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KINETICS OF GLASS DISSOLUTION AND ZEOLITE FORMATION UNDER HYDROTHERMAL CONDITIONS

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Abstract—After a temperature-dependent period when little dissolution occurs, the dissolution of rhyolitic glass can be described by $dC/dt = k(C_s - C)$, where C_s is the concentration of dissolved silica at saturation, C is the instantaneous silica concentration, and k is a rate constant equal to 1.6×10^{-5}, 3.0×10^{-5}, and 4.5×10^{-5} sec^{-1} at 115°, 130°, and 140°C respectively, in 2 M Na-K carbonate solution at 1 kbar pressure. At 130°C, a C_s value of 0.177 M SiO_2 is reached in 30 hr, and phillipsite, clinoptilolite, and mordenite begin forming at 34, 64, and 76 hr, respectively, in 2 M CO_3, 1:1 Na/K. During glass dissolution and zeolite formation, the concentration of Al as $Al(OH)_4^-$ is buffered at 3.7×10^{-4} M by an unidentified phase. The ratio of SiO_2 to $Al(OH)_4^-$ at the onset of zeolite formation is 475. In 2 M CO_3 solution, phillipsite crystallization begins at 144 hr at 115°C, at 34 hr at 130°C, and at 20 hr at 140°C. Phillipsite crystallization begins at 48 hr in 1.5 M CO_3, at 168 hr in 1.0 M CO_3, and in excess of 550 hr in 0.2 M CO_3 at 140°C. In addition to OH^- catalysis, CO_3^{2-} appears also to catalyze the glass-dissolution and zeolite-formation processes.

Thermodynamically, phillipsite is unstable relative to clinoptilolite and mordenite in silica-rich alkaline hydrothermal solutions. Phillipsite forms first, followed by clinoptilolite, and then mordenite. Phillipsite formation is favored by runs of one-week duration, temperatures less than 150°C, and K-rich fluids. Clinoptilolite formation is favored in runs of more than one week, temperatures less than 150°C and K-rich fluids. Mordenite formation is favored by runs of more than one week, temperatures greater than 140°C, and Na-rich fluids. In 8-day runs at 140°C, clinoptilolite formation was favored by liquid : solid reactant (volume : mass) ratios less than 1.0, mordenite by ratios from 0.85 to 1.5, and phillipsite by ratios greater than 1.5. The mechanism of formation of the different zeolites, particularly phillipsite, may involve silica-cyclic tetramers which are abundant in concentrated solutions under alkaline hydrothermal conditions but which are almost absent in dilute low-temperature solutions. Thus, the results of hydrothermal experiments may not be directly applicable to zeolite formation at low temperatures.

Key Words—Clinoptilolite, Dissolution, Kinetics, Mordenite, Phillipsite, Synthesis, Volcanic glass, Zeolite.

INTRODUCTION

Zeolites can be readily synthesized in a few hours under hydrothermal conditions, and much information exists on synthetic zeolites and the solution chemistry of zeolite synthesis. A major problem, however, as Sand (1980) discussed, is in relating the results of zeolite synthesis at high temperatures and pressures to the formation of zeolites in nature. A promising avenue of attack on this problem involves kinetic studies in which zeolites typical of low-temperature conditions are synthesized from natural reactants under chemical conditions similar to those in which the natural minerals are thought to form.

The present study is an outgrowth of clinoptilolite-synthesis studies reported by Hawkins *et al.* (1978). Several hundred hydrothermal runs were made under various combinations of time, temperature, and chemical conditions in which the zeolites phillipsite, clinoptilolite, and mordenite were formed from volcanic glass. In many of these runs, the silica and alumina contents of the fluid phase were determined after various treatment times. From these data, rate constants for the dissolution of volcanic glass and for the formation of the different zeolites were obtained. A model suitable for computer simulation of the process of glass dissolution and zeolite formation was derived. Finally, some speculations on the mechanism of zeolite formation and applications of experimental results to natural systems are presented.

EXPERIMENTAL

Synthesis

The synthesis conditions of this study were similar to those reported by Hawkins *et al.* (1978). The formation of phillipsite, clinoptilolite, and mordenite from volcanic glass was studied as a function of time, temperature, molarity of the carbonate solution, ratio of Na to K in the solution, and solid : liquid ratio of the reactants. Reconnaissance studies showed that over the range of 0.02–2 kbar, pressure did not affect the course of the reactions; therefore, subsequent studies were carried out at 1 kbar pressure. The chemical composition (wt. %) of the starting volcanic glass is (Sheppard and Gude, 1968) SiO_2, 72.78; Al_2O_3, 11.89; Fe_2O_3, 0.55; FeO, 0.99; MgO, 0.22; CaO, 0.55; Na_2O, 3.03; K_2O, 5.31; H_2O+, 3.86; H_2O-, 0.21; Total, 99.39.

The reactions were carried out in welded, 2.5-mm i.d. gold capsules that were 2 cm in length. Twenty milligrams of ash and 25 μliter of the carbonate solution were used. Each experiment was run in duplicate. As

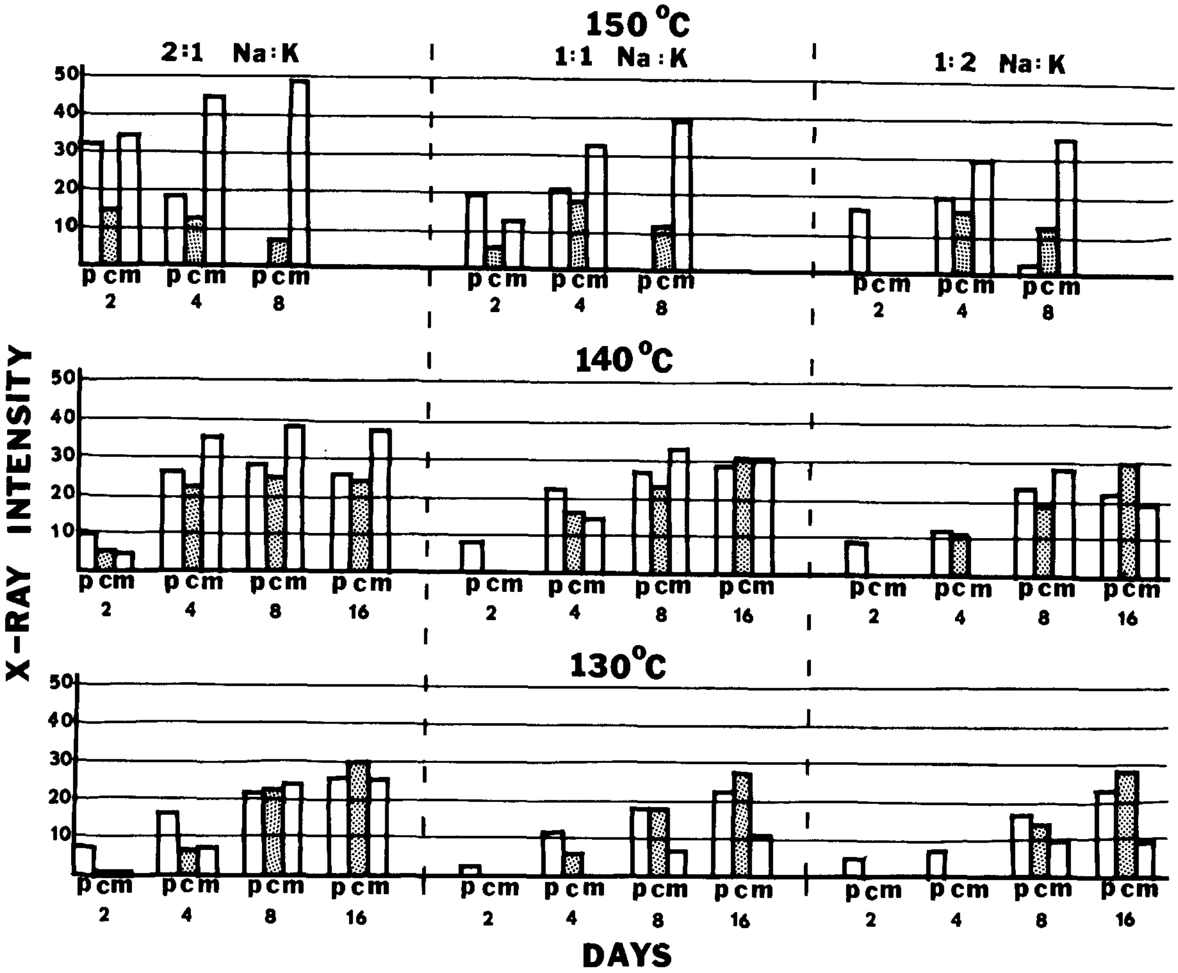

Figure 1. Relative quantities of phillipsite (p), clinoptilolite (c), and mordenite (m) formed in 2 M alkali carbonate solution, 2:1, 1:1, and 1:2 in Na:K at 130°, 140°, and 150°C and 1 kbar.

many as four capsules were placed in single cold-seal pressure vessels; the vessels were sealed; and the desired pressure-temperature conditions reached with a Tem-Pres HR-4B hydrothermal unit. After an appropriate time dictated by the experimental design, the pressure vessels were quenched, and the capsules were weighed to test for leakage during the run. The content of each capsule was transferred to a 0.45-μm Millipore filter and washed three times with distilled water to remove soluble carbonates. The washed product was then mounted on a glass microscope slide for X-ray powder diffraction (XRD) analysis. Relative quantities of the various zeolites were estimated from the XRD patterns.

Solution studies

To determine the effect of time, temperature, and carbonate molarity on the dissolution rate of the glass and on the rate of formation of the various zeolites, additional hydrothermal runs were made at 115°, 130°, and 140°C in 2.0 M carbonate solution, 1:1 Na:K, and at 140°C in 2.0, 1.5, 1.0, and 0.2 M carbonate solution, also 1:1 in Na and K.

For solution analyses, the hydrothermal procedure described above was followed except that 40.0 mg of glass and 50.0 μliter of carbonate solution were added to gold capsules, 4 cm long and 2.5 mm i.d. Runs were made in duplicate, with two capsules per vessel. Upon completion of a run and after weighing the capsules, the sealed capsule was rinsed with distilled water and placed in a 25-ml evaporating dish to which was added 1 ml of 2 M carbonate, 1:1 Na:K, solution and 2 ml of distilled water. Each capsule was opened while immersed in this solution, and the contents of the evaporating dish were transferred to a 10-ml plastic syringe. The mixture was filtered through a 0.45-μm filter into a calibrated 10.0-ml polystyrene tube; the solid was washed twice with distilled water, and the volume of the solution was then brought to 10.0 ml with distilled water. The tubes were capped and saved for analysis

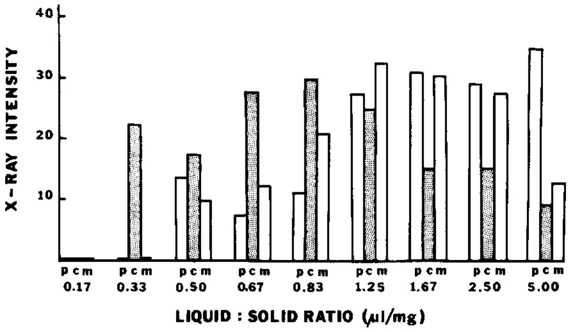

Figure 2. Relative quantities of phillipsite (p), clinoptilolite (c), and mordenite (m) formed in 2 M alkali carbonate solution, 1:1 Na:K at 140°C, 1 kbar at different reactant liquid : solid ratios.

for aluminum and silica. The solid phase was retained and examined by XRD and scanning electron microscopy (SEM).

Analysis

The concentration of Si and Al in the filtrate was determined by atomic absorption spectrometry using either nitrous oxide-acetylene flame excitation or graphite-furnace excitation (depending on the concentrations) and a Perkin-Elmer Model 5000 atomic absorption spectrometer. The solid phases were identified by XRD and examined by SEM using a JEOL-JSM-35 scanning electron microscope having a KEVEX energy-dispersive X-ray spectrometer.

RESULTS AND OBSERVATIONS

The results of the various hydrothermal experiments are shown graphically in Figures 1–6. A complete listing of analytical results is available from the author upon request. The following general observations can be made from Figures 1 and 2: (1) Phillipsite forms first, followed by clinoptilolite, then mordenite. This sequence is particularly evident in the 130°C runs and in the K-rich 140°C runs. (2) Zeolite formation increases with increasing temperature. (3) In 150°C runs, phillipsite, and possibly clinoptilolite, are unstable with respect to mordenite. (4) Phillipsite formation and persistence is favored in hydrothermal runs of about one week duration, temperatures less than 150°C, and K-rich fluids. Clinoptilolite formation is favored in hydrothermal runs of 1–2 weeks duration, temperatures less than 150°C, and K-rich fluids. Mordenite formation is favored in hydrothermal runs greater than one week duration, temperatures greater than 140°C (especially greater than 150°C), and Na-rich fluids. (5) For reactions at 140°C and 8 days duration, phillipsite formation is favored by liquid:solid reactant volume ratios greater than 1.5, clinoptilolite formation by ratios less than 1.0, and mordenite formation by ratios of 0.85 to 1.5.

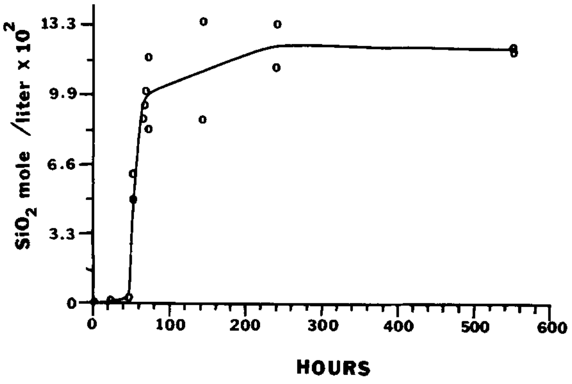

Figure 3. Silica concentration (mole/liter) vs. time (hr) for dissolution of rhyolite glass in 2 M alkali carbonate solution, 1:1 Na:K, at 115°C and 1 kbar.

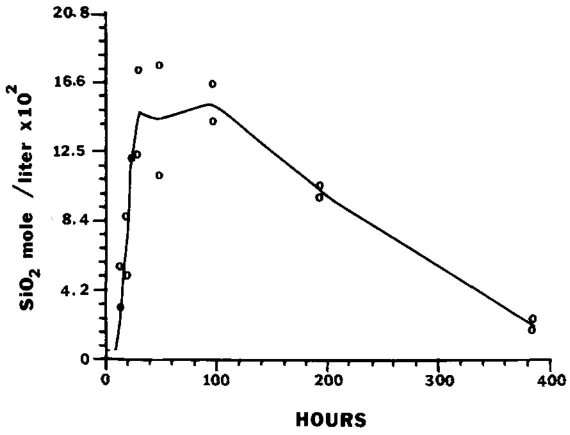

Figure 4. Silica concentration (mole/liter) vs. time (hr) for dissolution of rhyolite glass in 2 M alkali carbonate solution, 1:1 Na:K, at 130°C and 1 kbar.

From Figures 3–6 the following general observations can be made: (1) An induction period is required for glass dissolution, and its duration decreases with increasing temperature and carbonate concentration. (2) The rate of glass dissolution increases with increasing temperature and carbonate concentration. (3) The maximum silica concentration increases with increasing temperature and carbonate concentration. (4) The time required for the appearance of the first zeolite crystals (phillipsite) decreases with increasing temperature and carbonate concentration. For example, 74 hr is required at 115°C in 2 M carbonate solution; 20 hr is needed for the same system at 140°C. At 140°C and 1.0 M CO_3 solution, 166 hr is needed, while in 0.2 M CO_3 at 140°C, no zeolites were detected after 500 hr. (5) The total aluminum concentration for all conditions was about 3.7×10^{-4} M as $Al(OH)_4^-$, and there was no systematic change in concentration. At the time of zeolite formation, the $SiO_2:Al_2O_3$ ratio in solution was about 950 compared with 5.5 in the glass.

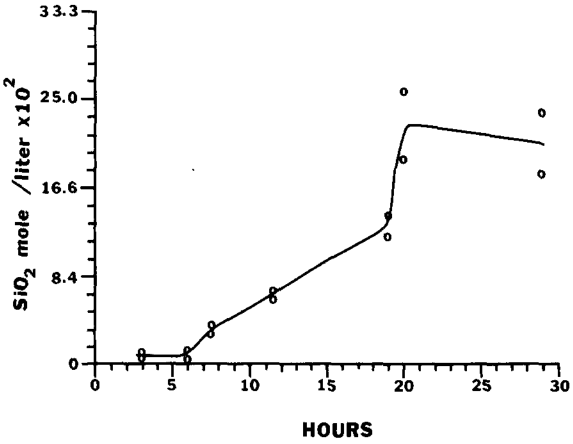

Figure 5. Silica concentration (mole/liter) vs. time (hr) for dissolution of rhyolite glass in 2 M alkali carbonate solution, 1:1 Na:K, at 140°C and 1 kbar.

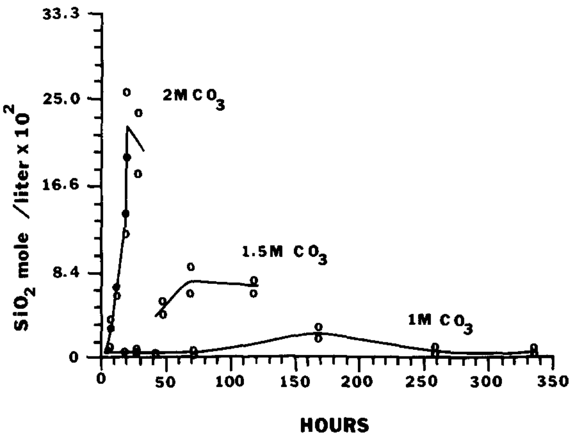

Figure 6. Silica concentration (mole/liter) vs. time (hr) for dissolution of rhyolite glass in 2 M, 1.5 M, and 1 M alkali carbonate solution at 140°C and 1 kbar.

DISCUSSION

Kinetics of glass dissolution

A "two-stage" dissolution process seems required. The first stage corresponds to an "induction" period characterized by a slow rate of dissolution, and the second stage corresponds to rapid dissolution of glass. Changes in silica concentration during the induction period could not be observed because of silica contamination (2 ppm) in the reagents. A two-stage process is required because the concentration changes occurring during rapid dissolution do not pass through zero time. Helgeson (1971) suggested that dissolution of various minerals follows a parabolic rate equation which describes a process resulting from diffusion of Si through different layers of reaction products on the surface of the mineral. Sicks (1975) postulated that two first-order reactions best describe the dissolution process. From the present results, it is impossible to distinguish between these models. However, over the steeply rising part of the dissolution curve, the data fit reasonably well Sicks' dissolution model of the form $dC/dt = -k(C_s - C)S$, where k is a first-order rate constant, C_s is the SiO_2 concentration at saturation, C is the SiO_2 concentration at any time t, and S is the surface area of the solid per unit volume of solution.

Using the data from Figures 3 and 4, the rate constants were derived from a least-squares fit of a linear function to a plot of $\log(C_s - C)/C_s$ vs. time in seconds. These constants are 1.6×10^{-5}, 3.0×10^{-5}, and 4.5×10^{-5} sec^{-1} for 115°, 130°, and 140°C, respectively in 2 M carbonate. These rate constants were then used in the Arrhenius equation $k = Ae^{-Ea/RT}$ to estimate the activation energy E_a for the glass dissolution and to estimate the rate constant at 140°C. Experimentally, the data for 115° and 130°C were more precise than those for 140°C, and the experimentally derived rate constant for 140°C was inconsistent with the other two; this rate constant was therefore estimated from the other two. Note that these values are *apparent* rate constants holding only for the conditions and material studied and that the surface area term is not included explicitly in the rate-constant calculations. The surface area of the glass in this study is about 2500 cm^2/g as estimated from the dimensions of the shards; thus the surface area-to-liquid volume ratio was about 2000 cm^2/cm^3.

The activation energy of 13 kcal/mole found in this study is lower than published values of 17–20 kcal/mole (Sicks, 1975) for glass of comparable composition. The difference is attributed to catalysis by hydroxide and carbonate ions in the present study.

Glass dissolution and the zeolite-formation process

Dissolution of glass as a function of time is represented schematically in Figure 7. Here, time interval A represents changes in solution composition occurring during the induction period. Time interval B represents the rapid dissolution of the glass as approximated by the differential equation:

$$dC/dt = k(C_s - C). \qquad (1)$$

Saturation of the solution with silica and the onset of zeolite crystallization are shown at time interval C. Time interval D corresponds to continued dissolution of the glass as described by Eq. (1) and to the simultaneous precipitation of zeolites which remove silica at a slightly faster rate than that provided by dissolution of the glass. Empirically, the variation in silica concentration with time during time interval D can be approximated by a linear function:

$$C = mt + b. \qquad (2)$$

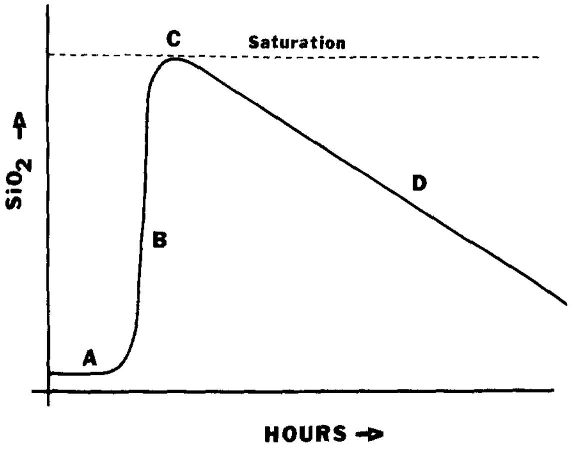

Figure 7. Generalized diagram depicting rhyolite glass dissolution vs. time in 2 M alkali carbonate solution. Section A represents the ingestion period; section B, exponential glass-dissolution; section C, solution saturation and beginning of zeolite formation; and section D, simultaneous glass dissolution and zeolite growth.

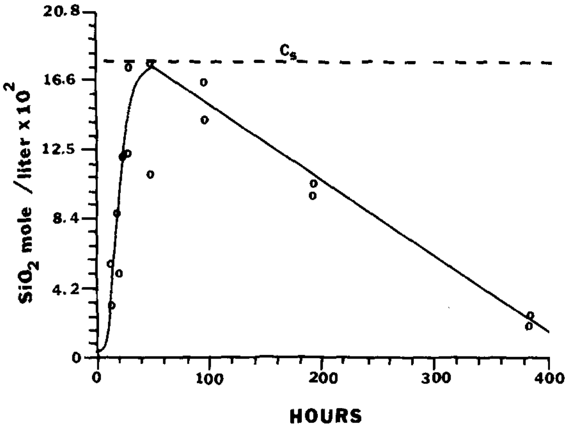

Figure 8. Calculated silica concentration (mole/liter) vs. time (hr) for dissolution of rhyolite glass in 2 M alkali carbonate solution at 130°C and 1 kbar. C_s is the SiO_2 concentration at saturation.

The quantity of glass that dissolves during time interval D can be obtained by substituting the expression for C (Eq. (2)) into Eq. (1) and integrating. The resulting expression is of the form:

$$C_{glass} = mt + nt^2.$$

Besides the silica contributed by the glass during this time interval, the solution also contributes silica. Taking this quantity into account, the total "concentration" of silica during zeolite crystallization for time interval D is of the form:

$$C_{zeolites} = mt + nt^2.$$

Ninety-eight percent of the silica contribution to zeolite formation comes from the glass dissolution during time interval D.

Table 1. Equations for glass dissolution and zeolite formation at 130°C, 2 M CO_3, 1 kb.

Section A. Ingestion period:

$C = 0.003$ mole/liter SiO_2
$t_i = 36{,}000$ sec (10 hr)
$C_{sol} = C_{sat}(1 - e^{-kt'})$

Section B. Glass dissolution:

$k = 3.0 \times 10^{-5}\ sec^{-1}$
t' (sec) $= t_{actual} - t_{induction}$
C = mole/liter
$C_{sat} = 0.177$ mole/liter

Section D. Concentration of silica in solution:

$C = -1.27 \times 10^{-7}$ (mole/liter-sec)t + 0.177 mole/liter
$t_0 = 146{,}000$ sec (40.6 hr)
$t = t_{actual} - t_0$

Concentration of silica contributed by glass dissolution during zeolite formation:

$C_{glass} = 1.04 \times 10^{-5}$ (mole/liter-sec)t + 1.88×10^{-12} (mole/liter-sec^2)t^2

Concentration of silica contributed by glass and solution to form zeolites:

$C_{zeolite} = 1.06 \times 10^{-5}$ (mole/liter-sec)t + 1.88×10^{-12} (mole/liter-sec^2)t^2

Table 1 shows the group of equations and rate constants for the different sections of the dissolution curve shown in Figure 7. A graph of the *calculated* concentration of silica (mole/liter) vs. time (hr) for glass dissolution at 130°C in 2 M carbonate solution is shown in Figure 8, on which the observed values are also plotted. These equations can be used to simulate the process of glass dissolution and zeolite formation and to provide a check on the internal consistency of the rates and compositions used. Thus, if the actual compositions of the coexisting zeolites were known, the dissolution rate and zeolite-growth rates could be adjusted by means of these equations to yield a consistent set of rate equations. Without compositional data for the zeolites, the system is too indeterminant to warrant such an attempt.

Wollast (1975) discussed the dissolution of silica coupled with the formation of secondary phases. According to Wollast, maximum silica concentration depends upon the relative rates of glass dissolution and removal of silica by clay or zeolite formation. Thus, the maximum concentration is not necessarily the saturation value of silica. The system studied here seems to be an example of Wollast's general model. However, the maximum silica concentration must be at or close to the saturation value for noncrystalline silica because the observed quantities of zeolite formed at or soon after this maximum were insufficient to limit the silica concentration as required by a dynamic maximum.

The solution need not become saturated with silica before zeolite growth occurs; however, in this study the glass-dissolution rate was fast relative to the zeolite-nucleation rate, and saturation was reached before significant zeolite growth occurred. The solution must, therefore, be highly supersaturated with respect to the zeolites, leading to the formation of many nuclei and to subsequently slow growth of many small crystals as Fyfe *et al.* (1978) discussed.

Zeolite equilibria

Until recently, thermodynamic data for zeolites were lacking. Kosiur (1981), using the method of Tardy and Garrels (1974, 1976, 1977), estimated the standard free energies of formation of zeolites and interpreted marine zeolite assemblages in light of these data. Using Kosiur's data and other standard compilations of thermodynamic data (e.g., Krauskopf, 1967), the activity diagram shown in Figure 9 was derived for conditions approximating those of the present study. The zeolite compositions and reactions used are as follows:

$$1.79\ \text{Phillipsite} + 0.19\ K^+ + 4.84\ H_4SiO_4 = \text{Clinoptilolite} + 0.19\ Na^+ + 9.04\ H_2O \qquad \log K_{eq} = 23.6$$

$$1.65\ \text{Phillipsite} + 5.40\ H_4SiO_4 + 0.97\ Na^+ = \text{Mordenite} + 0.97\ K^+ + 9.74\ H_2O \qquad \log K_{eq} = 19.8$$

$$0.92\ \text{Clinoptilolite} + 1.15\ Na^+ + 0.93\ H_4SiO_4 = \text{Mordenite} + 1.15\ K^+ + 1.40\ H_2O \qquad \log K_{eq} = -1.62$$

where:

Phillipsite = $K_{0.98}Na_{0.32}Al_{1.3}Si_{2.7}O_8 \cdot 3H_2O$, Clinoptilolite = $K_{1.95}Na_{0.38}Al_{2.33}Si_{9.67}O_{24} \cdot 6H_2O$, and Mordenite = $K_{0.65}Na_{1.5}Al_{2.15}Si_{9.85}O_{24} \cdot 6H_2O$.

The clinoptilolite composition used is that for clinoptilolite synthesized under similar conditions (Hawkins *et al.*, 1978). Phillipsite was assumed to be K and Al rich, the latter reflecting the high pH conditions of the synthesis, a dependency shown by Mariner and Surdam (1970). Mordenite was assumed to be Na and Al rich and slightly more silicic than clinoptilolite.

As Kosiur (1981) discussed, significant variations in free energy of formation result from rather small changes in the chemical composition of the zeolites. These cause major shifts in the stability fields of the different zeolites. Because of this major effect of composition and the fact that only assumed compositions were available, no attempt was made to adjust the free energies of formation from standard conditions to those of the hydrothermal runs.

The liquid-composition trajectory shown in Figure 9 is based on a Na/K of 1 in the liquid prior to glass dissolution. In the glass this ratio is 0.87. Dissolution of the glass causes a slight K enrichment, but the Na/K ratio is dominated by the initial liquid composition. Furthermore, no zeolites formed until saturation was reached, thus no phases removed K or Na prior to silica saturation. As a result, the liquid trajectory starts at log Na/K = 0 and parallels the abscissa until saturation. Upon formation of phillipsite and clinoptilolite (both K-rich zeolites), the Na/K ratio increases, leading to the formation of mordenite. At the end of the hydrothermal run, whether mordenite or a combination of mordenite and clinoptilolite dominate depends upon the composition of these phases; the determining factors are the relative silica content and the Na/K ratio of the two zeolites. Phillipsite was unstable at the high-silica activities; however, only at 150°C was the instability of phillipsite with respect to mordenite and clinoptilolite(?) and clinoptilolite with respect to mordenite evident (Figure 1).

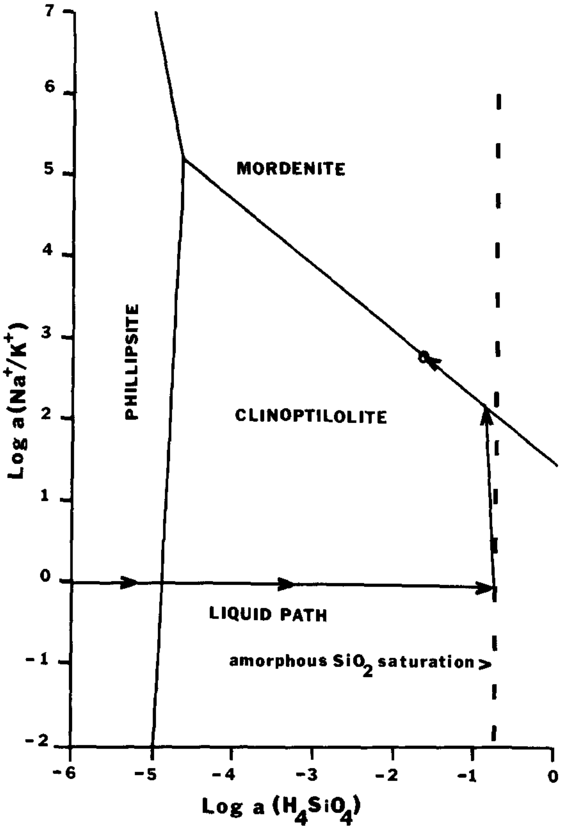

Figure 9. Logarithmic activity diagram depicting equilibrium-phase relations among phillipsite, clinoptilolite, and mordenite in 2 M alkali-carbonate solution.

Effect of carbonate concentration on glass-dissolution rate

The glass-dissolution rate was affected by the carbonate concentration (Figure 6); higher carbonate concentrations caused faster dissolution rates. This effect

Table 2. Observed ingestion times for glass dissolution and maximum silica concentrations for various temperatures, carbonate concentrations, and hydroxide-ion activity sets.

Temperature (°C)	(OH^-) (mole/liter)	(CO_3^{2-}) (mole/liter)	Ingestion time (hr)	Maximum SiO_2 concentration (mole/liter)
115	0.15	2.0	48	0.135
140	0.17	1.0	72	0.030
130	0.20	2.0	10	0.176
140	0.21	1.5	30	0.089

may be due in part to the catalytic effect of hydroxide ion (OH^-) on the dissolution of silica (Fyfe *et al.*, 1978). Carbonate itself, however, seems also to have catalyzed the reaction.

Table 2 shows calculated hydroxide-ion activities as a function of carbonate concentration and temperature (Helgeson, 1967). A role for carbonate is suggested by a comparison of hydroxide concentration in 2 M CO_3 at 130°C with that in 1.5 M CO_3 at 140°C; or in 2 M CO_3 at 115°C with that in 1.0 M CO_3 at 140°C, for which pairs the hydroxide activities are about the same. Because the rate of silica dissolution increases with increasing temperature, it was expected that for the *same* OH^- *value*, the faster dissolution rate should be associated with the *higher-temperature* member of the pair. The data of Table 2 show that the ingestion time for glass dissolution was shorter and that the maximum silica concentration was larger for the *higher-carbonate* member of the pair. In making these calculations, no attempt was made to correct the carbonate concentration or hydroxide-ion activity for the very high ionic strength of the system. More rigorous calculation would change the absolute values of the hydroxide-ion activities, but the relative values should be the same, and Table 2 should be valid for illustrative purposes.

Effect of carbonate concentration on zeolite-formation rate

Figure 6 shows that zeolite growth is a function of the carbonate concentration. Kerr (1966a) showed that zeolite-growth rate is first order with respect to the quantity of zeolite produced and that the rate of zeolite formation is dependent on the concentration of active soluble species (dissolved SiO_2, $Al(OH)_4^-$). He also suggested that the concentration of the active species should depend on the concentration of hydroxide ion. Hayhurst and Sand (1977) showed that phillipsite nucleation and growth are second-order reactions with respect to OH^-. Although the carbonate and/or hydroxide ions clearly affect zeolite-growth rates, the present data are inadequate to quantify these effects.

Effect of solid : liquid ratio of reactants

Figure 2 shows that the solid : liquid ratio of the reactants strongly affects the relative quantity of different zeolites formed at a specific time during hydrothermal runs in 2 M CO_3, 1:1 Na:K, at 140°C and 1 kbar, 8 days duration. The relative quantity of zeolites formed under high liquid : solid ratios (right side Figure 2) corresponds to that formed during earlier stages of zeolite growth under lower liquid : solid ratios (cf. Figure 1 for which liquid : solid is 1.25). The zeolite assemblages observed under low liquid : solid ratios may represent a more mature assemblage. The reason for this effect is not clear.

The aluminum problem

A surprising result of these studies was the low concentration of Al in solution. The Al concentration was expected to increase linearly and proportionally to the linear increase in the silica concentration as the glass dissolved, as found by Mariner and Surdam (1970). The Al concentration (as $Al(OH)_4^-$) observed in the present study was about 3.7×10^{-4} mole/liter. For the hydroxide-ion activities expected in 2 M carbonate at temperature, the calculated $Al(OH)_4^-$ concentration in equilibrium with gibbsite is 4.2×10^{-4} mole/liter. This perhaps fortuitous agreement suggests that the Al concentration is buffered by gibbsite. Attempts to observe directly this predicted gibbsite phase by SEM and KEVEX analysis were unsuccessful. May *et al.* (1979) studied the solubility of hydroxy-aluminum solids in alkaline systems and suggested that an unidentified phase (boehmite?) less soluble than gibbsite controls the Al concentration in alkaline solutions. Holdren and Berner (1979) suggested that Al forms a fine-grained precipitate that maintains the Al concentration at very low levels. They were unable to locate or identify this phase. Detailed SEM studies and microprobe analyses of the solid phases are needed to resolve this question.

SPECULATIONS ON THE MECHANISM OF ZEOLITE FORMATION

The structure of phillipsite is dominated by 4-membered rings of SiO_4 tetrahedra (Breck, 1974). The structure of clinoptilolite (Alberti, 1975) is similar to that of heulandite and has a characteristic configuration of 4- and 5-membered rings of SiO_4 tetrahedra. The mordenite structure (Breck, 1974) is characterized by 5-membered rings. Baes and Mesmer (1976) showed that at high pH (>10) the dominant dissolved silica species is the tetramer $Si_4O_8(OH)_4^{4-}$ with lesser quantities of $SiO(OH)_3^-$ and $SiO_2(OH)_2^{2-}$. In solutions of low ionic strength, the dominant dissolved silica species is $SiO(OH)_3^-$. The tetramer $Si_4O_8(OH)_4^{4-}$ is either absent or is present in negligibly low concentrations. The dominant Al species is $Al(OH)_4^-$ (Baes and Mesmer, 1976).

The dominance of tetramers both in concentrated solution and in phillipsite is striking. It is suggested here that phillipsite forms by a condensation reaction involving the silica tetramers. Because tetramers are the major silica species, the condensation reaction dominates, and phillipsite is the first zeolite to form. Such a process involving selective removal of the tetramers might then lead to an increase in the ratio of monomeric to tetrameric species and then to the easier formation of zeolites such as clinoptilolite in which 4- and 5-membered (tetramer + a monomer) rings are present, and finally to 5-membered structures such as mordenite. The role of silica-cyclic tetramers was emphasized by Hayhurst and Sand (1977). The present study draws attention to the abundance of the tetrameric species in solution under conditions suitable for zeolite formation.

SEM observations of the products of this study and of natural zeolite assemblages show pitting of the glass surface due to dissolution (cf. Mumpton, 1973) along with an intimate association of zeolites and glass shards. The pitting suggests that glass dissolution does not proceed uniformly over the surface but is more rapid at sites of excess surface energy. In the present study, no secondary protective surface could be seen on the glass. Both of these aspects were discussed by Holdren and Berner (1979) in their study of feldspar dissolution.

The question also arises, why do zeolites form close to the glass and not some place in the solution relatively remote from the glass surface? Zeolites should nucleate anywhere in solution, but growth depends upon the supply of nutrients. It is suggested that the zeolites form on or very close to the dissolving phases (glass, gibbsite?, boehmite?) in response to the high flux of nutrients from these phases and not because of some structural similarity of parent and daughter phases.

APPLICATION TO NATURAL SYSTEMS

The results of this study are most applicable to geothermal systems, especially those such as the Hot Dry Rock Project (Cremer *et al.*, 1980) in which hot, fresh, commonly glassy rock is fractured and water is pumped through the fractures. The rate constants from the present study may be applicable to the rate of dissolution of such rock and to the kind and quantity of secondary minerals such as zeolites that form during the development of the geothermal system.

At present, the results of this study cannot be adequately extrapolated to low-temperature conditions, inasmuch as both the glass-dissolution behavior and the dissolved silica species seem different in the hydrothermal system from those at low temperatures. In the hydrothermal system, large silica monomers such as the cyclic tetramers are abundant and probably play an important role in zeolite formation under these conditions. In the more dilute, low-temperature systems, large monomers are much less abundant. Rate equations derived for hydrothermal conditions involving large monomers will be inapplicable at low temperatures where these monomers are essentially absent.

Critical information needed to understand zeolite formation under all conditions is the amount and kind of silica monomers and polymers present in solution and their behavior during zeolite formation. These data coupled with reliable analyses of the aqueous fluid and coexisting zeolites and with more thermodynamic data for zeolites will ultimately permit more complete understanding of zeolite formation under natural conditions.

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Резюме—После периода, зависящего от температуры, во время которого выступают малые растворения, растворение риолитового стекла может быть описано как $dC/dt = \kappa(C_S - C)$, где C_S = концентрация растворенного кремнезема при насыщении, C = мгновенная концентрация кремнезема, и κ = постоянная скорости, равная $1{,}6 \times 10^{-5}$, $3{,}0 \times 10^{-5}$, $4{,}5 \times 10^{-5}$ $сек^{-1}$ при 115°, 130°, и 140°C соответственно в 2 M Na-K карбонатных растворах при давлении 1 кбар. При 130°C величина C_S 0,177 M SiO_2 достигается в течение 30 часов и начинается образование филлипсита, клиноптилолита и морденита на 34, 64, и 76 часу соответственно в 2 M CO_3 1:1 Na/K. Во время растворения стекла и образования цеолита концентрация Al как $Al(OH)_4^-$ амортизирована при $3{,}7 \times 10^{-4}$ M неидентифицированной фазой. Отношение SiO_2 и $Al(OH)_4^-$ при появлении образования цеолита равно 475. В 2 M CO_3 растворе кристаллизация филлипсита начинается на 144 часу при 115°C, на 34 часу при 130°C, и на 20 часу при 140°C. Кристаллизация филлипсита начинается на 48 часу в 1,5 M CO_3, на 168 часу в 1,0 M CO_3, и после более 550 часов в 0,2 M CO_3 при 140°C. Дополнительно к катализу OH^- появляется также CO_3^{2-}, чтобы катализировать процессы растворения стекла и образования цеолита. Филлипсит является термодинамически нестабильным по отношению к клиноптилолиту и мордениту в кремнеземобогатых щелочных гидротермальных растворах. Сначала образуется филлипсит, за ним следует клиноптилолит и потом морденит. Образованию филлипсита способствовали условия опытов продолжительностью одной недели при температуре менее 150°C и для K-богатых жидкостей. Образованию клиноптилолита благоприятствовали условия опытов продолжительностью более одной недели при температуре менее 150°C и для K-богатых жидкостей. Образованию морденита способствовали условия опытов продолжительностью более одной недели при температуре более 140°C и для Na-богатых жидкостей. Во время 8-дневного периода при 140°C образованию клиноптилолита способствовало соотношение жидкость : твердый реагент (объем : масса) менее, чем 1,0, морденита—соотношение от 0,85 до 1,5 и филлипсита—соотношение более 1,5. Механизм образования различных цеолитов, в особенности филлипсита, может включать кремнеземные циклические тетрамеры, которые многочисленны в концентрированных растворах при щелочных гидротермальных условиях, но которые почти отсутствуют в разбавленных низкотемпературных растворах. Таким образом, результаты гидротермальных экспериментов не могут быть непоредственно использованы при образовании цеолита при низких температурах. [E.C.]

Resümee—Nach einem temperaturunabhängigen Zeitabschnitt, in dem die Auflösung gering ist, kann die Auflösung von Rhyolithglas durch $dC/dt = k(C_s - C)$ beschrieben werden, wobei C_s die Konzentration an gelöstem SiO_2 bei Sättigung und C die augenblickliche SiO_2-Konzentration ist; k, eine Geschwindigkeitskonstante beträgt $1{,}6 \times 10^{-5}$, $3{,}0 \times 10^{-5}$, und $4{,}5 \times 10^{-5}$ sec^{-1} bei 115°, 130°, und 140°C in 2 M Na-K-Karbonatlösungen und bei 1 kbar Druck. Bei 130°C wird ein C_s-Wert von 0,177 M SiO_2 in 30 Std erreicht; Phillipsit, Klinoptilolith und Mordenit beginnen nach 34, 64 bzw. 76 Stunden, sich in einer 2 M CO_3, 1:1 Na/K zu bilden. Während der Auflösung des Glases und der Zeolithbildung wird die Al-Konzentration als $Al(OH)_4^-$ durch eine nicht identifizierte Phase bei $3{,}7 \times 10^{-4}$ gepuffert. Das SiO_2 zu $Al(OH)_4^-$ Verhältnis beträgt zu Beginn der Zeolithbildung 475. Die Kristallisation von Phillipsit beginnt in 2 M CO_3-Lösung nach 144 Stunden bei 115°C, nach 34 Stunden bei 130°C, und nach 20 Stunden bei 140°C. In 1,5 M CO_3 beginnt die Phillipsitkristallisation nach 48 Stunden, in 1,0 M CO_3 nach 168 Stunden, und nach über 550 Stunden in 0,2 M CO_3 bei 140°C. Zusätzlich zur Katalysierung durch OH^- scheint auch CO_3^{2-} die Auflösung des Glases und die Zeolithbildung zu katalysieren.

Thermodynamisch ist Phillipsit im Vergleich zu Klinoptilolith und Mordenit in SiO_2-reichen alkalischen hydrothermalen Lösungen instabil. Phillipsit bildet sich zuerst, danach entsteht Klinoptilolith und danach Mordenit. Die Phillipsitbildung wird durch eine Reaktionszeit von 1 Woche, Temperaturen unter 150°C und K-reichen Lösungen begünstigt. Klinoptilolith bildet sich bevorzugt bei Reaktionszeiten über einer Woche, Temperaturen unter 150°C und K-reichen Lösungen. Die Mordenitbildung wird durch Reaktionszeiten über einer Woche, Temperaturen über 140°C, und Na-reichen Lösungen begünstigt. Bei einer Reaktionszeit von 8 Tagen und bei 140°C wird die Bildung von Klinoptilolith durch ein Lösung/Festsubstanz-Verhältnis unter 1,0 begünstigt, die von Mordenit durch Verhältnisse von 0,85 bis 1,5 und die von Phillipsit durch Verhältnisse über 1,5. Der Bildungsmechanismus der verschiedenen Zeolithe, vor allem der von Phillipsit, kann mit zyklischen SiO_2-Tetrameren zusammenhängen, die in konzentrierten Lösungen unter alkalischen hydrothermalen Bedingungen häufig sind, aber in verdünnten niedrig temperierten Lösungen nahezu fehlen. Aus diesem Grund können die Ergebnisse der hydrothermalen Experimente nicht direkt auf die Zeolithbildung bei niedrigen Temperaturen angewendet werden. [U.W.]

Résumé—Après une période dépendante de la température pendant laquelle se passe peu de dissolution, la dissolution de verre rhyolitique peut être décrite comme $dC/dt = k(C_s - C)$, où C_s est la concentration de la silice dissoute au point de saturation, C est la concentration instantannée de silice, et k est un taux constant égal à $1{,}6 \times 10^{-5}$, 3×10^{-5}, et $4{,}5 \times 10^{-5}$ sec^{-1} à 115°C, 130°C, et 140°C, respectivement, dans une solution carbonate 2 M Na-K à 1 kbar de pression. A 130°C, une valeur pour C_s de 0,177 M SiO_2 est atteinte en 30 heures, et de la phillipsite, de la clinoptilolite, et de la mordenite commencent à se former en 34, 64, et 76 heures respectivement, dans 2 M CO_3, 1:1 Na/K. Pendant la dissolution du verre et la formation de zéolite, la concentration d'Al en tant qu'$Al(OH)_4^-$ est amoindrie à $3{,}7 \times 10^{-4}$ par une phase non-identifiée. La proportion de SiO_2 à $Al(OH)_4^-$ au début de la formation de la zéolite est 475. Dans une solution 2 M CO_3, la cristallisation de phillipsite commence après 144 heures à 115°C, après 34 heures à 130°C, et après 20 heures à 140°C. La cristallisation de phillipsite commence après 48 heures dans 1,5 M CO_3, après 168 heures dans 1,0 M CO_3, et après plus de 550 heures dans 0,2 M CO_3 à 140°C. En plus de la catalyse d'OH^-, CO_3^{2-} semble aussi catalyser les procédés de dissolution de verre et de formation de zéolite.

Thermodynamiquement parlant, la phillipsite est instable en comparaison avec la clinoptilolite et la mordenite dans des solutions hydrothermales alkalines riches en silice. La phillipsite est formée en premier lieu, suivie de la clinoptilolite et puis de la mordenite. La formation de phillipsite est favorisée par des expériences d'une semaine, des températures sous 150°C, et des fluides riches en K. La formation de clinoptilolite est favorisée par des expériences de plus d'une semaine, des températures sous 150°C et des fluides riches en K. La formation de mordenite est favorisée par des expériences de plus d'une semaine, des températures plus élevées que 140°C, et des fluides riches en Na. Dans des expériences de 8 jours à 140°C, la formation de clinoptilolite était favorisée par des taux de réaction liquide : solide (volume : masse) plus bas que 1,0, celle de la mordenite par des taux de 0,85 à 1,5, et celle de la phillipsite par des taux plus élevés que 1,5. Le mécanisme de formation des différentes zéolites, particulièrement de la phillipsite, peut impliquer de tétramères silice-cycliques qui abondent dans des solutions concentrées sous des conditions hydrothermales alkalines, mais qui sont quasi absentes dans des solutions diluées à basses températures. Ainsi, les résultats d'expériences hydrothermales ne peuvent pas être directement appliquables à la formation de zéolite à de basses températures. [D.J.]