Experimental Evaluation of Geochemical Conditions
in Geothermal Energy Systems

A Quarterly Report to the
U.S. Energy Research and Development Administration
On National Science Foundation Grant Number AER 74-08473
for
September to December, 1976

THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA
THE PENNSYLVANIA STATE UNIVERSITY
COLLEGE OF EARTH AND MINERAL SCIENCES

Dedicated to education and research in mineral exploration, use, and conservation; understanding and development of materials; and the preservation of our environment.

FIELDS OF WORK

EARTH SCIENCES: Geology, Mineralogy, Petrology, Geophysics, Geochemistry, Meteorology, and Geography

MINERAL ENGINEERING: Mineral Economics, Mining, Mineral Preparation, and Petroleum and Natural Gas


INTERDISCIPLINARY GRADUATE PROGRAMS AND INSTITUTES:
Mineral Engineering Management
Earth Science

ASSOCIATE DEGREE PROGRAMS:
Materials Technology
Mining Technology

ANALYTICAL AND STRUCTURAL STUDIES:
Wet Chemical Analysis of Silicate and Carbonate Rocks, X-ray Crystallography, Electron Microscopy and Diffraction, Electron Microprobe Analysis, and Spectroscopic and other Instrumental Analysis
Experimental Evaluation of Geochemical Conditions in Geothermal Energy Systems

Report to the U.S. Energy Research and Development Administration
On the Quarter September to December, 1976

H. L. Barnes, Co-principal Investigator
W. F. Downs, Project Associate

Covering information from the following contributors:

Static System
  C. W. Burnham, R. L. Erickson

Isotope Experiments
  H. Ohmoto, D. R. Cole

Alteration Experiments
  D. M. Kerrick, G. C. Solomon

Kinetic Functions
  J. D. Rimstidt

Silica Analysis
  J. Devine, N. Suhr

Mathematical Modeling
  C. Sammis, T. Li
During the second quarter of the budget year 1977, our efforts on the project "Experimental Evaluation of the Geochemistry of Geothermal Systems" have progressed in several directions. Our results are grouped under six headings in the enclosure report.

I. Static Measurements

The first set of enclosures provide for you the additional kinetic data collected since our last report from the static system experiments using the biotite adamellite (LA-11) and either air-saturated distilled water or 0.1 m NaCl brine at 200°C. Runs have now been completed at 250°C and the experiments for 300°C are in preparation. As explained in our introductory report, long term kinetic data from the static system are used in conjunction with the data from the circulating systems to determine both rates of equilibration and equilibrium concentrations. These data are submitted as an addition to our body of experimental data and detailed interpretation will be postponed until the data set is more complete.

II. Isotopic Geochemistry

Our research into geothermometry and fluid origins continued based on the stable isotope geochemistry of geothermal systems. Analyses were made of oxygen isotopic ratios of both solution samples and solids, mineral and rock samples, both before and after reaction. Tables of the raw isotopic values have been included in preceding reports, with isotopic (δ18O) values expressed in per mil (‰) deviation from "Standard Mean Ocean Water" (SMOW). Interpretation
Enclosure Set 1

**Static System 1, Run 5**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Elapsed Time (Hrs)</th>
<th>SiO₂ ( \times 10^3 )</th>
<th>Na⁺ ( \times 10^3 )</th>
<th>K⁺ ( \times 10^4 )</th>
<th>Ca²⁺ ( \times 10^4 )</th>
<th>Al³⁺ ( \times 10^5 )</th>
<th>Fe²⁺ ( \times 10^5 )</th>
<th>Mg²⁺ ( \times 10^5 )</th>
<th>SO₄²⁻ ( \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.1</td>
<td>162</td>
<td>4.73</td>
<td>8.94</td>
<td>7.52</td>
<td>1.94</td>
<td>1.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.2</td>
<td>330</td>
<td>5.02</td>
<td>8.20</td>
<td>6.16</td>
<td>1.00</td>
<td>7.26</td>
<td>1.63</td>
<td>&lt;0.25</td>
<td></td>
</tr>
<tr>
<td>15.3</td>
<td>498</td>
<td>5.36</td>
<td>7.74</td>
<td>6.12</td>
<td>0.53</td>
<td>7.85</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.4</td>
<td>670</td>
<td>5.46</td>
<td>7.74</td>
<td>5.78</td>
<td>0.36</td>
<td>15.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.5</td>
<td>834</td>
<td>3.74</td>
<td>6.68</td>
<td>4.80</td>
<td>0.66</td>
<td>15.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.6*</td>
<td>834</td>
<td>0.7</td>
<td>0.17</td>
<td>0.21</td>
<td>0.12</td>
<td>1.37</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Rock material: LA-11 Biotite Adamellite

Reaction fluid: Air saturated distilled water

Temperature: 200°C

Pressure: 5000 psi

*Sample 15.6 is the condensed steam fraction collected after the vessels were emptied of liquid.*
Enclosure Set 1

Static System 2, Run 3

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Elapsed Time (Hrs)</th>
<th>SiO₂ (mx10³)</th>
<th>Na⁺ (mx10³)</th>
<th>K⁺ (mx10³)</th>
<th>Ca²⁺ (mx10⁵)</th>
<th>Al³⁺ (mx10⁵)</th>
<th>Fe²⁺ (mx10⁵)</th>
<th>Mg²⁺ (mx10⁵)</th>
<th>SO₄²⁻ (mx10⁴)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.1</td>
<td>162</td>
<td>4.44</td>
<td>0.1</td>
<td>5.50</td>
<td>2.58</td>
<td>0.78</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23.2</td>
<td>330</td>
<td>4.16</td>
<td>0.1</td>
<td>5.24</td>
<td>1.64</td>
<td>1.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23.3</td>
<td>498</td>
<td>4.13</td>
<td>0.1</td>
<td>5.52</td>
<td>1.32</td>
<td>0.39</td>
<td>0.25</td>
<td>&lt;0.25</td>
<td></td>
</tr>
<tr>
<td>23.4</td>
<td>666</td>
<td>4.88</td>
<td>0.1</td>
<td>5.84</td>
<td>1.09</td>
<td>0.39</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23.5</td>
<td>836</td>
<td>4.76</td>
<td>0.1</td>
<td>5.50</td>
<td>0.93</td>
<td>0.39</td>
<td></td>
<td></td>
<td>2.37</td>
</tr>
<tr>
<td>23.6*</td>
<td>836</td>
<td>2.80</td>
<td>0.07</td>
<td>4.48</td>
<td>0.66</td>
<td></td>
<td></td>
<td></td>
<td>&lt;0.20</td>
</tr>
</tbody>
</table>

Rock material: LA-11 Biotite Adamellite

Reaction fluid: Air saturated 0.1 m NaCl solution

Temperature: 200°C

Pressure: 5000 psi

*Sample 23.6 is the condensed steam fraction collected after the vessels were emptied of fluid.
of these values is as follows. Figure 2a is a plot of the change in δ¹⁸O of the reacting solution as a function of time. The solutions sampled were reacting with the granitic gneiss (LA-6) and the rock-water oxygen atomic ratio was nearly one. This plot demonstrates that the shift in oxygen isotopic composition is a function of temperature and, especially, salinity of the brine. Air-saturated distilled water experiments show the smallest amount of change in isotopic composition and within this group the low temperature run is the closest to its initial value. Increasing salinity produces both an increase in the rate of isotopic exchange and the apparent steady state shift. Once again, within a series of experiments at a given salinity, an increase in temperature produces a corresponding increase in the rate of exchange.

Figure 2b allows easy comparison between the oxygen isotopic shifts of both the rock material and the reaction fluid for the granitic gneiss-sodium chloride brine runs. Oxygen was removed from the altered rock material in steps. The first reaction removed approximately 5% of the oxygen from rock chips of 1 mm nominal diameter. This surface leaching would, of course, cause isotopic zoning within individual rock fragments. Both the water and the rock shifted isotopically toward one another, but the surface layer on the rock shifted considerably farther than did the bulk rock fragments.

Equilibrium conditions based on the alkali feldspar-water data of O'Neil and Taylor (Am. Min., v. 52, pp. 1414-37) are also plotted in figure 2b. In no case are the isotopic shifts large enough to reach equilibrium. Increases in salinity and/or temperature increased the respective shifts and brought the solution and rock material closer
Figure 2a

Granite Gneiss (Circulating System) (R/W)₀ = 1

Δδ¹⁸O%H₂O %

Log Time (Hrs.)

300°C 1m NaCl
200°C 0.1 NaCl
170°C 0.1 NaCl
300°C H₂O
200°C H₂O
150°C H₂O
Figure 2b
to equilibrium.

To determine which minerals the rock material contributed to the oxygen shift, alkali feldspar was examined in detail. The granitic gneiss used in the first series of runs contained the major minerals alkali feldspar, plagioclase and quartz. Numerous studies have demonstrated that quartz is nearly impervious to isotope exchange even under metamorphic conditions. The isotopic exchange, therefore, is limited to either or both of the alkali and plagioclase feldspars. Figure 2c demonstrates that the alkali feldspars are isotopically zoned in the same manner as the whole rock fragments. Most of the isotopic exchange is contained in the outer 8-10% of the mineral grains and little or no exchange occurred in the middle of the grains. Mass balance calculations using our whole rock and alkali feldspar data indicate that the magnitude of the oxygen isotopic shift in plagioclase was limited to a maximum of 0.5°/oo. The relative isotopic depletions of the mineral phases can be ranked in the following order: alkali feldspar > plagioclase > quartz.

Further isotopic experiments were run using the same reaction fluids and but with disks of biotite adamellite (LA-11) in contrast to the disaggregated samples previously used. The major difference between the LA-6, granitic gneiss, and LA-11 is the presence of approximately 17% biotite in the latter rock type. By comparing isotopic shifts in the two rock types, the effect of biotite on the system can be determined. The oxygen atomic ratio of rock to brine in the second series of experiments is approximately 0.1.

Figure 2d shows the oxygen isotope shifts for the solution and whole rock starting material at various combinations of temperature,
Figure 2c

K-feldspar (Circulating System)

\[ \frac{10^6}{T^2} \]

\[ S^{18}O_{\%} \]

- Stripping
  - 1st 8-10%
  - 2nd 35%
  - 3rd 55%
  - Total Kspar

\( (R/W)_o = 1 \)

T °C

170° 200° 300°
Figure 2d
brane concentration and run times. Because the duration of the low temperature runs greatly exceeded those at higher temperatures, the magnitude of the oxygen shift is exaggerated. However, reaction rates are still clearly enhanced by increases in either reaction temperature or salinity.

The effects on reaction rates are shown on figures 2e and 2f by the oxygen isotope shift of alkali feldspar and biotite, respectively, as a function of temperature and brine salinity. The same trend, of increasing isotopic exchange with increasing temperature and salinity, is demonstrated by both of these minerals. The effects are more pronounced in biotite than in alkali feldspar – a maximum shift of 2.9 ‰ in biotite versus 1 ‰ in feldspar.

Be combining data from presently active geothermal areas and from hydrothermal ore deposits, which represent ancient geothermal systems, we find a correlation between salinity and change in the oxygen isotopic composition of water within the system (figure 2g). Conventional explanations have previously attributed large shifts in the $\delta^{18}O$ of geothermal solutions compared to the $\delta^{18}O$ of the recharge water to extreme temperatures at depth. We believe that the effect of salinity is as large, if not larger, than the temperature effect and must be considered in any interpretation of a solution's isotopic composition.

III. Alteration Experiments

An effort was made to determine the dominant rate controlling reactions for the dissolution of biotite adamellite in low salinity brines as a model for geothermal alteration processes. To start
Figure 2e

$10^6/T^2$

$\delta^{18}O_{\%oo}$

K-feldspar (Disc Experiments)

Initial Kspar

$\delta^{18}O_{\%oo}$

$T \, ^\circ C$

$300^\circ$ $250^\circ$ $200^\circ$

$0.1m$ $0.5m$ $1m$

$(R/W)_0 = 0.1$
samples obtained from our circulating systems were analyzed for the major rock-forming elements. Initially, we knew that alteration reactions involve both incongruent and congruent dissolution of mineral phases as well as simple hydration and ion exchange reactions. Figure 3a of the third set of enclosures lists six reactions which are either observed or inferred from the solution chemistry or analyses of the solid products of rock alteration. These reactions occurred in various combinations in all of the experiments. Vermiculite has been identified as an alteration product of biotite via both x-ray diffraction and energy dispersive spectroscopy techniques. The alteration of chlorite to clay was observed in thin section but has not yet been substantiated by spectroscopic work. The feldspar-to-mica alteration was detected in high temperature, high salinity experiments by x-ray diffraction. The congruent dissolution of quartz has been studied in detail as part of the Bureau of Mines scaling project and is used in conjunction with the other solution data to determine the contribution that each alteration reaction makes to the total solution chemistry. The final two reactions in figure 3a are inferred from solution analyses.

The treatment of the alteration data is shown by a series of figures. Figure 3b is a plot of dissolved species concentration as a function of time for one experiment, and is representative of the initial plot made for each experiment. Figure 3c compares observed silica data for the solution altering the rock sample versus the expected silica control for simple dissolution of quartz, both expressed in terms of the rate equation parameters, $-\ln (1-S)$ and time. By comparison, we deduce that less than 5% of the total silica in solution
Reactions:

\[ K(Fe^{2+}Mg_{2}) AlSi_{3}O_{10}(OH)_{2} + nH_{2}O = K_{1-x}(Fe^{3+}Fe^{2+}Mg_{2}) AlSi_{3}O_{10}(OH)_{2-x} nH_{2}O + xK^{+} + xOH^{-} \]

Vermiculite

Chlorite \equiv Clay (?)

\[ \frac{3}{2} K\text{-feldspar} + H^{+} = \frac{1}{2} \text{Musc.} + 3SiO_{2} + K^{+} \]

Incongruent Solution of Feldspars

(Primarily An_{30})

\[ K\text{-feldspar} + Na^{+} = \text{Albite} + K^{+} \]

T°C: 175-300 200; 285; 300 175-300

Salinity m: 0.1-1 1; 0.5; 1 0.1-1
200°C  0.5 m NaCl: \( \frac{\text{Area}_{\text{rock}}}{\text{mass}_{\text{H}_2\text{O}}} = 0.2 \text{ cm}^2 \text{ g}^{-1} \)

\[  \begin{align*} 
  &\text{K}^+ \quad \circ \\
  &\text{Ca}^{2+} \quad \triangle \\
  &\text{SiO}_2 \quad \square 
\end{align*} \]

Figure 3b
Predicted Rate for
$\text{SiO}_2_{\text{qtz}} + 2\text{H}_2\text{O} \rightarrow k_2 \text{H}_4\text{SiO}_4_{\text{aq}}$

Indicates Less Than
$5\% \sum \text{H}_4\text{SiO}_4_{\text{aq}}$ is from Quartz.

$A_{\text{qtz}} = 0.5 \text{cm}^2 \text{g}^{-1}$

Figure 3c
originates from the dissolution of quartz and the remainder is due to the alteration of other mineral phases.

A clue to the source of the dissolved silica is found in the distribution of calcium in the experiment. There are only two calcium-bearing mineral phases in rock LA-11, plagioclase and epidote. Pre- and post-run analyses of epidote indicate no chemical change. The plagioclase, however, is partially dissolved and shows considerable reaction rims. The \((\text{SiO}_2/\text{Ca}^{2+})\) aqueous mole ratio in these samples are 3:1, which corresponds to the ratio for the stoichiometric dissolution of \(\text{A}_n\text{Si}_3\text{O}_8\) plagioclase.

Rate functions are determined for the alteration reactions as follows. Figure 3d is an abbreviated derivation of the complete rate equation for the ion exchange reaction for the albitization of potassium feldspar. In Figure 3e, the reaction parameter is given as a function of time, and the values of \(k_+\) and \(k_-\) are calculated from the slope of this straight line together with the measured quantities of \(A/m\) and the concentration of the initial brine.

Activation energies can also be derived from these data. By determining values of \(k_+\) and \(k_-\) at a series of temperatures, an Arrhenius plot can be made to determine activation energies as shown by Figure 3f for the albitization reaction. The linearity of these plots lends credibility to the hypothesis that potassium feldspar–albite buffers control the alkali content of the solution.

Confirming the specific alteration reaction is a series of energy dispersive photos of one of our reacted biotites (Figure 3g). There is little or no change in the magnesium and iron contents of this particular sample toward the (upper) altered surface. The potassium,
K-feldspar + Na$^+\xrightarrow{k_+} \text{Albite} + K^+$

Net Rate $= \left(\frac{d\langle K^+ \rangle}{dt}\right)_{PT,m} = \frac{A\gamma}{m} \left[ k_+(Na^+) - k_+(K^+) \right]$

Assuming: $a_{\text{solids}} = 1; \gamma_{K^+} = \gamma_{Na^+}$

Integrating With $(Na^+) = (Na^+_0) - (K^+)$

Yields

$$-\ln \left[1 - \frac{(K^+)}{(K^+_0)}\right] = k_+ \left[ \frac{A\gamma(Na^+_0)}{m(K^+_0)} \right] t$$
$200^\circ C \quad 0.5 \text{m NaCl} \quad \frac{A}{m} = 0.07 \text{cm}^2 \text{g}^{-1}$

Integrated Rate Equation,

$$-\ln \left[ 1 - \frac{(K^+)}{(K_e^+)} \right] = k_+ \left[ \frac{A\gamma(Na^+)}{m(K_e^+)} \right] t$$

$k_+ = 9 \times 10^{-10} \text{ kg cm}^{-2} \text{ sec}^{-1}$

$k_- = 4 \times 10^{-7} \text{ kg cm}^{-2} \text{ sec}^{-1}$
Arrhenius Plot:

\[ \ln \frac{k_2}{k_1} = \frac{\Delta E_{\text{act.}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]

\[ \Delta E_{\text{act.}}^+ = 10.3 \text{ Kcal mole}^{-1} \]

\[ \Delta E_{\text{act.}}^- = 1.0 \text{ Kcal mole}^{-1} \]

\[ (N_0) = 0.1 - 1.0 \text{ m} \]

Figure 3f
Figure 3g
however, has been preferentially leached along the contacts between mica sheets. This biotite flake came from within the interior of the rock disc. Such potassium depletion indicates that the aqueous solution travels along grain boundaries and cleavage planes as it passes through the sample.

IV. Kinetic Functions

Following conventional kinetic derivations, we have been using rate equations involving concentrations. Because this usage causes inconsistencies in thermodynamic applications of the resulting equations, we have taken absolute rate theory and modified these functions as shown on Enclosure 4. The example used is the silica-water equilibria but the principles are identical for other systems and have been used here in the treatment of alteration in Enclosure 3.

V. Silica Analysis

Earlier reports have described problems that arose from our use of the standard analytical method for silica using atomic absorption spectrophotometry. Investigation of these difficulties has led to a revised manuscript entitled "Determination of Silicon in Water Samples" by J. C. Devine and N. H. Suhr in Enclosure 5. Because the majority of published silica analyses are produced by A.A., one must evaluate the validity of such numbers prior to using them in any research.

VI. Papers Presented

Enclosure 6 is a list of presentations made by researchers associated with the PSU geothermal research group. At this stage in our research project, we feel that our results will be better reported
by publication rather than oral presentation of our observations and conclusions; consequently, we are now accepting fewer invitations to present papers.

Enclosure 7 contains extended abstracts for talks given by H. L. Barnes at the E.R.D.A. Geothermal Brine Chemistry Program Review and C. G. Sammis at the Second Workshop on Geothermal Reservoir Engineering at Stanford University. Also enclosed are copies of the abstracts of the four talks presented at the annual meeting of the Geological Society of America in mid November. The final section of enclosure 7 consists of the extended abstracts for the presentation made to the Electrochemical Society in mid October by W. F. Downs.
Enclosure 4. Rate Equations for Silica-Water Reactions

The rate of reaction between these two phases is directly proportional to the interfacial area (A) between them.

\[
\frac{\partial n_{H_4SiO_4}}{\partial t} \bigg|_{P,T} = A k_+ a_{SiO_2} a_{H_2O}^2
\]

and

\[
-\frac{\partial n_{H_4SiO_2}}{\partial t} \bigg|_{P,T} = A k_- a_{H_4SiO_4}
\]

so

\[
\frac{\partial n_{H_4SiO_4}}{\partial t} \bigg|_{P,T} = A \left( k_+ a_{SiO_2} a_{H_2O}^2 - k_- a_{H_4SiO_4} \right)
\]

Since

\[
C_{H_4SiO_4} = \frac{n_{H_4SiO_2}}{m}
\]

where \( m \) is the mass of water

\[
\frac{\partial (C_{H_4SiO_4} \cdot m)}{\partial t} \bigg|_{P,T} = m \left( \frac{\partial n_{H_4SiO_4}}{\partial t} \right)_{P,T,M} + C_{H_4SiO_4} \left( \frac{\partial m}{\partial t} \right)_{P,T,C}
\]

assuming \( m \) is constant

\[
\frac{\partial C_{H_4SiO_4}}{\partial t} \bigg|_{P,T,M} = \frac{A}{M} \left( k_+ a_{SiO_2} a_{H_2O}^2 - k_- a_{H_4SiO_4} \right)
\]
also

\[ a_{H_4SiO_4} = \gamma_{H_4SiO_4} c_{H_4SiO_4} \]

so

\[
\left\{ \frac{\partial(a_{H_4SiO_4} / \gamma_{H_4SiO_4})}{\partial t} \right\}_{P,T,M} = \frac{1}{\gamma_{H_4SiO_4}} \left\{ \frac{\partial \gamma_{H_4SiO_4}}{\partial t} \right\}_{P,T,M,\gamma} + a_{H_4SiO_4} \left\{ \frac{\partial(1/\gamma_{H_4SiO_4})}{\partial t} \right\}_{P,T,M,a}
\]

assume \( \gamma_{H_4SiO_4} \) is constant

\[
\left\{ \frac{\partial a_{H_4SiO_4}}{\partial t} \right\}_{P,T,M,\gamma} = \frac{A}{M} \gamma_{H_4SiO_4} (k^+ a_{SiO_2} a_{H_2O}^2 - k^- a_{H_4SiO_4})
\]

\[
k^+ = \frac{A}{M} \gamma_{H_4SiO_4} a_{SiO_2} a_{H_2O}^2 k^+
\]

\[
k^- = \frac{A}{M} \gamma_{H_4SiO_4} k^-
\]

\[
\begin{bmatrix}
(a_{H_4SiO_4})_{2} \\
(a_{H_4SiO_4})_{1}
\end{bmatrix}
\]

\[
\int_{t_1}^{t_2} dt = \int_{t_1}^{t_2} \frac{d(a_{H_4SiO_4})}{k^+ - k^- a_{H_4SiO_4}}
\]

\[
\int_{t_1}^{t_2} = \frac{1}{-k^-} \ln (k^- k^+ a_{H_4SiO_4})
\]

\[
\begin{bmatrix}
(a_{H_4SiO_4})_{2} \\
(a_{H_4SiO_4})_{1}
\end{bmatrix}
\]
defining $S$

$$S = \frac{Q}{K} = \frac{a_{H_4SiO_4}}{a_{SiO_2}a_{H_2O}^2} \cdot \frac{1}{K_{eq}}$$

therefore

$$\Delta t = -\frac{1}{k^-} \ln \left( \frac{1-S_2}{1-S_1} \right)$$

In most systems

$$H_4SiO_4 = 1$$

so

$$a_{H_4SiO_4} = m_{H_4SiO_4}$$

and

$$\left( \frac{\partial a_{H_4SiO_4}}{\partial t} \right)_{P,T,m,\gamma} = \left( \frac{\partial m_{H_4SiO_4}}{\partial t} \right)_{P,T,m}$$

Unit Analysis

Differential rate equation

$$\left( \frac{\partial a}{\partial t} \right)_{P,T,m,\gamma} = \frac{A}{M} \gamma_{H_4SiO_4} k_+ a_{SiO_2} a_{H_2O}^2$$

$$k_+ = \left( \frac{\partial a}{\partial t} \right) \left( \frac{M}{A} \right) \gamma_{H_4SiO_4} \left( \frac{1}{a_{SiO_2}} \right) \left( \frac{1}{a_{H_2O}^2} \right)$$

$$k_+ = \text{sec}^{-1} \text{kg/cm}^2 = \text{kg/cm}^2 \text{ sec}$$

$$\left( \frac{\partial a}{\partial t} \right)_{P,T,m,\gamma} = \frac{A}{M} \gamma_{H_4SiO_4} k - a_{H_4SiO_4}$$
\[ k_- = \left( \frac{\partial m}{\partial t} \right) \left( \frac{M}{A} \right) \left( \frac{1}{\gamma_{H_4SiO_4} a_{H_4SiO_4}} \right) \]

\[ k_- \text{ sec}^{-1} \text{ kg/cm}^2 = \text{ kg/cm}^2 \text{ sec} \]

Integrated Rate Equation

\[ \Delta t = - \frac{m}{A \gamma_{H_4SiO_4}} \frac{1}{k_-} \ln \left( \frac{1-S_2}{1-S_1} \right) \]

\[ k_- = \frac{m}{\Delta t A \gamma_{H_4SiO_4}} \ln \left( \frac{1-S_2}{1-S_1} \right) \]

\[ k_- \text{ kg/cm}^2 \text{ sec} \]

Equilibrium constant

\[ \text{Keq} = \frac{k_+}{k_-} = \frac{\text{ kg cm}^{-2} \text{ sec}^{-1}}{\text{ kg cm}^{-2} \text{ sec}^{-1}} \]

note: If \( \left[ \frac{\partial m}{\partial t} \right] \) is used in the differential rate equation instead of \( \left[ \frac{\partial a}{\partial t} \right] \), the units of \( k_- \) will not agree with the units of \( k_- \) in the integrated rate equation.
Determination of Silicon in Water Samples

by

John C. DeVine and N. H. Suhr
Mineral Constitution Laboratories
The Pennsylvania State University
University Park, Pennsylvania 16802
Experimental

Standard Preparation

Silica standards may be purchased or prepared by following the procedures given in various papers and texts (3,4,5). With the exception of one available standard,* all are made from various soluble sodium silicates. The silica or silicon content is specified; however, the sodium content is variable or in many instances unknown. Since we have found a definite enhancement of silicon by sodium, these standards are of dubious value.

The most common procedures for making up silicon standards involve sodium silicates. For accurate work, though, we and others (4) have found that silicon in the standards has to be determined gravimetrically, since hydrous sodium silicates have indefinite water contents.

Another procedure (5) recommends fusing 2.1393 g of high purity silicon dioxide (SiO₂) with 4.60 g of Na₂CO₃, dissolving in water and diluting to 1000 ml. The composition is difficult to fuse, forming a water soluble sinter, rather than a melt. However, it requires no standardization and sodium content is known.

In our laboratories we followed another procedure which was initially used for the determination of silica by colorimetry. The stock solution is made by fusing 0.5000 g high purity silicon dioxide with 5.000 g of Na₂CO₃, dissolving in water and diluting to 500 ml. This solution is easy to make, requires no

*Spex Industries, Metuchen, N. J.
standardization, but does have a much higher sodium to silicon ratio, which is a disadvantage.

The best alkali free silica standard for studying the effect of sodium that we have obtained requires the use of a special high temperature-pressure vessel (6). An excess of quartz sand (-1 mm + .125 mm) is heated in the vessel at 250°C with distilled water. After quenching and diluting, the silica content is determined gravimetrically. For this study, a silica solution prepared in this manner gave a content of 392 ppm SiO₂.

Apparatus

All work was performed on a Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer using a nitrous oxide-acetylene flame and other parameters as recommended by the manufacturer.

Procedure

For the determination of silica by AAS, 1.00 ml aliquots of geothermal waters were diluted with 10.00 ml of distilled water for a dilution factor of eleven. For the determination by colorimetry, 1.00 or 2.00 ml aliquots were made up to 25.00 ml for a dilution factor of 25 or 12.5. Standards for both procedures were made from the same 1000 ppm SiO₂ stock solution which contained 5850 ppm Na₂O. A comparison of the results obtained by the two methods is shown in Table I.

The values obtained by colorimetry were generally in good agreement with expected values. The atomic absorption values, however, were unacceptably low.
### Table I

Comparison of SiO₂ Values by AAS and Colorimetry

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂, ppm</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AAS</td>
<td>Colorimetry</td>
</tr>
<tr>
<td>1</td>
<td>14</td>
<td>41</td>
</tr>
<tr>
<td>2</td>
<td>92</td>
<td>129</td>
</tr>
<tr>
<td>3</td>
<td>129</td>
<td>198</td>
</tr>
<tr>
<td>4</td>
<td>158</td>
<td>218</td>
</tr>
<tr>
<td>5</td>
<td>168</td>
<td>221</td>
</tr>
<tr>
<td>6</td>
<td>194</td>
<td>262</td>
</tr>
<tr>
<td>7</td>
<td>201</td>
<td>226</td>
</tr>
<tr>
<td>8</td>
<td>197</td>
<td>219</td>
</tr>
<tr>
<td>9</td>
<td>200</td>
<td>227</td>
</tr>
<tr>
<td>10</td>
<td>194</td>
<td>249</td>
</tr>
<tr>
<td>11</td>
<td>211</td>
<td>244</td>
</tr>
<tr>
<td>12</td>
<td>220</td>
<td>277</td>
</tr>
</tbody>
</table>

While colorimetry gave good results, it involved a long, tedious process of evaporation and fusion. Atomic absorption was preferred, providing the low values could be corrected, since the procedure was much faster and required less skill. Since sodium was the other major element present in the standard solution, it seemed that sodium was having more effect on the silica determination than anticipated.
In order to investigate the effect of sodium on the determination of silica, a series of standards were made by dilution of the 1000 ppm SiO$_2$, 5850 ppm Na$_2$O stock solution. Then a series of 10.0 ppm SiO$_2$ samples (starting from the same stock solution) were prepared with varying sodium content. Silica was then determined in the 10.0 ppm solutions as in unknown samples. Data are listed in Table II.

Table II
Enhancement Effect of Sodium on the Determination of SiO$_2$ by AAS

<table>
<thead>
<tr>
<th>Actual SiO$_2$, ppm</th>
<th>Na$_2$O, ppm</th>
<th>Apparent SiO$_2$, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standards</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>585</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>468</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>351</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>234</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>117</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>&quot;Unknowns&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>59</td>
<td>10.2</td>
</tr>
<tr>
<td>10.0</td>
<td>199</td>
<td>11.8</td>
</tr>
<tr>
<td>10.0</td>
<td>399</td>
<td>13.0</td>
</tr>
<tr>
<td>10.0</td>
<td>479</td>
<td>13.8</td>
</tr>
<tr>
<td>10.0</td>
<td>619</td>
<td>15.2</td>
</tr>
</tbody>
</table>
From this, it was evident that the sodium increased the observed silica values. One approach to avoid this was to swamp out the effect with a large excess of sodium. Five thousand ppm Na$_2$O was added to each silica standard, giving a range of 5000 to 5585 ppm Na$_2$O. Again, a series of 10.0 ppm SiO$_2$ samples was made up, varying the Na$_2$O content from 59 to 25059 ppm and run as unknowns. The results are shown in Figure 1. Up to 25000 ppm Na$_2$O, no levelling out of the enhancement effect was noted. The correct value for SiO$_2$ was found at approximately 5000 ppm Na$_2$O. However, if sodium in the sample was increased by the amount that it varied in the standards, there was a positive error of about ten percent. Furthermore, at 5000 ppm Na$_2$O and above there was a problem of burner clogging and contamination of subsequent samples.

Price (2) has noted that in the determination of silica in siliceous materials, many workers add lanthanum to overcome the ionization effect caused by calcium, iron or sodium. This was tried with no apparent decrease in silica enhancement (Table III).

If sodium enhances the values for silica, then sodium in the standards must cause the apparent silica values of samples to be low. Since there was sodium in all the standards and samples used, it was difficult to judge its effect. Consequently, starting with the pure silica stock solution mentioned previously, a set of standards was made up having no sodium. A series of 10.0 ppm SiO$_2$ samples was made from the same stock solution, with the Na$_2$O content varying from 0 to 200 ppm, and run as unknowns. The results are shown in Table IV.
Figure 1. Effect of Adding a Large Excess of Sodium to 10.0 ppm SiO<sub>2</sub> Samples. Range of Na<sub>2</sub>O in Standards: 5000-5585 ppm.
Table III
Lanthanum Addition to Standards and Samples

<table>
<thead>
<tr>
<th></th>
<th>Actual SiO₂, ppm</th>
<th>Na₂O, ppm</th>
<th>La, ppm</th>
<th>Apparent SiO₂, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Standards</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>585</td>
<td>10,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>468</td>
<td>10,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>351</td>
<td>10,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>234</td>
<td>10,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>117</td>
<td>10,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>10,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>&quot;Unknowns&quot;</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>585</td>
<td>10,000</td>
<td></td>
<td>100.0</td>
</tr>
<tr>
<td>80</td>
<td>585</td>
<td>10,000</td>
<td></td>
<td>81.4</td>
</tr>
<tr>
<td>60</td>
<td>585</td>
<td>10,000</td>
<td></td>
<td>62.3</td>
</tr>
<tr>
<td>40</td>
<td>585</td>
<td>10,000</td>
<td></td>
<td>43.1</td>
</tr>
<tr>
<td>20</td>
<td>585</td>
<td>10,000</td>
<td></td>
<td>23.7</td>
</tr>
<tr>
<td>0</td>
<td>585</td>
<td>10,000</td>
<td></td>
<td>5.1</td>
</tr>
</tbody>
</table>
Table IV
Enhancement Effect of Sodium on the Silica Determination Using Pure Silica Standards and the Effect of the D₂ Background Correcting Device

<table>
<thead>
<tr>
<th>Actual SiO₂, ppm</th>
<th>Na₂O, ppm</th>
<th>Apparent SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standards</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>9.8</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
<td>10.4</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
<td>10.7</td>
</tr>
<tr>
<td>40</td>
<td>0</td>
<td>11.2</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>11.8</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>12.2</td>
</tr>
<tr>
<td>&quot;Unknowns&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>0</td>
<td>12.9</td>
</tr>
<tr>
<td>10.0</td>
<td>5</td>
<td>13.7</td>
</tr>
<tr>
<td>10.0</td>
<td>10</td>
<td>14.3</td>
</tr>
<tr>
<td>10.0</td>
<td>20</td>
<td>16.5</td>
</tr>
<tr>
<td>10.0</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>200</td>
<td></td>
</tr>
</tbody>
</table>
If the enhancement effect were a light scattering effect, then the use of a deuterium ($D_2$) background correcting device should have remedied the problem. This was tried with some decrease in the enhancement but a noticeable increase in instability. Consequently, the $D_2$-lamp was not used in any further studies (see Table IV).

It was obvious that sodium, even in small amounts, had a pronounced effect and must be controlled closely in samples and standards. When the sodium contents of the solutions were adjusted to be exactly equal, silica values of the geothermal samples were in good agreement with colorimetric values and expectations.

To complete the study, a stock silica solution containing potassium (1000 ppm $SiO_2$ and 5000 ppm $K_2O$) was made by fusing high purity silicon dioxide with potassium carbonate. The effect of potassium on the determination of $SiO_2$ was checked by running known silica and variable $K_2O$ content samples versus silica-$K_2O$ standards (Table V). No enhancement of silica by potassium was observed.

A further comparison was made by running the potassium-based standards and the sodium-based standards as unknowns against the pure silica standards (Table VI). Again, sodium enhanced the determination of silica but potassium did not.

Conclusion

The enhancing effect of sodium on the silica determination was more pronounced than expected. As little as 10 ppm $Na_2O$
Table V

Effect of Potassium on SiO$_2$

<table>
<thead>
<tr>
<th></th>
<th>Actual SiO$_2$, ppm</th>
<th>K$_2$O, ppm</th>
<th>Apparent SiO$_2$, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standards</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;Unknowns&quot;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>50</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>200</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>350</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>500</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>650</td>
<td>10.3</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>1000</td>
<td>10.1</td>
<td></td>
</tr>
<tr>
<td>Actual SiO₂, ppm</td>
<td>K₂O, ppm</td>
<td>Na₂O, ppm</td>
<td>Apparent SiO₂, ppm</td>
</tr>
<tr>
<td>-----------------</td>
<td>----------</td>
<td>-----------</td>
<td>-------------------</td>
</tr>
<tr>
<td><strong>Standards</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td><strong>&quot;Unknowns&quot;</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>500</td>
<td>0</td>
<td>99</td>
</tr>
<tr>
<td>80</td>
<td>400</td>
<td>0</td>
<td>79</td>
</tr>
<tr>
<td>60</td>
<td>300</td>
<td>0</td>
<td>59</td>
</tr>
<tr>
<td>40</td>
<td>200</td>
<td>0</td>
<td>39</td>
</tr>
<tr>
<td>20</td>
<td>100</td>
<td>0</td>
<td>19</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>585</td>
<td>104</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
<td>468</td>
<td>84</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
<td>351</td>
<td>63</td>
</tr>
<tr>
<td>40</td>
<td>0</td>
<td>234</td>
<td>43</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>117</td>
<td>22</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
enhanced SiO\textsubscript{2} by approximately 1 ppm (see Table IV). At the 100 ppm level of SiO\textsubscript{2} the effect was negligible with 1\% enhancement. But, at 10 ppm SiO\textsubscript{2}, the effect was 10\% and at the 1 ppm SiO\textsubscript{2} level, the enhancement was 100\%.

Potassium-based standards had no measurable effect on the silica determination and they could be used to analyze sodium-free samples. It is rare, however, to encounter this condition. Thus, it would be well to determine Na\textsubscript{2}O in the sample first, then adjust the standards and/or the samples to exactly the same concentration of sodium.

The enhancement effect of Na on Si is not entirely an ionization or background absorption/light scattering effect. The use of a D\textsubscript{2} lamp for background correction did not adequately compensate for the enhancement (although it did improve it slightly) and the fact that a sample containing no SiO\textsubscript{2} and 585 ppm Na\textsubscript{2}O gave a definite absorption signal rules out an ionization effect also. Just what other factors are causing the enhancement is still to be determined. This means that the sodium content of standards and samples must be identical in order to get an accurate silica determination in waters by AAS.

References


Presentations Made by PSU Geothermal Group
(May - December, 1976)


* Speaker
Abstract: Experimental Evaluation of Geochemical Conditions in Geothermal Energy Systems

H. L. Barnes, The Pennsylvania State University

There are six dominant areas where our research has been concentrated.

1. An experimental system has been developed in order to evaluate the reaction kinetics of geothermal systems to 350°C and 3500 psi. A hydrothermal fluid is circulated through rock fragments in a 1.1' reaction vessel which is maintained at a selected temperature, T1. The fluid then passes through an isothermal heat exchanger where any precipitate is collected. A double valve sampling system and a constant volume circulation pump which returns the solution to the reaction vessel complete the circuit. As a solution sample is removed, the fluid is replaced from a reservoir by a compressed air-driven piston pump. This system is in routine use for determining pertinent fluid-solids kinetics.

Samples of two rock types, a biotite adamellite and a granitic gneiss, both from the Nacemiento Mountains, N. Mex. have been used as starting materials. These rocks are part of the basement complex being tested by the Los Alamos Scientific Laboratory as a dry geothermal reservoir. Prior to use, either these rocks or other mineral samples more disaggregated and characterized for chemical and isotopic composition, surface area and texture. Both air-saturated distilled water and NaCl brines were used as hydrothermal solutions.

2. Results indicate which reservoir reactions are dominant for these typical rocks and their kinetics. Interpretation of the concentrations of SiO₂, Na, K, Ca and Al versus time indicates that about 60% of the (H₄SiO₄) in solution is derived initially from feldspars which dissolve stepwise.

For example, the biotite-adamellite has been reacted with NaCl solutions at 200-300°C. Alteration products were dense coatings of illite on K-feldspar surfaces at 300°C, 1.0m, and sparse coatings at 200°C, 1.0m and 285°C, 0.5m; vermiculite replaced biotite during all the runs. Biotites exhibited marked swelling, and induced fracturing along adjacent grain boundaries. Vermiculite-encrusted biotites in the interior of adamellite provide evidence that solution migration occurred along grain boundaries and microfractures.

Moderately dilute aqueous NaCl solutions in a dry hot rock geothermal system in granitic terrain would promote alternation in the reservoir. The resulting exothermic reactions:

\[ \frac{3}{2} \text{K-feldspar} + \text{H}^+ = \frac{1}{2} \text{Mica} + \text{Qtz.} + \text{K}^+ \]

\[ \text{Biotite} + 4\text{H}_2\text{O} + \text{M}^+ = \text{M-vermiculite} + \text{K}^+ \]

occurring in relatively short amounts of time, would contribute to heat
extraction from the system. The $\Delta V_{\text{solids}}$ of the vermiculite reaction would enhance microfracturing and open new rock surface to the fluid.

These reactions are typical of those controlling permeability during either extraction or reinjection and also indicate that the extractible heat is likely to be dominated by these alteration reactions.

3. The isotopic composition of geothermal fluids is used to approximate both the source of the fluids and their reservoir temperatures. Consequently, the kinetics of reactions and their fractionation factors are of direct application. For example, solution samples obtained from our experimental circulating geothermal system were analyzed for oxygen isotopes. The $\delta^{18}O$ value of $\text{H}_2\text{O}$ interacted with granite gneiss increased with time and with increasing temperature at rates of $\Delta_{\text{final}} - \Delta_{\text{initial}} \approx 0.05\%/\log \text{ hr.}$ (0.25% after 30 hours) at 300°C, 0.04%/$\log \text{ hr.}$ (0.20% after 30 hours) at 200°C and 0.025%/$\log \text{ hr.}$ (0.1% after 30 hours) at 150°C.

With addition of NaCl, the rate of oxygen isotope exchange increased significantly. For example, with 0.1m NaCl reacted with granite gneiss at 200°C, the $\Delta_{\text{final}} - \Delta_{\text{initial}}$ increased rapidly to 2.15% in the first 30 hours. This $\delta^{18}O$ shift was accompanied by rapid increase in the K$^+$ concentration in the solution. After 30 hours, the cation concentration in solution reached steady state equilibrium and the increase in the $\delta^{18}O\text{H}_2\text{O}$ values was small. The contrast between the rate curves of the NaCl-solution and of pure-water reflects a difference in mechanisms of oxygen isotopic fractionation probably due to cation exchange reactions during alteration of feldspars and biotite as well as to oxygen exchange controlled by diffusion.

Similar effects of NaCl concentration on the degree of $\delta^{18}O$ shift are also observed in natural geothermal systems (hot springs; ore-forming fluids).

These results mean that there must be a major correction for salinity when using the isotopic composition observed in wells or springs to estimate that for geothermometry of the reservoir.

4. Scaling rates depend on the kinetics of quartz, carbonates, sulfides, and oxides in solution. We have determined the rate constants for quartz for this purpose.

The rate of reaction between quartz and water

$$\text{SiO}_2(s) + 2\text{H}_2\text{O} \rightarrow H_4\text{SiO}_4(aq)$$

depends predominantly upon two variables: 1) the ratio of interfacial area ($A$) between the two phases to the mass ($m$) of water and 2) the chemical potential driving the reaction. Hence, a rate equation can be derived:
Here, \( k_+ \) and \( k_- \) are the reaction rate constants for the forward and reverse rates respectively. Our rate measurements in both under- 
 saturated and supersaturated systems confirm this relationship and 
 independent experimental evidence shows it is valid for a wide range 
 of \( A/V \) ratios.

The activation energies for this reaction are very high causing the 
 rates to be very temperature dependent. Rate constants for two tem­ 
 peratures are listed below along with activation energies determined 
 from a number of experiments.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( k_+ )</th>
<th>( k_- )</th>
<th>Activation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>105°C</td>
<td>( 4.8 \times 10^{-16} ) moles cm(^{-2}) sec(^{-1})</td>
<td>( 5.4 \times 10^{-13} ) cm(^{-2}) sec(^{-1})</td>
<td>28.3 Kcal/mole</td>
</tr>
<tr>
<td>202°C</td>
<td>( 6.8 \times 10^{-13} ) moles cm(^{-2}) sec(^{-1})</td>
<td>( 1.4 \times 10^{-10} ) cm(^{-2}) sec(^{-1})</td>
<td>21.5 Kcal/mole</td>
</tr>
</tbody>
</table>

Since dissolving reactions which are controlled by aqueous diffusion 
 have activation energies of 4 to 5 Kcal/mole, there is no doubt that 
 the rate of this reaction is controlled by silica bond forming and 
 breaking.

These results show that with careful design, quartz precipitation can 
 be prevented by rapid cooling of the fluid.

5. To field test our kinetic data, we have designed a portable system for 
 measuring the rate of scale formation from geothermal fluids using 
 adjustable thermal quenching. A replaceable helical copper coil is 
 contained in a two-foot length of six-inch diameter pipe containing 
 mixed geothermal and domestic waters. The weight of scale deposited 
 by the flow of geothermal fluid through the coil is measured by weight 
 difference and the scale composition by analysis of the sectioned 
 coil.

Scales from the Salton Sea brines (Magmamax I) are a complex mixture 
 of carbonates (aragonite), sulfides (galena + Cu - Fe sulfides), and 
 some silicates. There is a possibility of quenching this scale-into 
 solution (if there is not extensive flashing) to minimize scaling.

5. Results of our hydrothermal experiments are being incorporated in 
 numerical modeling of geothermal reservoirs.

Although significant chemical energy exists, it cannot always be 
 extracted. For the case of dissolving-precipitation reactions, 
 solubilities are too low for chemical heat to make a contribution, 
 i.e., thermal energy is extracted far faster than chemical energy 
 under all flow conditions. In the case of alteration reactions, 
 however, the reaction rate is not limited by solubility, and, 
 depending on the alteration rate, significant chemical energy may 
 be extracted. We have delineated the combination of flow parameters,
crack parameters, heats of reaction and alteration rates for which chemical energy associated with the alteration may be extracted.

Permeability changes associated with alteration reactions may be written explicitly in terms of temperature, flow velocity, crack parameters, water chemistry, and appropriate alteration rate equation. This larger system of equations may be combined and solved. The large volume changes and chemical heats associated with the reactions suggests they may play an important role in permeability changes and thermal history of an evolving geothermal system.

In progress are (1) the experimental extension of quartz kinetics to cristobalite and amorphous silica and the influence of salinity and complexing on silica scaling, (2) experimental refinement of silicate alteration kinetics, (3) characterization of Salton Sea scales and thermodynamic interpretation of dominant reactions, and (4) extension of field tests to the effects of flashing on the kinetics of scale formation.
Effects of Hydrothermal Chemistry on Reservoir Evolution

Charles G. Sammis, Todd M.C. Li, and William F. Downs

Department of Geosciences, Pennsylvania State University, University Park, PA, 16802

Although the corrosion and scaling problems associated with handling geothermal fluids are well known, the effects of hydrothermal reactions are often overlooked in geothermal reservoir modeling. Water-rock chemistry can be expected to affect the evolution of a reservoir in at least three ways: (a) the heats of reaction may contribute directly to the energy production, (b) the viscosity and thermodynamic properties of water are affected by the dissolved solids - this is especially important in two-phase regimes, and (c) the porosity and permeability change with time due to dissolving and precipitation as well as due to the volume change associated with alteration.

Chemical Energy

Table 1 summarizes the important hydrothermal reactions in a granitic source rock together with the heats of reaction and associated volume changes. Note that the available chemical energy is comparable to the thermal energy while the associated volume changes are an order of magnitude larger than those due to thermal contraction.

Table 1

<table>
<thead>
<tr>
<th>IMPORTANT REACTIONS IN GRANITIC ROCK</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CHEMICAL REACTIONS TAKEN FROM HELGESON, 1969)</td>
</tr>
</tbody>
</table>

| PROCESS | Heat released per mole of solid vol. change per 100g of initial min. solid vol. change per 100g of initial min.  
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>HYDROTHERMAL ALTERATION</td>
<td></td>
</tr>
<tr>
<td>$2NaAlSi_3O_8(s) + 2H^+ + H_2O \rightarrow Al_2Si_2O_5(OH)_4(s) + 4SiO_2(s) + 2Na^+$</td>
<td>Low Albitè</td>
</tr>
<tr>
<td></td>
<td>11.21</td>
</tr>
<tr>
<td>$3KAlSi_3O_8(s) + 2H^+ \rightarrow KAl_2Si_3O_10(OH)_2(s) + 6SiO_2(s) + 2K^+$</td>
<td>Microcline</td>
</tr>
<tr>
<td></td>
<td>2.96</td>
</tr>
<tr>
<td>DISSOLVING AND PRECIPITATION</td>
<td></td>
</tr>
<tr>
<td>$SiO_2(s) + 2H_2O \rightarrow H_2SiO_4(aq)$</td>
<td>α-quartz</td>
</tr>
<tr>
<td></td>
<td>-6.22</td>
</tr>
<tr>
<td>COOLING</td>
<td></td>
</tr>
<tr>
<td>GRANITIC ROCK (300°C) \rightarrow GRANITIC ROCK (65°C)</td>
<td></td>
</tr>
<tr>
<td>$(\rho_R = 2.65 \text{ g/cm}^3, \ C_R = 0.25 \text{ cal/g°C, } \beta_R = 2.5 \times 10^{-3/°C})$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.875</td>
</tr>
</tbody>
</table>
Although significant chemical energy exists, it cannot always be extracted. One of the first questions we addressed (Morris, 1975; Morris and Sammis, 1975) was the delineation of reservoir conditions under which one could expect to extract significant chemical heat. For the case of dissolving-precipitation reactions, a comparison of thermal energy with chemical energy leads to a simple relation between solubility and heat of reaction for a given ratio of chemical to thermal energy extracted. Because the rate of dissolving is controlled by the solubility at the outlet temperature, the resulting relation is independent of all crack and flow parameters. In the case of quartz, the solubility at 300°C is too low for chemical heat to make a contribution - thermal energy is extracted far faster than chemical energy under all flow conditions.

In the case of alteration reactions, however, the reaction rate is not limited by solubility and, depending on the alteration rate, significant chemical energy may be extracted. Morris (1975) has delineated the combinations of flow parameters, crack parameters, heats of reaction and alteration rates for which chemical energy associated with the alteration may be extracted. One of the objectives of our experimental program is to determine alteration rates in typical reservoir rocks, and thus assess the importance of such reactions to the total thermal regime.

Numerical Model for Single-phase Flow Including Porosity and Permeability Changes

The changes in porosity and permeability associated with both dissolving and alteration reactions are easily incorporated into the standard finite difference schemes commonly used in numerical reservoir modeling. The molality of each important solute may be treated as a dependent variable to be found together with the temperature and velocity fields. In addition to the standard three equations for the conservation of mass, momentum, and energy, an equation may be written for the conservation of each solute species. Such an equation directly incorporates permeability changes associated with dissolving and precipitation. It requires, as an additional constitutive relation, the experimentally determined rate equation. Permeability changes associated with alteration reactions may be written explicitly in terms of the temperature, flow velocity, crack parameters, water chemistry, and appropriate alteration rate equation. This larger system of equations may be combined and solved using exactly the same numerical scheme employed by Harlow and Pracht (1972). Using their notation (variables are defined in Table 2), the energy balance equation is

\[
\frac{\partial}{\partial t} \{ [b_w \rho_R (1-\theta) + b_w \rho \theta] T \} + \nabla \cdot \rho_w b_w \theta \frac{\partial T}{\partial \theta} = \nabla \cdot [K_R (1-\theta) \nabla T] + \rho_w b_w T S \quad (1)
\]

and the mass and momentum balance equations may be written in the form

\[
\frac{\partial \theta}{\partial t} - \nabla \cdot \left[ KD \frac{\nabla \phi}{\mu} + \bar{g} \theta (T-T_0) \right] = S \quad (2)
\]

\[
\bar{u} \theta = -K_0 \frac{\nabla \phi}{\mu} + \bar{g} \theta (T-T_0) \quad (3)
\]

The equation of state of water

\[
\rho_w = \rho_0 (1-R_w (T-T_0)) \quad (4)
\]
and a porosity-permeability relation

$$k = \left( \frac{4d_C^2}{5} \right) \left( \frac{\theta^3}{(1-\theta)^2} \right)$$

are also required. It also is important to include the temperature dependence of the viscosity of water

$$\mu = \frac{0.279}{T(°C)-3.8} \left( \frac{gm}{cm \ sec} \right)$$

If we only consider the dissolution and precipitation of SiO2

$$SiO_2-(S) + 2H_2O \rightleftharpoons H_4SiO_4$$

we can write two more balance equations: the conservation of SiO2 during the reaction,

$$\frac{\partial}{\partial t} \left[ \bar{W}_R \rho_R (1-\theta) \right] + \frac{\partial}{\partial t} \left[ \frac{m_{H_4SiO_4}}{10^3} \bar{M}_{SiO_2} \rho_\omega \theta \right]$$

and the mass balance for SiO2 in solution

$$\frac{\partial}{\partial t} \left[ \frac{m_{H_4SiO_4}}{10^3} \bar{M}_{SiO_2} \rho_\omega \theta \right] = \frac{\partial}{\partial t} \left[ \frac{m_{H_4SiO_4}}{10^3} \bar{M}_{SiO_2} \rho_\omega \theta \right] - \nabla \cdot \left[ \frac{m_{H_4SiO_4}}{10^3} \bar{M}_{SiO_2} \rho_\omega \theta \right] + \rho \bar{M}_S$$

The subscript R indicates that we only consider the part of the subscripted expression which is due to the reaction. The time rate of change of molality \([\partial m/\partial t]_R\) is given in terms of experimentally determined rate constants, \(k_+\) (for the forward dissolution reaction) and \(k_-\) (for the reverse precipitation reaction) by the rate equation

$$\left( \frac{\partial a_{H_4SiO_4}}{\partial t} \right)_{P,T,M} = \frac{A}{\rho_w} \{ k_+ a_{SiO_2} a_{H_2O} - k_- a_{H_4SiO_4} \}$$

If we assume a pure quartz–water system \(a_{SiO_2} = a_{H_2O} = 1\). The activity of \(H_4SiO_4\) may be written in terms of the molality

$$a_{H_4SiO_4} = \frac{\gamma_{H_4SiO_4}^0 m_{H_4SiO_4}}{\gamma_{H_4SiO_4} m_{H_4SiO_4}}$$

The reference state is chosen such that \(\gamma^0 = m^0 = 1\). If we also assume \(\gamma_{H_4SiO_4} = 1\) (true only for pure water) equation (10) may be written

$$\left[ \frac{\partial m_{H_4SiO_4}}{\partial t} \right]_{P,T,M} = \frac{1}{\rho_w} \left( \frac{A}{\bar{V}} \left[ k_+ - k_- a_{H_4SiO_4} \right] \right)$$

In general we can write \(\bar{A}/\bar{V} = (\text{Fracture Parameter})/\theta\) where the fracture parameter can be readily found for simple assumed fracture geometries.
Following Harlow and Pracht (1972), these equations may be solved in the following sequential order: (a) the energy balance equation (1) (in finite difference form) is solved for $T$ at the new time step using the values of $\theta$, $u$, and $T$ at the previous time step; (b) equations (8), (9), and (12) are used to find $\theta$ and $m$ at the new time step; (c) equation (2) is solved for new values of $\phi$; and (d) equation (3) is solved for new values of $u$. The procedure is then repeated for the next time step. We are currently working on such a solution procedure for simple reservoir configurations.

**Kinetics of the Dissolution and Precipitation of SiO$_2$**

In order to implement the above scheme, the rate constants $k_+$ and $k_-$ must be known. These have been determined experimentally by measuring $m$ as a function of time in the apparatus shown in Figure 1 (Barnes and Rimstidt, 1975)

\[
\begin{align*}
k_+ &= 2.03 \, e^{-28.3/RT} \text{ moles/cm}^2\text{sec} \\
 k_- &= 3.30 \, e^{-22.5/RT} \text{ moles/cm}^2\text{sec}
\end{align*}
\]

where the activation energies are in kcal/mole. The rate-constants are only weakly dependent on pressure and salinity of the solution. In the case of saline brines, the major effect on the kinetics of quartz dissolution is to lower $a_{H_2O}$ in (10) (Lindsay and Liu, 1968) and slightly lower $\gamma_{H_4SiO_4}$ in (11).

**References**

Barnes, H.L., and J. D. Rimstidt, Control of Silica Scaling, in Geothermal Reservoir Engineering, ed. P. Kruger and H.J. Ramey, Jr., SGP-TR-12, Stanford University, 1975.


Table 2 Summary of Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ</td>
<td>porosity, open volume for water flow (per unit volume)</td>
</tr>
<tr>
<td>ρ_w</td>
<td>density of water, a function of temperature</td>
</tr>
<tr>
<td>ρ_R</td>
<td>density of rock</td>
</tr>
<tr>
<td>u</td>
<td>water velocity</td>
</tr>
<tr>
<td>S</td>
<td>source or sink of water from surface pipes (volume per unit volume)</td>
</tr>
<tr>
<td>p</td>
<td>water pressure</td>
</tr>
<tr>
<td>g</td>
<td>acceleration of gravity</td>
</tr>
<tr>
<td>u</td>
<td>coefficient of water viscosity</td>
</tr>
<tr>
<td>k</td>
<td>permeability</td>
</tr>
<tr>
<td>b_R, b_w</td>
<td>specific heats of rock and water, respectively</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>&lt;T&gt;</td>
<td>average water temperature at a given depth</td>
</tr>
<tr>
<td>T_0</td>
<td>reference temperature for thermal expansion</td>
</tr>
<tr>
<td>T_s</td>
<td>source or sink temperature</td>
</tr>
<tr>
<td>K_R</td>
<td>thermal conductivity of rock</td>
</tr>
<tr>
<td>φ</td>
<td>(p-p_0)/p_0 where p_0/p_0 is a function of depth only</td>
</tr>
<tr>
<td>d_c</td>
<td>measure of average crack spacing</td>
</tr>
<tr>
<td>β_w</td>
<td>volumetric expansion coefficient of water</td>
</tr>
<tr>
<td>m</td>
<td>molality</td>
</tr>
<tr>
<td>M</td>
<td>molecular weight</td>
</tr>
<tr>
<td>W_R</td>
<td>grams quartz per gram of rock</td>
</tr>
<tr>
<td>a</td>
<td>activity</td>
</tr>
<tr>
<td>(A/V)</td>
<td>surface area per unit water volume, a function of fracture geometry</td>
</tr>
<tr>
<td>k_+</td>
<td>rate constant for the forward dissolving reaction</td>
</tr>
<tr>
<td>k_-</td>
<td>rate constant for the reverse precipitation reaction</td>
</tr>
<tr>
<td>γ</td>
<td>activity coefficient</td>
</tr>
<tr>
<td>M</td>
<td>mass</td>
</tr>
</tbody>
</table>
ABSTRACT FORM

Exact format shown on instruction sheet must be followed.

'GEOTHERMAL SYSTEMS: MEASUREMENTS ON HYDROTHERMAL KINETICS

DOWNS, W. F., and BARNES, H. L., Department of Geosciences, The Pennsylvania State University, University Park, Pennsylvania 16802

An experimental system has been developed in order to evaluate the reaction kinetics of geothermal systems to 350°C and 3500 psi. A hydrothermal fluid is circulated through rock fragments in a 1.12 reaction vessel which is maintained at a selected temperature, T₁. The fluid then passes through a heated connecting tube (at T > T₁) to an isothermal heat exchanger (at T < T₁) where any precipitate is collected. A double valve sampling system is next in line downstream and is followed by a constant volume circulating pump which returns the solution to the reaction vessel. As a solution sample is removed, the fluid is replaced from a reservoir by a compressed air-driven piston pump. The circulation path is heated either by immersion in a constant temperature water bath or by heating coils. Typically the water bath is maintained at 65°C, the minimum to which geothermal energy can be extracted economically.

Samples of two rock types, biotite adamellite and a granitic gneiss, both from the Nacimiento Mountains, N. Mex. have been used as starting materials. These rocks are part of the basement complex being tested by the Los Alamos Scientific Laboratory as a dry geothermal reservoir. Prior to use, either these rocks or other mineral samples are disaggregated and characterized for chemical and isotopic composition, surface area and texture. Both air-saturated distilled water and NaCl brines were used as hydrothermal solutions.

Interpretation of the concentrations of SiO₂, Na, K, Ca and Al versus time indicates that about 60% of the (H₄SiO₄) in solution is derived initially from feldspars which dissolve stepwise via the formation of a "protonated feldspar" surface.

☐ Oral  ☐ Poster  ☐ Symposium (title of symposium)

Speaker  W. F. Downs  ☐ Student paper  ☐ GSA Student Associate

Is senior author a member of GSA (so he/she may receive Abstracts with Programs)?  ☐ Yes  ☐ No

Percentage of paper previously presented  0

I will be available to serve as a cochairman for a technical session on or concerning

For correspondence purposes, list address of senior author if different from above

Phone numbers and dates where senior author can be contacted  814-865-7573 (anytime)
RATES OF QUARTZ-WATER REACTIONS

RIMSTIDT, Donald, and BARNES, H. L., Department of Geosciences, The Pennsylvania State University, University Park, Pennsylvania 16802

The rate of reaction between quartz and water

\[ \text{SiO}_2(s) + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4(aq) \]

depends predominantly upon two variables: 1) the ratio of interfacial area (A) between the two phases to the volume (V) of water and 2) the chemical potential driving the reaction. Hence, a rate equation can be derived:

\[ \frac{\partial [\text{H}_4\text{SiO}_4]}{\partial t} = \frac{A}{V} \left( k_+ a_{\text{SiO}_2} a_{\text{H}_2\text{O}} - k_- a_{\text{H}_4\text{SiO}_4} \right) \]

Here, \( k_+ \) and \( k_- \) are the reaction rate constants for the forward and reverse rates respectively. Our rate measurements in both undersaturated and supersaturated systems confirm this relationship and independent experimental evidence shows it is valid for a wide range of A/V ratios.

The activation energies for this reaction are very high causing the rates to be very temperature dependent. Rate constants for two temperatures are listed below along with activation energies determined from a number of experiments.

\[
\begin{array}{c|cc}
\text{Temperature} & k_+ & k_- \\
105^\circ \text{C} & 4.8 \times 10^{-16} \text{ moles cm}^{-2} \text{sec}^{-1} & 5.4 \times 10^{-13} \text{ cm}^{-2} \text{sec}^{-1} \\
202^\circ \text{C} & 6.8 \times 10^{-13} \text{ moles cm}^{-2} \text{sec}^{-1} & 1.4 \times 10^{-10} \text{ cm}^{-2} \text{sec}^{-1} \\
E_{\text{act}} & 28.3 \text{ Kcal/mole} & 21.5 \text{ Kcal/mole} \\
\end{array}
\]

Since dissolving reactions which are controlled by aqueous diffusion have activation energies of 4 to 5 Kcal/mole, there is no doubt that the rate of this reaction is controlled by silica bond forming and breaking.

Phone numbers and dates where senior author can be contacted 814-865-7573
EXPERIMENTAL HYDROTHERMAL ALTERATION OF GRANITIC ROCKS, WITH IMPLICATIONS FOR DRY, HOT-ROCK GEOTHERMAL ENERGY

SOLOMON, George C., and KERRICK, Derrill M., Department of Geosciences, The Pennsylvania State University, University Park, Pennsylvania 16802

Biotite-adamellite core sections from the PG basement of the Jemez Plateau, New Mexico have been reacted with aqueous NaCl solutions (0.1m-1.0m) at 200-300°C and 200 bars for 4-96 hours in a circulating system modeled after a proposed dry, hot-rock geothermal experiment being conducted by the Los Alamos Scientific Laboratory in that area. The rock surface area: volume solution ratio was 0.2cm²/ml. Alteration products were dense coatings of illite on K-feldspar surfaces at 300°C, 1.0m, and sparse coatings at 200°C, 1.0m and 285°C, 0.5m; vermiculite replaced biotite during all the runs. Biotites exhibited marked swelling, and induced fracturing along adjacent grain boundaries. Vermiculite-encrusted biotites in the interior of adamellite provide evidence that solution migration occurred along grain boundaries and microfractures.

Moderately dilute aqueous NaCl solutions in a dry hot rock geothermal system in granitic terrain would promote alteration in the reservoir. The resulting exothermic reactions:

$$\frac{3}{2} \text{K-feldspar} + \text{H}^+ = \frac{1}{2} \text{Mica} + 3 \text{ Qtz.} + \text{K}^+,$$

Biotite + 4H₂O + M⁺ = M-vermiculite + K⁺, $

occurring in relatively short amounts of time, would contribute to heat extraction from the system. The AV solids of the vermiculite reaction would enhance microfracturing and open new rock surface to the fluid. This study shows that the P/T stability range of vermiculite, generally considered to be restricted to the supergene environment, may be extended to higher P/T hydrothermal conditions.

* M⁺ is any exchangeable cation (not necessarily monovalent).

### Oral □ Poster □ Symposium __________________________ (title of symposium)

Speaker George C. Solomon □ Student paper □ GSA Student Associate

Is senior author a member of GSA (so he/she may receive Abstracts with Programs)? □ Yes □ No

Percentage of paper previously presented 0

I will be available to serve as a cochairman for a technical session on or concerning 0

For correspondence purposes, list address of senior author if different from above

Phone numbers and dates where senior author can be contacted 814-865-7573 (after July 12, 1976)
EFFECT OF NaCl ON THE RATE OF OXYGEN ISOTOPIC EXCHANGE REACTIONS BETWEEN ROCKS AND WATER

COLE, David R., and OHMOTO, Hiroshi, Department of Geosciences, The Pennsylvania State University, University Park, Pennsylvania 16802

Solution samples obtained from an experimental circulating geothermal system were analyzed for oxygen isotopes. The $\delta^{18}O$ value of pure H$_2$O (initial $\delta^{18}O$ = -10.41‰) interacted with granite gneiss ($\delta^{18}O$(w.r.) = +7.8‰, $\delta^{18}O$(qtz.) = +8.1‰, $\delta^{18}O$(plag.) = +6.6‰, $\delta^{18}O$(Kspar) = +7.5‰) increased with time and with increasing temperature at rates $\frac{\Delta \delta^{18}O_{\text{final}} - \delta^{18}O_{\text{initial}}}{\log \text{hr}}$ at 100°C, 0.04‰/log hr. (0.20‰ after 30 hours) at 200°C, 0.025‰/log hr. (0.1‰ after 30 hours) at 150°C.

With addition of NaCl, the rate of oxygen isotope exchange increased significantly. For example, with 0.1m NaCl reacted with granite gneiss at 200°C, the $\Delta \delta^{18}O$—initial increased rapidly to 2.15‰ in the first 30 hours. This $\delta^{18}O$ shift was accompanied by rapid increase in the K$^+$ concentration in the solution. After 30 hours, the cation concentration in solution reached steady state equilibrium and the increase in the $\delta^{18}O$ values was small. The contrast between the rate curves of the NaCl-solution and of pure-water reflects a difference in mechanisms of oxygen isotopic fractionation probably due to cation exchange reactions during alteration of feldspars and biotite as well as to oxygen exchange controlled by diffusion.

Similar effects of NaCl concentration on the degree of $\delta^{18}O$ shift are also observed in natural geothermal systems (hot springs; ore-forming fluids).

Phone numbers and dates where senior author can be contacted 814-865-3565 anytime
EXPERIMENTAL EVALUATION OF THE GEOCHEMISTRY
OF GEOTHERMAL SYSTEMS

W. F. Downs and H. L. Barnes; Department of Geosciences,
Pennsylvania State University, University Park, Pa. 16802

In order to evaluate the rates of dissolution and precipitation of mineral
components from rock-water reactions, an experimental model of natural geothermal
systems has been designed and fabricated. For use in these dynamic hydrothermal
units, several rock types (similar to those found in the holes drilled for the
Los Alamos Scientific Laboratory's "Dry Geothermal System") were collected in the
vicinity of the Nacimiento Mountains. These samples (approximately 75 lbs. each)
were cored and the remainder crushed to major axes of between 1 and 6 mm, about
the grain size of the coarser minerals.

Each circulating system consists of an 1125 ml., 310 stainless steel reaction
vessel connected via 316 stainless steel tubing to a series of heat exchangers,
a double valve sampling system, a circulating pump and a reservoir-fed pressure
pump. The last heat exchanger in the series is maintained at 65°C in a constant
temperature water bath which also contains the solution sampling system and the
circulating pump. The sampling system permits the extraction, without contamina­
tion, of 5 ml. samples from the circulating solution with no significant perturba­
tion of the conditions within the pressurized system. Analysis of these samples
provides the basis for deriving reaction rate constants.

In order to maintain pressure in the hydrothermal circuit, it was necessary
to design a constant volume circulating pump capable of operation at 65°C and
10,000 psi. A simple reciprocating, twin-piston pump was fabricated using "O"
ing seals and teflon seats. Each stroke of the pump is tallied on a counter
and, from the known displacement, the total volume of fluid pumped through the
rock fragments is known accurately and reliably, as required for analysis of
reaction rates.
Initially only one low temperature heat exchanger was used. During the course of the first series of experiments, it was found that if the solution was rapidly quenched to 65°C, the rate of precipitation of dissolved species was negligible and the circulating solutions simply approached equilibrium with the rock material at the temperature of the reaction vessel. For example, in an experiment at 300°C with air-saturated, distilled water, the line between the reaction vessel and the heat exchanger was maintained at about 280°C. This line was nearly clogged with a precipitate later identified as a mixture of truscotite (Ca₂Si₄O₉(OH)₂) and quartz (SiO₂); however, the heat exchanger contained no in situ deposits but only a few fragments which had been dislodged from the precipitate in the tubing. Residence times for the fluid in the tubing and the heat exchanger were seven and 44 minutes, respectively. Apparently the reaction rate at 280°C was fast enough to allow precipitation of scale in this short interval. Conversely, although the solution was more grossly supersaturated and had a relatively long residence time in the heat exchanger, reaction rates for the formation of scale were slow enough at 650°C that no scale formed. This principle is generally useful for scale control. However, the rate of deposition of silica scale is a complicated function of silica concentration, temperature, salinity, temperature gradient, turbulence, flow rate, substrate roughness, suspended solids content, pressure, and perhaps other variables.

One of the major objectives of this study was to attempt to understand the mechanism of reaction for the dissolution of the various mineral phases. The granitic gneiss that has been used in the majority of the experiments run to date consists of 40% quartz, 25% alkali feldspar and 25% plagioclase feldspar. Rudimentary mass balance calculations indicate that only 60% of the silica in solution (H₄SiO₄) can be accounted for by the decomposition of feldspar and the remainder from the dissolution of quartz. Several investigators, most recently
Busenberg and Clemency (1976), have suggested that the feldspar minerals decompose in a series of step-wise reactions. The first reaction entails a simple ion exchange between the protons in solution and the alkalies within the feldspars. The second step involves the breakdown of this "protonated feldspar" to release both silica and more alkalies. We tested this hypothesis by a series of experiments at the same temperature and with the same rock material. If the above hypothesis were correct, the alkalies should go into solution at a higher rate during the initial run and silica should show a retarded rate of dissolution compared to later runs. Both of these phenomena were observed. The higher rate of dissolution of silica in the later experiments indicates that the "protonated feldspar" remained on the surface of the feldspar from the initial run and thus allowed silica to start dissolving immediately. The rate of dissolution of silica and alkalies is, apparently, a function of the volume of solution with which the rock material has previously reacted. This factor is important in tracing the evolution of geothermal systems because water circulating in a geothermal reservoir may contact fresh rock surfaces along young fractures as well as the altered rock surfaces dominant in reservoirs.

The experiments that have been completed to date have used both air-saturated distilled water and 0.1 m sodium chloride brine as starting fluids. Several experiments of 400 to 500 hour duration have been run in the same apparatus and corrosion has been limited to a slight discoloration of the reaction vessel. Each reaction vessel and heat exchanger is periodically pressure tested at 10,000 psi and we have had no failures.

No attempt has been made to simulate the extremely concentrated brines found in the Salton Sea Area, California. Through the cooperation of the U.S. Bureau of Mines, a site has been made available to test reaction rates of the extremely concentrated brines found in the Nyland K.G.R.A., Imperial Valley, California.
A small volume heat exchanger has been constructed which will allow the geothermal fluids to pass through several temperature decrements to obtain data for the rate of scale formation. These results on a natural complex geothermal fluid should provide direct design information on the degree of quenching necessary to minimize scale formation.