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The use of a surface complexation model to describe the kinetics of ligand-promoted dissolution of anorthite

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Abstract—The dissolution of anorthite ($CaAl_2Si_2O_8$) in the presence of fluoride and oxalate was studied under controlled pH and CO_2 conditions. The dissolution of anorthite in the absence of complex-forming ligands was nearly pH independent between pH 5 and 9. The presence of complex-forming ligands resulted in a dissolution rate that increased linearly with decreasing solution pH. The dissolution data were modeled using the theory that the reaction rate is proportional to the surface concentration of activated sites. Surface activated sites are formed by the adsorption of protons and complexing ligands. On anorthite, the proton-promoted activated sites are probably Si centered and the ligand-promoted activated sites Al centered. Two surface chemistry models were combined in order to describe the overall reaction. At pH values less than 4.2, the rate of the proton-promoted dissolution was linearly proportional to Γ^4, where Γ is the surface concentration of adsorbed protons. The rate of the ligand-promoted dissolution was found to be linearly related to the surface concentration of adsorbed ligand.

These findings suggest that for most natural systems, pH and complexing ligands have a synergistic effect on feldspar dissolution. The observation in nature that Ca-rich plagioclase feldspars are less resistant to weathering than Na-rich feldspars can be attributed to the increased reactivity of organic ligands towards Ca-rich feldspars. The increased reactivity is attributed to the higher proportion of Al in the Ca-feldspars.

INTRODUCTION

IT HAS LONG BEEN recognized that the chemical weathering of minerals in soils is of fundamental importance in the maintenance of soil fertility, the genesis of soils and the formation of clay minerals. The most ubiquitous group of primary minerals in soils are the feldspars. Feldspar weathering has been cited as a possible source to soil solutions of Ca^{2+} and alkalinity (SUAREZ 1977; SUAREZ and RHOADES, 1982) and K^+ (SADUSKY and SPARKS, 1985). Since the weathering of minerals is an acid-consuming reaction, the environmental impact of acid deposition on granitic watersheds may be closely related to the weathering rate of the feldspars in the watershed (ESHLEMAN and HEMOND, 1985). It has been proposed that proton adsorption is the mechanism that controls the dissolution rate of silicates (AAGAARD and HELGESON, 1982) and oxides (STUMM *et al.*, 1985).

There is a growing recognition of the importance of organic acids and chelates in the weathering process. It is felt by some (KRUMBEIN and DYER, 1985; ECKHARDT, 1985) that the processes of mineral weathering are completely controlled by biological activity through CO_2 production and excretion of organic acids.

The role of organic ligands (predominately humic and fulvic acids) in the weathering process has generally been attributed to the capacity of these ligands to form organo-metallic complexes (WRIGHT and SCHNITZER, 1963; HUANG and KELLER, 1972; BAKER, 1973; TAN, 1975).

The aggressive nature of fluoride toward Al containing minerals has been recognized as a result of the work of HUANG and JACKSON (1965) on clays, oxides, and soils.

According to STUMM *et al.* (1980, 1983, 1985) and AAGAARD and HELGESON (1982) the inner-sphere adsorption of protons, organic ligands, and fluoride on oxides and aluminosilicates weakens critical crystal lattice bonds at the site of adsorption, and thus increases the rate of dissolution. Adsorption occurs on the surface metal sites through ligand exchange reactions on the basis of the amphoteric nature of these sites (PARKS and DE BRUYN, 1962).

STUMM *et al.* (1983, 1985), FURRER and STUMM (1983), and ŽUTIĆ and STUMM (1984) found accelerated rates of aluminum and iron oxide dissolution in the presence of various organic acids and fluoride ions. They proposed a surface complexation model to describe the dissolution of metal oxides and suggested that a similar mechanism may also regulate the dissolution of aluminosilicate minerals. FURRER and STUMM (1986) determined that in the absence of complex-forming ligands, the rate of oxide dissolution was proportional to the *n*th power of the surface concentration of protons. In the presence of ligands, a ligand-promoted reaction occurred and the two mechanisms were not affected by one another and both occurred simultaneously. These findings were described by the following equation:

$$R_{total} = R_H + R_L = k_H(SOH_2^+)^n + k_L(S - L) \quad (1)$$

where the total rate (R_{total}) is equal to the sum of the proton-promoted rate (R_H) and the ligand-promoted rate (R_L). The proton-promoted rate is proportional to the concentration of adsorbed protons (SOH_2^+) or the surface charge density raised to some power (n) and the ligand-promoted rate is proportional to the concentration (activity) of surface activated sites formed from the adsorption of ligands (S − L), where S stands for the surface metal center that adsorbs protons and ligands. No back reactions are included in this model, because the reactions were investigated sufficiently far from equilibrium to neglect them. Other studies (unpublished data) have shown no effect of dissolution products on the rate of anorthite dissolution. FURRER and STUMM (1986) developed a theory based on the probability of a metal center having two or three adsorbed protons to show that the exponent, n, was equal to the number of adsorbed hydrogen ions at an activated site. They observed that $n = 3$ for δ-Al_2O_3 and n

= 2 for BeO and suggested that the exponent, n, may be equal to the oxidation state of the metal center. Zinder *et al.* (1986) found that $n = 3$ for the reductive dissolution of α-FeOOH. In phyllosilicates it has been assumed that the active metal centers for both proton and hydroxide ion adsorption are the alumino-sites and the silanol sites (Si) complex only hydroxide anions (Sposito, 1984). This suggests that for feldspars, activated sites are preferentially formed on Al metal centers. Extrapolating the theory of Furrer and Stumm (1986) to feldspars, an activated site should have three adsorbed protons ($n = 3$).

Aagaard and Helgeson (1982) hypothesized that the activated complex on alkali feldspar in acid solutions is $((H_3O)AlSi_3O_7OH)^+$ or $((H_3O)AlSi_3O_8(H_3O))^+$, that is, the alkali cation is replaced by a hydrogen ion and the alumino-site protonates. This suggests that $n = 2$ in the Furrer and Stumm model. Under alkaline conditions the reaction rate would be related to the surface concentration of deprotonated hydroxyl groups.

The following study was undertaken to determine the rate of anorthite ($CaAl_2Si_2O_8$) dissolution in the presence of complexing ligands (fluoride and oxalate) and to determine whether the dissolution rate could be explained on the basis of surface protonation/deprotonation and the surface concentration of complex-forming ligands.

MATERIALS AND METHODS

A rock sample containing anorthite and pyroxene from Grass Valley, CA was obtained from Ward Scientific. The rock was crushed to release the individual crystals, passed through a magnetic separator, and then hand picked to obtain clean anorthite. The mineral was ground and sieved to various size fractions, thoroughly washed in distilled water and dried. Table 1 shows the anorthite analysis using HF digestion in a closed vessel (Lim and Jackson, 1982). The analysis is nearly the same as that reported by Deer *et al.* (1966) for Grass Valley anorthite (An_{93}). The presence of Mg and Fe are likely due to minor pyroxene contamination. All experiments were carried out in a constant temperature room at 298.15 ± 0.1 K. Reactions were carried out in polyethylene bottles mounted on a wrist-action shaker modified to operate at 80 cycles per minute. This agitation was not vigorous enough to suspend the mineral. Once a day the bottles were thoroughly mixed by hand. It is generally accepted that stirring rate has little or no effect on the rate of feldspar weathering (Aagaard and Helgeson, 1982), since the rate of hydrolysis is too slow for interstitial aqueous diffusion to be rate-limiting.

Samples were withdrawn from the settled suspensions with a syringe at given time intervals and filtered through 0.1 μm cellulose nitrate membrane filters which were prerinsed with the solutions. Samples were stored until the end of the reaction, when all samples were analyzed at one time. Solution concentrations were corrected for changes in the solution:solid ratios due to acid or base additions and solution sample removal, by calculating the total mass of solid dissolved previous to each sampling time. Dissolved mass removed in each sample was included in the running total and the cumulative amount of mineral dissolved is expressed on a mmol m^{-2} basis. The pH of the suspension was measured *in situ* at the time of sampling, after calibration with pH buffers to within ±0.01 pH units. Calcium was measured by atomic absorption spectrophotometry after addition of acidified La_2O_3. Silicon was determined with the heteropoly blue method (American Public Health Assoc., 1976) using ascorbic acid as the reducing agent (Technicon Auto Analyzer II* Industrial Method No. 105-71 W/B). Aluminum was determined colorimetrically using hydroxyquinoline after the removal of interfering cations (Fe) using a preliminary extraction procedure (May *et al.*, 1979). Fluoride and oxalate were measured using ion chromatography. Surface area of the ground anorthite was determined by single point Kr adsorption at liquid N_2 temperature using a Quantasorb Jr.* (Quantachrome Corp.). The 20–50 μm size fraction of anorthite had a measured surface area of 0.50 $m^2\ g^{-1}$. The point of zero charge (PZC) of the anorthite was measured by microelectrophoresis using a Zeta-Meter 3.0 system.*

TABLE 1
Chemical analysis of
Grass Valley anorthite

	wt % ± std. dev.*
SiO_2	43.64 ± 1.22
Al_2O_3	33.02 ± 1.25
CaO	18.67 ± 0.30
Na_2O	0.76 ± 0.01
Fe_2O_3	0.79 ± 0.01
MgO	0.23 ± 0.01
K_2O	0.05 ± 0.01

* n=5

Adsorption isotherms of F^- on anorthite were determined by adding anorthite to solutions of known F^- concentration and pH and fixed ionic strength. After reacting for 10 minutes the solutions were separated from the mineral and reanalyzed for F^-. Adsorbed F^- was taken as the difference between these values. Isotherms were determined at several pH values and at a mineral:solution ratio of 50 g L^{-1}.

The concentration of adsorbed protons and the point of zero net proton adsorption were determined by potentiometric titration of the anorthite in 5.0 mM NaCl with 5.0 mM HCl and NaOH using the method of Parks and de Bruyn (1962). The total number of reactive sites was calculated from the titration data.

RESULTS AND DISCUSSION

The effect of pH on the dissolution rate of anorthite was determined from the following experiment. Anorthite (0.2 g, 50–100 μm) was added to 0.030 L of 5.0 mM NaCl in 50 ml polyethylene centrifuge tubes. The suspensions were adjusted to pH values of 3, 4, 5, 6, 7, 8, 9, and 10 using HCl and NaOH. Every three days, for 12 days, the pH values were measured and the solutions replaced with fresh solutions and the pH values of the suspensions adjusted to the target pH values. The four sets of samples were filtered and analyzed for Ca and Si.

Figure 1 (Exp. 1) shows that the release of Si from anorthite was nearly independent of pH between pH 5 and 9. Large increases in the dissolution occurred at both low and high pH. These data are consistent with Helgeson *et al.* (1984) who maintain that feldspar dissolution is pH independent between pH 3 and 8 at 25°C for all feldspars and with the findings of Knauss and Wolery (1986) for albite dissolution. The rapid dissolution at low pH is termed the proton-promoted rate and at high pH is termed the hydroxide-promoted rate.

The second experiment was a sequential rinse (batch) reaction at constant pH. One gram samples of anorthite (20–50 μm) were added to 0.20 L of 5.0 mM NaCl, 0.5 mM NaF + 4.5 mM NaCl, and 0.05 mM NaF + 4.95 mM NaCl in duplicate. In order to maintain the pH constant at 5.5, 5.0 mM HCl was added daily or more often. The pH varied no

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* Trade names and company names are included for the benefit of the reader and do not imply endorsement or preferential treatment of the product by the USDA.

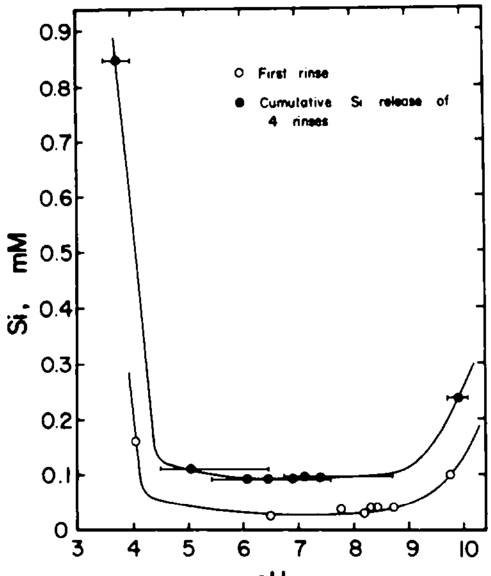

FIG. 1. Experiment 1. The cumulative release of Si to solution *vs.* solution pH for four sequential rinses. The pH values at time of sampling are plotted. The mineral:solution ratio was 6.67 g L^{-1}.

more than 0.2 pH units over the course of the reactions. After 13 days, the solutions were replaced with fresh solutions (same composition as the original solutions) and the pH maintained at 5.5. This was repeated again after 13 days and then again after 16 days. After the third set of solutions, the 4th series of reactions was performed at all three F^- concentrations at pH 3.5 and maintained for 9 days at constant pH. The anorthite was subsequently rinsed in distilled water, dried, and reacted at pH 3.3 in the absence of F^-.

Figure 2 (Exp. 2) shows the release of Si to solution from anorthite under constant pH and three concentrations of F^-. There was an initial rapid release of Si followed by a near linear release with time. Many researchers have attributed this initial rapid release to the removal of high energy broken edges and dissolution of small particles adhering to the surfaces (HOLDREN and BERNER, 1979; HELGESON *et al.*, 1984; RIMSTIDT and DOVE, 1986). In addition, there was an initial non-linear release at the beginning of each rinse which could not be attributed to solution carry-over from the previous rinse. This nonlinearity may be due to Si desorption after being placed in a fresh, Si-free solution. There appears to be a trend in decreasing reaction rate with each subsequent rinse. This observation is being investigated further. For this study, we have used all three rates as representing the dissolution at pH 5.5.

Figure 3 shows the release of Si for the dissolution reaction of anorthite at pH 3.5 (with 0.5 mM F^-, 0.05 mM F^-, and without F^-) and at pH 3.3 (in the absence of F^-). In contrast to pH 5.5, at pH 3.5, the ligand-promoted dissolution was very small compared to the acid-promoted rate. That is, the rates for the 0.0, 0.05, 0.5 mM F^- runs at pH 3.5 were nearly all the same. Also shown on Fig. 3, for comparison, are the dissolution data at pH 5.5.

Figure 4 shows the degree to which there was stoichiometric release of Ca and Si to solution (Si/Ca mole ratio = 2.18 for this mineral specimen). In the first rinse, a large excess of Ca relative to Si was released into solution for all reactions. This pulse of Ca is attributed to surface exchange of Ca^{2+} for H^+ and Na^+ as well as leaching of Ca from the crystal structure. Following the initial pulse of Ca to solution, the anorthite dissolved stoichiometrically (Ca and Si) for all subsequent rinses. Al release was also stoichimetric at the low pH runs (<4.2). At higher pH runs, Al activity became nearly constant and was apparently controlled by $Al(OH)_3$ precipitation, based on calculations using the program WATEQ (TRUESDELL and JONES, 1974). The depth to which Ca was leached from the crystal structure was calculated from the amount of excess Ca (Ca minus ½ Si in mmol L^{-1}) and assuming that the Ca was removed uniformly over the whole surface. The calculated leached layer thickness that developed in this experiment was 2.5–3.0 nm. This is in agreement with WOLLAST and CHOU (1985) who found that albite developed an alkali

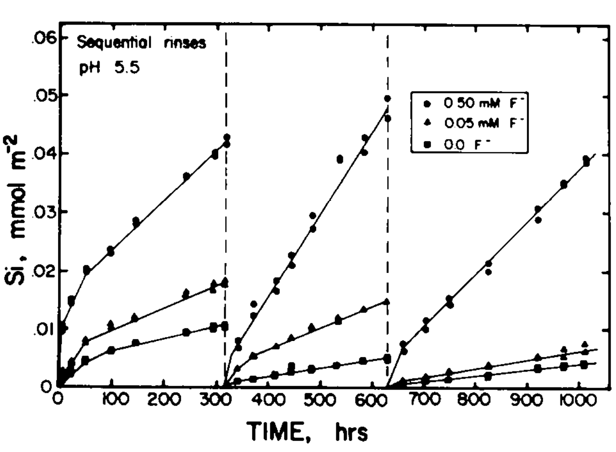

FIG. 2. Experiment 2. Silica release from anorthite for three sequential rinses at pH 5.5 in 5.0 mM NaCl, 4.95 mM NaCl + 0.05 mM NaF, and 4.5 mM NaCl + 0.5 mM NaF. The mineral:solution ratio was 5.0 g L^{-1}.

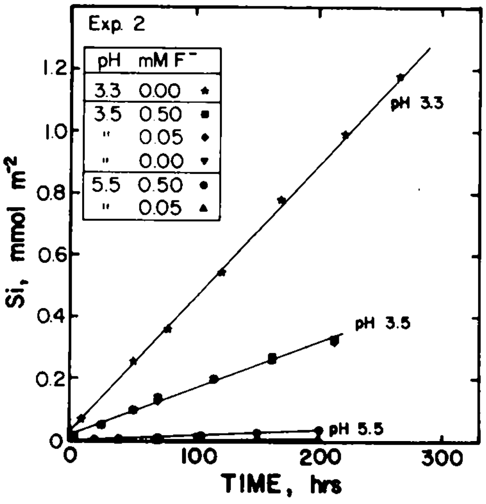

FIG. 3. Experiment 2. Silica release from anorthite at pH 3.3 (without F^-), and pH 3.5 and 5.5 (0.5 mM F^-, 0.05 mM F^-, and without F^-). Symbols for the pH 5.5 data are the same as Fig. 2.

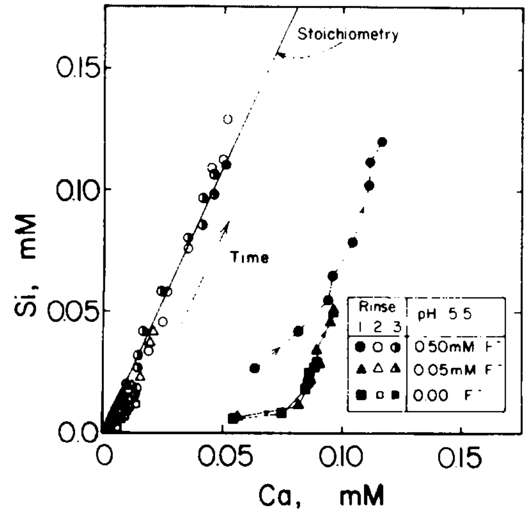

FIG. 4. Experiment 2. Stoichiometric release of Ca and Si from anorthite during sequential rinses at pH 5.5. The stoichiometric release line is equal to a Si/Ca mole ratio of 2.18.

depleted layer of 2.5–2.8 nm. The fact that the release was stoichiometric after the first rinse (Fig. 4) shows that Si adsorption was not an important process in these dissolution studies. STÖBER (1967) proposed that Si adsorption was a mechanism that affects the dissolution kinetics of SiO_2 minerals.

The dissolution kinetics of the pyroxene separated from the anorthite were nearly the same as the anorthite (unpublished data). The contribution of Si to solution from this minor contaminant was therefore insignificant.

The third experiment was a pH free-drift, controlled CO_2 experiment. One gram samples of anorthite (20–50 μm) were added to 0.15 L of 5.0 mM NaCl, 0.05 mM NaF + 4.95 mM NaCl, 0.5 mM NaF + 4.5 mM NaCl, 5.0 mM NaF, and 2.5 mM $Na_2C_2O_4$. Each of these solutions was maintained at constant PCO_2. Mixtures of CO_2 + air from compressed cylinders were continuously bubbled into the reaction bottles after first being saturated with water vapor by passage through a train of 4 gas scrubbers. These experiments utilized mixtures with CO_2 partial pressures of 0.95, 9.5, 94.2 kPa.

The release of Si to solution under controlled CO_2 conditions (pH free drift, Exp. 3) is given in Fig. 5a (experiments with 0.5 mM F^-, 0.05 mM F^-, and without F^-) and Fig. 5b (experiments with 5.0 mM F^-). Initial parabolic Si release was observed, followed by approximately linear release. This variable release rate was apparently due to changing pH during the reaction. The rate of dissolution was taken as the slope of this later portion of the curve. Si release was enhanced by the presence of F^- and increasing PCO_2 (lower pH).

The rate of anorthite dissolution increased linearly with decreasing solution pH for Exp. 3 (Fig. 6). The data indicate that the reaction is increasingly dependent on pH as the amount of F^- is increased. Since the reaction was done under pH free drift conditions (constant PCO_2) a time-averaged pH is plotted and the bars show the pH range over the linear release portion of the reaction. The various CO_2 partial pressures controlled the solution pH values within the indicated range (Fig. 6). At pH values less than 4.2 (suspension F12) the rate was not linear with pH, because the proton-promoted rate became a significant component of the total rate. Also plotted on Fig. 6 is the rate data for the dissolution of anorthite in the presence of 2.5 mM $Na_2C_2O_4$. The affinity of oxalate for oxide surfaces is approximately the same as that of fluoride (ŽUTIĆ and STUMM, 1984), and this also appears to be true for anorthite surfaces. From the data in Fig. 6 it is apparent that the effect of one mole of oxalate on the reaction rate is equivalent to 2 moles of F^-. We suspect that feldspar dissolution occurs at an activated complex with two adsorbed F^- ions or one oxalate ion. Since the alumino-sites are spa-

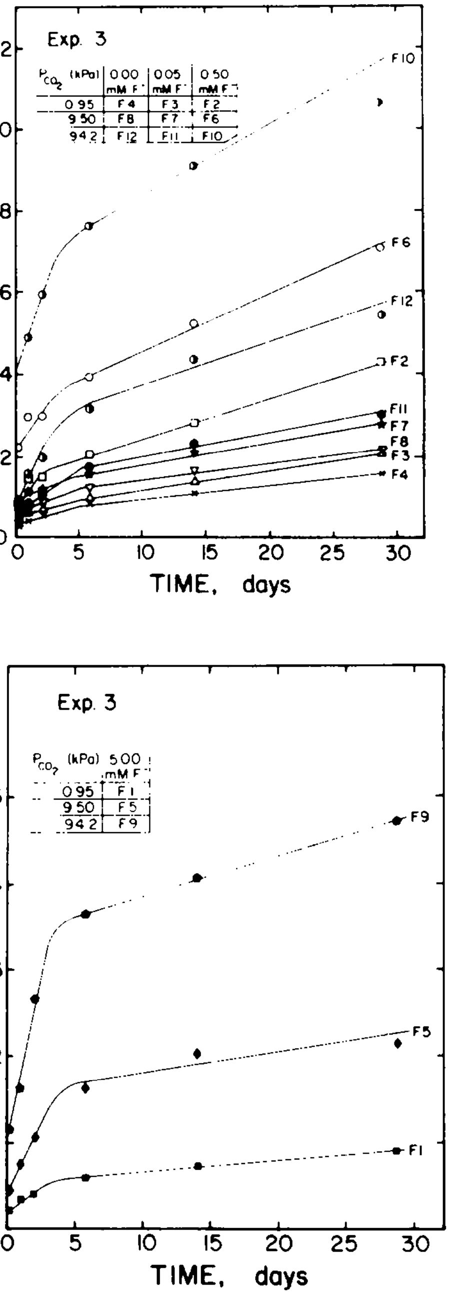

FIG. 5a, b. Experiment 3. Silica release from anorthite under constant pCO_2 (pH free drift) in the presence of F^-.

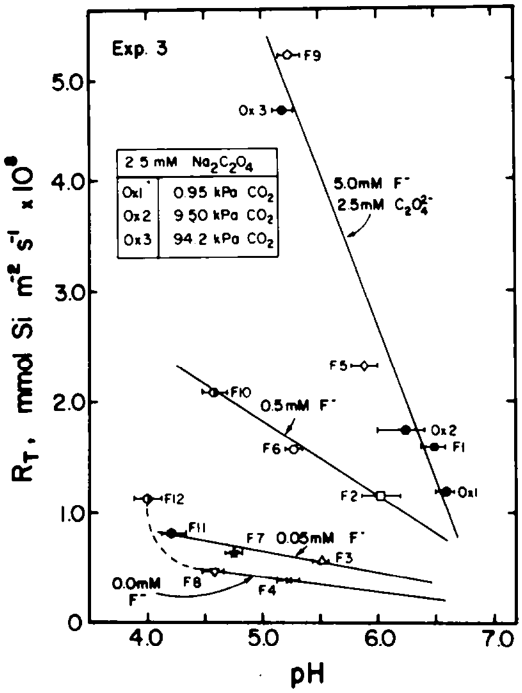

FIG. 6. Experiment 3. Linear dissolution rate *vs.* pH (constant pCO_2) at various concentrations of fluoride and oxalate. Point marks time averaged pH values and bars show the pH range over the time period that the rate was determined.

tially separated from one another by silicon-sites, an oxalate ion is unable to adsorb by bridging at two separate sites. Rather, it is forced to attach at a single alumino-site as constrained by the geometry of the surface and the size of the molecule. In other words, the oxalate ion forms a bidentate complex with an alumino-site.

The linear relationship between the dissolution rate and pH obtained in the presence of F^- (at intermediate pH values) is related to F^- adsorption. The dissolution data discussed above are in agreement with the F^- adsorption isotherms given in Figs. 7 and 8. That is, the dissolution data show an increasing effect of F^- as the pH decreases from 7 to 4 and the isotherms show increasing F^- adsorption with decreasing pH. At F^- concentrations up to 1.0 mM, the adsorption of F^- on anorthite was linear with concentration and pH.

An additional experiment was done to examine the effect of boric acid on the dissolution rate since other workers have used H_3BO_3 as a buffer and background constituent in dissolution studies (MAST and DREVER, 1987; KNAUSS and WOLERY, 1986). This experiment was a batch reaction at constant pH 5.0 ± 0.2 in a background of 5.0 mM NaCl with and without 0.5 mM $Na_2C_2O_4$ and/or 5.0 mM H_3BO_3. One ppm Hg^{2+} was added to all of these suspensions to retard the decomposition of oxalate (MAST and DREVER, 1987).

We found no effect of 5.0 mM H_3BO_3 on the dissolution reaction, either in the presence or absence of oxalate (data not shown). At pH 5.0, H_3BO_3 is largely a neutral species ($pK = 9.24$) and therefore does not adsorb on the feldspar surface. Thus, boric acid is not expected to affect the rate of dissolution at low to intermediate pH values.

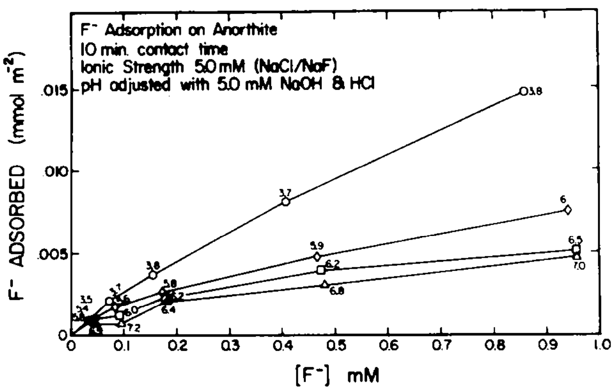

FIG. 7. Fluoride adsorption on anorthite in 5.0 mM NaCl/NaF (constant ionic strength). The solution pH is shown next to each point and the equilibration time was ten minutes.

Proton-promoted dissolution

Several rate laws have been proposed for oxide, silicate, and alumino-silicate dissolution kinetics (STÖBER, 1967; PACES, 1973; BUSENBERG and CLEMENCY, 1976; AAGAARD and HELGESON, 1982; BALES and MORGAN, 1985; CHOU and WOLLAST, 1985; TOLE *et al.*, 1986; FURRER and STUMM, 1986). The CHOU and WOLLAST (1985) model considers a back reaction involving Al^{3+}. Additional studies have shown no effect of Al on the rate of dissolution of anorthite (manuscript in preparation). Only the FURRER and STUMM (1986) model for oxide dissolution considers the effect of complexing ligands on the rate and the authors have suggested its use for describing the dissolution of alumino-silicates.

Several of these models are based on the concept that the rate is proportional to the solution hydrogen ion activity. That is:

$$\text{Rate} = k[H^+]^{\alpha} \qquad (2)$$

and a plot of log rate *vs.* pH yields a straight line with slope equal to α. For feldspar dissolution, the log rate *vs.* pH plots generally do not yield a straight line over all pH values. HELGESON *et al.* (1984) have proposed a two-region model made up of a pH-dependent reaction and a pH-independent reaction. For the pH dependent region (acidic), Eqn. (2) was

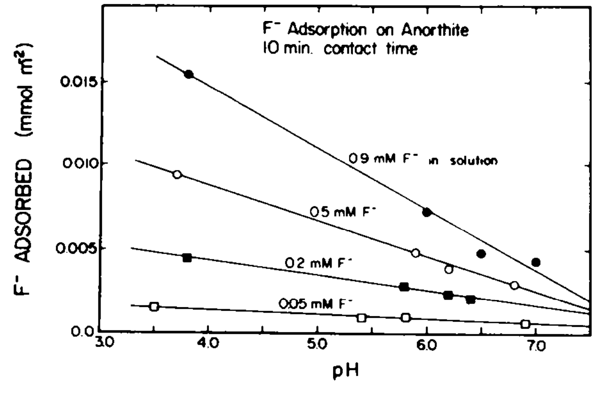

FIG. 8. Fluoride adsorption on anorthite plotted as a function of solution pH in 5.0 mM NaCl/NaF (constant ionic strength).

proposed to describe the dissolution of feldspars. Using data from several sources they determined that the equation was applicable at pH values < 2.9 (at 25°C) and that α was equal to 1.0. That is, the dissolution rate in the pH-dependent region was first order with respect to hydrogen ion activity. STUMM *et al.* (1985) reported fractional exponents that ranged from 0.33 to 0.8 for several other primary minerals. CHOU and WOLLAST (1985) reported dissolution data for albite with an exponent (α) equal to 0.5 in the acid-dependent region.

HELGESON *et al.* (1984) also reported that the dissolution reaction was pH-independent between pH 2.9 and 8.0. In the alkaline dissolution region (pH > 8) workers have found fractional exponents varying from 0.3 to 0.4 for albite dissolution (HELGESON *et al.*, 1984; CHOU and WOLLAST, 1985).

Figure 9 shows that the data for the three experiments, carried out in the absence of F^- and $C_2O_4^{2-}$, are not linear when plotted as log rate *vs.* pH. Rather, the graph shows pH-dependent and pH-independent regions as previously discussed. The pH-independent region had a rate of $10^{-8.6\pm0.1}$ mmol m^{-2} s^{-1} ($10^{-15.6}$ mol cm^{-2} s^{-1}) which is in excellent agreement with the value $10^{-15.5\pm0.3}$ mol cm^{-2} s^{-1}, reported by HELGESON *et al.* (1984) for anorthite, albite, and K-feldspar. A straight line fitted through our data from the acid-dependent data region (pH < 4.2) has a slope (α) of 2.7 which is larger than values previously reported for other minerals. There were insufficient data to determine accurately the pH *vs.* rate relationship in the alkaline region. Also plotted on Fig. 9 are model lines which will be discussed next.

The oxide dissolution model of FURRER and STUMM (1986) is similar to Eqn. (2) except that the acid-promoted dissolution rate is proportional to the concentration of adsorbed protons (Γ), that is:

$$R_H = k_H(\Gamma)^n \quad \text{when} \quad S - L = 0. \qquad (3)$$

The surface concentration of adsorbed protons and hydroxide ions as a function of pH is given in Fig. 10 for anorthite and shows that very few net protons or hydroxide ions are adsorbed from pH 5 to 9. The shape of this titration curve appears to most closely resemble those observed for SiO_2 (TADROS and LYKLEMA, 1967). WOLLAST and CHOU (1985) have postulated the formation of a residual layer at the albite surface which is enriched in Si. The pH at the point of zero net proton adsorption (pH ≃ 6.8) differs from the pH at the point of zero charge (PZC = 2.8) due to preferential removal of Ca^{2+} from the surface. The total number of sites was calculated from the potentiometric titration (Fig. 10) assuming the *pK* values occur at pH 2.8 and 10.7 and the titration is symmetrical about the *pK* values. This method only slightly overestimates the adsorption and the maximum number of sites as a result of dissolution reactions at low and high pH values. Based on calculated dissolution rates and a titration time of 5 minutes, less than 1.0% of the total acid or base consumed can be attributed to dissolution. Using the titration data the total number of sites was calculated to be 0.12 mmol m^{-2}.

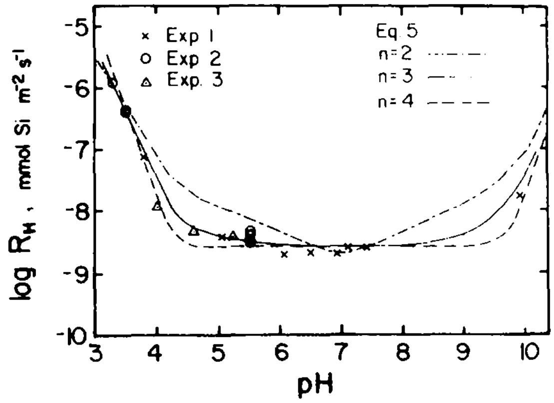

FIG. 9. The log of the proton-promoted rate *vs.* solution pH. Equation (4) plotted for n = 4 (dashed line), n = 3 (solid line), and n = 2 (dash/dot line).

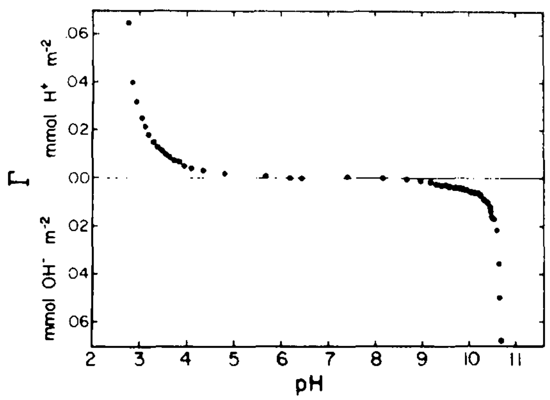

FIG. 10. Proton and hydroxide ion adsorption on the anorthite surface (20–50 μm) as determined by potentiometric titration with 5.0 mM HCl and 5.0 mM NaOH in 5.0 mM NaCl.

Figure 11 shows that log (R_H) *vs.* log (Γ) for anorthite is not linear and that feldspars do not behave in the same way as oxides. In order to model anorthite dissolution kinetics, we have expanded Eqn. (3) to include a rate of decomposition for the neutral surface species. In addition, it was assumed that the deprotonated surface species (SO^-) are as reactive as the protonated sites (SOH_2^+). This was assumed because the single high pH point from Exp. 1 fell on the line with the low pH data (Fig. 11). CHOU and WOLLAST (1985) found that albite dissolution was not symmetrical with respect to

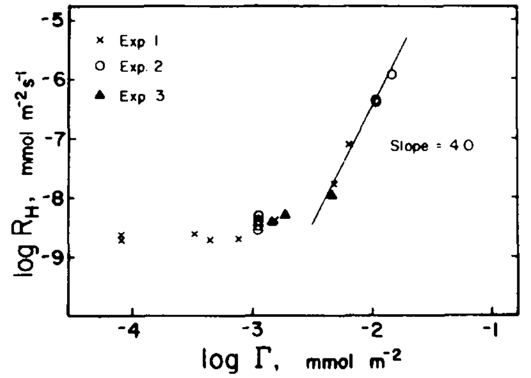

FIG. 11. The log of the proton-promoted rate *vs.* the log of the net concentration of adsorbed protons and hydroxide ions.

pH. No information was given on surface charging with pH so that nonsymmetrical dissolution may be attributed to nonsymmetrical surface charging with pH on albite.

The following equation was tested for its ability to model the dissolution data:

$$R_H = k_H(\Gamma)^n + k_0(\mathrm{SOH}) \tag{4}$$

where R_H is the proton/hydroxide-promoted rate in mmol m^{-2} s^{-1}, k_H is the dissolution rate constant for the activated complex, (Γ) is the net surface concentration of adsorbed protons and hydroxide ions in mmol m^{-2}, n is the slope of the log R_H *vs.* log Γ plot for the pH dependent reaction, k_0 is the dissolution rate constant for the uncharged surface sites in s^{-1}, and SOH is the concentration of uncharged sites in mmol m^{-2}. The product $k_0(\mathrm{SOH})$ is the rate of dissolution at $\Gamma = 0$. The uncharged sites (SOH) were calculated as the difference between the maximum number of sites as determined by titration and the number of charged sites. At most pH values SOH $\approx$ total sites and $k_0(\mathrm{SOH})$ is essentially a constant. At pH 3.3, 12% of the total sites are charged and at pH 9.9 only 4% are charged. Thus a simplifying assumption would be to keep $k_0(\mathrm{SOH})$ constant. The data in the pH-dependent region (pH < 4.2 and >9) have a slope of 4.0, $r^2 = 0.991$ (Fig. 11). Plotted on Fig. 9 are the lines for values of $n = 3$ and $n = 2$. The value of $n = 3$ fits the transition region between pH 4.2 and 5.5 a little better than $n = 4$, and $n = 2$ fits the data the poorest. It appears that there may be two different surface activated sites on anorthite. The proton/hydroxide-promoted sites are likely Si centered and the ligand-promoted sites Al centered. This is in agreement with the potentiometric titration data discussed above and the observation that the Si oxidation state is 4 and $n = 4.0$. This also agrees with the observation of FURRER and STUMM (1986) that for oxides the ligand-promoted sites are independent of the proton-promoted sites. The dissolution rate of chrysotile ($Mg_3Si_2O_5(OH)_4$), which lacks Al, is almost unaffected by oxalate and catechol (BALES and MORGAN, 1985) and therefore supports the postulate that Al is the reactive metal center for organic ligands.

Ligand-promoted rate

The ligand-promoted rate (R_L) was determined as the difference between the total rate (R_T) and the proton-promoted rate (R_H). Figure 12 shows the relationship between ligand-promoted rate and the concentration of adsorbed $F^-(S - L)$ from experiments 2 and 3. The concentration of adsorbed $F^-(S - L)$ was determined from Fig. 8 after correcting for F^- ion pairs using a modified GEOCHEM program (PARKER *et al.*, 1987). The slope of this line is k_L, the ligand-promoted rate constant.

This ligand-promoted rate can be incorporated into the model by adding the term $k_L(S - L)$ to Eqn. (4) resulting in the overall equation as follows:

$$R_T = k_H(\Gamma)^n + k_0(\mathrm{SOH}) + k_L(S - L). \tag{5}$$

The following constants were determined for anorthite dissolution from pH 3 to 10 and F^- and oxalate concentrations up to 1.0 mM and in the absence of back reactions:

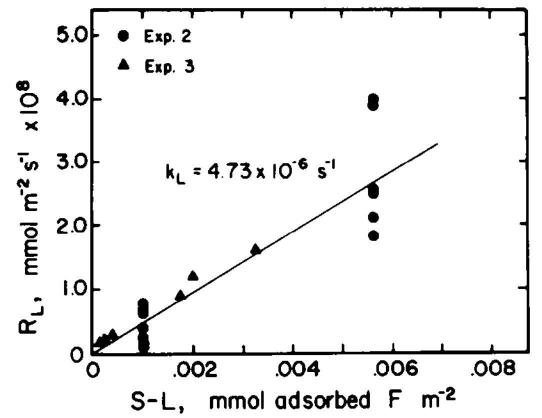

FIG. 12. Ligand-promoted dissolution rate *vs.* the concentration of adsorbed fluoride (experiments 2 and 3).

$$R_T = 37.0(\Gamma)^{4.0} + 2.09 \times 10^{-8}(\mathrm{SOH}) + 4.73 \times 10^{-6}(S - L). \tag{6}$$

The rate of anorthite dissolution in the presence of 0.5 mM oxalate (Exp. 4) at pH = 5.0 was measured at 6.26×10^{-8} mmol m^{-2} s^{-1} and was not used in the determination of the model. Assuming that adsorption and reactivity of oxalate are equal to F^-, the estimated rate of reaction using Eqn. (6) is 6.00×10^{-8} mmol m^{-2} s^{-1} which is very close to the measured rate. This confirms the observation that oxalate has the same effect as fluoride on dissolution rate and supports the proposed model.

Figure 13 shows the predicted rate *vs.* measured rate for all of the data from experiments 1, 2, 3, and 4 which covers a span of over 3 orders of magnitude in rate. The one to one agreement is good at the higher rates and mediocre at low rates. This poor fit at low rates is being investigated and may be due to a steady decrease in rate with repeated use of the mineral.

Applying this model to various F^- concentrations shows that the ligand-promoted rate is a significant component of the total rate in the pH region from 3.5–8.5 (Fig. 14) and that it makes the overall-rate dependent on pH in the intermediate pH range. This is in contrast to the pH independence in the absence of complexing ligands (Fig. 1). The reason for this dependence is the pH dependence of ligand adsorption. This has important implications for the weathering of feldspars in natural systems. In most natural systems (pH 4.5–7.5), the presence of organic ligands make the weathering rate of anorthite dependent on pH. The organic ligand concentration and pH have a synergistic effect on feldspar dissolution kinetics.

The relationship between feldspar composition and organic ligand reactivity is shown in Fig. 15. MAST and DREVER (1987) showed no effect of oxalate on the dissolution of oligoclase (An_{12}) at pH 4. ERICH and BLOOM (1987, and pers. commun.) showed that 0.1 mM oxalate at pH 4 increased the dissolution rate of labradorite (An_{54}) 132% over dissolution in the absence of oxalate. This study with anorthite (An_{93}) showed a 221% increase in dissolution rate under comparable conditions. Increases in the mole fraction of Ca

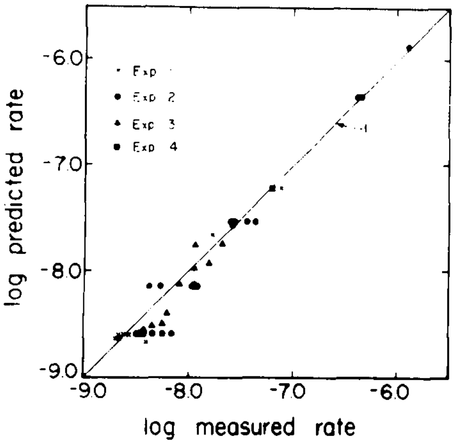

FIG. 13. Measured rate *vs.* predicted rate for all data from experiments (1, 2, 3, and 4). Predicted rates were calculated using Eqn. (6).

in the plagioclase increases the relative reactivity of the feldspar towards organic ligands due to a higher proportion of Al in the structure. The findings of HUANG and KIANG (1972) show the qualitative effect of organic acids toward various plagioclase minerals. All five of the plagioclase minerals studied, had nearly the same dissolution rate in water. The rate of dissolution of these feldspars in organic acids was proportional to the anorthite mole fraction of the minerals. This observation is attributed to the increased Al content of the high-Ca plagioclase minerals, rather than to the high Ca content. The concept that the ligand-promoted rate is dependent on the Al sites is supported by the finding that there is no effect of oxalate or catechol on chrysotile dissolution (BALES and MORGAN, 1986).

Since HELGESON *et al.* (1984) have shown (from recalculated data) that the proton-promoted dissolution rates of albite, anorthite, and K-feldspar are all approximately equal, the observations in nature that Ca-rich feldspars weather faster than Na-rich feldspars (GOLDRICH, 1938; CLAYTON, 1988) can be attributed to the effect of organic ligands on the dissolution rate. That is, organic ligands show increasing reactivity toward feldspars with increasing Al (anorthite) composition. In general, the degree to which organic ligands increase the dissolution of silicates depends on their Al content. Since Fe also has a high affinity for ligand-complexation, the reactivity of organics towards Fe-containing silicates is probably directly proportional to their Fe content as well.

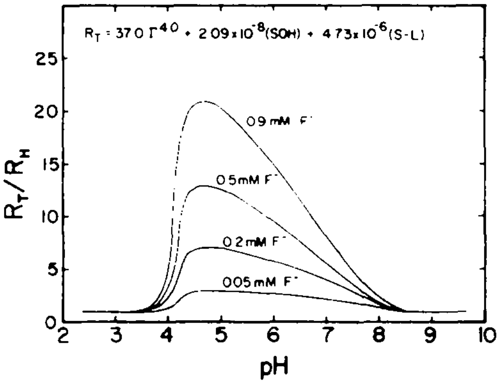

FIG. 14. Model predictions (Eqn. 6) for the ratio of proton + ligand-promoted dissolution rate to proton-promoted rate for various solution F^- concentrations.

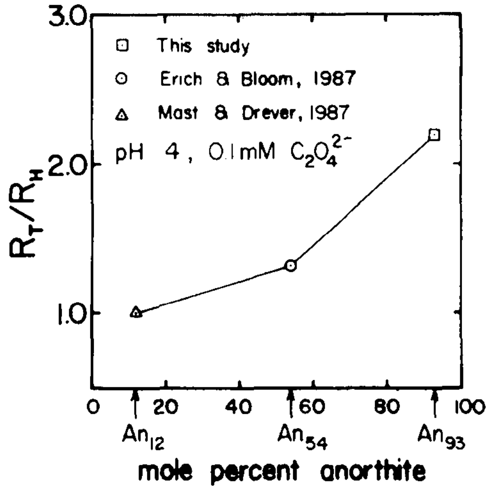

FIG. 15. The effect of oxalate on the dissolution rate relative to the rate in the absence of oxalate at the same pH *vs.* the mole percent Ca in the plagioclase. A ratio of 1.0 represents no effect of oxalate on the rate of dissolution.

CONCLUSIONS

The dissolution of anorthite was found to be nearly pH independent between pH 5 and 9 in the absence of complexing ligands. In the presence of complexing ligands (F^- and $C_2O_4^{2-}$) the rate becomes linearly proportional to pH, between pH 4.2 and 9. At pH values less than 4.2, the proton-promoted rate was much more significant than the ligand-promoted rate. The data were modeled using a surface complexation model with two types of reactive sites. The proton-promoted dissolution appears to occur at Si centered sites and the ligand-promoted dissolution at Al centered sites. In addition, the hydrolysis of uncharged Si sites contributes to the dissolution, especially in the pH-independent region. The proton-promoted rate was proportional to the net concentration of adsorbed protons raised to the fourth power. This is in agreement with the postulate of FURRER and STUMM (1986) that the exponent is equal to the oxidation state of the metal center. The ligand-promoted rate of dissolution was linearly proportional to the concentration of adsorbed ligand and is also in agreement with the findings of FURRER and STUMM (1986) on oxides.

The susceptibility of plagioclase minerals to organic ligand attack is proportional to Al content, *i.e.* anorthite mole fraction.

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