ROLE OF POLYMERIZATION IN THE DISSOLUTION OF NEPHELINE, JADEITE, AND ALBITE GLASSES: TOWARD BETTER MODELS FOR ALUMINOSILICATE DISSOLUTION. S.L. Brantley[1], J. Hamilton[2], C.G. Pantano[3], L. Criscenti[1], J. D. Kubicki[1]. Pennsylvania State University (Dept of Geosciences, Penn State University, University Park, PA 16801, brantley@geosc.psu.edu), [2]Johns Manville Inc., [3]Dept of Materials Science and Engineering, Pennsylvania State University.

Introduction: Dissolution and precipitation of feldspar is an important reaction in many environmental systems, as plagioclase feldspar is the most common mineral in the crust. However, the mechanism of dissolution of feldspar has remained in dispute despite twenty or more years of analysis of feldspar dissolution. We are pursuing an approach toward better understanding of feldspar dissolution by investigating reactivity of aluminosilicate glasses of variable composition.

In particular, to investigate the effects of Al/Si ratio on plagioclase dissolution without complications of varying Na/Ca content or exsolution, three glasses with varying Al/Si ratio (albite, jadeite, nepheline) were synthesized. Glass powders were then prepared and dissolved at various values of pH in batch reactors under ambient conditions. Solution chemistry was analyzed by inductively coupled plasma -optical emission spectroscopy or -mass spectrometry. In addition, alteration of the glass surface was investigated using X-ray photoelectron spectroscopy, secondary ion mass spectrometry, and Fourier transform infrared spectroscopy.

Dissolution results: Many similarities in dissolution behavior between plagioclase crystals and this suite of glasses were observed: 1) dissolution was slowest at near-neutral pH and increased under acid and basic conditions, 2) dissolution rate at all pH values increased with increasing Al/Si ratio, 3) the pH dependence of dissolution was higher for the phase with Al/Si = 1 than the phase with Al/Si = 0.3, 4) after acid leaching, the extent of Al-depletion of the altered surface increased with increasing bulk Al/Si ratio from Al/Si = 0.3 (albite) to 0.5 (jadeite), but then decreased in nepheline (Al/Si = 1.0), which dissolved stoichiometrically with respect to Al, and 5) little to no Al depletion of the surface of any glass occurred at pH > 7. However, in contrast with some observations for plagioclase dissolution, log(rate) increased almost linearly with Al content, and *n*, the slope of the log(rate)-pH curve at low pH, varied smoothly from albite to jadeite to nepheline (n = 0.3, 0.6, 1.0 respectively). At high pH, the slope of this curve, *m*, did not differ between glasses ($m = -0.4 \pm 0.1$).

Mechanistic interpretation: These results are consistent with an identical mechanism controlling dissolution of nepheline, albite, and jadeite glass, although no Si-rich layer can develop on nepheline because of the lack of Si-O-Si linkages.

Such a conclusion is consistent with a transition state for these aluminosilicates at high pH consisting of a deprotonated Q_3^{Si} hydroxyl group (where Q_v^x refers to an x atom in a tetrahedral site with v bridging oxygens) or a five-coordinate Si site after nucleophilic attack by OH^-, and, at low pH, a protonated $Q_4^{Al}OQ_4^{Si}$. At low pH, we infer that $Q_4^{Si}OQ_4^{Al}$ linkages are rate-limiting because they are presumed to hydrolyze more slowly than $Q_v^{Si}OQ_w^{Si}$ ($v,w \leq 3$). According to this model, dissolution rate increases from albite to jadeite to nepheline because hydrolysis of Al-O-Si linkages becomes more energetically favorable as the number of Al atoms per Si tetrahedral increases, a phenomenon documented by geometry optimizations using *ab initio* methods (for example, Figure 1). However, a model wherein $Q_4^{Al}OQ_4^{Si}$ linkages are faster to hydrolyze than lower connectivity linkages between Si atoms ($Q_v^{Si}OQ_w^{Si}$, $v,w \leq 3$) may also explain aspects of this data.

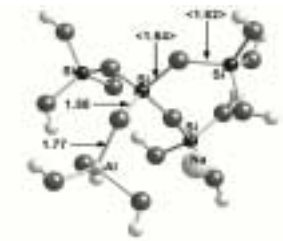

Figure 1. Optimized geometry (HF/3-21G**) of the *Q^4Si(AlNa)* molecule, the primary structural unit in albite glass. The bond lengths in brackets are average values. Optimized geometries were also calculated for the primary structural units in jadeite and nepheline glass. The average Si-O bond length within *SiOSi* linkages (~1.64 Å) and the average Al-O bond length within *AlOSi* linkages (~1.77Å) do not change as Al is added to the network. However, the average bond length of Si-O bonds within *AlOSi* linkages increases from ~1.58 Å in albite to ~1.60 Å in jadeite to ~1.62 Å in nepheline glass.

Further computational and experimental measurements are needed to distinguish among models of aluminosilicate dissolution.