaction with basalt at S/R of 3 during 473 hours. Important levels of all elements appeared in solution, with some erratic scatter in the data probably caused by analytical difficulties connected with the homogeneous nucleation of silica aggregates in solution. The solutions highly supersaturated with SiO_2 tended to form particles of filterable size on standing at room temperature for a few minutes. The high trace element contents reported in Table 3-2 probably are representatives of compositions of solutions in the cell before sampling. Initially pure H_2O clearly is capable of extracting significant amounts of trace elements from basalt.

Basalt-300°C-2% NaCl. Table 3-12 presents trace element levels for Ba, As, Tl, B, Pb, and Li in 2% NaCl solutions reacted with basalt at 300°C for 842 hours. Absolute levels were higher than in H_2O . Most elements rose to steady values except for B, which showed a steady increase.

Table 3-15

CONCENTRATION OF DISSOLVED SPECIES DURING THE INTERACTION OF RHYOLITE AND 20% NaCl AT 300°C, 500 BARS

Sample (Hrs.)	pH	Cl*	SiO ₂	Na*	K*	Ca	Mg	Fe
1 (0)	4.1	124	946	71.3	0.59	148	14.0	31.5
2 (47)	4.9	127	1235	69.4	10.57	377	10.4	181
3 (95)	5.05	125	1266	67.9	10.87	416	6.5	200
4 (239)	5.00	125	1328	69.7	11.41	453	3.3	215
5 (599)	5.00	123	1350	70.1	10.78	468	2.3	196
6 (935)	5.01	130	1435	70.9	10.27	480	2.3	190

*Concentration in parts per thousand

Figure 3-9. Concentrations of trace elements during the interaction of rhyolite and 2% NaCl at 300°C, 500 bars.

Table 3-16

CONCENTRATIONS OF DISSOLVED SPECIES DURING THE INTERACTION OF BASALT AND
20% NaCl AT 300°C, 500 Bars

Sample (Hrs.)	pH	Cl*	SiO ₂	Na*	K	Ca	Mg	Fe
1 (0)	5.05	125	547	73.7	1991	115	3.46	8.4
2 (1)	4.75	—	755	80.6	2713	149	4.37	19.4
3 (25)	4.60	126	1415	73.8	3540	190	6.32	85.3
4 (63)	4.58	128	1395	71.8	3690	231	7.72	126
5 (145)	4.83	119	1389	80.1	3780	246	7.84	144
6 (457)	4.95	126	1277	74.3	3970	328	8.42	137
7 (767)	4.90	130	1025	—	4090	502	3.99	75
7 (767)	4.90	127	713	74.3	4240	488	4.39	76

(—) Not analyzed

*Concentration in parts per thousand

Figure 3-10. Concentrations of trace elements during the interaction of rhyolite and 10% NaCl at 300°C, 500 bars.

Basalt-300°C-10% NaCl. Table 3-14 and Figure 3-11 show trace element data on As, Au, B, Ba, Bi and Tl in 10% NaCl solutions reacted with basalt at 300°C for 823 hours. Levels tended to be somewhat higher than for 2% NaCl, with the exception of Pb and As.

Andesite-300°C-0.1% NaCl. Table 3-7 presents data on Ni, As, B, and Pb contents of 0.1% NaCl solutions reacted with andesite at a S/R of 10 at 300°C for 2032 hours. The data cannot be compared directly with data for the basalt and rhyolite reactions because of the differences in experimental conditions, but it is clear that important levels of the trace elements are released from andesite. Steady states were attained by most elements after a few hundred hours.

Solid Phases

Rhyolite products. The solid phases produced by the reactions of rhyolite with solution are tabulated in Table 3-17 along with the experimental conditions. The following section discusses the experiments arranged according to temperature and solution types.

300°C-H₂O. The rhyolite glass after reacting 460 hours at 300°C completely transformed to a fine-grained mixture of K-feldspar, albite, alpha-cristobalite and mordenite, shown in the SEM photograph of Figure 3-12. K-feldspar is a disorder sanidine structure containing 85% KAlSi₃O₈, according to X-ray diffraction examination; K-feldspar is shown in the center of Figure 3-12 as euhedral tabular crystals that range up to 3 µm in length. Albite occurs as aggregates of finer crystals visible in the lower right of Figure 3-12. Alpha-cristobalite, visible as interpenetrating crystals up to 3 µm in length in the center of Figure 3-13, is well ordered with a d(101) spacing of 4.04 Å. Mordenite, which occurs in small amounts as fibers in Figures 3-12 and 3-13, ranges from 0.2 µm to 10 µm in length.

300°C-2% NaCl. In contrast to the reaction with pure H₂O, rhyolite glass reacted incompletely with 2% NaCl solution in 836 hours at 300°C. The reaction produced coatings of alteration minerals on glass shards (Figure 3-14). The most important alteration product was a zeolite in a tabular habit that resembles the characteristic habit of clinoptilolite (euhedral coffin-shaped crystals) but with atomic spacings close to those of ferrierite (Na-K-Mg-Al tectosilicate). Semi-quantitative analysis by SEM indicates that the phase contains major K, Na, Al, Fe, and Si, but is low in Mg. Other

Figure 3-11. Concentrations of trace elements during the interaction of basalt and 10% NaCl at 300°C, 500 bars.

Table 3-17

RUN CONDITIONS AND REACTION PRODUCTS FROM RHYOLITE EXPERIMENTS

Run No.	Temp °C	P _{fluid} bars	Solution Type	Ratio Solution to Rock	Duration (Hours)	Run Products
1	300	500	Distilled H ₂ O	3/1	836	Sanidine + albite + cristobalite + mordenite
2	300	500	2% NaCl	3/1	836	K-Al zeolite (clinoptilolite - ferrierite) mordenite
3	300	500	10% NaCl	3/1	839	K-Al zeolite (clinoptilolite - ferrierite) mordenite + analcime
4	300	500	20% NaCl	3/1	935	Bladed unknown phase
5	200	500	Distilled H ₂ O	3/1	577	unreacted glass shards
6	200	500	2% NaCl	3/1	2469	unreacted glass shards

Table 3-18

RUN CONDITIONS AND REACTION PRODUCTS FROM BASALT EXPERIMENTS

Run No.	Temp °C	P _{fluid} bars	Solution Type	Ratio Solution to Rock	Duration (Hours)	Run Products + (plagioclase + diopside)
1	300	500	Distilled H ₂ O	3/1	473	Unreacted material (smectite)
2	300	500	2% NaCl	3/1	842	clay (smectite) + zeolite (chabazite + clinoptilolite)
3	300	500	10% NaCl	3/1	870	clay (smectite) + mordenite + analcime(?)
4	300	500	20% NaCl	3/1	769	Albite + clay.
5	200	500	1000 ppm NaCl	3/1	882	unreacted material (smectite?)
6	200	500	2% NaCl	3/1	1152	unreacted material (smectite?)

Figure 3-12. SEM photograph of alteration products from rhyolite-H₂O experiment at 300°C, 500 bars.

Figure 3-13. SEM photograph of alteration products from rhyolite-H₂O experiment at 300°C, 500 bars.

Figure 3-14. SEM photograph of alteration products from rhyolite-2% NaCl experiment at 300°C, 500 bars.

Figure 3-15. SEM photograph of alteration products from rhyolite-10% NaCl experiment at 300°C, 500 bars.

alteration products included K-feldspar and albite up to 8 μm long that overlie the earlier zeolite crystals.

300°C-10% NaCl. The reaction of rhyolite glass with 10% NaCl for 839 hours produced results similar to the reaction with 2% NaCl, except that analcime appeared in small quantities. Cores of unreacted glass were coated by the fine-grained reaction products, which were made up mostly of the same zeolite as found in the 2% NaCl experiment. Analcime occurs as euhedral twinned crystals up to 6 μm long (center of Figure 3-15) that typically sit on the earlier formed zeolite. Other minerals include mordenite, albite and K-feldspar.

300°C-20% NaCl. The reaction of rhyolite glass with 20% NaCl at 300°C for 935 hours was incomplete, as observed with other NaCl reactions, but the only alteration product was a fine-grained bladed material which was non-crystalline according to X-ray examination. The solid contained Si, Al, Fe, K and Cl, according to semi-quantitative SEM analyses. We conclude that this solid is probably a poorly crystallized clay.

200°C-H₂O-2% NaCl. No reaction products were produced at 200°C. Examination by SEM of cell contents after 800 hours of reaction showed only pitted glass fragments. The strong effect of temperature on reaction rates was well illustrated by the slowness of the 200°C breakdown.

Basalt products. The reactions of basalt powder with solutions tended to be incomplete. Mostly small amounts of clay were produced with lesser zeolites and albite. The crystalline minerals in the basalt tended to remain unreacted. Table 3-18 presents a list of the basalt reaction products.

300°C-H₂O. The reaction of basalt with distilled H₂O at 300°C and 800 hours produced minor amounts of poorly crystallized, fine, smectitic clay mixed with unreacted materials. Original plagioclase and pyroxene showed no signs of alteration.

300°C-2% NaCl. Basalt reacted with 2% NaCl for 842 hours at 300°C formed reaction products visible in SEM photographs but too low in amount to be detected by the X-ray diffractometer in the presence of crystalline original minerals. The SEM photograph of Figure 3-16 shows 2 kinds of textures: the platelets of probable clay on the right; and less organized, poorly

Figure 3-16. SEM photograph of alteration products from basalt-2% NaCl experiment at 300°C, 500 bars.

Figure 3-17. SEM photograph of alteration products from basalt-2% NaCl experiment at 300°C, 500 bars.

crystallized clay on the lower left; whether these are two different clays or different habits of the same clay is not known. A distinctly different clay that occurs in plates as large as 3 μm in length and 0.5 μm or less in thickness is shown in Figure 3-17. Another phase, shown in Figure 3-18, which perhaps is a zeolite, makes up thin rectangular euhedral crystals that perch on plagioclase and pyroxene grains. The crystalline primary minerals appear to have provided sub-strates suitable for nucleation and growth of this secondary mineral.

300°C-10 % NaCl. Basalt reacted with 10% NaCl for 870 hours at 300°C produced several alteration minerals as tight coatings on rock particles. The most abundant was smectite, which was closely associated with typical bent fiber crystals of mordenite (Figure 3-19). A phase tentatively identified as a zeolite occurs as single and intertwinning euhedral-to-subhedral grains (Figure 3-20) and as small single crystals embedded in clay (Figure 3-19). The crystal shapes resemble analcime (Mumpton and Ormsby, 1976).

300°C-20% NaCl. Basalt reacted with 20% NaCl for 900 hours at 300°C formed smectitic clay and secondary albite. Grain surfaces had been etched.

200°C-0.1 and 2% NaCl. No alteration products were detectable by X-ray examination in the basalt reacted with 0.1 and 2% NaCl for 900 hours.

Andesite products. Table 3-19 gives the reaction products of andesite.

300°C-0.1% NaCl. Japan andesite (JA1) reacted with 0.1% NaCl for 2033 hours at 300°C produced tight coatings of a fine, disordered clay (smectite), visible in the SEM photograph of Figure 3-21. X-ray diffractometer examination of unglycolated and glycolated clay showed the expansion of the 15 Å spacing to 17 Å typical of smectite.

200°C-0.1% NaCl. Andesite reaction with 0.1% NaCl at 200°C at the normal 10/1 and at 10/1 solution to rock ratios produced products identical to the 200° experiment.

400°C-0.1% NaCl. Andesite reacted extensively with 0.1% NaCl at 400°C during 530 hours, to produce chlorite and epidote. Chlorite occurs in tabular and aligned grains (Figure 3-22) that contain, in decreasing amounts,

Figure 3-18. SEM photograph of alteration products from basalt-2% NaCl experiment at 300°C, 500 bars.

Figure 3-19. SEM photograph of alteration products from basalt-10% NaCl experiment at 300°C, 500 bars.

Figure 3-20. SEM photograph of alteration products from basalt-10% NaCl experiment at 300°C, 500 bars.

Figure 3-21. SEM photograph of alteration products from andesite-0.1 % NaCl experiment at 300°C, 500 bars.

Table 3-19

RUN CONDITIONS AND REACTION PRODUCTS FROM ANDESITE EXPERIMENTS

Run No.	Temp °C	P _{fluid} bars	Solution Type	Ratio Solution to Rock	Duration (Hours)	Run Products + (Qtz + albite)
1	300	500	1000 ppm NaCl	10/1	2033	Smectite clay
2	200	500	"	10/1	739	"
3	200	500	"	50/1	1375	"
4	400	1000	"	10/1	530	swelling chlorite epidote

Figure 3-22. SEM photograph of alteration products from andesite-0.1% NaCl at 400°C, 500 bars.

Si, Al, Fe, and Na, according to semi-quantitative SEM analyses. Examination by X-ray indicates that the chlorite is a swelling type that shows a change of the 14.7 Å atomic spacing to 16.4 Å upon glycolization.

Summary on Reaction Products

The nature and extent of alteration depended on temperature, crystallinity and rock type; reactivity was greater at higher temperature, greater glassiness and higher concentrations except for the pure H₂O reaction with rhyolite. Smectite was most commonly formed as a metastable mineral from the more acidic solutions. Feldspars and zeolites may represent more stable forms. Quartz or other silica phases did not form except for cristobalite in one experiment, in spite of the high level of SiO₂ in solution.

Section 4

DISCUSSION

COMPARATIVE SOLUTION BEHAVIOR

The following sections compare and discuss general solution behavior (pH; SiO₂; Na, K, Ca, Mg; and trace elements) between the different experiments and as a function of time. We then propose various models which may explain this behavior which take into account previous experimental and theoretical studies.

pH. The pH, as measured under room conditions, showed a variety of behavior. Most experiments showed initial drops from the original pH value of 7 to about 5, followed by a return toward higher pH's, during which the pH passed through broad maxima or rose monotonically. The pH at constant time (720 hours was arbitrarily selected for illustration) varied with rock type, solution composition, temperature, and solution-to-rock ratios. Figure 4-1 shows room temperature pH of solutions reacted with rhyolite and basalt at 300°C, 500 bars and a 3/1 solution-to-rock ratio, plotted against NaCl concentration. Higher pH values were found for solutions reacted with rhyolite as compared to basalt, and lower pH's were found for the higher NaCl concentrations. The pH of solutions reacted with andesite (a rock intermediate to rhyolite and basalt in composition) is not comparable with the pH of solutions reacted with rhyolite and basalt, because experimental conditions were not the same (different solution to rock ratio and initial solution concentrations). However, pH values of solutions reacted with andesite at 200, 300 and 400°C (at a solution-to-rock ratio of 10/1) in other experiments in our laboratory became lower with temperature increase, similar to the temperature effect on pH values of other solution types. One experiment with andesite at a 50/1 solution-to-rock ratio showed a pH of 6.5 after 720 hours, in contrast to a pH of 7.1 for a 10/1 ratio at the same conditions (200°C, 300 bars, 0.1% NaCl).

The tendency for pH of solutions to become acid initially and the return toward alkalinity has been observed commonly in our laboratory in other rock-solution reactions as well. The reaction of basalt with seawater, for example (5, 12), produced initial pH values of about 2.5 and steady state values of about 5. Both Bischoff and Dickson (5) and Seyfried (12) concluded that H⁺ was produced by

Figure 4-1. pH vs NaCl content of solution of 300°C experiments.

the reaction of Mg^{+2} and H_2O in solution with the rock to form oxy- or hydroxy-clay, a reaction that releases H^+ . The H^+ ion was subsequently steadily consumed by a slower reaction of H^+ with silicate solids in the production of other minerals. However, our initial solutions lacked high levels of Mg^{+2} , and clearly, other mechanisms operate. The following reactions may possibly account for the pH behavior of the solutions.

1. Rapid formation of oxy- or hydroxy-solid phases or solution species (simplified reaction):

Hirano and Oki (35) presented evidences that support the existence of this reaction.

2. Surface interactions of silicate particles with H_2O . Hydroxide, OH^- , can be incorporated in the surface layer, freeing H^+ . For example, powdered quartz reacts with H_2O , releasing H^+ , until the charge imbalance on fractured surfaces is compensated for by high H^+ concentration in solution. This mechanism would be greatly influenced by the amount of total surface area of the grains. Our experiments used powders ground to certain maximum grain sizes in unsorted condition; hence, they were of large net surface areas. Experiments with different solution-to-rock ratios show differential effects in accord with this mechanism. (10/1 solution-to-rock ratio, compared to 30/1, showed acidities about twice as high).
3. Rapid extraction from rocks of acid-forming compounds. Examples are CO_3 , H_2S or FeS_2 , which react with H_2O to form H^+ . For example, CO_2 behaves as follows:

4. Acid producing metastable reactions of solution and solid phases, early, when systems are far from equilibrium. With time, of course, the system approaches some steady state or equilibrium configuration. Many workers have pointed out that natural reactions commonly consume or produce H^+ . A simple example is the reaction of mica with solution to form albite:

The equilibrium constant for the reaction is:

$$K_R = \frac{a_{K^+} a_{H^+}}{a_{H_4SiO_4} a_{Na^+}}$$

In many of our experiments with NaCl solutions, a_{Na^+} is large and relatively constant. Therefore a different constant can be written that incorporates a_{Na^+} :

$$\frac{1}{K_R} = \frac{a_{K^+} a_{H^+}}{a_{H_4SiO_4}}$$

The system is initially far from equilibrium, and the $a_{H_4SiO_4}$ rapidly rises to anomalously high levels. For the solution to drive toward an equilibrium configuration the $a_{K^+} a_{H^+}$ product must likewise increase. In some reactions, the a_{H^+} may change more rapidly than the a_{K^+} , causing an initial buildup of H^+ . The slower but steady building up of K^+ at relatively constant $a_{H_4SiO_4}$ and a_{Na^+} requires H^+ to drop. The pH behavior of the solutions, therefore, in part reflects the initial strong departure from equilibrium followed by a slow adjustment toward equilibrium.

Some of our recent experiments on the reaction of sorted (200 to 100 mesh) rhyolite glass with NaCl solutions confirms that a strong grain size effect exists. However, all three reaction mechanisms would be influenced by the changed reaction rates caused by the elimination of the finest fraction. Using the sized fraction, the solutions do not become acid but drive initially toward alkalinity (pH 9) and then slowly move toward neutrality. The reaction products formed at alkaline conditions do not include clay. Glass dissolution, as well as precipitation of new phases, is enhanced by the alkalinity. The avoidance of the rapid formation of metastable clay and the accompanying H^+ permits other solid phases to form that, once formed, control the subsequent course of the reaction.

The pH values at elevated conditions depend on the differential changes in solution equilibria with temperature, pressure, and concentrational factors. The pH at the experimental conditions can be calculated from knowledge of changes in equilibrium constants with temperature and pressure. Several computer programs exist, such as SOLVEQ by M. Reed (36), that simplify the calculation of the complex set of variables needed to estimate in-situ pH values.

In relatively simple systems such as those of these experiments which involve only small amounts of CO_2 , SO_4^{2-} and H_2S , in-situ pH's can be estimated

by simple calculations. By ascribing the major effect on pH to the hydrolysis of NaCl, the H^+ concentration at elevated temperatures can be estimated from data on the ionization of NaCl, HCl and NaOH. At 300°C, some Na, K, and Cl form non-dissociated soluble complexes, such as $NaCl^0$ and KCl^0 . The amount of free K^+ , Na^+ , and Cl^- can be calculated from disassociation constants (4-1) (37). The H^+ concentration in solution at temperature relates to HCl and free Cl^- by

$$H^+ = \frac{HCl K_{diss}}{a_{Cl^-}} \quad (4-1)$$

Strictly speaking, the tendency for Na^+ to react with OH^- to form NaOH must be taken into account, but the dissociation of NaOH is large at 300°C relative to the dissociation of HCl.

In-situ pH's calculated by using the steady state values for the higher salinity experiments (2, 10, 20% NaCl) are listed in Table 4-1 along with the calculated activities of Na^+ and K^+ . As expected, the calculated in-situ pH's are higher than the measured pH's. However, buffering agents such as $SO_4^{=}$ or CO_2 could affect these values strongly. Ellis and Mahon (2), assuming that in-situ pH's were neutral, were able to account for the room temperature pH values of their solutions by chloride hydrolysis. Neutral pH at 500 bars is ~ 5.5 at 300°C. The calculated pH values for 300°C range from 6.0 to 7.1 for the experiments. The solution-solid phase reactions drive the solutions to slightly alkaline conditions by silicate mineral hydrolysis reactions, as suggested earlier. The calculated free H^+ concentration at the elevated temperatures of the andesite experiments is close to the measured room temperature values, a result of the small concentrations of NaCl in the solutions, $1.6 \times 10^{-2}M$.

SiO₂. Silica behaved characteristically in 18 of the 19 experiments. Commonly SiO₂ rose to maxima or to nearly constant values after 1 to 15 days of reaction, to levels well above quartz solubility at the conditions. Beyond the maxima, drops in SiO₂ contents took place slowly for most experiments. Figure 4-2 shows steady state silica concentrations as a function of temperature. Most of the long-time steady state concentrations cluster around amorphous silica solubility, with some SiO₂ concentrations closer to cristobalite solubility and only one near quartz solubility. This departure from equilibrium values is a striking feature that results from the kinetically dominated dissolution behavior of silicate minerals and glass.

Table 4-1

CALCULATED ACTIVITIES OF STEADY STATE COMPONENTS IN SOLUTION AT 300° C

Experiment no.	pH _{300°}	aH ⁺	aK ⁺	aNa ⁺	aCa ²⁺
Rhyolite-2%NaCl	7.17	3.8×10^{-8}	.013	.0935	1.05×10^{-5}
Rhyolite-10%NaCl	6.6	1.28×10^{-7}	.026	.28	1.02×10^{-4}
Rhyolite-20%NaCl	6.6	1.28×10^{-7}	.038	.49	2.05×10^{-4}
Basalt-2%NaCl	6.17	3.8×10^{-7}	.0091	.096	8.6×10^{-5}
Basalt-10%NaCl	6.03	4.7×10^{-7}	.0199	.31	1.8×10^{-4}
Basalt-20%NaCl	6.5	1.63×10^{-7}	.0156	.51	2.13×10^{-4}

Figure 4-2. SiO₂ concentrations as functions of temperature for all experiments.

The maximum contents of SiO_2 in solution depend on temperature, rock type and solution concentration. In general, maxima were higher for higher temperatures, other factors constant. A tendency existed for maximum SiO_2 to be progressively higher in solutions reacted with rocks of higher SiO_2 contents (order of increasing SiO_2 : basalts, andesite, rhyolite). Solutions of lower ionic strength tended to develop higher maximum SiO_2 contents. Particularly high levels were found in the initially pure H_2O solutions.

The chemical reactions responsible for the anomalously high maximum SiO_2 contents are not well understood. Silicate glass has a known higher solubility than silicate minerals of equivalent bulk composition; therefore, if kinetic barriers prevent nucleation and growth of SiO_2 -containing solids, high SiO_2 values would be predicted. However, even in the presence of crystalline phases, such as quartz or K-feldspar, solutions take on excess concentrations of SiO_2 which, after 30 days, remain greatly above quartz solubility.

The reaction of fused SiO_2 glass with H_2O solutions in the presence of quartz nuclei provides a simplified example:

For equilibrium between quartz and solution, the chemical potentials of SiO_2 , μ_{SiO_2} , must be equal in both phases:

$$\mu_{\text{SiO}_2}(\text{q}) = \mu_{\text{SiO}_2}(\text{aq})$$

For supersaturation between solution and quartz:

$$\mu_{\text{SiO}_2}(\text{aq}) > \mu_{\text{SiO}_2}(\text{q})$$

That is, the thermodynamic tendency is for SiO_2 to migrate spontaneously from solution to the quartz grains until the SiO_2 in solution falls to levels that no longer sustain quartz growth. Obviously, since our solutions rapidly attain SiO_2 contents far above equilibrium values, the absolute rate for the glass-solution reaction exceeds the absolute rate of growth of quartz.

This result is reasonable and predictable from established modes of kinetic dissolution of solids of the same composition with different atomic structures.

However, as Morey, et al. (38) pointed out, H_2O solutions energetically reacted with pure quartz are capable of overshooting the equilibrium concentrations by orders of magnitude. The effect was explained by the higher Gibbs free energy of powdered quartz, which develops large surface areas, thin edges, and sharp points. This accords with Morey et al.'s (38) observation that solutions reacted gently with previously leached powdered quartz slowly develop equilibrium SiO_2 concentrations. The influence of solution on nucleation and growth is well illustrated by our results as well as those of Morey and others (38) that solutions with anomalously high levels of SiO_2 return only slowly toward equilibrium values. The SiO_2 in solution may form polymeric aggregates or complex species which, once developed, are difficult to break and permit release of SiO_2 to growing silica phases. The reaction of quartz with solution is best explained by the properties of both solids and solution. Steady-state SiO_2 concentrations (after 30 days) were 1.5 to 2.5 times larger than quartz solubility under the conditions. A pure SiO_2 phase, cristobalite, formed in one experiment only. The SiO_2 content of solutions remained high even for systems that should not stably form an SiO_2 phase; the formation of metastable phases such as montmorillonite or zeolites did not lower the SiO_2 contents of solutions even to the quartz solubility levels.

Obviously, the SiO_2 contents of our solutions could not be used to predict the temperatures of the experiments. This conclusion does not necessarily hold for natural systems; only in unusual circumstances in which the departure from equilibrium is abnormally great, such as strongly increased temperatures accompanying intrusion of hot igneous magma into water-containing host rocks would this effect be important. The major application of this data would be to predict effects of injecting hot brines into cold, glassy rocks, or of injecting cold fluids into hot dry rocks. Metastable overshoots of SiO_2 in solution could lead to subsequent deposition of solids in pores and fractures in rocks, with consequent reduction of permeability.

Mg, Ca, Na, K. Trends in major element compositions with time for most experiments indicate that approximate steady states are attained; however, steady state values do not imply equilibrium. They reflect a kinetic balance between the influx of chemicals to the solution from the altering rocks and from the solution to the solid phases as secondary minerals form.

In most experiments, Mg is removed almost quantitatively from solution with time, and definitely shows an affinity for the solid phases. Even at high NaCl

concentrations, (basalt, 10 and 20% NaCl, and rhyolite, 20% NaCl), only 2 to 5 ppm Mg was present in solution. Mg is a common component in zeolites and clays. Seyfried (12) found similar results in his experiment with seawater and basalt at 300° with initial Mg concentration of >1200 ppm. Nearly all of the Mg is incorporated into the run products (Mg-rich smectite) within 100 to 1000 hours, depending on rock-to-water ratio.

Ca increases in concentration quickly and approaches steady state levels within 50 to 100 hours. The absolute level of Ca depends on the NaCl concentration, temperature and rock type. Comparison of data from the 2% experiments with both rock types at 200 and 300°C indicates that the 200°C experiments attain a greater Ca concentration than the 300°C. Apparently low-solubility calcium silicate forms at 300°C. Seyfried (12) reacted a glassy basalt with a 2.57% NaCl solution and found wairakite ($\text{Ca}(\text{Al}_2\text{Si}_4)\text{O}_{12} \cdot 2\text{H}_2\text{O}$) as a stable phase in his experiments. Wairakite or a similar phase is probably present in some of the NaCl-basalt-rhyolite experiments, but in amounts undetectable by X-ray or SEM.

Na was initially removed from solution to some extent in nearly all NaCl experiments except for the 10% and 20% NaCl experiments, in which possible Na loss was less than can be detected by the accuracy of the analysis. In some experiments, Na increases slightly following the early decrease. The early removal may result from the initial release of K and Ca to solution and the electrical neutrality requirements of the solution. The Na may exchange with H^+ on surfaces or, more probably, is incorporated into a secondary phase such as albite. Seyfried (12) accounts for the early removal of Na from solution during reaction of basalt and NaCl by the formation of albite. Albite ($\text{NaAl} \cdot \text{Si}_3\text{O}_8$) is present in many of these experiments as well as analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) in the 10% rhyolite experiment and possibly in the 10% NaCl basalt experiment. The formation of albite in other basalt-seawater experiments has been verified by Mottl (9) and Hajash (10). Hajash found analcime present in some of his basalt-seawater experiments.

K increases quickly in concentration, followed by substantial decreases with time in the rhyolite 2 and 10% NaCl experiments at 300 C. In some of the basalt, 10% and 20% NaCl, and the rhyolite, 20% NaCl, experiments at 300 C, the K concentration continually increased. An exception was the 2% NaCl-basalt experiment in which the K decreased significantly after the 200 hours. A possible explanation is that is that the supersaturation and nucleation of a K-bearing silicate depend on some critical ratio of K to Na in solution. Solutions high in NaCl (10 and 20% NaCl solutions reacted with basalt, and 20% NaCl reacted with rhyolite) have

too much Na relative to K in the rocks for the appropriate ratio to be reached. Solutions low in NaCl (2% NaCl solution reacted with basalt) can extract enough K from rocks to permit growth of the K-bearing phase (zeolite), which, once formed, controls the K to Na ratio in solution. The K to Na ratio for several reactions is plotted versus time in Figure 4-3. Apparently, K/Na must be 1/9 or higher before nucleation takes place at about 190 hours of a phase, the growth of which also consumes SiO_2 from solution as evidenced by the sharp drops in SiO_2 concentration. However, at 200°C the K-bearing phase did not nucleate even though solutions attained seemingly appropriate K to Na ratios, a reflection of the slower reaction rates at 200°C .

Trace Elements

All rocks reacted significantly with aqueous NaCl solutions and pure H_2O to solubilize trace elements found in natural systems. Rhyolite tended to give up somewhat higher levels than basalt or andesite. Differences existed among the rock types but the fragmentary data do not justify efforts to establish characteristic associations of trace element assemblages with rock type. Solutions contained elements that are found in geothermal fluids, but at higher concentrations, which is probably a consequence of the difference between experimental and natural conditions. The experiments involved the rapid reaction of powdered fresh rocks with solution, whereas geothermal fluids pass slowly through the pores and channels of rocks that may have been transited by large quantities of previously flowing fluids. The nature and levels of trace elements in the experimental solutions reflected rock types, NaCl concentrations, solution-to-rock ratios, and reaction times.

NaCl effect on rhyolite reaction. Steady state or end-of-experiment, trace element levels, plotted versus % NaCl in Figure 4-4, show the strong effect of NaCl concentration. Mn, Pb and Tl increase in concentrations at increasing rates, in contrast to the initially more soluble elements, B, As, and Fe, which increase at decreasing rates. The NaCl contributes to at least three effects: ionic strength, complex ion formation, and pH, which, in turn, effect the trace element levels.

NaCl effect on basalt reactions. Steady state or end-of-experiment concentrations of trace elements are plotted versus NaCl concentration in Figure 4-5. The positive effect of NaCl increase on most of the trace element concentrations is clearly illustrated. The reactions released from the basalt elements found in geothermal fluids, altered rocks, and ore deposits.

Figure 4-3. Molar K/Na ratios as a function of time for selected experiments.

Figure 4-4. Steady state trace element concentrations vs NaCl content for rhyolite-300°C experiments, 500 bars.

Figure 4-5. Steady state trace element concentrations vs NaCl content for basalt experiments at 300°C, 500 bars.

CORRELATION OF WATER CHEMISTRY AND ALTERATION MINERALOGY

The calculations of the activities of dissolved species in solution can be done for the experimental solutions by use of physical chemical generalizations and available data. The activities of Na^+ , K^+ , H^+ , and Ca^{++} , evaluated using the modified Debye-Huckel formula (40) are listed in Table 4-1.

The logs of activity ratios of our solutions have been plotted on appropriate diagrams calculated by Helgeson (33) using thermodynamic data and compositions of solutions that are thought to be in equilibrium with these assemblages of minerals from the Salton Sea geothermal area. We use these diagrams to illustrate both the chemical evolution of the fluid with time and the approach to equilibrium boundaries of the steady state solution compositions.

Figure 4-6 is a $\log a\text{Ca}^{++}/a\text{H}^+$ vs. $a\text{Na}^+/a\text{H}^+$ diagram with the steady state solution compositions from all of the 300°C-NaCl experiments plotted on it. The basalt experiments are shown with a B and the rhyolite experiments indicated with an R, the salinity is also shown beside the rock type. This diagram illustrates a nearly linear relationship between the activity ratios of the steady state values. We interpret this as implying that exchange reactions are controlling the activities of Ca and Na. We do not intend to imply that bulk equilibrium between either albite and zoisite or wairakite has been obtained by using these diagrams, but rather to show that these ion exchange reactions involving cations such as Na, Ca and K can show near equilibrium values regardless of the presence or absence of the equilibrium assemblage.

Figure 4-7 is an identical diagram to figure 4-6 in which the solution activities at different time for the basalt-2% NaCl experiment. The activity ratios change during the initial 194 hours and move towards the montmorillonite-albite boundary due to initial formation of montmorillonite. The trend reverses and the solution compositions approach the albite-wairakite boundary as phases other than the montmorillonite appear. By 842 hours the solution activity ratios plot directly on the wairakite-albite stability line. This may be coincidence, however wairakite could have formed since it has been observed by Seyfried (12) in rather similar experiments. We were unable to observe it using the X-ray or SEM techniques. Regardless of whether wairakite formed it is apparent from these diagrams that ion exchange reactions are rapid enough that the solution activity ratios show near equilibrium values and follow time dependent paths which in this case are close to those predicted by observation of the secondary phases. Bulk equilibrium between phases may not be necessary for ion exchange equilibrium to occur. The

Figure 4-6. Calculated activity diagram for the system $\text{NaCl}-\text{CaCl}_2-\text{HCl}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 300°C with steady state values of selected 300°C runs.

Figure 4-7. Calculated activity diagram for the system $\text{NaCl}-\text{CaCl}_2-\text{HCl}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 300°C with points representing the changing solution compositions of the basalt-2% NaCl run.

success of the Na-K-Ca geothermometer may be a direct result of the rapidity of the ion-exchange reactions.

Figure 4-8 is a $\log a\text{Na}^+/a\text{H}^+$ vs $\log a\text{K}^+/a\text{H}^+$ diagram showing all of the NaCl 300°C experiments. Close agreement is observed between data points for the reactions basalt-2% NaCl and rhyolite-2, 10 and 20% NaCl and the equilibrium boundary between K-feldspar and albite. As stated earlier this agreement represents an attempt by the solution and the solids to obtain ion-exchange equilibrium. We believe that both K feldspar and trace amounts of albite are forming in the rhyolite experiments along with the Na-K zeolite, however, no trace of K feldspar have been observed in the basalt 2% NaCl experiment. Plagioclase and the Na-K zeolite have, however been observed. These results are significant in that the ratios of the alkalis are controlled at values almost identical to the K feldspar-albite boundary even though these phases are not present in the alteration assemblage. We believe that the surfaces of the minerals are controlling exchange reactions, and that these surfaces develop similar compositions. These results experimentally support the theoretical predictions by Dibble and Tiller (40) who have, based on a non-equilibrium surface model, derived a model for water-rock interaction at low temperatures. Since a specific ratio of Na/K is required, a solution initially high in Na relative to K will extract and exchange K in the solids for Na in solution. If the total available K in the rock is not enough to reach this ratio the solution compositions would plot in the albite stability field. This is observed in the basalt 10 and 20% NaCl experiments.

Figure 4-9 is a $\log a\text{Na}^+/a\text{H}^+$ vs. $\log a\text{K}^+/a\text{H}^+$ diagram showing the calculated activity ratios of the rhyolite-2% NaCl experiment at different times in the experiment. Extraction of K from the rock into solution and incorporation of Na into the solid results in initial movement of the calculated activity into the K feldspar stability field. Later precipitation of the K-Na zeolite removes substantial potassium from solution and moves the activity towards the K feldspar-albite boundary. At steady state, we would predict that the solution activity ratios for this experiment would coincide closely with the albite-K feldspar equilibrium line even though the tabular Na-K zeolite may be the dominant K-bearing phase, and may persist metastably under these conditions.

APPLICATION TO NATURAL SYSTEMS

In order to relate the observations made during the experimental study to processes occurring in natural hydrothermal systems one must consider that many

Figure 4-8. Calculated activity diagram for the system NaCl-KCl-HCl-Al₂O₃-SiO₂-H₂O at 300°C with steady state values of the 300°C experiments.

Figure 4-9. Calculated activity diagram for the system NaCl-KCl-HCl-Al₂O₃-SiO₂-H₂O at 300°C with points representing the changing solution compositions of the rhyolite-2% NaCl run.

of the chemical reactions occurring in the experiments may be metastable or non-equilibrium. However, the alteration in active hydrothermal systems often represents non-equilibrium as well. Classical thermodynamic equilibrium is determined only by the temperature, pressure and bulk composition of the system. When the reactions are kinetically controlled, other variables such as fluid flow and time may also play a major role in determining the alteration assemblage and the composition of the associated fluid phase. In this section we discuss the six major factors which affect the alteration in natural systems and relate these to the variables deduced from the agitated experiments described above. The important controls in natural hydrothermal systems are temperature, pressure, rock type, permeability, fluid composition and duration (42).

Temperature

The effect of temperature in both natural and experimental systems is profound. In natural hydrothermal systems a uniform assemblage of secondary phases occurs in nearly all hydrothermally altered rocks at temperatures above 280°C (albite, K-feldspar, illite, chlorite, Fe epidote, calcite, quartz, and pyrite), however at lower temperatures, both zeolite and clay minerals are more common (analcime, mordenite, wairakite, clinoptilodite, smectite) (42). In both the rhyolite and basalt experiments at 300°C, clays and zeolites are the most common phases, and albite forms as a later phase, perhaps at the expense of the early formed zeolites. At 200°C, only poorly crystallized clays and/or amorphous material were found.

The differences between natural and experimental assemblages at similar P-T conditions are due to kinetics and the effects of solution variables (e.g., pH, salinity) on the kinetics. The alteration of glass to form secondary phases involves irreversible multi-step reactions where both rates of dissolution of the glass and rates of nucleation and growth of secondary phases determine the overall reaction rate (43). In the low-temperature experiments, dissolution rates far exceed growth rates of secondary phases hence, concentrations of most components in the solution are being determined by solubility of the original material.

High concentration levels of many components are found in the solutions of the 200° experiments. However in the 300° experiments, dissolution of the glass may set initially high solution levels for many components, on the other hand, increased growth rates for secondary phases such as zeolites results in a overall decrease in solution concentrations. Concentration levels are then determined either by the solubility of the secondary phase (zeolites) or is set at some intermediate value between the solubilities of the glass and this secondary phase.

In order to explain the apparent metastable crystallization of abundant zeolites at 300° in both rhyolite and basalt experiments we refer to a recent model for zeolite paragenesis in altered tuffs by Dibble and Tiller (44). In the previous paragraph the relationship between the dissolution and growth rates and the overall rate of alteration was discussed. If the dissolution rate of the original material is very rapid the solution can become supersaturated in a short time with respect to many aluminosilicates. The secondary phase which may nucleate and grow under these conditions may not be the equilibrium phase but rather some metastable intermediate phase. The growth kinetics of these phases are determined by interface attachment reactions (43) and in general the more stable the phase the slower the growth rates. With time, the metastable phases dissolve to form more stable phases until the equilibrium assemblage under the conditions is formed (44). This sequence of formation of minerals with increasing stability and decreasing solubility is observed in the low-temperature alteration of glassy tuffaceous rocks and at higher temperatures in hydrothermally altered rocks (45).

We are duplicating this sequence of irreversible alteration reactions in these closed experiments. Clay with highest solubility forms early, later zeolites form as solution concentrations decrease. Finally, after all the glass has dissolved, albite (K feldspar) forms.

Pressure

The rock powder-fluid mixture in the agitated experiments is under a uniform hydrostatic (non-directed) pressure. Grains exert no stress on other grains. In a natural system, this case is never realized except in rare instances (self sealed zones). Pressure in reservoirs can be separated into lithostatic and hydrostatic components. Lithostatic pressure results from the weight of the column of rock above the reservoir, hydrostatic is the weight of the column of pore water above the reservoir. Depending on the density, porosity, and permeability of the rock, the ratio of lithostatic to hydrostatic pressure can range from 1 to greater than 10.

Browne (42) suggests that pressure has little direct effect on hydrothermal alteration except when fluid pressure is reduced to the point where boiling occurs. Recent studies on pressure solution (45) suggest that mineral solubilities are significantly increased in areas of high stress. The area at grain-grain contacts would be subjected to a net force proportional to the difference between the lithostatic and hydrostatic pressures (effective stress). Free surfaces of grains (regions in contact with the open pores in the rock) would be subjected to a stress closer to hydrostatic pressure. High dissolution rates at the regions of grain-grain contacts could lead to either precipitation of the same phase in the low stress (unbounded) regions, or if the growth rates of the stable phase are low, compared to the dissolution rates of the stressed phase, metastable phases could nucleate and grow in these regions (46).

Dibble and Nur (46) have postulated that chemical-mechanical equilibrium is obtained only when the fluid pressure and the lithostatic pressure are equal. In natural systems where the permeability has been reduced by some mechanism commonly pore fluid pressure approaches lithostatic pressure (42). Where fluid conductivity is maintained to the surface, lithostatic is usually larger than hydrostatic pressure.

Rock Type

In silica and alumina rich reservoir rocks, the rock type influences the type of alteration predominately in the lower temperature systems $<280^{\circ}\text{C}$ (42). Above this temperature as stated previously, a "similar assemblage" of stable hydrothermal minerals (feldspars, quartz, etc.), is consistently found in nearly all geothermal systems whether the reservoir rocks are sandstones, basalts or rhyolites. Browne (42) suggests that parent rock influences the alteration assemblage mainly through bulk rock permeability and porosity. Zeolite formation seems to be influenced strongly by the initial rock type at temperatures $<280^{\circ}\text{C}$. High silica zeolites (mordenite, clinoptilolite) are found in siliceous rhyolites of Yellowstone (47, 48) and New Zealand (49) while lower silica zeolites (chabazite, laumontite thomsonite) are associated with basalts of Iceland (50). This association does not hold for those experiments where the types of zeolite found (Na-K ferrierite, mordenite and analcime) occur in experiments using basalt and rhyolite.

Comparing experiments using different starting rocks (basalt, andesite and rhyolite) and similar experimental conditions, we find nearly identical secondary mineral assemblages. The main differences lie in the relative proportions of the

secondary phases. Solution compositions show little difference from basalt to rhyolite experiments of the same initial salinity with respect to SiO_2 and Al concentrations. Solutions are obtaining similar degrees of supersaturation leading to the formation of an identical assemblage of zeolites in either experiment. The zeolites observed (mordenite-clinoptilolite) in these experiments have, from other field and experimental studies, been associated with a high SiO_2 activity in the pore fluid (42). These results are consistent with the very high levels of SiO_2 found in every experiment. Perhaps the unsized nature of the starting materials is helping maintain higher solubilities especially in the basalt experiments.

The secondary mineral assemblage found in the various experiments using different rock types at 300°C are very similar, in support of observation made on natural hydrothermal systems. However, the assemblages formed are not those that suggest equilibrium. We have found that in the experiments, variation in fluid composition is not sufficient to discriminate among the different starting rock types.

Permeability

Permeability in natural systems is finite and often shows sharp variations with depth, however, because of the mixing of the rock-powder and fluid, the permeability of the experimental system is assumed infinite. Browne (42) suggests that permeability may be as important as temperature in determining the formation of hydrothermal minerals, primarily through the input of water necessary for the hydration reactions. Keith and others (48) found that for glassy reservoir rocks in the Yellowstone geothermal system, glass persists even to elevated temperatures. They suggest that this is a results of the low permeability of the partially altered glass, and the necessity for a fluid phase to be present for glass alteration to proceed.

Another factor not considered by Browne (42) is that fluid might have access to the rocks, but the fluid flow rates are so slow that it may affect the rates of dissolution and alteration reactions. A more thorough discussion of the effects of flow rate and permeability are discussed in (51).

Fluid Composition

Hydrothermal fluids in natural systems are thought to represent fluids at various stages of evolution with respect to the reservoir rocks. Often these fluids have been interpreted to show near equilibrium with respect to silicates (quartz,

feldspars, zeolites) as indicated by the successful application of the quartz and Na-K-Ca geothermometer. The results of the experiments have shown that ion exchange equilibrium may have been attained without having bulk equilibrium in the system. Close fit of data points on activity-activity diagrams in which exchangeable components (Na, K, Ca, Mg) are plotted against one another do not necessarily indicate that bulk equilibrium has been established within the system. Bulk equilibrium is determined by equilibrium among both network forming species (Al, Si, Fe⁺³) and exchangeable ions (C, Na, Mg, K)(41).

In open systems where the fluid can act as a source or sink of components, metasomatism can occur. This process leads to changes in the bulk composition of the rock. The results of the high salinity rhyolite experiment (20% NaCl) suggest that the approach to an equilibrium state has been impeded by the almost quantitative removal of K from the rocks. In this case, the fluid is acting as a sink for the K and as a source for the Na. The slower kinetics for the formation of pure Na phases at the near neutral pH's in the experiment leads to the formation of poorly crystallized K deficient material. In natural systems, Na metasomatism is fairly common. Highly altered regions in the drill cores from Yellowstone (47, 48) commonly show assemblage quartz+analclime+clay. Bulk chemical analysis show that most of the K has been removed from the rock during alteration.

Duration

The evolution of natural geothermal system is a subject of considerable importance. Work in several areas suggests that hydrothermal activity can be maintained for periods up to several million years (42). Core samples from active areas commonly show gradual progressive mineralogical transition due to elevated temperature and pressure from burial. Overprinted on this gradation are sharp mineralogical changes thought to be due to differences in fluid flow or fluid composition (47, 48). There exists a complex interrelationship of the above mentioned variables (particularly temperature, permeability or fluid flow, and fluid composition) to the types and rates of changes in mineralogy that occur, during the evolution of a natural system.

Detailed petrographic studies such as those done on the Yellowstone drill cores (47, 48) have revealed much on the paragenetic relationship between primary and secondary minerals and can be used to affix relative times to such events as fracturing and fracture cementation (53). The duration of hydrothermal activity is much harder to affix a time scale to and is usually constrained by relative

events such as cessation of fracturing or sealing reactions. The secondary minerals in these fractures can be dated by some radiometric method and compared to dates of material from early formed fractures and/or pores.

Section 5

CONCLUSIONS

The experiments conducted for this project were performed to investigate the kinetics and steady state geochemical processes occurring in natural geothermal systems. Fluid compositions in these experiments rapidly approach steady state values, however, the chemical and mineralogical evidence suggests that these steady state conditions do not represent true equilibrium. Solution pH ranges from near neutral to slightly alkaline, and appears to be buffered by mineral solution reactions. SiO_2 concentrations commonly reach highly supersaturated levels without subsequent decreases. These concentrations are close to those of amorphous silica solubility at the experimental temperature. Activities of exchangeable cations (Na, K, Ca, Mg) appear to be controlled at near equilibrium levels by rapid ion exchange reactions even though as previously stated, bulk equilibrium was not obtained in the system. Trace element concentrations in solution are commonly higher than those observed in natural hydrothermal waters of comparable salinity and temperature, again testifying to the kinetic rather than equilibrium nature of these studies.

The degree to which the rock powder reacted depends on the starting material and temperature, the rhyolite glass reacted almost completely in 30 days at 300°C , while the basalt was only partially altered. The secondary phases formed at 300°C consist of Na-K zeolites, clays, and Na-rich feldspar. The starting rock type appears to predominately affect the relative proportions rather than the types of various secondary minerals formed. Slower growth kinetics at 200° prevented the formation of identifiable secondary phases except for traces of clay.

The data from the experiments suggests that chemical equilibrium was not obtained during the experiments. The complexity and non-equilibrium nature of mineral-solution interactions in many natural systems is evidenced by the occurrence of many coexisting minerals. Many of these minerals are thought to represent metastable phases, whose formation is controlled by kinetic factors. Insight into the actual mechanisms operating in natural hydrothermal systems requires understanding how a minimum of 5 or 6 variables each affects the chemical and physical development of the system. Predicative estimates are possible only at the most

basic levels. Future experimental work in this area should consist of evaluating the effects of temperature, fluid flow, rock and solution composition (pH, ionic strength) and directed stress on the time dependent changes in alteration mineralogy. Detailed experimental studies on surface properties, dissolution-growth kinetics, and changes in properties with changes in composition of the numerous minerals and phases found in natural systems is then required for a more complete understanding.

Section 6

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