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DISSOLUTION RATES AND SURFACE CHEMISTRY OF FELDSPAR GLASS AND CRYSTAL

Final Technical Report

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By

S. Brantley and C. Pantano

College of Earth and Mineral Sciences
The Pennsylvania State University
University Park, PA 16802

DOE Patent Clearance Granted
Mark P. Dvorscak
1830 252-2393
E-mail: mark.dvorscak@ch.doe.gov
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College of Earth and Mineral Sciences, The Pennsylvania State
University, Univ Pk, PA 16802

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Title: Dissolution of Feldspar in the Field and Laboratory

PI: Susan L. Brantley, 814 863 1739 (ph and fax; Brantley@geosc.psu.edu)
coPI: Carlo G. Pantano (814 863 2071, ph; 814 865 0016 fax;
pantano@ems.psu.edu)

Objectives: Three questions were investigated in this project: 1) What are the structures of altered layers on dissolving crystalline and glassy feldspars in laboratory and field systems? 2) What techniques can be used to investigate dissolution of feldspar in the field or laboratory? 3) How is feldspar weathering affected by internal porosity and surface coatings?

Project Description: One of the highly debated questions today in low-temperature geochemical kinetics centers upon the rate and mechanism of dissolution of feldspar, the most common mineral in the crust. In this project, the mechanisms of feldspar dissolution were investigated by emphasizing experiments with feldspar glass and crystal while comparing surface and solution chemistry. Specifically, laboratory work focussed on the structure of altered surface layers on feldspars, the rate of dissolution of feldspar crystal and glass, and the presence of porosity and surface coatings on feldspars. In a complementary field project, the use of Sr concentrations and isotopic ratios were used to calculate feldspar dissolution rates.

Feldspar Dissolution in the Laboratory. Initial effort focused upon investigating how to prepare samples from the field and laboratory for spectroscopic surface analysis (Hamilton and Pantano, 1997; Mellott et al., 2001). One important finding was that the surface compositions of dissolving feldspars measured with x-ray photoelectron spectroscopy (XPS) of powder samples and polished crystals and glasses, after similar dissolution treatment, are identical. This is especially important since, as described below, many of our naturally weathered samples are in powder form. We enhanced the accuracy of our XPS measurements through the use of a cleaning technique which reduces the concentration of hydrocarbons on the sample surface. This technique, ultra-

violet ozone cleaning (UVOC), removes surface hydrocarbons through a photosensitized oxidation process and is ideal for removing carbonaceous material from the surfaces of materials – even naturally weathered materials – to be analyzed with XPS. Using these methods of sample preparation, and focussing on solution chemistry far from equilibrium the surface chemistry and dissolution behavior of crystalline and amorphous albite was studied using both powder and bulk samples. In flow-through experiments ranging from 3000-5000 h, the dissolution rate of both crystalline and amorphous albite decreased from pH 2 (log rate ≈ -14.5 (mol Si cm⁻² s⁻¹)) to pH 6 (log rate ≈ -15.3 (mol Si cm⁻² s⁻¹)), but increased in raising the pH to 9 (log rate ≈ -15.2 (mol Si cm⁻² s⁻¹)). These results represent the only published systematic dissolution rates for albite glass.

Our data has shown that the dissolution rate of the albite glass is insignificantly faster than that of the albite crystal (e.g. at pH 2, albite crystal vs. glass showed log dissolution rates of -14.5 vs. -14.4 (mol Si cm⁻² s⁻¹)). Although the dissolution rates of crystalline and amorphous albite are almost indistinguishable, formation of altered surface layers is more extensive on glass than on crystal surfaces, especially in the early stages of dissolution at pH 2 (Hamilton et al., 2000; Mellott et al., 2002).

In contrast to extensive leaching at pH 2, extent of leaching of Na and Al on both phases was much less significant at pH 9 (again, however, the glass leached slightly more than the crystal). Although previous to our work many researchers had reported upon the alteration of crystalline albite under acid conditions (and our results corroborate and expand upon much of this earlier work), few investigators have determined the controls on feldspar dissolution and surface chemistry at neutral and high pH. Furthermore, the results in the literature are sometimes contradictory as to whether Si- or Al-leached layers form or whether the surface layer remains stoichiometric. Our observations show that discrepancies in the literature concerning the leaching of Al from albite at high pH are undoubtedly related to the solution chemistry of individual experiments.

Depth profiles of Si, Al, and Na were also measured on leached crystal surfaces using angle-resolved x-ray photoelectron spectroscopy (ARXPS). The extent of Na and Al depletion in the near-surface layer of albite under the experimental conditions was observed to decrease with increasing temperature (Chen et al., 2000). The lower depletion of Al and Na at higher temperature is interpreted as the result of competition between dissolution of the surface layer and diffusion of Al and Na through the surface layer and into solution.

This work, as well as reports in the literature, suggest that the composition of the leached layer may vary with the local solution conditions, temperature, and

structure of the dissolving substrate. We have looked at this effect by investigating glasses whose Al/Si composition can be readily varied (Hamilton and Pantano, 1997; Hamilton et al., 2001). Specifically, the glass network structure was systematically altered by substituting alumina for silica in the system $\text{Na}_2\text{O}-x\text{Al}_2\text{O}_3-(3-x)\text{SiO}_2$ join. Across our model glass join, the dissolution rate at pH 2 is extremely slow until the alumina concentration is increased to 15–20 mol%, at which point the dissolution rate increases drastically.

Fully polymerized glasses (albite, jadeite, and nepheline composition), two Na-aluminosilicate glasses containing non-bridging oxygens, and albite crystal were dissolved under ambient conditions and analyzed using nuclear magnetic resonance spectroscopy (NMR). Using NMR we showed, for the first time, that octahedral Al forms on the surface of albite when it dissolves at pH 2 (Tsomaia et al., 2002). The fraction of octahedral aluminum with respect to total Al in the surface leached layer of glasses increases with increasing Al/Si ratio of the bulk glass. The NMR data also document repolymerization of the silicon network on the surface of nepheline glass, documenting alteration of the connectivity and coordination number of Al and Si during dissolution. Secondary ion mass spectrometry, X-ray photoelectron spectroscopy, and Fourier-transform infrared reflection spectroscopy (FTIRRS) were also used to document characteristics of the surface layers on all glasses after dissolution.

Feldspar Dissolution in the Field. To extrapolate our measured kinetics from the lab to the field, the mechanism of reaction must be the same (see discussion in Kump et al., 2000). However, investigators have wondered if the discrepancy among laboratory and field dissolution rates for feldspars (which can be as high as 5 orders of magnitude) could be caused by a difference in mechanism between laboratory and field. In this project, we discovered that, under the acidic pH conditions of a natural soil, weathered albite surfaces, like laboratory-dissolved samples, are Na- and Al-depleted (Nugent et al., 1998, 1998). To our knowledge, this was the first documentation of Al-depletion in naturally weathered feldspar surfaces similar to depletions observed in the laboratory. This coating is important because 1) it can be largely undetected under scanning electron microscopy, 2) it is difficult to remove, 3) it develops over months to years in acid soils, 4) it contributes to surface chemistry measurements, and 5) it may partially inhibit the rate of dissolution in the field.

A second set of experiments to investigate field rates of feldspar dissolution was pursued for the unconsolidated sand comprising the Cape Cod aquifer. Sands in this aquifer are dominantly quartz and feldspar, and dissolution of the feldspar occurs as water flows downgradient. Feldspar dissolution was assessed by analyzing the rate of change of alkalis and Si downgradient through the groundwater flow regime. In addition, we ran several laboratory experiments in which Cape Cod feldspar was dissolved after

various pretreatments. The measured dissolution rate of the untreated Cape Cod feldspar was significantly slower than published rates for feldspars of similar composition, as well as slower than our own measured rates for a laboratory-ground feldspar of similar composition. In contrast, harshly etched Cape Cod feldspar (etched with HCl so as to remove much of the surface coating) dissolved at a rate only slightly slower than the reported feldspar rates for pristine, laboratory ground samples. Thus, removal of the surface coating caused a rate acceleration of about an order of magnitude for the Cape Cod aquifer sands. Other than the work of Nugent et al. (1998) reported here, we believe that this is the first documentation that a surface coating -- in this case, a coating of Si, Al and Fe -- can significantly inhibit dissolution of a feldspar.

Unfortunately, however, even if the laboratory dissolution rate for the untreated aquifer feldspar (feldspar with the surface coating) is used, the laboratory dissolution rate is still faster than the field-calculated dissolution rate at Cape Cod (Brantley et al., in prep.). We hypothesize that this discrepancy is related to the chemical affinity of the groundwater, or to heterogeneities in fluid flow.

Using mercury porosimetry, quartz and feldspar samples collected from the Cape Cod aquifer have been shown to contain between 11 and 13% intragranular porosity in the unsaturated zone or between 4 and 19% porosity in the saturated zone. Calculated volume and surface area of pores reveal that most of the internal porosity of both the quartz and feldspar grains from the aquifer is present as mesoporosity. Building upon this observation, we systematically studied the presence of porosity in primary silicate minerals, and related it to specific surface area and dissolution kinetics (Brantley et al., 1999; Brantley and Mellott, 2000).

One final problem encountered in the Cape Cod study involved the observation that increases in Na with distance (i.e. with residence time in the subsurface) did not always match the increase in Si with distance assuming feldspar dissolution. Our work (Brantley et al., 1998) showed that Sr release from three endmember feldspar compositions begins nonstoichiometrically, but becomes stoichiometric with time (we also observed some significant isotopic changes in both feldspar powder and feldspar dissolution effluents over time). We have used these observations to help interpret Sr chemistry in the Cape Cod aquifer, as described by Brantley et al., (2001) and Bau et al. (subm).

Publications resulting from this work.

Work completed under DOE DE-FG02-95ER14547.A000 comprises the following theses:

- 1997 Nugent, Melissa, "Temporal Evolution of Feldspar Surfaces during the Initial Stages of In-situ Weathering" (M.S., Penn State University)
- 1999 Yau, Simmy, "Dissolution Kinetics of Feldspar in the Cape Cod Aquifer, Massachusetts: Calculation of Ground Water Residence Time" (M.S., Penn State University)
- 1999 Hamilton, J.P. "Effects of Structure, Composition, and pH on the Corrosion Behavior of Sodium-Aluminosilicate Glasses and Crystals" (Ph.D., Penn State University).
- 2000 Mellott, N.P., "Evolution of Surface Roughness with Aqueous Corrosion of Alkali and Alkaline-Earth Aluminosilicate Minerals and Glasses" (M.S., Penn State University)
- 2002 Alexander, B.A., "Controls on Groundwater Chemistry in the Cape Cod Aquifer, MA" (M.S., Penn State University)

and papers which are published, in press, or submitted:

- 1999 Brantley, S.L., A.F. White, M. Hodson. Surface area of primary silicate minerals, *in* Growth and Dissolution in Geosystems, B. Jamtveit and P. Meakin (ed.), Kluwer Academic Publishers, Dordrecht, 291-326.
- 1997 Hamilton, J. and Pantano, C.G., Effects of glass structure on the corrosion behavior of sodium-aluminosilicate glasses, J. Noncrystalline Solids 222, 167-174.
- 1998 Brantley, S.L., J.T. Chesley, L.L. Stillings. Isotopic ratios and release rates of Sr measured from weathering feldspars. Geochimica Cosmochimica Acta 62,1492-1500.
- 1998 Nugent, M.A., S.L. Brantley, C.G. Pantano, P.A. Maurice. The influence of natural mineral coatings on feldspar weathering. Nature 396, 527-622.
- 1998 Nugent, M., P. Maurice, and S.L. Brantley. The field dissolution rate of feldspar in a Pennsylvania (USA) spoDsol as measured by atomic force

- microscopy, Proc. Ninth Inter. Conference on Water-Rock Interactions, New Zealand.
- 2000 Chen, Y., S.L. Brantley, E. Ilton. X-ray photoelectron spectroscopic measurement of the temperature dependence of leaching of cations from the albite surface. Chemical Geology 163, 115-128.
- 2000 Kump, L., S.L. Brantley, M.A. Arthur. Chemical weathering, atmospheric CO₂ and climate, Earth and Planetary Science Reviews 28, 611-667.
- 2000 Hamilton, J., C.G. Pantano, S.L. Brantley. Dissolution rates of albite crystal and glass. Geochimica Cosmochimica Acta, 64, 2603-2615.
- 2000 Brantley, S.L., N. Mellott. Surface area and porosity of primary silicate minerals, American Mineralogist. 85, 1767-1783.
- 2001 Mellott, N.P., S.L. Brantley, J.P. Hamilton, C.G. Pantano. Evaluation of surface preparation methods for glass. Surface and Interface Analysis 31, 362-368.
- 2001 Brantley, S.L., M. Bau, S. Yau, B. Alexander. Interpreting kinetics of groundwater-mineral interaction using major element, trace element, and isotopic tracers, Proc. Tenth Inter. Conference on Water-Rock Interaction, Villasimius, Italy, Cidu, R. (ed.), Balkema, Rotterdam, 13-18.
- 2001 Hamilton, J., Brantley, S.L., Pantano, C.G., Criscenti, L., Kubicki, J. Dissolution of nepheline, jadeite and albite glasses: Toward better models for aluminosilicate dissolution. Geochimica Cosmochimica Acta 65, 3683-3702.
- 2002 Mellott, N.P., S.L. Brantley, C.G. Pantano, Topography of polished plates of albite crystal and glass during dissolution. *in* Water-Rock Interactions, Ore Deposits, and Environmental Geochemistry, A Tribute to David A. Crerar, Hellmann R. and Wood S. (ed.), The Geochemical Society, Spec. Pub. No. 7, pp. 83- 96.
- 2002 Tsomaia, N., Brantley, S.L., Hamilton, J.P., Pantano, C.G., Mueller, K.T., NMR evidence for formation of octahedral and tetrahedral Al and repolymerization of the Si network during dissolution of aluminosilicate glass and crystal. In press, American Mineralogist.

- 2002 Bau, M., B. Alexander, J.T. Chesley, N.P. Mellott, P. Dulski, S.L. Brantley. Impact of accessory feldspar and glauconite on strontium isotopes, solute concentrations, and REE-Y systematics in the Cape Cod aquifer, Massachusetts. In revision for Geochimica Cosmochimica Acta.
- 2003 Brantley, S.L. and White, A.F., Age-dating groundwater in the Cape Cod aquifer using mineral dissolution rates. In preparation for Geochimica Cosmochimica Acta.