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The Pennsylvania State University
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The Report For January - September, 1994 on the Project

KINETIC MEASUREMENTS ON THE SILICATES OF THE YUCCA MOUNTAIN POTENTIAL REPOSITORY

to

Los Alamos National Laboratory
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INTRODUCTION

The principal effort has been concentrated on the preparation of clean clinoptilolite, quartz, and boehmite and then reaction of the natural clinoptilolite solid solution to the Na-endmember, plus measurements of the endmember solubility to derive an accurate equilibrium constant for the clinoptilolite dissolution reaction, correctly speciated. We are very pleased with the consistency between the best calorimetrically measured and modeled equilibrium constants and those we have determined from 125°C to 265°C. These results now provide a basis for relating measurements of reaction rates to departures from equilibrium.

PREPARATION OF MATERIALS

The Castle Creek deposit is exceptionally pure in its clinoptilolite content (~95%) but contains small amounts of smectite (mineralogy and percentage estimated using XRD, SEM, and transmitted light microscopy). Samples (1-2 kg) from this deposit and several others (*e.g.*, Buckhorn, N.M.; Mud Hill, CA; Sheaville, OR; and Shoshone, CA) were obtained from F. Aplan (Dept. of Mineral Processing, PSU). Material from these deposits has been the focus of

on going studies on zeolite beneficiation and ion exchange capacity by the Mineral Processing Section at Penn State (*e.g.*, Carland, 1980; Mondale *et al.*, 1988).

Material from Castle Creek was carefully crushed in an agate mortar and sieved through a 150 mesh screen. To remove the impurity smectite, approximately 50 grams of the sieved material was placed in a 1L graduated cylinder along with a magnetic stirring bar and doubly distilled deionized water after which the resultant slurry was stirred gently for 10 minutes. The suspension was then allowed to settle for 5 minutes before decanting the overlying fluid. This process was then repeated. The supernatant fluid is enriched in a mixed layer clay (~90% smectite, 10% illite)(Srodon, 1980) and very fine-grained clinoptilolite (<3μm)(see Fig. 1). Analysis of the concentrated residual solids by particle counting using transmitted light microscopy revealed a purity of ~99% clinoptilolite had been achieved.

The bulk composition of the Castle Creek clinoptilolite is given in Table 1, as determined by ICP spectroscopy. In Fig. 2, the Castle Creek analysis is plotted on the ternary (K-Na-Ca+Mg) diagram showing compositional variations of natural clinoptilolites and heulandites, including data from the Yucca Mountain site (from Bowers and Burns, 1990). When compared to the available data, the Castle Creek clinoptilolite is the closest to the Na-endmember composition; however, significant amounts of CaO (0.72 wt.%), MgO (1.07 wt.%), and K_2O (2.34 wt.%) are present.

NA-EXCHANGE EXPERIMENTS

In order to produce an Na-endmember, we utilized the cation exchange properties of clinoptilolite. An initial exchange experiment was run at 90°C (±5°) with 25 g of clinoptilolite in 250 mL of 3M NaCl (Baker Reagent). The experiment was set up using standard laboratory glassware (500 mL Erlenmeyer flask with $\overline{\$}$ 24/40 joint connected to an adapter holding a condenser and thermometer port). A combination stirrer/hot plate was used as the heat source. The slurry was not continuously stirred to prevent attrition of the particles, but several times a

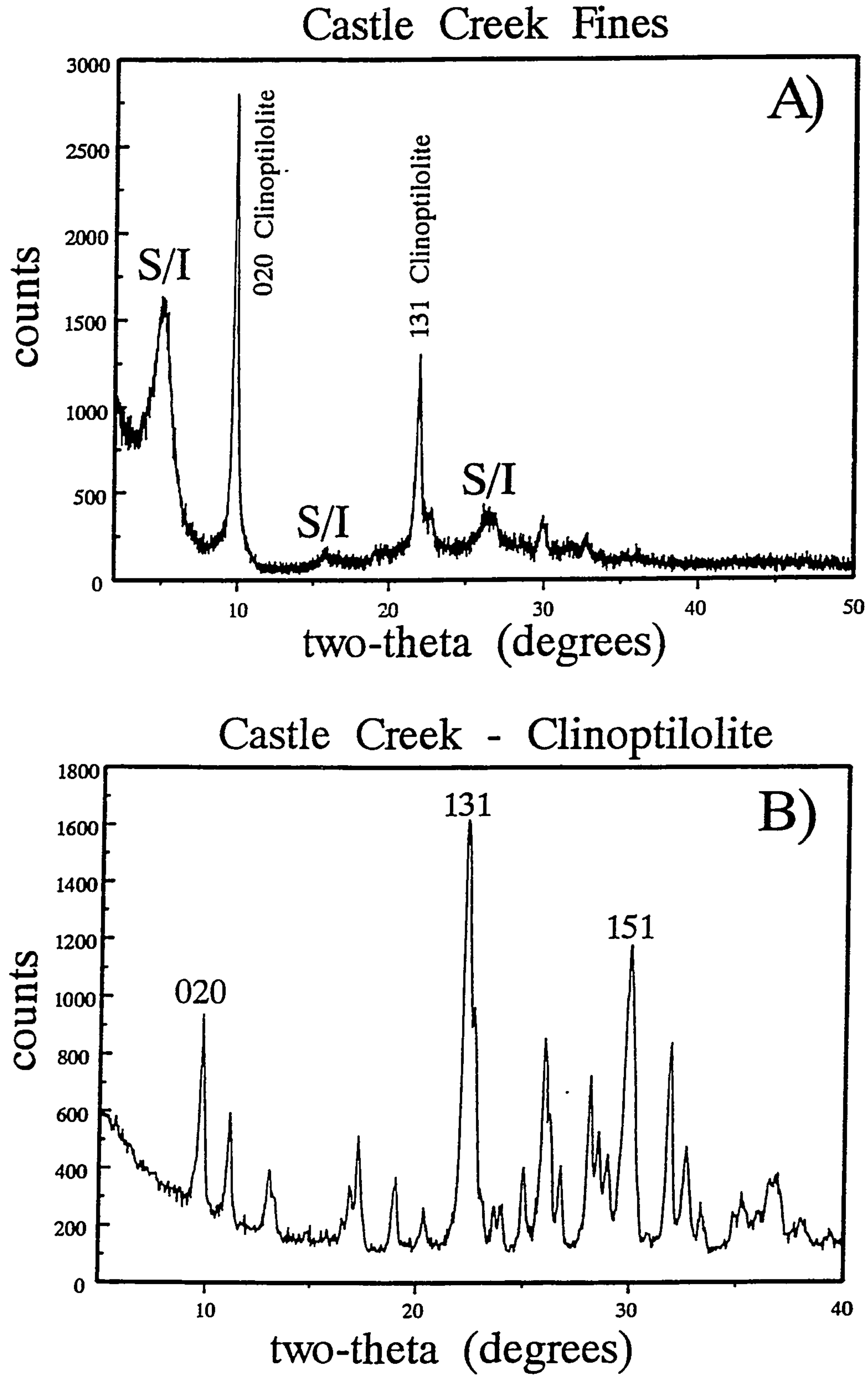

Figure 1. X-ray diffraction patterns from A) suspended solids containing mixed layer clay (smectite-illite) and very fine-grained clinoptilolite, and B) concentrated clinoptilolite (sample mounted on zero-background quartz plate). Analyses done with Ni filtered $Cu_{K\alpha}$ radiation at a rate of 2°θ per minute.

TABLE 1. Major element analyses of natural and Na-exchanged clinoptilolites

wt. %	**Succor Creek, NV**	**Castle Creek, ID**	**CC Exchanged (#7)**	**CC Exchanged (#9)**	**CC Exchanged final**
SiO_2	63.01	65.50	67.00	66.80	64.90
Al_2O_3	15.48	12.50	12.40	12.90	12.20
TiO_2	<0.02	0.08	0.06	0.07	0.08
Fe_2O_3	0.07	0.48	0.35	0.41	0.90
CaO	3.77	0.72	0.06	0.03	0.06
MgO	0.31	1.07	0.15	0.10	0.07
Na_2O	2.42	3.57	6.97	7.41	7.24
K_2O	1.25	2.34	0.68	0.55	0.25
LOI	15.48	13.10	12.60	11.2	13.8
Total	100.01	99.37	100.40	99.50	99.50
Si/Al	3.45	4.54	4.57	4.26	4.51
[Ca/(Na+K)]	0.63	0.08	0.005	0.005	0.008

Notes: Major elements by ICP spectroscopy; accuracy and precision ~3%. LOI, loss on ignition; measured gravimetrically on sample heated to 750°C overnight with an additional 3 hours at 900°C. Si/Al and [Ca/(Na+K)] are stoichiometric ratios. Succor Creek, NV- hand picked clinoptilolite supplied to Yale for initial experiments. Castle Creek, ID - analysis of purified material used in exchange experiments; #7 - Castle Creek material after 148 hours at 90°C in 3M NaCl (see text); #9 - Castle Creek material after 315 hours at 90° in 3M NaCl; final Castle Creek material after 890 hours at 120°C in 5M NaCl.

Calculated formulas (based on 72 oxygens):

Ideal clinoptilolite $(Na, K)_6 (Al_6 Si_{30} O_{72}) \cdot 24H_2O$

Succor Creek $(Na_{2.26} K_{0.76})(Ca_{1.93} Mg_{0.26}) (Al_{8.77} Si_{30.26} O_{72}) \cdot 24.8H_2O$

Castle Creek $(Na_{3.10} K_{1.25})(Ca_{0.35} Mg_{0.73}) (Al_{6.48} Si_{29.47} O_{72}) \cdot 20.0H_2O$

Castle Creek(#9) $(Na_{6.33} K_{0.32})(Ca_{0.03} Mg_{0.05}) (Al_{6.86} Si_{29.28} O_{72}) \cdot 17.0H_2O$

Castle Creek (final) $(Na_{6.33} K_{0.14})(Ca_{0.03} Mg_{0.05}) (Al_{6.53} Si_{29.42} O_{72}) \cdot 20.9H_2O$

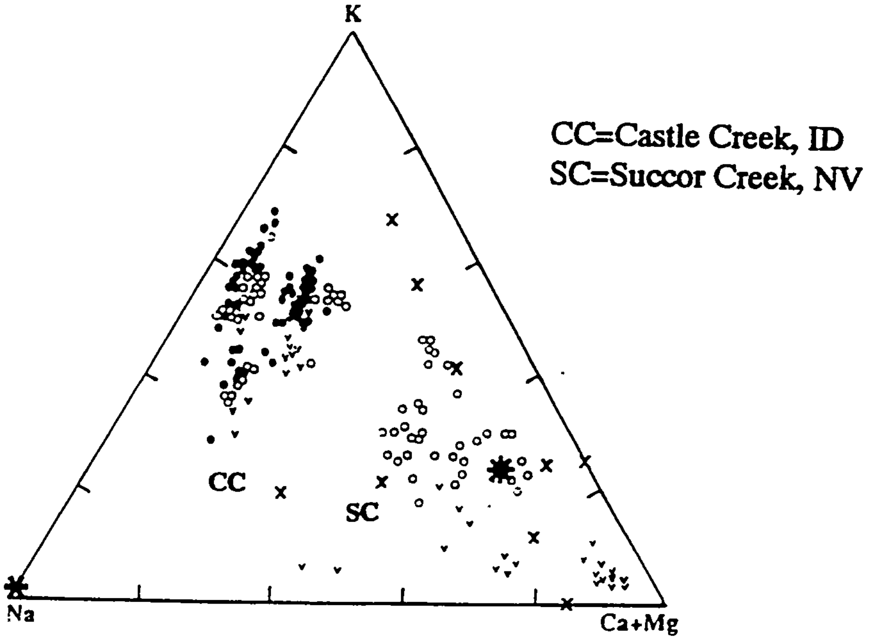

Figure 2. Ternary diagram showing compositional variations of natural clinoptilolites and heulandites (from Bowers and Burns, 1990). SC= Succor Creek clinoptilolite; CC= Castle Creek clinoptilolite; *=final Na-exchanged Castle Creek clinoptilolite..

day the slurry was mixed for several minutes using a magnetic stirring bar. Broadly similar exchange experiments have been described, for example, by Bish (1984), Pozas *et al.* (1989), and Liang and Sherriff (1993). About 500 mg of solid was collected *ca.* 10 times over a run of 315 hours. The NaCl solution was refreshed 3 times during the experiment. All solid samples were analyzed for Na and K and several samples had a complete major element analysis along with XRD.

The change in Na and K content and the calculated molar [Na_2O/Na_2O+K_2O] of the clinoptilolite as a function of time are shown in Fig. 3 and Fig. 4, respectively. Note that there is a rapid initial period of cation exchange over the first 50 hours of the experiment followed by a much slower exchange. Exchange rates are faster immediately after refreshing the NaCl solution. The composition of the final exchanged solid (after 315 hours) is given in Table 1. Note that Si/Al has remained constant indicating no change in mineralogy; this is confirmed by XRD. Ti and Fe have also remained constant suggesting the that trace impurities are present of

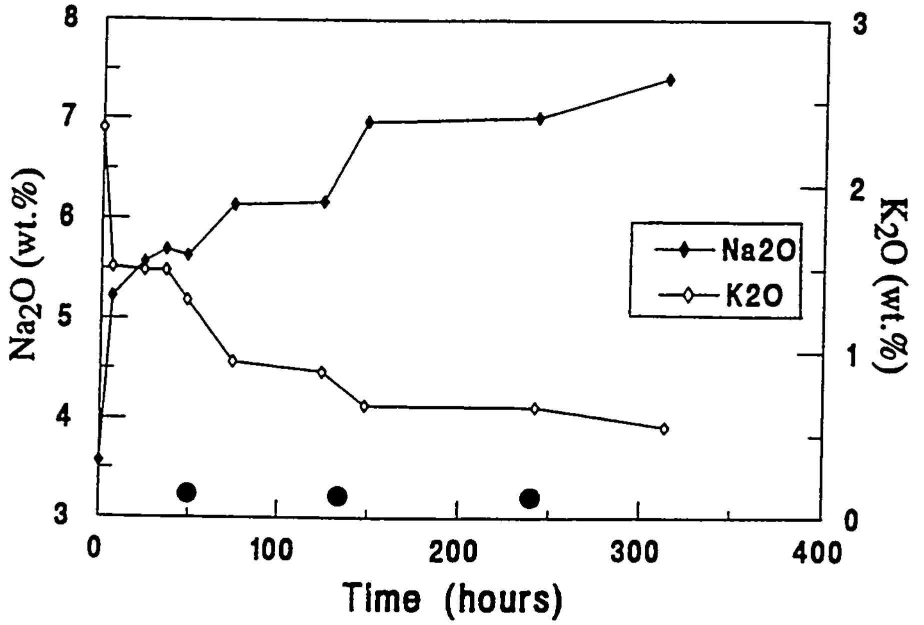

Figure 3. Results of Na-exchange experiment (90°C, 3M NaCl). Na_2O and K_2O vs. time, large dots represent times when the solution was refreshed.

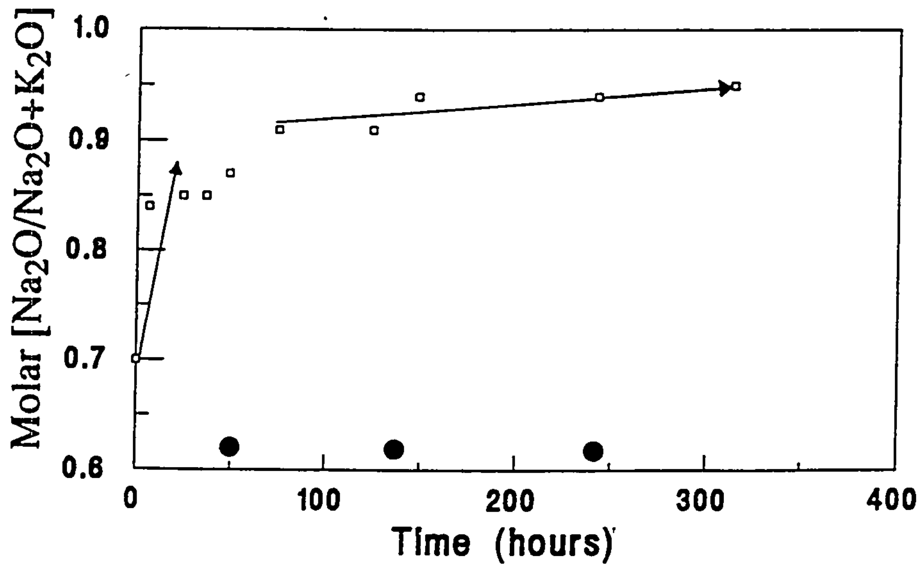

Figure 4. Results of Na-exchange experiment (90°C, 3M NaCl). molar $[Na_2O/(Na_2O+K_2O)]$ vs. time, large dots represent times when the solution was refreshed.

some non-exchangeable phase, possibly rutile and/or ilmenite, which must be very fine-grained as no opaque phases were observed using transmitted light microscopy. The divalent cations, Ca and Mg, are largely removed. Na has, of course, increased and K has decreased. The final molar [$Na_2O/(Na_2O+K_2O)$] was 0.95. We selected, as a goal a reasonable endpoint for the exchange, a K_2O~0.1-0.2 wt.% or molar [Na_2O/Na_2O+K_2O]~ 0.98-0.99. Also, note the decrease in LOI from 13.10 wt.% to 11.10 wt.%. This is, perhaps, due to the concentrated NaCl solutions slightly depressing the activity of water and the hydration state of this zeolite. More likely, however, the observed decrease in water content is related to the increase of Na as the exchangeable cation in the clinoptilolite (D. Bish, pers. comm.).

We have calculated partition coefficients with K_p=[molar Na/K in solution]/[molar Na/K in clinoptilolite]. The partition coefficient increases as K_2O decreases in the solid suggesting that the Na-endmember clinoptilolite is comparitively less stable than clinoptilolite with intermediate compositions (Fig. 5). This increased resistance to Na-exchange also indicates that periodic refreshing of the NaCl solution is required to achieve the Na/K desired.

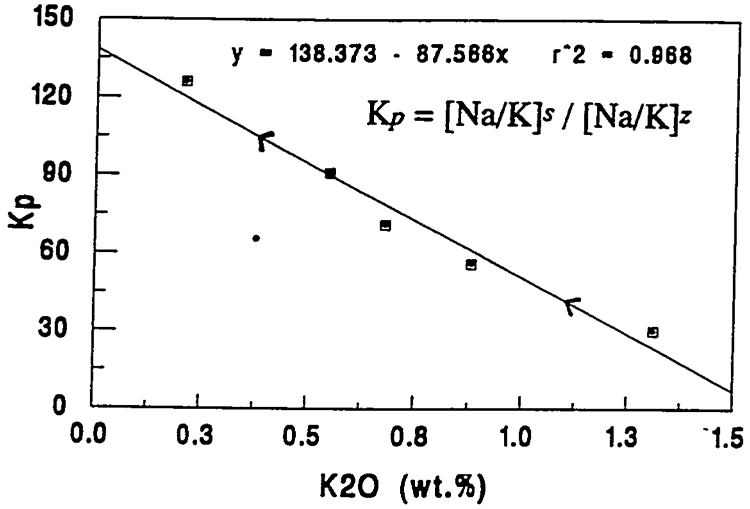

Figure 5. Partition coeficient vs. K_2O, arrows show direction of exchange (see text).

To assess whether increasing either or both temperature and NaCl concentration would materially speed up the exchange process without destruction of the clinoptilolite or production of any unwanted phase, additional experiments were run at 120°C using 5M NaCl. These experiments were run in titanium bombs placed in rocking furnaces. After an additional 150 hours, the K_2O content of several grams of the previously exchanged material decreased from 0.5 to 0.2 wt.%. XRD analysis indicated that there was no change in mineralogy.

We have also completed a 560 hour run at 120°C in 5M NaCl using a total of 150 grams of clinoptilolite. The solution was exchanged 6 times. The cation exchange, unexpectedly 'stalled' at a molar $[Na_2O/Na_2O+K_2O]$ of 0.93. We split this material into two separate batches (A&B) and after an additional 80 hours, batch A had a molar $[Na_2O/Na_2O+K_2O]$ of 0.96. We have continued exchange experiments on batches A&B for a total of an additional 330 hours. The final composition of combined batches A&B is given in Table 1. The final K_2O content and molar $[Na_2O/Na_2O+K_2O]$ value is 0.25 wt.% and 0.98, respectively. We are not aware of any other clinoptilolite, exchanged or natural, that approaches the Na-endmember as closely as the material we have produced. About 20 grams of this material has been supplied to the geochemists at Yale University, and about 10 grams was given to D. Bish at LANL. The material has been characterized using scanning electron microscopy. The clinoptilolite is in the form of foliated aggregates of euhedral tabular crystals (Fig. 6). Micro-fine particles have, for the most part, been removed using the ultrasonic cleaning and hydrothermal annealing techniques. The size of most of the clinoptilolite particles is between 10 and 100µm. The surface area of the clinoptilolite was measured to be 19.5 m^2/g from a three point BET N_2 adsorption isotherm with an estimated accuracy of ±10%.

We still have about 150 grams of non-exchanged, purified Castle Creek clinoptilolite. During the next year we will treat this material with KCl solutions to produce K-endmember clinoptilolite with subsequent experiments to determine solubility of this phase.

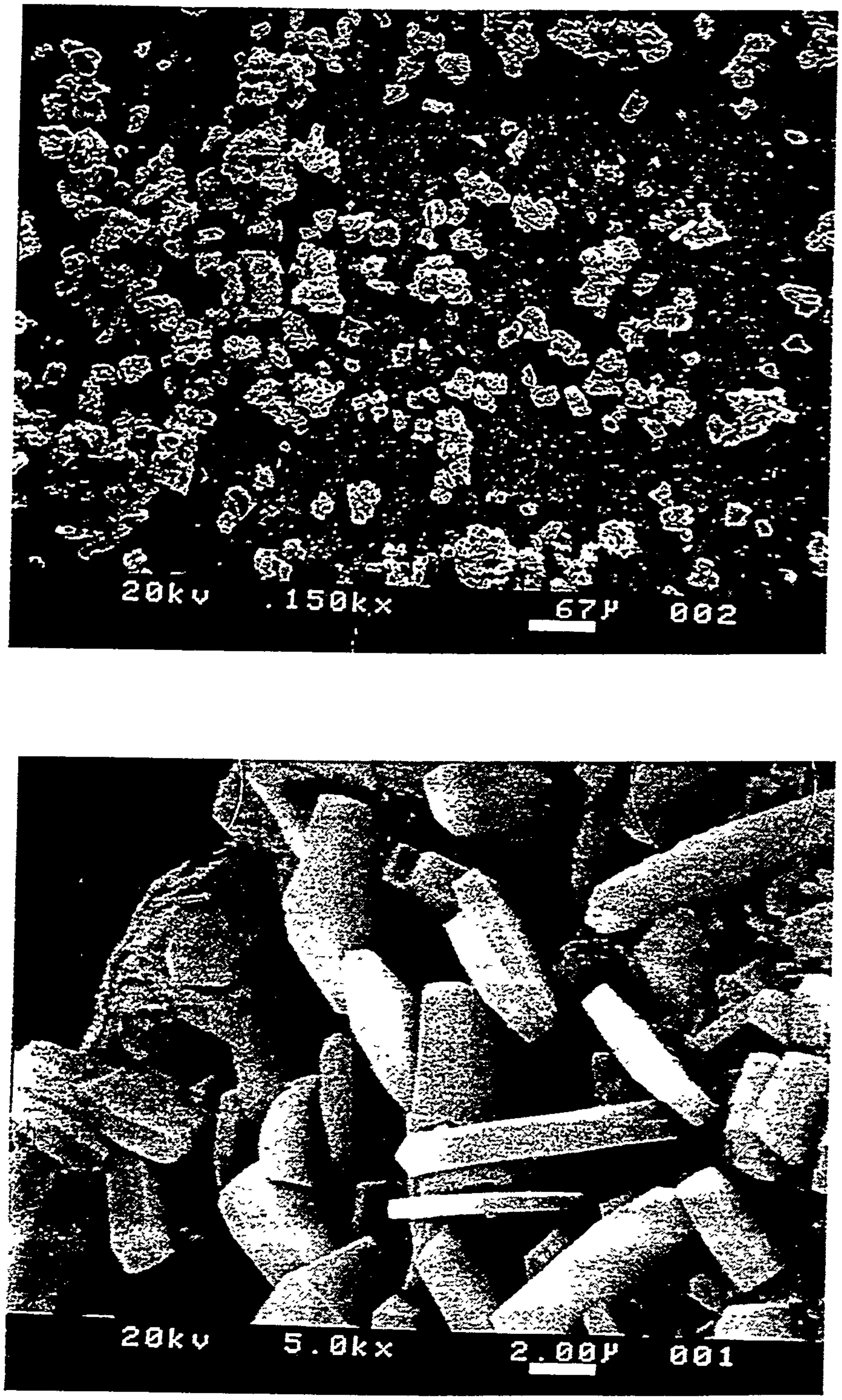

Figure 6. SEM images of the Na-clinoptilolite after hydrothermal treatment at 125°C in distilled water

CLINOPTILOLITE SOLUBILITY

Methods

The reversible solubility of Na-exchanged Castle Creek clinoptilolite was determined at 125°, 175°, 200°, 225°, and 265°C. These data will be used in upcoming experiments where the rates of clinoptilolite dissolution and precipitation will be measured both far from, and near to, the equilibrium conditions defined here.

The solubility of clinoptilolite was measured in aqueous solutions using a gold-plated, stainless steel autoclave (nominal volume 1100 mL) placed within a rocking, dual-wound furnace. Temperature was monitored and controlled using two chromel-alumel thermocouples inserted into the top and bottom of the autoclave. At the beginning of a run, 50 grams of well-rinsed, Na-exchanged clinoptilolite was placed in the autoclave along with 300 mL of nitrogen gas-purged, doubly distilled, deionized water (DDW) as recommended in the recent study by Butler *et al.* (1993). With these materials in the autoclave, it is purged with N_2 for 30 minutes and then sealed. Next, rocking is begun and the system brought up to temperature. The system was kept at constant temperature for a minimum of several days at each condition where the solubility was to be determined. Solution sampling was carried out using a double valve configuration (*e.g.*, Bourcier and Barnes, 1987). Usually, two aliquots of approximately 3 mL each were taken and each aliquot was filtered through an 0.2 µm cellulose acetate syringe filter. Aliquot 1 was used to measure pH and then diluted 5-10x with DDW and acidified with ultrapure HNO_3 so that the pH was near 2. The pH of the solution was measured with a Corning semi-micro combination electrode calibrated with NIST standard buffers. Aliquot 2 was only acidified with ultrapure HNO_3. Total Si, Al, Na, and K were measured by ICP spectroscopy on both aliquots. Analytical precision and accuracy for these elements is estimated to be better than ±5%.

We did not use a buffer to fix the pH in these experiments. From our Na-exchange experiments, we have found that the pH of a clinoptilolite-water-NaCl suspension is near 6.

Therefore, $Al(OH)_4^-$ is known to be the dominant Al species in solution. Consequently, we can consider the following solubility-controlling reaction for Na-clinoptilolite (based on 72 oxygens):

$$Na_6Al_6Si_{30}O_{72}\cdot 24H_2O + 48H_2O = 6Na^+ + 6Al(OH)_4^- + 30H_4SiO_4$$

The solutions were speciated at temperature using the program, SOLMINEQ (Kharaka *et al.* 1988). This program converts analytical concentrations of Al and Na to activities using activity coefficients calculated with the extended Debye-Hückel equation. For the neutral species H_4SiO_4, activity coefficients are derived from data on the solubility of amorphous silica as a function of temperature and salinity (Kharaka *et al.* 1988; Chen and Marshall, 1982). We have also utilized the recent thermodynamic data on aluminum speciation in hydrothermal solutions of Castet *et al.* (1993), Bourcier *et al.* (1993), and Wesolowski and Palmer (1994).

Results

The experimentally determined solubility data for temperatures between 125° and 265°C are presented in Table 2. For Na-endmember clinoptilolite the solubility product can be calculated using the equation

$$\log K_{sp} = 6\log a_{Na^+} + 6\log a_{Al(OH)4^-} + 30\log a_{H4SiO4^-} - 48\log a_{H2O}$$

The large stoichiometric coefficient of water in this solubility expression requires that an accurate estimate of the water activity be made. The activity of water can be calculated by considering the total molar dilution by all dissolved species

$$a_{H2O} = 55.55/(55.55 + \Sigma m_i)$$

where Σm_i is the sum of all dissolved species in moles/kg. Even in the most concentrated solutions of this study (*i.e.*, the highest temperature experiment), the calculated a_{H2O} does not drop below 0.9997. Therefore, the effect of water activity on the solubility product is negligible. However, this may not be the case if moderately concentrated buffers are used in similar experiments to control pH. We have calculated the solubility product based on the analytically determined mineral stoichiometry so that

$$\log K_{sp} = 6.33 \log a_{Na^+} + 6.53 \log a_{Al(OH)_4^-} + 29.42 \log a_{H_4SiO_4}$$

The contribution of other alkali elements (*e.g.*, K, Ca, Mg) have been neglected in the calculation of the solubility product. The molar [Na/Na+K], [Na/Na+Ca], and [Na/Na+Mg] values of the clinoptilolite used in this study are 0.98, 0.99, and 0.99, respectively; thus, errors accrued in the omission of these elements are expected to be small compared to experimental and analytical uncertainties. Table 2 shows the calculated values of the K_{sp} of clinoptilolite and the conditions of measurement.

In order to avoid deleteriously leaching the clinoptilolite, the volume of solution is small in the experimental system and only a limited volume was available for sampling. Consequently, we not did follow the solution composition by collecting many samples at any one temperature in order to track the approach to a steady state (*i.e.* equilibrium). However, we have evaluated the solubility and the attainment of equilibrium by approaching an apparent state of equilibrium from both undersaturated (upon heating) and supersaturated (upon cooling) conditions. Table 2 shows the time spent at constant temperature prior to sampling and the direction from which the temperature was approached. Prior to sampling after thermal equilibration, the reaction vessel remained for 339 hours at 125°C and the measured concentrations gave $\log K_{sp}$=-109.98; whereas, after 280 hours at 125°, $\log K_{sp}$= -107.20. The difference in the calculated $\log K_{sp}$ is 2.78 and indicates that the equilibrium was bracketed within a reasonable margin of error. At 175°C the difference in $\log K_{sp}$ between samples approached from both under- and super-saturated conditions is 1.62. These data indicate that the rate of equilibration is fast for the Na-exchanged clinoptilolite.

Figure 7 shows a plot of log K_{sp} vs. 1/T from which thermodynamic data such as ΔH_r and ΔS_r can be obtained. For example, log K_{sp} is related to ΔG_r by

$$\Delta G_r = -2.303\ RT \log K_{sp}$$

and

$$\Delta G_r = \Delta H_r - T\Delta S_r$$

substituting and solving for log K_{sp} gives

$$\log K_{sp} = -\Delta H_r/2.303\ RT + \Delta S_r/2.303\ \ R$$

Thus, the slope on a 1/T vs. log K_{sp} plot depends on the reaction enthalpy. We calculate a ΔH_r of 569.26 $kJmol^{-1}$ and ΔS_r of -653.7 $Jmol^{-1}{}^{\circ}K^{-1}$. The lack of curvature on Figure 7 indicates that, over the temperature interval between 125° and 265°C, the ΔH_r remains constant and that $(\Delta C_p)_r$=0. This is somewhat unexpected as reactions involving ionic aqueous species often have constant or more complicated ΔC_p functions. Extrapolation of our hydrothermal solubility measurements to lower temperatures gives a log K_{sp} = -133.01(±13.15) at 25°C. From the free energy of formation and enthalpy of formation of the various aqueous species involved in the dissolution reaction, $\Delta G_{f,\ 298}$ and $\Delta H_{f,\ 298}$ for Na-exchanged clinoptilolite

TABLE 2. Solubility data for Na-exchanged Castle Creek clinoptilolite

T (°C)	Direction	Si (mM)	Al (mM)	Na (mM)	pH_{25}	pH_T	Time	log K_{sp}
125	↑	4.82 (±1.40)	0.11(±0.04)	3.08(±0.50)	8.81	7.88	339	-109.98
125	↓	7.14 (±0.64)	0.13(±0.02)	1.13(±0.03)	6.84	6.10	280	-107.20
175	↑	9.30 (±1.24)	0.30(±0.11)	1.39(±0.08)	8.31	7.26	170	-101.07
175	↓	7.23	0.52	3.65	8.74	7.76	122	-99.45
200	↑	10.4 (±1.35)	0.30(±0.02)	1.97(±0.06)	8.76	7.74	96	-98.75
225	↑	12.52	0.54	4.02	8.63	7.58	103	-92.76
265	↑	17.42 (±1.66)	0.55(±0.04)	4.23(±0.04)	8.80	7.90	77	-89.32

Notes: ↑ denotes experiments where equilibration was approached from undersaturation; ↓ denotes experiments where equilibration was approached from supersaturation. Errors are 1σ of replicate samples.

may be computed. Thermodynamic data for $Al(OH)_4^-$, Na^+, and H_4SiO_4 were taken from Castet *et al.* (1993), Robie *et al.* (1978), and Rimstidt and Barnes (1980), respectively. The calculation yields

$$\Delta G_{f,\,298} = -38045.1(\pm 75.3)\ \mathrm{kJmol^{-1}}$$

and

$$\Delta H_{f,\,298} = -41091.1(\pm 46.0)\ \mathrm{kJmol^{-1}}$$

These values can be directly compared with calorimetric measurements on clinoptilolite by Hemingway and Robie (1984). These authors give

$$\Delta G_{f,\,298} = -37897.8\ \mathrm{kJmol^{-1}}$$

and

$$\Delta H_{f,\,298} = -41053.1\ \mathrm{kJmol^{-1}}$$

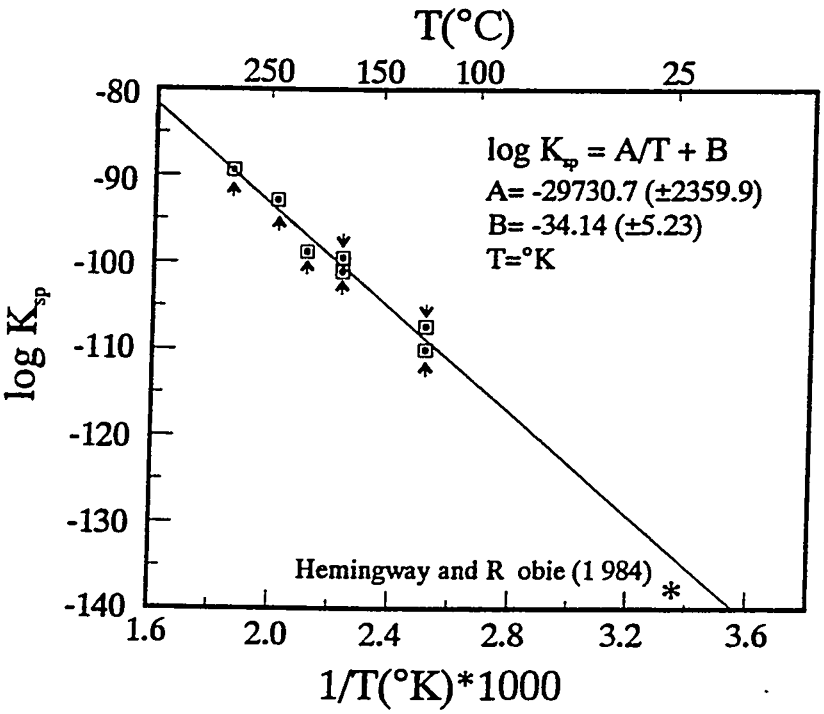

Figure 7. Plot of log Ksp vs. 1/T using Na-clinoptilolite solubility data. Log K_{sp} at 25°C (*) calculated from calorimetric data of Hemingway and Robie (1984) and thermodynamic data referenced in text; data for aqueous K, Ca, and Mg from Robie *et al.* (1977). Errors on slope and intercept are 1σ.

Hemingway and Robie (1984) used clinoptilolite from altered tuffs of the Big Sandy Formation, Mohave Co., AZ for their measurements of these values. The composition of this material was reported to be

$$Na_{0.56}K_{0.98}Ca_{1.50}Mg_{1.23}Fe_{0.3}Al_{6.7}Si_{29}O_{72}\cdot 22H_2O$$

The agreement between their calorimetric measurements and our solubility determinations is excellent. The apparent constancy of ΔH_r to 265°C adds confidence to the activity diagrams constructed by Bowers and Burns (1990) showing the stability fields of clinoptilolite. The large extrapolation from our higher temperatures to 25°C, however, makes tenuous any comment on relationships between compositional variability and differences in $\Delta G_{f,\ 298}$.

The solubility data will be used to adjust the concentrations of dissolved Na, Al, and Si of input solutions of our flow-through system so that either undersaturated or supersaturated conditions are present within the reaction vessle containing clinoptilolite. Table 3 lists calculated saturation indices of the experimental solutions for quartz, amphorous silica, and boehmite. The saturation index of quartz, $SI_{qtz.}$, for example, is defined as

$$SI_{qtz.} = m_{Si} / m^{\circ}_{Si}$$

where m_{Si} is the molality of Si in the aqueous solution and m°_{Si} is the molality of Si in a quartz-saturated solution. Solubility data for quartz, cristobalite, and amorphous silica are taken from Rimstidt and Barnes (1980) and the data of Castet *et al.* (1993) are used to calculate the saturation index of boehmite. Note that all experimental solutions are supersaturated with respect to quartz and undersaturated with respect to amorphous silica. They are slightly supersaturated with respect to cristobalite. As temperature increases, however, the probability of quartz nucleation increases and the persistence of metastable cristobalite or amorphous silica becomes less likely. Upon the complete loss of these metastable phases by quartz nucleation and growth, the concentration of silica in solution will be controlled by quartz. We expect that clinoptilolite

TABLE 3. Saturation indices for selected phases

T	Direction	$SI_{qtz.}$	$SI_{cris.}$	$SI_{ampsil.}$	$SI_{boem.}$
125	↑	3.37	2.33	0.59	4.98
125	↓	4.99	1.46	0.87	179
175	↑	3.01	1.49	0.72	8.07
175	↓	2.33	1.22	0.56	4.43
200	↑	2.48	1.27	0.67	1.34
225	↑	2.28	1.24	0.69	2.20
265	↑	2.24	1.18	0.77	0.57

will become unstable in solutions with the lower silica concentrations, for example, saturated with respect to quartz and will undergo reactions that convert clinoptilolite to mordenite and/or analcime. This possibility will be tested kinetically in the upcoming year. Our solubility experiments are being extended to temperatures above 265°C, and also 90° to ensure that our hydrothermal data may be compared easily for compatibility with the low temperature (25-80°C) values being measured at Yale University.

CRISTOBALITE KINETICS

The manuscript on the kinetics of dissolution and of precipitatioin of cristobalite, already accepted for publication by the editors of *Geochimica et Cosmochimica Acta*, has been revised on the basis of comments by several reviewers and has been returned to the journal for publication. A copy is being forwarded to LANL for use in the Yucca Mountain programs.

PLANNED ACTIVITIES FOR THE 1994 - 1995 FISCAL YEAR

Research over the next year will be focused in several areas:

1) Kinetic flow-through experiments on Na-clinoptilolite

2) Procurement and characterization of analcime

3) Synthesis and characterization of Na-mordenite

4) Hydrothermal solubility experiments of analcime and Na-mordenite

5) Synthesis via exchange of K-clinoptilolite

1) In recent months we have finished setting up the experimental flow-through apparatus that will be used to measure the rates of zeolite dissolution and precipitation as a function of reaction affinity at hydrothermal conditions. For example, quantities of boehmite and quartz have been prepared for use in controlling the Al and Si concentrations, respectively, for input into the reaction vessel. Boehmite is obtained by thermally treating gibbsite (Baker analyzed reagent aluminum hydroxide) at 250°C with distilled, deionized water for 24 hours (Fig.8). For quartz, we are using clear Brazilian quartz crushed and sieved to a size fraction of 0.1-0.3mm.

We plan to measure reaction rates at 125°, 175°, and 250°C at pH conditions ~7 and ~5. The pH condition will be selected so that either $Al(OH)_4^-$ or $Al(OH)_3^o$ is the dominant Al species in solution.

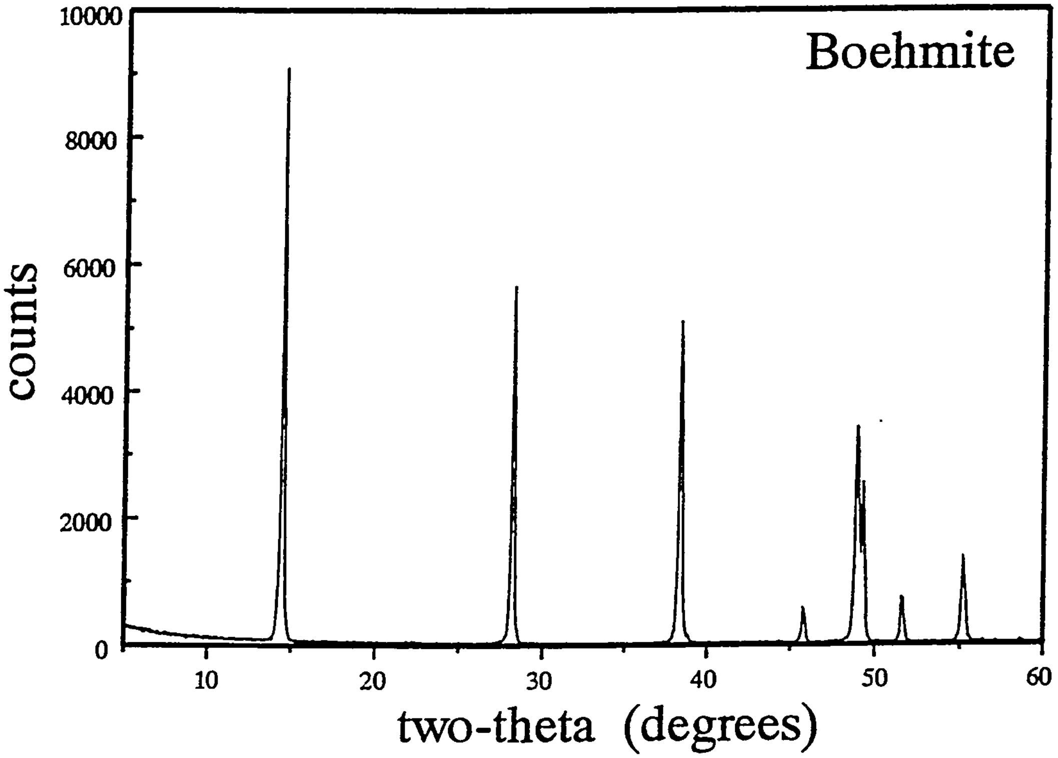

Figure 8. XRD pattern of synthesized boehmite to be used as Al source in flow-through experiments

2) We will obtain analcime from Mt. St. Hilaire, Quebec, Canada. The group at Yale has had success with this material; the composition of this analcime is very close to the exact ideal stoichiometry. We will take this material through the same purifying and annealing treatments that were successful in preparing the Na-clinoptilolite described in this report. Characterization will again be done using XRD, ICP, SEM, and BET.

3) We have been unsuccessful in locating natural deposits that contain >90% mordenite. It appears that mordenite is often associated with a variety of other zeolite and silicate minerals. An inability to purify such a mixture suggests that natural materials are inappropriate for use in kinetic experimental work. Therefore, our plan is to synthesize mordenite. There is a considerable literature describing methods to synthesize mordenite (*e.g.*, Bajpai, 1986). We are currently starting experiments where Al-isopropoxide, tetraethyl orthosilicate, and NaOH are used as sources for Al, Si, and Na, respectively. These components are mixed together in stoichiometric proportions to form a homogeneous melt. The melt is hydrated to form a gel which is sealed in a glass reaction tube with excess water and heated to 200°C overnight.

4) Once we have analcime and Na-mordenite, we will begin solubility measurements on these phases in the temperature range between 90° and 350°C. We will use the same methods used for Na-clinoptilolite described in this report.

5) In future experiments, the thermodynamics and kinetics of K-clinoptilolite and K-mordenite will need to be evaluated. We are confident that K-clinoptilolite can be prepared from the purified Castle Creek clinoptilolite using the same techniques that have been described in this report for the production of Na-clinoptilolite. Both the Na-mordenite and K-clinoptilolite will be supplied to Yale University for their use in low-temperature geochemical studies.

QUALITY ASSURANCE ACTIVITIES

On May 3, 1994 we met with a Quality Assurance representative and were introduced to QA policies and procedures. Since that time we have taken steps to initiate our lab into the QA system. For example, our balances were checked by a Los Alamos representative on 6/7/94. We are also in the process of getting several K-type thermocouples and our Pt-resistance thermometer calibrated so that we can check for accuracy any thermocouple used on the YMP using DP-105.

REFERENCES CITED

Bajpai, P.K. (1986). Synthesis of mordenite type zeolites: Zeolites, v. 6: 2-8.

Bish, D.L. (1984). Effects of exchangeable cation composition on the thermal expansion/contraction of clinoptilolite: Clays and Clay Minerals, v. 32: 444-452

Bourcier, W.L. and Barnes, H.L. (1987). Rocking autoclaves for hydrothermal experiments I. Fixed volume systems, *In* Hydrothermal Experimental Techniques, *Edited by* G.C. Ulmer and H.L. Barnes, J. Wiley & Sons.

Bourcier, W.L., Knauss, K.G., and Jackson, K.J. (1993). Aluminum hydrolysis constants to 250°C from boehmite solubility measurements: Geochim. Cosmochim. Acta, v. 57: 747-752.

Bowers, T.S. and Burns, R.G. (1990). Activity diagrams for clinoptilolite: Susceptibility of this zeolite to further diagenetic reactions: American Mineralogist, v. 75: 601-619.

Butler, I.B., Schoonen, M.A.A., and Rickard, D.T. (1994). Removal of dissolved oxygen from water: a comparison of four common techniques: Talanta, v. 41: 211-215.

Castet, S., Dandurand, J., Schott, J., and Gout, R. (1993). Boehmite solubility and aqueous aluminum speciation in hydrothermal solutions (90°-350°C): Experimental study and modeling: Geochim. Cosmochim. Acta, v. 57: 4869-4884.

Carland, R.M.P. (1980). Studies of cation exchange properties in natural sedimentary zeolites: MSc. thesis, The Pennsylvania State University, University Park.

Chen, C.A. and Marshall, W.M. (1982). Amorphous silica solubility IV. Behavior in pure water and aqueous sodium chloride, sodium sulfate, magnesium chloride, and magnesium sulfate solutions up to 350°C: Geochim. Cosmochim. Acta, v. 46: 279-287.

Hemingway, B.S. and Robie, R.A. (1984). Thermodynamic properties of zeolites: Low temperature heat capacities and thermodynamic functions of phillipsite and clinoptilolite and clinoptilolite. Estimates of the thermochemical properties of zeolitic water at low temperatures: American Mineralogist, v. 69: 692-700.

Kharaka, Y.K., Gunter, W.D., Aggarwal, P.K., Perkins, E.H., and DeBraal, J.P. (1988). SOLMINEQ88: A computer program for geochemical modeling of water-rock interactions: U.S. Geological Survey, Water Resources Investigations Report 88-4227.

Liang, J. and Sherriff, B.L. (1993). Lead exchange into zeolites and clay minerals: A ^{29}Si, ^{27}Al, ^{23}Na solid state NMR study: Geochim. Cosmochim. Acta, v. 57: 3885-3894.

Mondale, K.D., Mumpton, F.A., and Aplan, F.F. (1988). Properties and beneficiation of natural sedimentary zeolites: *In* Process Mineralogy VIII, *edited by* D.J.T. Carson and A.H. Vassiliou, The Minerals, Metals, & Materials Society, pp. 249-275.

Rimstidt, J.D. and Barnes, H.L. (1980). The kinetics of silica-water reactions. Geochim. Cosmochim. Acta, v. 44: 1683-1699.

Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1978). Thermodynamic properties of minerals and related substances at 298.15°K, and 1 bar pressure and at higher temperatures. USGS Bull. No. 1452.

Srodon, J. (1980). Precise identification of illite/smectite interstratifications by x-ray powder diffraction: Clays and Clay Minerals, v. 28: 401-411.

Wesolowski, D.J. and Palmer, D.A. (1994). Aluminum speciation and equilibria in aqueous solution: V. Gibbsite solubility at 50°C and pH 3-9 in 0.1 molal NaCl solutions (a general model for aluminum speciation; analytical methods): Geochim. Cosmochim. Acta, v. 58: 2947-2969.

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Supplement to
The Report For January - September, 1994 on the Project

KINETIC MEASUREMENTS ON THE SILICATES OF THE YUCCA MOUNTAIN POTENTIAL REPOSITORY

to

Los Alamos National Laboratory
September 16, 1994

George Kacandes and H. L. Barnes

An incongruent reaction important to this project is the reaction of smectite to illite. This reaction is being investigated in parallel with this project but with NSF support and is reported here because of the abundance of these minerals at Yucca Mountain. Smectite, illite and mixed-layered smectite/illite intermediates occur at the Yucca Mountain site as a result of past tuff/water interactions (Bish and Aronson, 1993). Repository-induced heating and hydrothermal circulation will result in further reaction of tuff to smectite and illite. The extent of this alteration process will depend on the temperature and the composition of the hydrothermal fluid. We are investigating the effect of solution chemistry on the illitization of precursor smectite in dilute KCl-bearing solutions under hydrothermal flow-through conditions (T= 200°, 250°, 300°C). The use of a flow-through apparatus allows us to control the composition of input solutions, and to monitor changes in clay and outlet solution composition. Reaction products closely match those found in nature and consist of mixed-layered smectite/illite clays which increase in illite content as reaction progresses. A 10Å non-expandable product forms upon completion. Solution parameters examined to date include silica activity and pH.

pH influences the specific mode of illitization. At pH's slightly below neutral, illitization involves net tetrahedral Al^{3+} for Si^{4+} exchange; while at basic pH's, illitization involves net octahedral Mg^{2+} for Al^{3+} exchange. This behavior reflects the relative pH-dependence of Al^{3+} and Mg^{2+} solubilities. At pH's slightly below neutral, Mg^{2+} is significantly more soluble than Al^{3+} and dissolution of precursor smectite results in the incongruent formation of Al-rich (muscovitic) illite layers. At pH's above neutral, the opposite effect results in the formation of Mg-rich (celadonitic) illite layers.

Aqueous silica activity affects the extent of illitization so that the illite content of mixed-layered products systematically increases with decreasing $aH_4SiO_4(aq)$. Complete illitization is rapidly achieved (e.g., 1000 hours) in solutions maintained well below quartz saturation. In solutions held above quartz saturation, illitization does not go to completion and a smectite-rich product is stabilized.

The results of this study may help explain illitization trends currently observed at the Yucca Mountain site. For example, Bish and Aronson (1993) have shown that the illite content of mixed-layered smectite/illite increases as the amount of high-silica glass decreases. Furthermore, these experimental results predict that illite formation may be instantaneous (on a repository time-scale), if aqueous silica activity is reduced by quartz formation or by fluid flow under relatively open system conditions. During the next contract year, we expect to complete a doctoral dissertation reporting on extended experiments in this system. This thesis will become part of our contract report next year.