An integrated model for feldspar dissolution under acid conditions

S.L. Brantley

L. Stillings

Department of Geosciences, Pennsylvania State University,
University Park, PA 16802, USA.
Department of Geological Sciences, University of Wyoming,
Laramie, Wyoming, USA.

Introduction

The global estimate of albite weathering as calculated from the flux of Na in rivers to the oceans, 10^{12} mol albite/y, is three orders of magnitude slower than the estimate based on laboratory measurements of albite dissolution at neutral pH, 10^{15} mol albite/y. To explain the discrepancy, geochemists have discussed effects ranging from hydrologic factors and the estimation of surface area in weathering lithologies to inhibition caused by oxide or organic coatings. However, scrutiny of the literature of laboratory feldspar dissolution reveals several discrepancies between experimental results and current models for dissolution, emphasizing that we are still unable to propose mechanism-based rate equations for feldspar, the most common rock-forming mineral of the earth's crust. Only with better insight into the mechanism of dissolution will we be able to predict mechanism-based weathering kinetics.

Experiments and theories of feldspar dissolution

Early theories of feldspar dissolution can be classified by the assumption of rate-limiting step: either 1) diffusion-limited leaching; or 2) surface-limited reaction models. Recently, Blum and Lasaga (1988, 1991) and Schott (1990) have adapted the surface protonation model for simple oxides to albite. This model has also been used by Amrhein and Suarez (1988) for anorthite, Brady and Walther (1992) for albite, and Schweda (1990) for microcline, and these models represent the current paradigm for feldspar dissolution. These models assume that the dissolution rate, R (mol/area s), at low pH is a function of the areal concentration of protonated surface sites, $[\equiv SOH]$ (mol/area):

$$R = k[\equiv SOH]^n \qquad (1)$$

where k is the rate constant, and n is the reaction order with respect to the surface species Schott (1990), Blum and Lasaga (1991), and Brady and

Walther (1992) argue that protonation of Al sites explains the pH-dependence of feldspar protonation at low pH.

Titration of feldspar-water suspensions with acid allows measurement of $[\equiv SOH]$ on the feldspar surface. For example, we have measured proton uptake onto microcline during slurry titrations as a function of ionic strength. Once a correction is made to remove the contribution of protons exchanged for potassium, the ionic strength dependence of proton adsorption on feldspar is insignificant. According to the proton-promoted dissolution model, therefore, feldspar dissolution should not be ionic strength dependent. However, Sjoberg (1989), Schweda (1990), and Stillings and Brantley (subm.) have documented that feldspar dissolution decreases with increasing ionic strength.

This contradiction suggests that a new rate model is needed that can explain these and other observations such as: 1) Steady-state dissolution rate of feldspar increases with increasing temperature, decreasing pH, and decreasing salt concentration in solution. 2) Surface hydration (permeation of protons and water into the surface) of feldspar also appears to increase with increasing temperature, decreasing pH, and decreasing salt concentration in solution. 3) Feldspar surfaces show alkali- and aluminum-leaching at low pH (< 6), and depth of leaching increases with decreasing pH and decreasing salinity of leachant solutions. 4) Dissolution is proportional to $\{H^+\}^{0.5}$ for both albite and microcline dissolution. 5) Rate of dissolution of albite and microcline are roughly similar; however, increasing the anorthite component increases the dissolution rate. 6) TMAC adsorbs onto siloxane sites on the silica surface; the presence of TMAC in solution also causes a decrease in feldspar dissolution rates. We propose a rate model for dissolution of feldspar under acid conditions which is based on the fact that at steady state, all feldspars dissolve stoichiometrically. Although dissolution occurs stoichiometrically, constant thickness leached layers form where dissolution

occurs in acidified dilute solutions. The rate-limiting step of dissolution is not diffusion through this leached layer, but rather, hydrolysis of the Si–O–Al bridging oxygens which accelerates the rate of silica network opening. We can predict an equation for the rate of this reaction:

$$R = k[Q_k^{Al}H] \qquad (2)$$

where k is the rate constant, and $[Q_k^{Al}H]$ refers to the number of moles of proton exchanged aluminum sites in the entire layer normalized by surface area. Note that this model differs from that of Blum and Lasaga (1991) in assuming that proton-exchanged rather than proton-adsorbed sites promote dissolution.

To predict the rate of this reaction, we need to predict the concentration of proton-exchanged aluminum-centered sites, $[Q_k^{Al}H]$. We can follow the derivation of Doremus (1975) and show that our proposed mechanism implies that the rate of dissolution is directly proportional to the leached layer thickness, D/a:

$$R = kc_{surf}^{Q_k^{Al}H}\left(\frac{D}{a}\right) \qquad (3)$$

where D is the diffusion coefficient for the surface leach layer, a is the linear rate of dissolution, and $c_{surf}^{Q_k^{Al}H}$ is the surface concentration of protonated aluminum sites. Because the leached layer thickness is a function of the concentration of proton-exchanged sites on the surface, the equation can be further simplified, and a Langmuir competitive isotherm can be used to describe the concentration of proton-exchanged sites on the surface:

$$R = k\left(\frac{k_H\{H^+\}}{1 + K_H\{H^+\} + K_M\{M^{b+}\}}\right) \qquad (4)$$

where R is the area-normalized rate of feldspar dissolution at steady state, k is the rate constant, K_H and K_M refer to the adsorption constants for H^+ and M^{b+} adsorption onto the exchange site, and the braces refer to activities of dissolved species. Where $n = 0.5$, the model predicts a pH dependence similar to that observed by Chou and Wollast (1984) for albite or Schweda (1990) for microcline. The model also predicts that increasing the concentration of dissolved M^{b+} inhibits the dissolution, as observed.

Conclusions

Because we have observed that dissolution rate and ion exchange of the feldspar surface are ionic strength dependent but proton adsorption is not, our model assumes that ion exchange controls the hydrolysis of Si within the leached, hydrated surface layer. The observed rate-inhibiting effect of dissolved salts is directly related to the inhibition of leaching within the surface: in quartz and kaolinite, where leached layers do not form, dissolved salts accelerate rather than inhibit dissolution. The rate of feldspar dissolution is therefore slowest at neutral pH where no leached layers form.

References

Amrhein, C., and Suarez, D.L. (1988) *Geochim. Cosmochim. Acta*, **52**, 2785–93.
Blum, A.E. and Lasaga, A.C. (1988) *Nature*, **331**, 431–3.
Blum, A.E. and Lasaga, A.C. (1991) *Geochim. Cosmochim. Acta*, **55**, 2193–201.
Brady, P.V. and Walther, J.V. (1992) *Amer. J. Sci.*, **29**, 639–58.
Chou, L., and Wollast, R. (1984) *Geochim. Cosmochim. Acta*, **48**, 2205–17.
Doremus, R.H. (1975) *J. Non-crystalline Solids*, **19**, 137–44.
Schott, J. (1990) Modeling of the dissolution of strained and unstrained multiple oxides: The surface speciation approach. In *Aquatic Chemical Kinetics* (ed. W. Stumm), John Wiley and Sons, New York, 337–66.
Schweda, P. (1990) *Kinetics and mechanisms of alkali feldspar dissolution at low temperatures*, Ph.D. dissertation, Department of Geology and Geochemistry, Stockholm University, 99p.
Sjoberg, L. (1989) Kinetics and non-stiochiometry of labradorite dissolution. In *Proc. of the 6th International Symp. on Water-Rock Interactions* (ed. D.L. Miles), Malvern, United Kingdom, A.A. Balkema, Rotterdam, 639–42.
Stillings, L.L. and Brantley, S.L. (subm) *Geochim. Cosmochim. Acta.*