Some factors affecting the dissolution kinetics of anorthite at 25°C

CHRISTOPHER AMRHEIN\(^1\) and DONALD L. SUAREZ\(^2\)

\(^1\)Department of Soil and Environmental Sciences, University of California, Riverside, CA 92521, USA
\(^2\)US Salinity Laboratory, US Department of Agriculture, Agricultural Research Service, 4500 Glenwood Drive, Riverside, CA 92501, USA

(Received January 31, 1991; accepted in revised form February 24, 1992)

Abstract—Batch dissolution experiments were conducted at 25°C to determine the effects of agitation, particle size, suspension density, wetting and drying cycles, drying temperature, sequential rinses, ionic strength, and the addition and removal of products on the rates of anorthite (An\(_{83}\)) dissolution. In general, the dissolution kinetics at constant pH were not zero order with respect to products in solution, and this nonlinear release persisted beyond the time when Ca and Si stoichiometric dissolution was reached. The failure to establish zero-order kinetics could not be attributed to the weathering of damaged surfaces or fine, broken particles. Leached layer depths, calculated from solution composition, ranged from 2.6–3.5 nm; but a Ca-depleted surface layer was observed by energy dispersive X-ray analysis only on the reaction fines. Agitation rate had a marked effect on dissolution rate, contrary to expectations based on a surface reaction control mechanism. Anorthite dissolution in the presence of cation- and anion-exchange resins produced zero-order kinetics at sustained high rates. We hypothesize that these linear rates were due to the continuous removal of Al from solution by the resins. Consistent with these results, there was no effect of added Ca or Si on the rate of reaction; but the addition of Al slowed the initial rate of reaction at pH 3.6 and 6.0 but not at pH 3.0. Long-term dissolution studies (up to 4.5 ys) resulted in final reaction rates over two hundred times slower than previously reported for feldspar dissolution. These data are consistent with the idea that the presence of Al in solution and the incorporation of Al into the hydrous silanol surface slow the rate of anorthite dissolution and are important factors affecting the rate over all time periods. The addition of KCl slowed the dissolution rate either through competitive exchange with structural Ca or adsorbed H, or by blocking the polymerization reactions at the surface.

INTRODUCTION

The kinetics and mechanisms of silicate mineral dissolution have received much attention lately yet are still not well understood (Heltgens et al., 1984; Brady and Waither, 1989; Eggleston et al., 1989; Casey et al., 1988, 1989; Muir et al., 1990). The hypothesis that aluminosilicate dissolution is limited by a surface-controlled reaction has received the most attention, while the alternative concept that the rate is controlled by a diffusion-limiting residual layer (Petrovic et al., 1976; Aagaard and Helgeson, 1982; Sjoberg, 1989; Hellmann et al., 1990) appears less accepted. The observations of nonstoichiometric release of ions to solution from silicate dissolution are universally observed in weathering studies (Paces, 1973; Busenberg and Clemency, 1976; Kodama et al., 1983; Chou and Wollast, 1984; Wollast and Chou, 1985; Bales and Morgan, 1985; Holdren and Speyer, 1986; Carroll-Webb and Waither, 1988). This nonstoichiometry has been associated with an initial decrease in the dissolution rate with time that has been attributed to the loss of small broken particles and "disturbed surfaces" that result from sample preparation (Petrovic et al., 1976; Holdren and Berner, 1979). Most researchers interpret their dissolution data far from equilibrium as zero order with respect to products in solution. However, good evidence exists that nonzero-order dissolution kinetics occur beyond the time period when disturbed material is thought to have been removed. Schott and PetIt (1987) observed nonlinear dissolution of garnet over a 187-day time period at pH 2, and Holdren and Speyer (1986) reported a continuously decreasing reaction rate of an alkali feldspar in a fluidized bed reactor at pH 4 over an 88-day time period, even though the stoichiometry of the dissolution was essentially constant. Casey et al. (1988) presented a plot of Si concentration vs. time for labradorite dissolution in 0.02 M HCl and DCI at 25 and 45°C that shows nonlinearity over the whole reaction period of 185 h. Holdren and Speyer (1987), who studied the dissolution kinetics of eight feldspars at a constant pH of 3 considered the dissolution rates to be zero order. However, the dissolution of the Grass Valley anorthite sample was clearly not zero order at any time during the 26-day reaction period. There is a possibility that these nonzero-order kinetics can be attributed to a leached layer or a back reaction involving accumulated products or secondary phases.

The presence of an altered surface layer is well established both with solution composition data (Nahon and Colin, 1982; Chou and Wollast, 1984; Wollast and Chou, 1985; Sjoberg, 1989) and with surface analysis techniques (Beusen and Giubels, 1983; Schott and PetIt, 1987; Casey et al., 1988, 1989; Muir et al., 1989, 1990; Hellmann et al., 1990). However, the exact role that this surface layer plays in controlling the rate of dissolution and the thickness of this layer is still not yet clear. Wollast and Chou (1985), Sjoberg (1989), and Muir et al. (1990) reported an increase in the thickness of the surface Si layer as pH decreased. Chou and Wollast (1984) and Wollast and Chou (1985) studied the dissolution rate of albite using a flow-through fluidized bed reactor and noted an influence of soluble Al on the reaction rate. Casey et al. (1988) speculated that aluminum adsorbs onto the surface, condenses and dehydrates the surface silanol polymers, and thus stabilizes the
hydration layer by adding a crosslink and decreases the overall rate of reaction. This hypothesis agrees with the observations of Nesbitt and Muir (1988) that naturally weathered oligoclase had altered surface layers depleted in Na, Ca, and Si but was enriched in Al to depths of 30–80 nm. This hypothesis may also explain the eightfold lower laboratory dissolution rate of glaciofluvial silt as compared to ground mineral specimens (Lundstrom and Ohman, 1990).

Schott and Pettit (1987) have proposed that a key step in the dissolution of silicate minerals may be the migration of water into the crystal structure. Wetting and drying is a realistic process for natural conditions and has not been examined to date. Drying might be expected to cause cracking and spalling of a leached layer and thereby increase the initial dissolution rate until the hydrous layer coated the surface once again.

It has also been assumed that aluminosilicate weathering should be unaffected by stirring because the measured rates are slower than predictions based on aqueous diffusion (Aagaard and Helgeson, 1982). However, it seems possible that agitation might strip the leached layer through abrasion and that this might account for the linear kinetics observed by several researchers.

The following experiments were designed to evaluate if nonzero-order dissolution kinetics of Grass Valley anorthite were associated with nonstoichiometry, dissolution of damaged surfaces and microparticles, changes in the solution composition with time, or a diffusion-controlled reaction. Several types of batch dissolution experiments were conducted, including sequential equilibrations of the same material and the addition and removal of soluble products, as well as studies to determine the effects of agitation, particle size, suspension density, ionic strength, wetting and drying cycles, and drying temperature on reaction rate. The dissolution rates in several long-term studies (up to 4.5 yrs) are reported.

MATERIALS AND METHODS

Grass Valley anorthite (An95) was separated from the host rock, crushed, sieved, and washed thoroughly with sonification in H2O. The anorthite was digested in a closed Teflon vessel with HF + aqua regia (procedure of Lim and Jackson, 1982) and was found to have the following elemental composition (in weight %): SiO2, 43.6 ± 1.22; Al2O3, 32.02 ± 1.25; CaO, 18.67 ± 0.30; Na2O, 0.76 ± 0.01; Fe2O3, 0.79 ± 0.01; MgO, 0.23 ± 0.01; and K2O, 0.05 ± 0.01. This analysis was replicated five times, and a National Institute of Standards and Technology (NIST) reference basalt rock was digested simultaneously to check for accuracy. Our analysis of the basalt was within 5% of the reported values. The chemical analysis is nearly identical to that reported for Grass Valley anorthite by Deer et al. (1966). The Mg and Fe values are attributed to a small pyroxene contamination (<3 mol% pyroxene, assuming all of the Mg and Fe were in the pyroxene). Grain counting under the polarized light microscope showed that the purity was 96% anorthite, 3% perthite, and 1% pyroxene. The three size fractions used in the experiments were 20–50 µm (0.50 m2 g–1), 50–100 µm (0.30 m2 g–1), and 100–250 µm (0.11 m2 g–1).

Surface area was determined by triple-point BET using Kr adsorption at liquid N2 temperature with a Quantasorb Jr. analyzer (Quantachrome Corp.). In general, the surface area of the mineral at the start of the reaction was used in calculating dissolution rates. In some instances, the surface area was measured before and after reaction. Some of the experiments used material from previous experiments, which is called “aged”. The material that had been washed initially in H2O was considered to be “unweathered” because of the short contact time with the water. Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) were used to check for surface morphology and the presence of leached layers. The anorthite samples were mounted on C stubs and C-coated. The samples were examined at an accelerating voltage of 20 kV in a JSM-U3 SEM (JEOL, Medford, MA). Energy-dispersive X-ray analysis was performed with a solid-state Si(Li) United Scientific detector and analyzed by a Tracer-Northern TN-2000 multichannel analyzer (Middleton, WI).

All experiments were carried out at constant temperature (25.0 ± 0.1°C) in polyethylene bottles either under fixed CO2 or controlled pH conditions. For reactions in the presence of CO2, mixtures of CO2 plus air from compressed cylinders were bubbled into the reaction bottles after first being saturated with water vapor. Reactions at constant pH required the addition of acid at least once a day (more frequently at the start of the reaction). The pH fluctuated a maximum of 0.2 pH units and, more typically, ±0.1 pH units between pH adjustments. The types of agitation applied to the reaction bottles were wrist-action shaker (80 cpm), reciprocating shaker (208 cpm), propeller stirrer, and quiescent. The wrist-action shaking was sufficiently gentle that the mineral was not suspended but instead accumulated between the bottom and side of the bottle. The reciprocating shaker continuously moved the mineral particles in the bottom of the bottles. The propeller shaker moved the settled material with light tumbling. The quiescent samples were agitated by hand once a day, and the material tended to settle uniformly over the bottom.

The suspensions were allowed to settle overnight or were centrifuged prior to sampling, and all solutions were then filtered through 0.1 µm prerinsed cellulose nitrate membrane filters. Samples were analyzed at the time of sampling (Experiments 6, 8–17) or stored until the end of the experiment when all samples were analyzed at one time (Experiments 1–5, 7, 18–20). Corrections for changing mineral: solution ratio and the amount of dissolved mass removed at each sampling were accounted for in the rate calculations. All solutions were analyzed for Ca, Si, and pH; and some of the solutions were also analyzed for Al, Na, K, Mg, and HCO3. All analyses were regularly checked against water-quality assurance standards from the NIST. If an analysis was within 5% of the NIST standard, it was deemed acceptable. Most analyses were within 2% of the NIST standard. All working standards were made up in appropriate background matrices to match the matrices of the samples. The pH of the solution was measured in situ at the time of sampling, after calibration of the pH meter/electrodes with pH buffers to within 0.01 pH units. Ca, Mg, Na, and K were measured by atomic absorption spectrophotometry, Ca and Mg after addition of acidified La2O3. Alkalinity was titrated with 0.010 M KH2PO4 (primary acid standard) to pH 4.40 under air. Silicate was determined with the heteropoly blue method (American Public Health Assoc., 1985) using ascorbic acid as the reducing agent (Technicon Auto-Analyzer II, Method No. 105-72 W/B). Aluminum was measured colorimetrically using hydroxyquinoline after the removal of interfering cations (Fe) by a preliminary extraction procedure (May et al., 1979) and by inductively coupled argon plasma spectrophotometry.

Specific descriptions of each experiment are given along with the results in the next section.

DESCRIPTION OF EXPERIMENTS AND RESULTS

Experiments 1 and 2: Sequential Rinsets

Distilled water at 94.2 kPa CO2 (continuously purged with CO2) was reacted with unweathered anorthite (50–100 µm) at mineral:water ratios of 10, 30, 70, and 140 g L–1. The suspensions were reacted on a wrist-action shaker for varying times, centrifuged, decanted; and fresh distilled water under 94.2 kPa CO2 was added to the mineral. Sampling occurred after 5, 7, 9, 6, 8, 19, 23, and 28 days for a total of nine solution changes for each suspension ratio. The total reaction time was 112 days.

The material from Experiment 1 was rinsed in distilled water and dried. This aged material was examined by SEM...
and was found to be free of small, adhering particles. The aged material was reweighed and reacted in a series of five sequential rinses in 5.0 mM NaCl under 94.2 kPa CO₂ at 140 g L⁻¹ mineral:water ratio (Experiment 2). Sampling times for these rinses were 1, 3, 5, and 79 days for a total of 91 days.

Figure 1 shows that in Experiment 1 the solution Si/Ca ratio was initially much lower than stoichiometry (Si/Ca mole ratio 2.18). With each subsequent rinse, the Si/Ca ratio in the solution increased until stoichiometric dissolution with respect to Si and Ca occurred. Further rinses maintained Si and Ca stoichiometric dissolution. The pH of the solutions at the time of sampling tended to increase with increasing mineral:solution ratio and increasing time as expected and ranged from 3.9-4.5 with a mean of 4.1. Unfortunately, Al concentrations were not measured on these solutions. Assuming stoichiometric release of Al with Si, using WATEQ (TRUEDELL and JONES, 1974), we calculated the solution concentrations at which halloysite and gibbsite could have formed (Fig. 1). The solutions were oversaturated with halloysite and gibbsite but undersaturated with amorphous Al(OH)₃.

The thickness of the surface leached layer was calculated from the molar volume of the mineral and the cumulative amounts of Ca and Si removed in each rinse, assuming that Ca leached uniformly from the surface. This leached layer thickness for the 10, 30, 70, and 140 g L⁻¹ mineral:solution ratios was 2.74, 2.85, 2.65, and 2.62 nm, respectively. Thus, the calculated leached layer thickness was independent of the extent of weathering because the leached layer thicknesses were nearly constant for all four suspensions.

Assuming a zero-order reaction with respect to Si concentration, we calculated the dissolution rates on a surface area basis from the time of solution change (time = 0; Si = 0) to the time of sampling. Figure 2 shows that the calculated zero-order dissolution rates were dependent upon the suspension ratio. That is, the feldspar in the low mineral: solution suspensions dissolved more rapidly than the feldspar in the high-ratio suspensions.

The rate data from Experiments 1 and 2 at a mineral: solution rate of 140 g L⁻¹ are shown in Fig. 3 and indicate that: (1) there was a steady decrease in the rate of release with increasing reaction time; and (2) at similar reaction times (rinses 2 and 3, and 11 and 12), the rate decreased with each subsequent rinse. Clearly, the reaction was not linear with time, even though stoichiometric dissolution had been reached. The reduction in reaction rate was almost two orders of magnitude for Si and over two orders of magnitude for Ca (initially 10⁻⁷.12 and final 10⁻⁹.48 mmol m⁻² s⁻¹). The “aged” material used in Experiment 2 also showed a decrease in rate with an increase in time of reaction (rinses 10-14). The Al concentrations were measured on samples 11-14 (Experiment 2) and showed that from 80-96% of the Al precipitated or remained in a leached layer (based on Si concentrations in solution). Even though the pH was free-drift (controlled by the PCO₂ and alkalinity generated from the weathering), the changes in pH were small due to the high

---

**Figure 1.** Experiment 1. The release of Ca and Si from anorthite in distilled water under 94.2 kPa CO₂ at four different mineral:water ratios. The solutions were replaced nine times over a period of 112 days. The pH at the time of sampling ranged from 3.9-4.5 with a mean of 4.1. The saturation points for gibbsite and halloysite were calculated assuming stoichiometric release of Al with Si.

**Figure 2.** Experiment 1. Zero-order dissolution rate was calculated from the time of solution change (t = 0; Si = 0) to the time of sampling, assuming a linear release over time.
Reaction time, days

FIG. 3. Experiments 1 and 2. Zero-order dissolution rate as a function of length of reaction for fourteen sequential rinses. Reactions 1-9 were in distilled water and 10-14 were in 5.0 mM NaCl, all under 94.2 kPa CO₂ and at 140 g L⁻¹ mineral:water ratio. Drying and reweighing occurred after Reaction 9. Numbers next to data represent the order of the sequential rinses. The average pH at time of sampling for rinses 10-14 was 4.4.

PCO₂ and are insufficient to explain the decreases in dissolution rate with increasing time or rinse cycle.

Experiment 3: Sequential Rinses with Wet /Dry Cycles

This experiment was conducted to confirm the results from the sequential rinse Experiments 1 and 2 and to determine the effects of drying on the dissolution rate. Washed, unweathered anorthite was reacted on a wrist-action shaker at a mineral:water ratio of 5.0 g L⁻¹ under constant pH conditions in 5.0 mM NaCl. The pH was maintained constant (±0.2 pH units) by daily additions of either 5.0 mM HCl (pH 5.5) or 100 mM HCl (pH 3.5). Two size fractions were used, 20-50 μm and 50-100 μm. They were reacted in replicate: one set with drying at 100°C between rinses; the other kept continuously wet. Three sequential reactions at pH 5.5 were carried out for times of 13, 13, and 16 days, followed by a fourth reaction adjusted to pH 3.5 for 9 days. Within each reaction period, the solutions were sampled 7 or 8 times.

The effect of wetting and drying cycles on the kinetics of dissolution demonstrated that there was no significant difference (p < 0.05) in reaction rate at pH 5.5 between the wet/dry system and the continuously wet system (data not shown). The reaction rate was different for the two size fractions; the coarser material had a greater dissolution rate on a surface area basis than the finer material, in agreement with the findings of Holdren and Speyer (1985, 1987).

The data in Fig. 4 show that there was no difference between the wet and dry treated samples reacted at pH 3.5 (fourth rinse in this series). Also, the Si, Al, and Ca release for this fourth rinse were not linear with time even though the material had been aged for 42 days at pH 5.5 and at a low mineral:water ratio. Stoichiometric dissolution of Ca and Si was observed for all but the first rinse at pH 5.5 (Al was not measured on the pH 5.5 solutions). The reaction at pH 3.5 resulted in Ca, Si, and Al stoichiometry in solution. Calculation of the leached layer thickness based on the cumulative amount of Si and Ca removed in the pH 5.5 reaction resulted in 2.8 and 2.9 nm for the coarse and fine fractions, respectively. There was no change in the leached layer thickness when samples were reacted at pH 3.5. This is not in agreement with the SIMS data presented by Muir et al. (1990), who found an increased leach layer thickness at pH 3.5 as compared to that at pH 5.7.

Experiment 4: Drying Temperature

"Well aged" anorthite (from Experiment 2; 50-100 μm) was dried at 75°C, 150°C, and 600°C for 24 h to test if the hydrous leached layer could be altered. These feldspars were then reacted in duplicate at suspensions of 3.33 g L⁻¹ in 5.0 mM NaCl and at pH 3.6 for 14 days. The pH of the solutions was adjusted daily with 1.0 M HCl. The solutions were sampled eleven times over the 14-day time period. The chemical composition of the solutions between duplicates was within 5%.

The material dried at 75 and 150°C had the same reaction rate as the material that had been maintained wet (p < 0.05). The material dried at 600°C had a 10% slower reaction rate (significantly slower at p < 0.05; data not shown). These data and the data from Experiment 3 suggest that at pH values 3.5, 3.6, and 5.5, the migration of water into the structure is not the rate-limiting step; rather it is either the protonation of the surface, or the partial spalation of the reacted surface and the development of hydrophobic pores in the surface (Schott and Pettit, 1987; Casey et al., 1989). The reduced dissolution rate of anorthite after heating to 600°C is likely the result of a reduction in the defect density (annealing), but it is a very minor effect that cannot account for the observed nonlinearity.

FIG. 4. Experiment 3. Dissolution of anorthite at constant pH 3.5, following the three sequential rinses at pH 5.5 with wet/dry and continuously wet cycles.
Experiment 5: Agitation

Anorthite dissolution reactions were carried out on a reciprocating shaker, wrist-action shaker, and quiescent (agitation only at the time of pH adjustment) to examine the effect of stirring rate on dissolution. Anorthite (50–100 μm, aged at pH 3.6 for 21 days) and unweathered, ultrasonically cleaned material (100–250 μm) were used. The initial suspension densities were 3.8 g L⁻¹ (50–100 μm) and 7.5 g L⁻¹ (100–250 μm), both in 5.0 mM NaCl. The pH was maintained at 3.6 (+0.2) by daily additions of 1.0 M HCl. All reactions were replicated, and the difference between replicates was less than 5%. To a separate set of suspensions, 1.0 mg L⁻¹ HgCl₂ was added to check if microbial activity was affecting the reaction rate. The specific surface area was measured before and after reaction on all samples using Kr adsorption, but the data plotted in Fig. 5 are based on the initial surface areas.

The well-aged material dissolved stoichiometrically with respect to Ca, Si, and Al. The fresh material showed preferential leaching of Ca over Si and Si over Al and gradually approached stoichiometric dissolution with time. The Si/Al and Ca/Al concentration ratios from the fresh material at the first sampling (1 day) were 1.5 and 8.4 times higher than stoichiometry. No solid phase was predicted to have precipitated in these solutions based on calculations using WATEQ (TRUESDELL and JONES, 1974). The addition of HgCl₂ (1.0 mg L⁻¹) had no effect on the rate of dissolution (p < 0.05), indicating that microbial films did not cause the nonzero-order kinetics. The plot of Si release vs. time (Fig. 5) shows that there was a significant increase in the dissolution rate of suspensions reacted on the reciprocating shaker (nearly double) as compared to the rates on the wrist-action shaker or quiescent. There was no significant difference between rates of reaction on the wrist-action shaker or quiescent (p < 0.05). The wrist-action shaker was sufficiently gentle to avoid movement of the feldspar on the bottom of the reaction bottle, which reduced sample abrasion as compared to the reciprocating shaker. The fresh, coarse material dissolved faster on a surface area basis than the aged fine material, confirming the observations made in Experiment 3. The surface area of the anorthite, as measured by Kr adsorption before and after reaction, is given in Table 1. The well-aged anorthite (50–100 μm) showed a decrease in surface area of up to 50%, which may explain the decrease in Si release rate with time. Correcting the dissolution rates plotted in Fig. 5 for the change in surface area over time tended to bring the rates closer together, but the finer material still dissolved slower than the coarse material on a surface area basis. There were no significant differences in surface area of the 100–250 μm anorthite with the different levels of agitation. The slight increase in surface area as a result of reaction was not significant. These observations emphasize the point that reactive site density is independent of surface area.

Experiments 6 and 7: SEM and EDX Investigations

A sample of anorthite (20–50 μm) was reacted in distilled water under 94.2 kPa CO₂ (pH approx. 4.4) for 267 days. The suspension density was initially 7.8 g L⁻¹, rising to 8.6 g L⁻¹ (due to periodic sampling of the solution) by the end of the time period. The suspension was mixed by a propeller stirrer.

The rate of dissolution, as determined by the Si and Ca concentrations, steadily decreased over the whole 267-day period. Aluminum concentration was nearly constant during the reaction and averaged 0.040 mM. Even though halloysite saturation was reached, the measured Si/Al ratios do not confirm precipitation. A leached layer thickness of 3.5 nm was calculated from the difference between the cumulative amounts of Si and Ca in solution.

During the course of the reaction, clay-sized fines were produced that could not be identified by X-ray diffraction or thermogravimetric analysis. The weathered feldspar and the reaction fines were examined using SEM and EDX analysis for evidence of a leached layer or a surface precipitate. Peak area ratios for the elemental analysis of the unweathered anorthite, weathered anorthite, and reaction fines are given in Table 2. There was no significant difference between the surface composition of the weathered and unweathered anorthite. No excess Al was detected by the EDX, even though Al precipitation occurred, based on Al analyses. Failure to confirm the presence of a leached or precipitate layer on the weathered material may be due to the depth of penetration of the EDX beam as compared to the calculated leached
The EDX analysis of the fines showed them to be greatly depleted in Ca and slightly depleted in Al (Table 2). The fines were apparently neither a gibbsite nor kaolinite type mineral since they contained a large proportion of Ca. It appears that the fines produced as a result of weathering were a "leached out" feldspar or a Ca-rich clay. The fines were 41% depleted in Ca relative to the starting material and had an Al/Si ratio 5% lower than the starting material. These findings are in agreement with HOLDREN and BERNER (1979), who found extensive leaching of Na (approximately 33-40% depleted in Na) in the ultrafines produced during albite weathering. HOLDREN and BERNER (1979) also found that the Al/Si ratio for the fines produced in albite weathering was the same as the original material. It is hypothesized that the Ca-depleted (or Na-depleted) layer was observed in the fines and not in the larger material because the depleted layer makes up a much greater percentage of the fines.

Samples of the weathered and unweathered feldspars were extracted for "poorly crystalline aluminosilicates" using boiling 0.5 M KOH for 2.5 minutes (JACKSON et al., 1986). The amount of poorly crystalline Si and Al extracted from the weathered anorthite using the KOH procedure was 0.16 and 0.06 mmol g⁻¹, respectively. For comparison, the amount of Si and Al extracted from the unweathered material was 0.16 and 0.06 mmol g⁻¹, respectively. These findings indicate that a small amount of poorly crystalline Si and Al may have accumulated on the surface of the feldspar. This amorphous material was not visible under the SEM, and the feldspar surfaces showed only very slight pitting or etching.

The anorthite from this long-term weathering (Experiment 6) was rinsed, dried, reweighed, and reacted in 5.0 mM NaCl under controlled CO₂ conditions (0.95, 9.5, and 94.2 kPa CO₂) for 29 days. The initial suspension densities were 6.7 g L⁻¹ and increased to 10 g L⁻¹ due to solution sampling. The suspensions were agitated by wrist-action shaker, and the solution pH values were controlled by the PCO₂ and alkalinity generated from the weathering. These solutions were sampled six times over the 29-day period and analyzed for Si, Ca, Mg, HCO₃⁻, and pH. Aluminum was measured only on the final solution after 29 days' reaction time. Changes in leached layer thickness were calculated based on solution composition.

Nonlinear release of Si and Ca was observed, and there was an excess of Si over Ca released to solution. That is, the leached layer (or hydrous Si layer) partly dissolved. This was also observed in other reactions where anorthite, previously weathered at pH 3.6, was reacted at pH 6.0 (Experiments 15 and 16) and is in agreement with MUIR et al. (1990). However, in earlier reactions going from pH 3.3–5.3 (Experiment 3), there was no change in the leached layer thickness.

In the final solutions, from 67–98% of the Al that was predicted to have dissolved based on Si concentrations precipitated or remained in a leached layer.

Experiments 8–16: Long-term Reaction Studies

Several very long-term batch studies (up to 4.5 ys) were carried out under various mineral:solution ratios and pH values. The conditions of each experiment and the dissolution rates are presented in Table 3. All reactions were quiescent, except for weekly agitation by hand. The rates of reaction were calculated assuming a linear release rate during the time period listed. Experiment 11 was run at a very high mineral: solution ratio (water-filled pore space) and may reflect the water/rock contact expected for aquifer materials. Generally, only Ca, Si, and pH were determined on these samples and, in a few cases, Al; however, earlier studies indicated that nearly constant Al concentrations were reached early at pH values > 4.5.

The Si/Ca mole ratios in solution reflect both nonstoichiometric and incongruent dissolution. When unweathered material was used, low Si/Ca ratios in solution resulted due to preferential leaching of Ca from the structure and the possible loss of Si due to halloysite or kaolinite precipitation. For long time periods, the Ca-release rates are a better measure of dissolution rates because Ca is not lost to precipitation. For short reaction times, preferential release of Ca over Si dominates. The data in Table 3 show a trend of decreasing dissolution rate with increasing time and increasing mineral: solution ratio and agree with the findings from Experiments 1 and 2. The slowest rate of dissolution (Ca-release data) was for the suspension density that approximated the rock mass/ water ratio in a saturated aquifer system (Experiment 11). This rate, 10⁻¹⁰.₅ mmol m⁻² s⁻¹, is over 200 times slower than the average dissolution rate of feldspars reported by HELGESON et al. (1984) of 10⁻⁸.₅±0.₃ mmol m⁻² s⁻¹ and AMRHEIN and SUAREZ (1988) of 10⁻₈.₆±0.₁ mmol m⁻² s⁻¹ for the pH-independent reaction. Similar rates were found in Experiments 12 and 13 and are consistent with the discrepancy between laboratory dissolution rates obtained after short time intervals and natural weathering rates for silicates which often differ by several orders of magnitude (VELBEL, 1986; CLAYTON, 1988). In agreement with this, LUNDSTROM and OHMAN (1990) reported a linear dissolution rate of natural silt (equal parts of microcline, oligoclase, quartz, and illite) of 10⁻¹⁰.₁ mmol m⁻² s⁻¹ at pH 5.1–5.3, which compares well with our long-term weathering rates.

The materials from Experiments 10 and 10A after 4.5 ys of reaction were examined under petrographic and scanning electron microscopes for evidence of leached layers or precipitated products. Approximately 5% of the feldspar grains were found to be aggregated together with an X-ray amorphous product that could not be identified. We extracted the original unweathered feldspar and the feldspar from Experiments 10 and 10A for poorly crystalline Si and Al using the
Table 3

<table>
<thead>
<tr>
<th>Exp</th>
<th>Size fraction µm</th>
<th>Mineral/ solution ratio</th>
<th>Weathered or unweathered material</th>
<th>Background electrolyte</th>
<th>pH during period of rate deter.</th>
<th>Si conc. at sampling</th>
<th>Ca&lt;sup&gt;2+&lt;/sup&gt; conc at sampling</th>
<th>TIME period of rate deter.</th>
<th>Si release rate, mmol m&lt;sup&gt;2&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Ca release rate, mmol m&lt;sup&gt;2&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Si/Ca mole ratio in sol'n</th>
<th>TIME at final sampling</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>20-50</td>
<td>g L&lt;sup&gt;-1&lt;/sup&gt; 1.26</td>
<td>new H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>4.3 4.6</td>
<td>0.356 0.23</td>
<td>179 421</td>
<td>1.49x10&lt;sup&gt;-8&lt;/sup&gt; 3.36x10&lt;sup&gt;-9&lt;/sup&gt;</td>
<td>0.10x10&lt;sup&gt;-9&lt;/sup&gt; 1.17</td>
<td>3.36</td>
<td>1.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.28</td>
<td></td>
<td></td>
<td>4.6-5.0</td>
<td>0.502 0.43</td>
<td>421-1228</td>
<td>4.40x10&lt;sup&gt;-9&lt;/sup&gt;</td>
<td>1.17</td>
<td>3.36</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>20-50</td>
<td>g L&lt;sup&gt;-1&lt;/sup&gt; 1.28</td>
<td>new H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>4.4-5.0</td>
<td>0.481 0.33</td>
<td>206-1228</td>
<td>5.30x10&lt;sup&gt;-9&lt;/sup&gt; 3.62x10&lt;sup&gt;-9&lt;/sup&gt;</td>
<td>1.46</td>
<td>3.36</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.30</td>
<td></td>
<td></td>
<td>4.9-4.9</td>
<td>0.404 0.31</td>
<td>206-1228</td>
<td>4.72x10&lt;sup&gt;-9&lt;/sup&gt; 3.53x10&lt;sup&gt;-9&lt;/sup&gt;</td>
<td>1.32</td>
<td>4.51</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>20-50</td>
<td>g L&lt;sup&gt;-1&lt;/sup&gt; 1.28</td>
<td>new H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>7.6-7.7</td>
<td>0.282 0.266</td>
<td>0-1228</td>
<td>4.25x10&lt;sup&gt;-9&lt;/sup&gt; 4.00x10&lt;sup&gt;-9&lt;/sup&gt;</td>
<td>1.06</td>
<td>4.51</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.30</td>
<td></td>
<td></td>
<td>7.7-7.9</td>
<td>N.D.</td>
<td>1228-1640</td>
<td>N.D.</td>
<td>2.80x10&lt;sup&gt;-9&lt;/sup&gt;</td>
<td>N.D.</td>
<td>4.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>20-50</td>
<td>g L&lt;sup&gt;-1&lt;/sup&gt; 1.26</td>
<td>new H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>7.2-7.5</td>
<td>0.33 0.93</td>
<td>0-1192</td>
<td>5.09x10&lt;sup&gt;-12&lt;/sup&gt; 1.43x10&lt;sup&gt;-11&lt;/sup&gt;</td>
<td>0.35</td>
<td>3.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>20-50</td>
<td>g L&lt;sup&gt;-1&lt;/sup&gt; 430.</td>
<td>new H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>7.1-7.7</td>
<td>0.31 0.06</td>
<td>0-1192</td>
<td>1.40x10&lt;sup&gt;-11&lt;/sup&gt; 3.88x10&lt;sup&gt;-11&lt;/sup&gt;</td>
<td>0.36</td>
<td>3.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>50-100</td>
<td>g L&lt;sup&gt;-1&lt;/sup&gt; 70.</td>
<td>new H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>6.2-6.6</td>
<td>0.152 0.078</td>
<td>139-920</td>
<td>1.06x10&lt;sup&gt;-10&lt;/sup&gt; 4.65x10&lt;sup&gt;-11&lt;/sup&gt;</td>
<td>1.96</td>
<td>2.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>50-100</td>
<td>g L&lt;sup&gt;-1&lt;/sup&gt; 3.0</td>
<td>&quot;aged&quot; 20mM NaCl</td>
<td>3.6</td>
<td>0.336 0.040</td>
<td>0-3</td>
<td>5.79x10&lt;sup&gt;-8&lt;/sup&gt; 6.43x10&lt;sup&gt;-8&lt;/sup&gt;</td>
<td>0.90</td>
<td>1.92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td></td>
<td>from NaCl</td>
<td>3.6</td>
<td>0.164 0.060</td>
<td>3-6</td>
<td>9.00x10&lt;sup&gt;-9&lt;/sup&gt; 1.83x10&lt;sup&gt;-9&lt;/sup&gt;</td>
<td>2.62</td>
<td>2.62</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.3</td>
<td></td>
<td>Exp1</td>
<td>3.6</td>
<td>0.339 0.164</td>
<td>8-19</td>
<td>1.38x10&lt;sup&gt;-9&lt;/sup&gt; 2.61x10&lt;sup&gt;-9&lt;/sup&gt;</td>
<td>2.07</td>
<td>2.07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>50-100</td>
<td>g L&lt;sup&gt;-1&lt;/sup&gt; 6.87</td>
<td>&quot;aged&quot; 20mM NaCl</td>
<td>6.0</td>
<td>0.0126 0.0085</td>
<td>0-1</td>
<td>7.23x10&lt;sup&gt;-8&lt;/sup&gt; 4.92x10&lt;sup&gt;-8&lt;/sup&gt;</td>
<td>1.47</td>
<td>2.19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td></td>
<td>at pH 3.6 NaCl</td>
<td>6.0</td>
<td>0.0177 0.0090</td>
<td>1-7</td>
<td>4.18x10&lt;sup&gt;-9&lt;/sup&gt; 4.02x10&lt;sup&gt;-10&lt;/sup&gt;</td>
<td>1.97</td>
<td>1.97</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>14.5</td>
<td></td>
<td>for 30 days</td>
<td>6.0</td>
<td>0.0297 0.0095</td>
<td>7-12</td>
<td>4.63x10&lt;sup&gt;-9&lt;/sup&gt; 3.86x10&lt;sup&gt;-10&lt;/sup&gt;</td>
<td>2.49</td>
<td>2.49</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>50-100</td>
<td>g L&lt;sup&gt;-1&lt;/sup&gt; 10.3</td>
<td>&quot;aged&quot; 5mM NaCl</td>
<td>6.0</td>
<td>0.0055 0.0087</td>
<td>0-1</td>
<td>2.06x10&lt;sup&gt;-8&lt;/sup&gt; 2.25x10&lt;sup&gt;-9&lt;/sup&gt;</td>
<td>0.92</td>
<td>2.17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.1</td>
<td></td>
<td>at pH 3.6 NaCl</td>
<td>6.0</td>
<td>0.020 0.0083</td>
<td>1-7</td>
<td>8.40x10&lt;sup&gt;-9&lt;/sup&gt; 1.33x10&lt;sup&gt;-9&lt;/sup&gt;</td>
<td>2.41</td>
<td>2.41</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.5</td>
<td></td>
<td>from</td>
<td>6.0</td>
<td>0.024 0.0097</td>
<td>7-13</td>
<td>4.12x10&lt;sup&gt;-9&lt;/sup&gt; 7.20x10&lt;sup&gt;-10&lt;/sup&gt;</td>
<td>2.89</td>
<td>2.89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.6</td>
<td></td>
<td>Exp 19</td>
<td>6.0-6.6</td>
<td>0.167 0.030</td>
<td>13-732</td>
<td>5.06x10&lt;sup&gt;-10&lt;/sup&gt; 1.03x10&lt;sup&gt;-10&lt;/sup&gt;</td>
<td>4.30</td>
<td>2.17</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

N.D. - Not Determined
“flash” 0.5 M KOH extraction method (JACKSON et al., 1986). The amount of Si extracted from the original unweathered material and from the Experiment 10 and Experiment 10A materials was 0.16, 0.38, and 0.47 mmol g\(^{-1}\). The amount of Al extracted from the original unweathered material and from the Experiment 10 and Experiment 10A materials was 0.06, 0.39, and 0.39 mmol g\(^{-1}\). Significant amounts of Si and Al had accumulated on the surfaces of the feldspar, and more Si accumulated at higher pH (Experiment 10A). The Si/Al molar ratios were nearly 1, supporting the EDX analysis from Experiment 6.

These findings suggest that two mechanisms are important in controlling the rate of dissolution: (1) the accumulation of products in solution exerts a back reaction that slows the dissolution rate; and (2) with time, the formation of a stabilized Al-O-Si polymer on the feldspar surface acts as a barrier to reaction. To investigate the effect of products on the reaction rate, two types of experiments were carried out: (1) cation and anion exchange resins were added to anorthite plus water suspensions in order to scavenge products produced from dissolution, and (2) products were added to solution prior to the start of the reaction. We hypothesized that if the accumulation of products had an effect on the dissolution rate, adding products would slow the rate of dissolution and removing products (with exchange resins) should speed up the reaction.

**Experiment 17: Product Removal with Exchange Resins**

Considering the possibility that the accumulation of products (particularly Al) may be slowing the rate of dissolution, we reacted anorthite in the presence of cation and anion exchange resins for a period of 38 days following the technique of CLEEMENCY and LIN (1981). Strong cation exchange resin Amberlite IR-120 (280–860 μm) was saturated with H\(^+\) and another batch of resin saturated with Na\(^+\), and both resins were rinsed with distilled water. Strong anion exchange resin Dowex 1-8X (280–860 μm) was saturated with OH\(^-\), another batch of the same resin was saturated with Cl\(^-\), and both resins were rinsed with distilled water. The H-saturated cation resin was mixed with an equal weight of OH-saturated anion resin to produce an H\(^+\)/OH\(^-\) mixed resin. Likewise, the Na-saturated resin was mixed with the Cl-saturated resin to produce a mixed Na\(^+\)/Cl\(^-\) resin. Unweathered anorthite (50–100 μm) was added to two series of 50 mL polyethylene centrifuge tubes. One set of tubes had anorthite (0.2 g) plus 75 mL deionized water plus 1.0 g of H/OH mixed resin; the other set of tubes had anorthite + water + Na/Cl mixed resin all in the same proportions. The H/OH resin mixture was an effective sink for all products produced from the weathering of the anorthite, including Si(OH)_4. The Na/Cl resin mixture adsorbed all Ca and Al and approximately 50% of the Si(OH)_4 that was released. The tubes were placed on a reciprocating shaker; and, at various time intervals, a tube from each set was destructively sampled by first centrifuging and decanting the aqueous phase. This aqueous phase was filtered through a 0.1 μm cellulose nitrate membrane filter, and the ions adsorbed on the resin extracted with three sequential rinses with 4 M HNO_3. Both the aqueous phase and the acid extract of the resin were analyzed for major cations and anions.

Shown in Figs. 6 and 7 are the amounts of Ca, Si, and Al released from the anorthite in the cation/anion mixed exchange resin experiments. The average solution pH in the Na/Cl and H/OH resin systems were 6.5 ± 0.1 and 6.8 ± 0.5, respectively. The pH measurements in the H/OH resin system are somewhat more variable due to the difficulty in determining pH in a very low electrolyte solution (average electrical conductivity 0.23 mS m\(^{-1}\)). In the Na/Cl resin system, the ionic strength of the solution increased with time as Na\(^+\) and Cl\(^-\) were released to solution from the exchange resins. The concentrations of Na and Cl in solution went from 1.0 mM at the start of the experiment to 2.9 mM at the end of the experiment. The reaction kinetics were linear for all elements (Ca, Al, and Si) after a short start-up (4 days) that can be attributed to disturbed surfaces and small particles. Figure 8 shows that the amount of Ca initially leached relative to Si was similar in both the Na/Cl and H/OH resin systems. Following this initial leaching, the Ca and Si data parallel the stoichiometric dissolution line indicating congruent, stoichiometric dissolution of Ca relative to Si. Figure 9 shows that Al was preferentially leached over Si in the H/OH resin system but not in the Na/Cl resin system, which suggests an accumulation of Al relative to Si on the surface. The only other time we observed Si/Al ratios that were less than stoichiometry was when freshly ground, unwashed anorthite (containing fines) was reacted at pH 7–9 (data not shown). This finding is in agreement with SÅBERG (1989), who reported an Al-enriched altered surface layer on labradorite weathered in alkaline solutions. Thus, the mechanism of Al retention in the hydrous surface layer must be dependent upon the surface pH. Additional evidence for this is given in Experiments 18 and 19.

Following the initial Ca leaching, the release of Al, Si, and Ca was linear and at sustained high rates. The steady-state dissolution rates in the H/OH and Na/Cl resin systems averaged 10\(^{-7.20}\) and 10\(^{-7.71}\) mmol m\(^{-2}\) s\(^{-1}\), respectively. The dissolution rate in the presence of the Na/Cl resin was 6–8 times faster than the average feldspar dissolution rates reported by HELGESON et al. (1984) and AMRHEIN and SUAREZ (1988) but was comparable to the initial dissolution rates at
Dissolution kinetics of anorthite

Anorthite + Na/Cl resins

0.20
0.15
0.10
0.05
0.00

0.05
0.10
0.15
0.20

0.01
0.02
0.03
0.04

0.00
0.005
0.010
0.015
0.020

FIG. 7. Experiment 17. Release of Ca, Si, and Al in the presence of Na\(^+\)/Cl\(^-\) saturated exchange resins.

pH 6 (Table 3; Experiments 15 and 16, 0–1 day). The dissolution rate in the presence of the H/OH resin was equivalent to the rate of reaction in the pH range of 3.5–3.8. This higher rate in the presence of H/OH resin is attributed to near saturation of the feldspar surface with H\(^+\). Even though the solution pH was near neutral, the presence of the H\(^+\) saturated exchange phase (which was present in a much greater amount than the feldspar exchange capacity) resulted in a Ca\(^{2+}\)/H\(^+\) exchange reaction. Assuming that the affinity of the resin and feldspar for H\(^+\) and Ca\(^{2+}\) were similar, the composition of both exchange phases (resin and feldspar) would have been similar. Previous work has shown that the rate of dissolution at pH values < 8 is proportional to the concentration of H\(^+\) adsorbed to the feldspar surface (Helgeson et al., 1984; Stumm et al., 1985; Amrhein and Suarez, 1988; Brady and Waltther, 1989).

At the end of the reaction, 1.4 and 3.6% of the added mineral had dissolved in the Na/Cl and H/OH systems, respectively. Under the conditions of the experiment, there was no change in the mineral:solution ratio with time, and less than 10% of the total exchange capacity of the resin was used.

These findings support the hypothesis that the accumulation of products (either in solution or incorporated in a hydrous layer or precipitate) is an important factor in the kinetics of dissolution, even after short time periods of reaction.

Experiments 18 and 19: Addition of Al, Si, and Ca

Anorthite, aged in distilled water for 212 days, was reacted for 13 days in solutions of constant ionic strength at pH 3.0 and in the presence of 0, 2, and 10 mM Al\(^{3+}\). Potassium chloride was added to adjust the ionic strength, and 1.0 M HCl was added daily to maintain pH. The addition of the acid made an insignificant change in the ionic strength. The suspensions were agitated on a wrist-action shaker for 14 days.

The dissolution of anorthite was independent of added Al (Fig. 10) at pH 3.0. The addition of 0.5 mM Al at pH 3.6 suppressed the initial Si release (approx. 50% lower), but then the rate was comparable to the other solutions without added Al (Fig. 10). This initial reduction in rate may be attributed to some displacement of adsorbed H\(^+\) at activated sites by Al\(^{3+}\). However, this was not observed at pH 3 in Experiment 18. The amount of Al added to the pH 3.0 and 3.6 suspensions did not exceed amorphous Al(OH)\(_3\) solubility, and the solutions remained undersaturated with any known mineral phases according to the WATEQ speciation program (Truebellel and Jones, 1974). Supernaturation with halloysite and amorphous Al(OH)\(_3\) was rapidly reached in the pH 6.0 suspension. The addition of products did not
affect the stoichiometry of dissolution and nonzero-order kinetics were observed for all treatments. We also observed a 31% decrease in the initial rate of dissolution at pH 6 when only 4.0 μmol L⁻¹ Al³⁺ was added to a solution of 5.0 mM NaCl. Brady and Walther (1989) postulated that albite dissolution from pH 8–3 is controlled by Al detachment. Below pH 3, the overall surface charge appears to become saturated and at pH values from 1–3, the penetration of H⁺ over distances of many unit cells occurs and controls the rate (Casey et al., 1989).

Experiment 20: The Effect of Ionic Strength

Figure 11 shows that increasing the ionic strength at constant pH (3.6 and 6.0) decreased the rate of reaction. Zero-order kinetics were not observed, even though the material had been well aged. The addition of KCl to the reaction decreased the reaction rates to a lesser extent than the rate decrease reported by Sjöberg (1989) for labradorite dissolution. At pH 3.6, the dissolution rate dropped an average of 0.13 log units as compared to 0.4 log units in the study of Sjöberg. These results are in qualitative agreement with Tole et al. (1986), who found that addition of 3.0 M NaCl at pH 5 and 60°C decreased the rate of nepheline (NaAlSiO₄) dissolution by an order of magnitude, and with Carroll-Webb and Walther (1988), who found a slightly lower dissolution rate of corundum and kaolinite at ionic strength 0.05 M as compared to 0.005 M (KCl buffer solutions). These observations differ from the findings of Rimstidt and Dove (1986), who found no effect of added CaCl₂ (0.001–1.0 M) on the rate of wollastonite dissolution. In addition, Sjöberg (1989) saw no effect of 0.01 M LiCl at pH 2 on the dissolution of labradorite.

Apparently, K⁺ and not Ca²⁺ or Li⁺ interferes with the H⁺ exchange at the surface or with the repolymerization of the silanol groups. If the dissolution rate under acid conditions were solely a function of the adsorbed H⁺ concentration or surface charge (Amrhein and Suarez, 1988; Brady and Walther, 1989) in the absence of ion exchange, then increasing the ionic strength should increase the dissolution rate. The double layer theory of constant potential surface predicts that an increase in the ionic strength will increase the surface charge density and the amount of protons adsorbed on the surface (McBride, 1989). However, feldspars have both constant potential and constant charge sites. The constant charge sites are associated with the tetrahedrally coordinated Al and form where Ca is leached from the structure. These sites may be subject to competitive cation exchange between K⁺ and H⁺ or K⁺ displacing structural Ca. We hypothesize that Ca²⁺ and Li⁺ do not have an inhibiting effect comparable to K⁺ because their hydrated radii are too large to fit into cavities in the repolymerized siloxane surface and, therefore, are not competitive with K⁺ or H⁺ on the exchange sites.

SUMMARY AND DISCUSSION

The dissolution of anorthite under controlled CO₂ and pH conditions did not exhibit zero-order kinetics with respect to the concentration of Ca, Si, or Al in solution, even after extensive aging. Sequential reaction of anorthite in water always
exhibited a decrease in reaction rate with each subsequent rinse at constant pH and a decrease in reaction rate with increasing suspension density. Possible explanations for these observations are: (1) the formation of variable thickness leached layers that limited dissolution via diffusion control; (2) the weathering of fines and damaged surfaces and; (3) a back reaction involving soluble or precipitated products that reduced the surface reactivity or formed a physical barrier to dissolution. The calculated uniform leached layer thicknesses were nearly the same for all suspension densities and were small, ranging from 2.6–2.9 nm over a pH range from 3.9–4.5, which suggests that the rate differences could not be attributed to diffusion through a Ca-depleted layer. These leached layer thicknesses agreed well with the 2.5–2.8 nm thicknesses reported for albite at pH 5.1–3.5 (WOLLAST and CHOU, 1985). However, the integrity or reactivity of this leached layer as a result of Si-O-Al or Si-O-Si repolymerization could not be determined and may play a role in determining the rate. Secondly, these nonzero-order kinetics could not be attributed solely to the weathering of fine, broken particles and disturbed surfaces or to the lack of stoichiometric dissolution because nonzero-order dissolution was observed even after extensive aging of the feldspar and after stoichiometric dissolution had been reached. Thirdly, the effect of back reactions involving products appeared to be important in determining the dissolution rate.

Drying of the feldspar at 75, 100, or 150°C had no effect on the rate of reaction, suggesting that the migration of water into the crystal, low-temperature annealing, or leached layer sloughing as a result of drying were not important factors controlling the dissolution rate.

There was no simple correlation between weathering rate and specific surface area of the material. That is, the fine-size fraction material dissolved slower than the coarser sized material, on a surface area basis, in agreement with the findings of HOLDREN and SPEYER (1987), suggesting that reactive site density was not directly proportional to surface area.

Energy-dispersive X-ray analysis of the weathered and unweathered feldspar showed evidence of a leached layer or precipitated phase in the fine fraction, consistent with the calculated leached layer thickness and excess penetration depth of the EDX beam.

Increased agitation approximately doubled the rate of dissolution over a quiescent system, implying that alteration of the surface layer or surface sites through abrasion was an important factor in determining the rate. Thus, studies using fluidized bed reactors will have higher weathering rates relative to the quiescent or low-flow systems, which we consider to correspond better to natural conditions.

Long-term weathering studies showed a decrease in dissolution rate with time and suspension density, suggesting that product accumulation (either in solution or incorporated into a surface layer) was an important factor in controlling the rate. The weathering of anorthite at a mineral-solution ratio comparable to a saturated aquifer had an average dissolution rate of $10^{-10.8}$ mmol m$^{-2}$ s$^{-1}$ over a 3.3 y period, which is over two hundred times slower than previously reported laboratory rates for anorthite dissolution.

The removal of soluble products using cation and anion exchange resins resulted in zero-order kinetics at sustained high rates for 38 days near neutral pH. These high linear rates ($10^{-7.20}$ and $10^{-7.21}$ mmol m$^{-2}$ s$^{-1}$ in the H/OH and Na/Cl resins, respectively) are attributed to low Al in solution and the lack of a condensed silanol surface protective layer.

The addition of Ca or Si to the initial reaction solution had no effect on anorthite dissolution. Added Al did not affect the rate at pH 3.0 but did decrease the initial rate by 50 and 31% at pH 3.6 and 6.0, respectively. These findings are somewhat different from those reported by WOLLAST and CHOU (1985), who observed a reduction in albite dissolution at pH 3 in the presence of dissolved Al. This may be due to differences in the surface pH of albite and anorthite at a solution pH of 3 or to the effects of the KCl used to adjust the ionic strength. These findings support the hypothesis of CASEY et al. (1988) that adsorbed Al condenses and dehydrates surface silanol polymers, decreasing the overall rate of reaction, and that this reaction is pH-dependent. The Al-enriched surfaces of naturally weathered oligoclase observed by NESBITT and MUIR (1988) and the low laboratory dissolution rates of similar material at pH 5.1–5.3 reported by LUNDSTROM and OHMAN (1990) may also be explained by these findings.

Further evidence that the accumulation of soluble products decreases the rate of reaction was mentioned in the studies of WOGELIUS and WALther (1991), who found that the rate of olivine dissolution decreased as the pumping rate in a fluidized bed reactor was decreased. Steady-state dissolution rates were reached at both pumping speeds, but the dissolution rates varied by 0.56 log units even though the pH was kept constant at 5.7. This finding suggests that the dissolution rate of Al-free silicate minerals may be affected by back reactions involving Mg or Fe. The other explanation for this observation is a decrease in agitation and abrasion at the lower pumping rate resulted in a decreased rate, comparable to the effects observed in this study.

Increasing concentration of KCl at pH 3.6 and 6.0 decreased the dissolution rate of anorthite. This is contrary to the prediction that an increase in the ionic strength should increase the adsorption of protons on a constant potential surface at constant pH and, thus, increase the rate. These results indicate K$^+$ exchange for H$^+$ at the reactive sites results in a reduction of the dissolution rate. Major solution cations such as Ca, Na, and Mg are expected to have little effect on reaction rates because of their hydrated size.

Acknowledgments—We thank C. Irma Lopez and J. D. Wood for assistance in the laboratory. This paper has benefited greatly by reviews from S. A. Carroll, R. Wollast, J. V. Walther, and H. W. Nesbitt.

Editorial handling: G. Sposito.

REFERENCES


