

Altered layers on dissolving albite. II. Model

Carrick M. Eggleston
Stanford University, Stanford CA, U.S.A.

Roland Hellmann
Universite Paul Sabatier - C.N.R.S., Toulouse, France

ABSTRACT: In an X-ray photoelectron spectroscopy study of hydrothermally altered albite (see Hellmann et al., this volume) we found that Na and Al were preferentially removed from the surface, forming leached layers nearly 1000 Å thick (depending on pH). In this paper we use the Michalske-Freiman (1983) model for breakage of Si-O-Si linkages, together with molecular orbital calculations, to construct a mechanistic conceptual model for leached layer formation and network dissolution which is consistent both with surface reaction rate control and with the formation of thick leached layers. We propose that the leached layers consist of partially depolymerized and repolymerized silicate species.

1 INTRODUCTION

As water moves over or through rocks or soils, chemical reactions occur which directly affect both the composition of the water and often the composition and structure of mineral surfaces. Understanding these reactions is crucial to our ability to predict the chemical evolution of fluids in watersheds, aquifers, diagenetic environments, and hydrothermal systems. Many of these settings are also focal points of environmental concerns, such as acid rain and groundwater contamination, which have focused scientific attention on short term geochemical processes in which chemical kinetics is a necessary part of predictive modeling efforts.

In particular, several models have been proposed to describe mineral dissolution. These can be generally grouped into diffusion models and surface-reaction models; silicate dissolution is now generally thought to be surface-reaction controlled. Most recently, surface-complexation models (e.g. Pulfer et al., 1984; Furrer and Stumm, 1986; Blum and Lasaga, 1988) have extended the surface-reaction concept to the description of the pH-dependence of dissolution rates.

However, the mechanisms by which surface complexes accelerate or retard dissolution are not understood. Aagaard and Helgeson (1982), among others, use transition state theory (TST) to interpret feldspar dissolution and postulated the formation of activated complexes of the form $(\text{H}_3\text{O}^+)\text{AlSi}_3\text{O}_8(\text{H}_3\text{O}^+)$ (for acid conditions). However, such stoichiometric activated complexes are not consistent with the formation of altered layers that we and others observe; Petit et al. (1987), Nesbitt and Muir (1988), Mogk and Locke (1988), and Casey et al. (1988) have found alteration of feldspar and chain silicate surfaces

to depths of over 1000 Å as a result of dissolution in natural and laboratory settings at 25 to 75°C.

Our combined X-ray photoelectron spectroscopy (XPS) and dissolution rate/stoichiometry results for hydrothermally altered albite (presented in Hellmann et al., this volume) show similar deep alteration, but suggest that dissolution is nevertheless not rate-controlled by transport of reactants and products through the leached layers. The purpose of this discussion is to propose a mechanistic conceptual model for dissolution which is consistent both with surface-reaction rate-control and with the formation of altered layers.

2 HYDROLYSIS REACTIONS

It is clear that dissolution must proceed via the rupture of various bonds at mineral surfaces in contact with water. Na-O, Al-O, and Si-O bonds in albite have different strengths and should therefore rupture at different rates during aqueous attack. The dissolution rate and the formation of leached layers both depend on the relative strengths of these bonds under various aqueous conditions.

2.1 Ion exchange

Upon initial contact of albite with water, Na^+ exposed at the surface exchanges for H^+ or H_3O^+ in the solution (see Chou and Wollast, 1984; Blum and Lasaga, 1988). The sequential, angle-resolved XPS results of Eggleston et al. (1987) show that most of the sodium is removed from a thin surface layer within the first hour of albite immersion. Low energy electron

diffraction (LEED), which is a probe of surface structure, shows that no significant changes in the surface diffraction pattern take place during $\text{Na}^+=\text{H}^+$ exchange (Eggleston et al., 1989), suggesting that little if any disruption of the aluminosilicate network takes place. Further release of Na^+ must await the breakage of Al-O-Si and Si-O-Si linkages so as to provide access to deeper Na^+ sites. The remainder of the discussion thus focuses on the mechanisms of hydrolysis of the aluminosilicate network.

2.2 Network hydrolysis

The hydrolysis reactions described below are treated within the framework of transition state theory. We (Hellmann et al., this volume) postulate the formation of activated complexes at bridging oxygen (O_{br}) sites. The mechanisms of bond rupture have been studied in the silicate fracture literature; our formulation follows the Michalske-Freiman (1983) model, which defines steps in the reaction of H_2O with an O_{br} linkage:

Step 1 (fig. 1a): A water molecule is adsorbed at the siloxane when the lone pair on the water interacts with an Si and a proton from the water forms a hydrogen bond with the O_{br} . Step 2 (fig. 1b): the Si- O_{br} and O-H bonds in the siloxane and water, respectively, cleave to form two silanol groups. Step 3 (fig. 1c): Hydrogen bonded silanol groups may dissociate to form isolated silanol groups. This basic sequence of steps is used to describe bond breakage during slow fracture of silicate glasses (Michalske and Bunker, 1984) and quartz (Atkinson and Meredith, 1981).

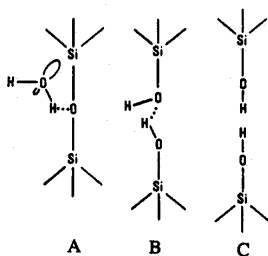


Fig. 1 Idealized representation of reaction between water and an Si-O-Si linkage. Steps A - C are discussed in the text. A. Adsorption of water at O_{br} . B. Cleavage of an Si-O bond and dissociation of water. C. Formation of silanols. After Michalske and Freiman (1983).

Using TST we may write the reaction as follows:



where \ddagger designates an activated complex in which an Si-O bond is breaking. Although several elementary

reactions must take place (adsorption, dissociation of H_2O , etc.) during this overall reaction, we have chosen the breakage of the Si-O bond as the "critical" activated complex because it is likely to be the slowest, and therefore rate-controlling, elementary reaction occurring during the sequence of fig. 1. TST assumes that an equilibrium is established between reactants (in this case H_2O) and the activated complex:

$$K^\ddagger = \frac{[\text{act.cpx}]^\ddagger}{[\equiv\text{Si}-\text{O}-\text{Si}\equiv][\text{H}_2\text{O}]} \quad (2)$$

Using classical rate theory we write the rate equation:

$$\text{Rate} = k'[\text{act.cpx}]^\ddagger \quad (3)$$

which can be rearranged using eqn (2) to give

$$\text{Rate} = k'K^\ddagger[\equiv\text{Si}-\text{O}-\text{Si}\equiv][\text{H}_2\text{O}] \quad (4)$$

The values of k' and K^\ddagger can be calculated using the Eyring equation, which relates the energetic configuration of the reactants and of the activated complex to the reaction rate:

$$\text{Rate} = \kappa(kT/h) \frac{q^\ddagger}{q_A q_B} \left[\exp[E_a/RT] \right] (A)(B) \quad (5)$$

where κ = transmission coefficient, T is $^\circ\text{K}$, h is Planck's constant, q 's are partition functions describing the partitioning of energy between the accessible vibrational, rotational, and translational energy levels of the system, E_a is an activation energy, and R is the gas constant. (A) and (B) are reactant concentrations, in this case $[\equiv\text{Si}-\text{O}-\text{Si}\equiv]$ and $[\text{H}_2\text{O}]$. We may generalize eqs. (1) - (5) for different kinds of reactants (i.e. $A = \text{H}_2\text{O}, \text{H}_3\text{O}^+, \text{H}^+, \text{OH}^-$, etc. and $B = \text{Al}-\text{O}-\text{Si}$ or $\text{Si}-\text{O}-\text{Si}$ linkages in albite). The partition functions and E_a 's for these various reactants, and therefore also of the activated complex, are likely to be different, resulting in different reaction rates. It is important to point out that eqn (5) describes the rate of breakage of O_{br} linkages, not the dissolution rate. The dissolution rate, defined as the rate of release of, for example, Si to bulk solution, is related to eqn. (5) in a somewhat complicated way which we discuss below.

It is beyond the scope of this paper to attempt a rigorous calculation of reaction rates using eqn. (5). However, Hellmann et al. (this volume) point out that the pH dependence of our Si release rate and leached layer thickness results are qualitatively consistent with the energetics of interaction of H^+ , H_3O^+ , OH^- , and H_2O with O_{br} sites given by molecular orbital (MO) calculations (de Jong and Brown, 1980b). The preferential leaching of Al over Si that we observe can be explained by MO calculations (de Jong and Brown, 1980a and Geisinger et al., 1985) which show that Al- O_{br} bonds have a smaller overlap population than Si- O_{br} bonds and are thus somewhat weaker. The pH dependence of albite dissolution observed by Knauss and Wolery (1986) and Blum and Lasaga (1988) is also consistent with eqn. (5). Casey et al. (1988) used a similar TST/partition function argument to rationalize the isotope dependence ($\text{H}_2\text{O}-\text{HCl}$ vs. $\text{D}_2\text{O}-\text{DCl}$) of labradorite dissolution.

Thus it seems reasonable to use the breakage of O_{br} linkages, faster at $Al-O_{br}$ bonds and slower at $Si-O_{br}$ bonds, as a conceptual framework with which to interpret the depolymerization of the aluminosilicate network of albite.

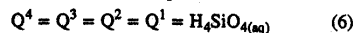
3 DEPOLYMERIZATION/REPOLYMERIZATION

3.1 Depolymerization

In bulk albite, Al and Si are tetrahedrally coordinated by O, and each O is shared between two tetrahedra. Therefore, for hydrolysis of O_{br} linkages to release a molecule of silicic acid (H_4SiO_4) to solution, for example, each of the four O_{br} linkages around an Si must be broken. We adopt the Q^n notation, where n = the number of O_{br} around an Si. Thus, if we break an O_{br} bond between two Q^4 species, we create two Q^3 species via eqn (1). Hydrolysis of the remaining O_{br} linkages will create a population of $Q^{n<3}$ species. Similar depolymerization applies to the hydrolysis of tetrahedrally coordinated Al, but with the added complication that Al becomes octahedrally coordinated by water.

If, as we have argued above, Al-O bonds break more quickly than Si-O bonds, we can envision a reaction sequence such as that shown in fig. 2. Fig. 2a shows an Al site after initial ion exchange (see above); fig. 2 b shows an Al site with two of the O_{br} linkages broken (H_2O or OH coordinating the Al are not shown). Fig. 2c shows complete removal of the Al, leaving residual silanol groups. The silanol groups are thought to behave amphotericly; at low pH, they adsorb H^+ to become $Si-OH_2^+$. Such positively charged sites can affect the strength of remaining O_{br} linkages (providing a mechanistic basis for surface-complexation models) as well as provide adsorption sites for negative ions such as Cl^- . We have observed invasion of leached layers by Cl^- during dissolution of albite in HCl solutions (see Hellmann et al., this volume).

In well ordered low albite, leaching of Al via the steps in fig. 2 creates a population of Q^3 species within the leached layer. Continued depolymerization via eqn (1) will lead to creation of Q^2 and Q^1 species. We propose that eventually a steady state is reached in which detachment of Q^1 species equals the rate at which they are created by depolymerization of $Q^{n>1}$ species. As dissolution proceeds at steady-state, Q^4 species within albite (and presumably of other silicate minerals) must traverse the sequence



Therefore, the surface region of dissolving minerals should consist of these partially depolymerized $Q^{n<4}$ species. The = signs in eqn (6) are meant to allow for the possibility of back reactions, i.e. repolymerization (discussed below).

Evidence for partially depolymerized silica in dissolving silicate near-surface regions exists in the literature. On the basis of site density arguments, Yates and Healy (1976) postulate a three-dimensional

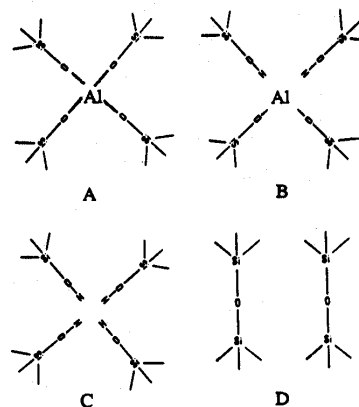


Fig. 2 Idealized representation of a sequence of depolymerization and repolymerization reactions resulting in leaching of Al and a reduced O/Si ratio (as we observe with XPS; see Hellmann et al., this volume). The sequence is discussed in the text.

layer of OH-bearing species on precipitated amorphous silica. Similar conclusions are reached by Fleming (1986) and Zaborski et al. (1989). Kulkarny (1972) and Kulkarny and Somasundaran (1977) attribute variations in the electrokinetic behavior of quartz to variations in the number of partially polymerized silica species at the surface after aging in pretreatment solutions. Miller and Linton (1985) present XPS evidence for the formation of silanol groups in amorphous SiO_2 after hydrothermal attack. Bunker et al. (1988) present strong Raman and NMR evidence supporting the formation of silanols and partially polymerized species in glass surfaces during leaching of boron from a borosilicate glass.

3.2 Repolymerization

In addition to depolymerization reactions, there is strong evidence that residual silanol groups may repolymerize (e.g. see Casey et al., 1988, and Bunker et al., 1988) as suggested in eqn (6). Such repolymerization is illustrated in fig. 2d. Repolymerization reactions of this type can create an open, porous structure within the leached layer; the structure is also probably distorted (see Bunker et al., 1988). It is important to note that in going from fig. 2c to fig. 2d via the reverse of eqn. (1), two oxygens are lost relative to both the original albite and to the leached albite. This is consistent with the reduced O/Si ratio we observe in leached layers on hydrothermally altered albite (Hellmann et al. this volume).

4 CONCLUDING COMMENTS

We have presented a conceptual model designed to explain our observation of formation of thick (ca. 1000Å) leached layers on dissolving albite (see Hellmann et al., this volume, for the spectroscopic results). It is hoped that these mechanistic arguments will be of use in explaining leached layer formation on other minerals, as well as in providing insight into the reactivity, structure, and chemical nature of mineral surfaces resulting from dissolution reactions.

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