

## INFLUENCE OF POLYMERIZATION ON SILICATE GLASS AND MINERAL DISSOLUTION: CALCULATED REACTION PATHS AND ACTIVATION ENERGIES USING *AB INITIO* METHODS.

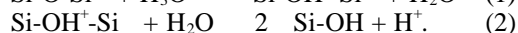
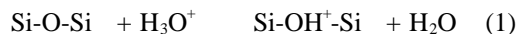
L. J. Criscenti, S. L. Brantley, and J. D. Kubicki. Department of Geosciences, Pennsylvania State University, University Park, PA 16802 (louise@geosc.psu.edu).

**Introduction:** The rate-limiting step for quartz and feldspar dissolution is thought to be the hydrolysis of either Si-O-Si or Si-O-Al bonds. However, the rates of silicate dissolution are a function of polymerization [1]. For example, the dissolution rate for a fully-polymerized structure such as quartz is slower than that for a depolymerized structure such as enstatite. In silicate glasses, silanol groups promote the hydrolysis of adjacent Si-O-Si bonds, leading to depolymerization and dissolution of the silicate network [1]. Therefore, groups of  $Q^1_{Si}$  (Si sites with one bridging O and three non-bridging O) depolymerize more readily than  $Q^2_{Si}$ ,  $Q^3_{Si}$ , and  $Q^4_{Si}$  groups. For aluminosilicate dissolution, Hamilton et al. [2] have hypothesized that the hydrolysis of  $Q^1_{Al}OQ^1_{Si}$  may be slower than the hydrolysis of  $Q^m_{Si}OQ^n_{Si}$  ( $m, n \geq 3$ ). In this study, we investigate this hypothesis with *ab initio* methods to calculate the reaction paths and activation energies for the hydrolysis of  $Q^1_{Si}$ ,  $Q^2_{Si}$ , and  $Q^3_{Si}$  model clusters. By evaluating relative activation energies for the dissolution of different silicate species, we plan to evaluate the relative rates of dissolution.

**Approach:** Initial calculations to model dissolution have been performed by bringing  $H_3O^+$  into close proximity with a bridging O near the  $Q^1_{Si}$ ,  $Q^2_{Si}$ , and  $Q^3_{Si}$  model clusters in a manner similar to that used in previous work [3,4]. We approximated these mineral surface species with  $H_6Si_2O_7$ ,  $H_8Si_3O_{10}$  and  $H_{10}Si_4O_{13}$  clusters, respectively. A  $Q^3_{Si}$  has one SiOH surface site and is bonded to three bridging O atoms that link it to the bulk structure (Fig. 1). Four water molecules were included in each cluster to account for short-range solvation of  $H_3O^+$  and one surface SiOH group.

We used Hartree Fock calculations with the basis set (3-21G(p,d)) to optimize cluster geometries along silicate dissolution paths and to calculate frequencies to identify stable and transition-state configurations. Geometry optimizations for stationary points and transition states were also calculated using a hybrid density functional theory method, B3LYP/6-31G(d), to improve calculated energies and structures. Reaction paths were calculated in both forward and backward directions to establish the lowest energy pathway on the potential energy surface given one constrained interatomic distance. This approach differs from that of Pelmenschikov et al. [5] who modeled  $Q^3_{Si}$ ,  $Q^2_{Si}$ , and  $Q^1_{Si}$  hydrolysis with  $H_2O$ , neglecting the effects of solvation, assuming a single transition-state, and fixing a crystalline framework.

**Results:** We studied the reaction path for  $Q^3_{Si}$  in the most detail. At least two elementary steps, proton transfer and hydrolysis, are involved in dissolution:



Preliminary results suggest that these two steps are also critical to the dissolution of  $Q^1_{Si}$  and  $Q^2_{Si}$ . Fig. 1 shows that each of these two steps is coincident with a maximum in system energy. After the formation of  $Si-OH^+-Si$ , the  $H_2O$  molecule is progressively constrained to approach  $Q^3_{Si}$  until Si becomes 5-coordinate. Continuing to decrease the bond length between  $H_2O$  and  $Q^3_{Si}$  results in Reaction (2).

Each energy barrier should be associated with a transition state defined by a saddle point on the potential energy surface. Calculated frequencies for each maximum in energy include one imaginary frequency, suggesting that these optimized geometries represent transition state configurations.

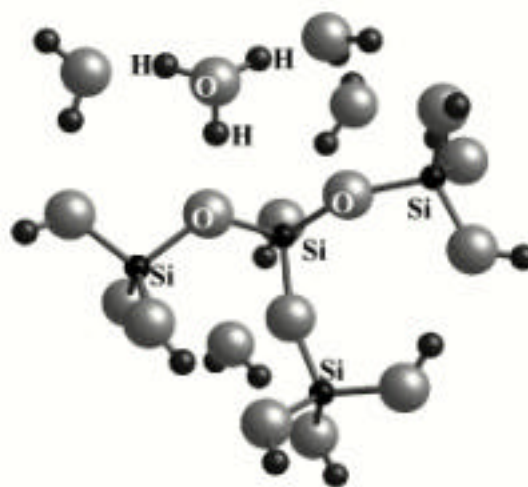


Fig. 1. Initial  $H_{10}Si_4O_{13}-H_3O^+ \cdot 4(H_2O)$  cluster.

Single point calculations using DFT theory on the HF/3-21G(d,p) structures predict that the  $E_a$  for protonating the bridging O is +137 kJ/mol, and the  $E_a$  for Si-OH<sup>+</sup>-Si bond-breaking is +161 kJ/mol. These

$E_a$  are high, so we are re-optimizing these clusters with B3LYP/6-31G(d) calculations. The calculated change in energy for the complete reaction is +44 kJ/mol. Comparison of reaction path calculations for  $Q^3_{Si}$ ,  $Q^2_{Si}$  and  $Q^1_{Si}$  will provide a basis to evaluate the effects of silicate polymerization on silicate dissolution rates.

**References:** [1] Bunker B. C. et al. (1988) *Phys. Chem. Glasses*, 29, 106-120. [2] Hamilton J. et al. (submitted). [3] Xiao Y. and Lasaga A. C. (1994), *GCA*, 58, 5379. [4] Pelmenschikov A. et al. (2000) *J. Phys. Chem. B*, 104, 5779-5783.