

PROJECT SUMMARY

PROJECT TITLE: Quantifying Silica Reactivity in Subsurface Environments: Reaction Affinity and Solute Matrix Controls on Quartz and SiO₂ Glass Dissolution Kinetics

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RESEARCH OBJECTIVE: Our goal is to develop a quantitative and mechanistic understanding of amorphous silica, SiO₂(am), dissolution kinetics in aqueous solutions. A knowledge of fundamental controls on the reactivity of simple Si—O bonded phases is the baseline of behavior for understanding highly complex silica phases. In the Earth, silicate minerals comprise >70% of the crust and dominate virtually every subsurface system. More importantly for the objectives of this EMSP project, the silicates are important because compositionally complex glasses will become the front line of defense in containing radioactive wastes in the nation's long term and interim storage strategies. To date, the behavior of SiO₂(am) is largely inferred from studies of the better known crystalline polymorphs (e.g. alpha-quartz). In the first step towards constructing a general model for amorphous silica reactivity in the complex fluid compositions of natural waters, we are determining the dissolution behavior as a function of temperature, solution pH and cation concentration. With these data we are determining relationships between SiO₂ glass structure and dissolution rates in aqueous solutions, as described below.

RESEARCH PROGRESS AND IMPLICATIONS:

1) Interactions with Users: Tank Focus Area and Workshop Meetings

The 1998 EMSP conference in Chicago was an important meeting for our project. The symposium, enabled P.I. Dove to establish valuable contacts with focus area 'users' having specific needs for the findings of our EMSP project related to the urgency of problems in the Tank Focus Area (TFA). Since 1998, our working relations have developed through interactions with TFA scientists and engineers on the problems of waste glass properties. Dove presented the results of EMSP research findings to a TFA subgroup at a Product Acceptance Workshop held in Salt Lake City during December 1998. Travel costs to this workshop were paid from EMSP research funds. In January 2000, Dove attended a similar meeting in Atlanta with participants from PNNL, SRL and BNF to discuss new issues and make another level of decisions on the Product Acceptance goals.

Our current EMSP-funded research has interfaced well with the ongoing glass corrosion studies in the Applied Geochemistry Group at PNNL (contacts: Dr. R. Holdren and Dr. P. McGrail). Shortly after the Chicago conference, our EMSP-funded Postdoc, Dr. Jonathan Icenhower was hired by the same PNNL group. Icenhower brings his experience in silica-water reactivity and the experimental expertise in mineral-water reaction kinetics. With the Icenhower move from postdoc to a staff scientist position at PNNL, our EM project facilitated information transfer from the 'university to user' environment. Similarly, one of our EMSP M.S. students, Mr. Troy Lorier, will be visiting Savannah River Laboratory to discuss a possible position in the glass group (contact: Dr. Bill Holtzscheiter). His thesis research on silica geochemistry meshes with on-going efforts at SRL. In short, our current EMSP project has gone well beyond the strictly academic goals of producing high quality scientific knowledge to establish connections with actual users and produce new talent for the waste immobilization effort.

2) EMSP 96-10 Project Highlights

1.3 EMSP 96-10 Project Highlights.

This section is intended to highlight the scope of findings made to-date on the current project.

1.3.1. The dissolution kinetics of amorphous silica into sodium chloride solutions: Effects of temperature and ionic strength. (Icenhower and Dove, in press, *Geochim. Cosmochim. Acta*). The kinetics of amorphous silica, SiO_2 (am), dissolution was determined in deionized water (DIW) and NaCl solutions at temperatures that span 40-290°C. The model is carefully underpinned with experimental data from our laboratory and assesses all of the published amorphous silica data to produce a critically evaluated comprehensive model. Using two sources of pure SiO_2 glass (fused purified quartz and pyrolyzed SiCl_4), dissolution rates were measured in our lab by applying three types of reactor systems to assess kinetic behavior over the full temperature range. Dissolution rates of the two materials are similar within experimental error.

Figure 2 a,b.

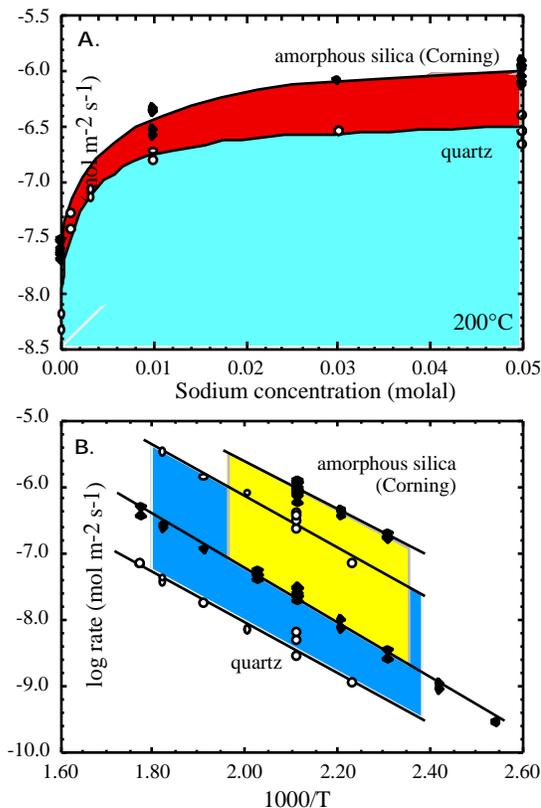
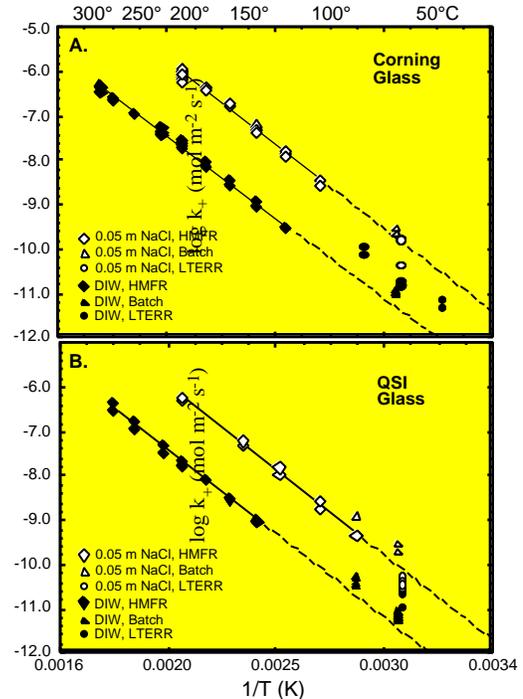


Fig. 1 a,b



Absolute rates of amorphous silica dissolution exhibit an experimental activation energy, $E_{a, \text{xp}}$, of 82.4 ± 3.0 and 78.9 ± 1.8 kJ mol^{-1} for the fused quartz and pyrolyzed silica, respectively (**Fig 1**). These values are similar to each other and to estimates for quartz within experimental errors. Absolute dissolution rates of the amorphous silica in DIW are $\sim 10\text{X}$ faster compared to quartz (**Fig 2a,b**). Amorphous silica dissolution rates in near-neutral pH solutions are strongly dependent upon the concentration of NaCl such that 0.05 molal sodium ion enhances rates by 30X compared to deionized water. Results of this study show that NaCl can greatly modify the reactivity of amorphous silica.

The findings step toward the larger goal of understanding silica polymorph reactivity in the complex fluid compositions of natural systems. Recent findings that quantify

the effects of dissolved solutes on quartz dissolution rates allow us to suggest that other major solutes found in natural waters will also enhance the dissolution rates of amorphous silica in a systematic and predictable manner. Continuing work towards a comprehensive model of silica reactivity will be able to assess these effects.

1.3.2. Dissolution kinetics of quartz in aqueous mixed cation solutions.

(Dove, 1999, *Geochim. Cosmochim. Acta*). The dissolution kinetics of quartz is quantified in dilute

mixtures of magnesium, calcium, barium and sodium chloride salts in near-neutral pH solutions over the temperature range of 175 to 295°C.

Measurements using single salt solutions show that the rate-enhancing effects increase in the order:

$Mg^{2+} < Ca^{2+} = Na^{+} < Ba^{2+}$ (Fig 3).

Barium ion increases dissolution rates by 114X compared to new, slower rates found for deionized water ($10^{-8.11}$) at 200°C.

Experimental activation energies, E_{xp} , measured for each salt solution are similar within experimental

errors (Fig 4). In solution mixtures of two salts, dissolution rates are a nonlinear combination of the bulk concentrations of cations in solution such that rates are limited by the cation with the *smallest* rate-enhancing effect. That is, a small fraction of magnesium ion in the mixture limits the net dissolution rate to an extent disproportionate to its bulk concentration. A comparison of Fig. 5 with Fig 6 shows that this behavior is more pronounced for salt mixtures of 2+:1+ cations (i.e. Mg^{2+} and Na^{+}) than 2+:2+ cations (i.e. Mg^{2+} and Ba^{2+} or Ca^{2+}).

The behavior observed in salt mixtures is quantified by an empirical expression based upon a competitive cation-surface interaction model. The kinetic model assumes that salt-enhanced dissolution rates are determined by the intrinsic ability of each type of cation, i , to enhance rates ($k_{mx,i}$) and their concentration(s) at the surface ($K_{ad,i}$). Estimates of these parameters are obtained by fitting the

Fig. 3 Comparison of IIA and IA cation solutes on quartz dissolution rate

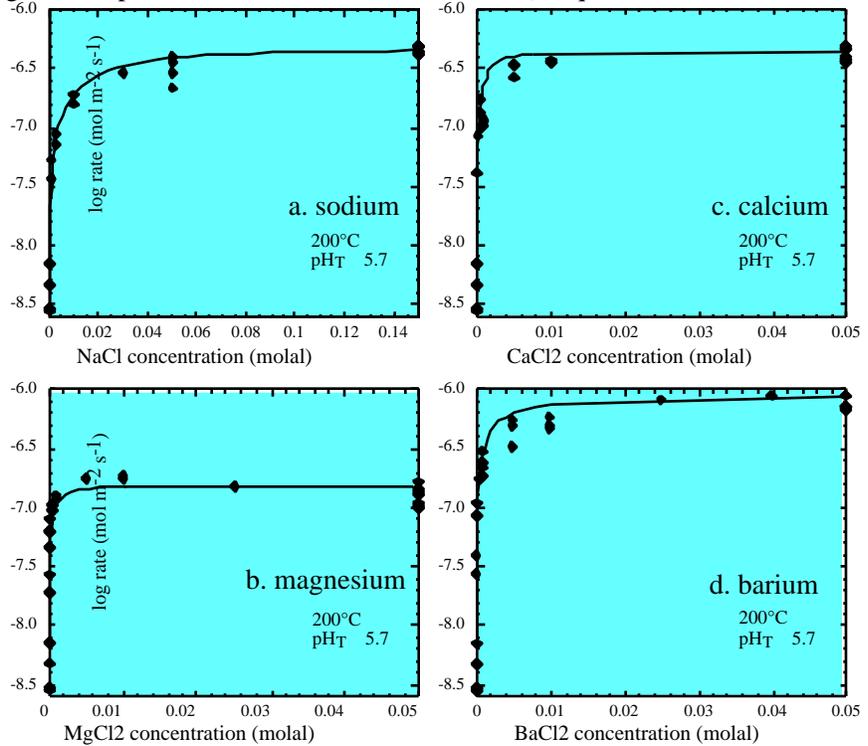


Fig. 4 Temperature dependence of quartz dissolution in deionized water and 0.05 M chloride salts.

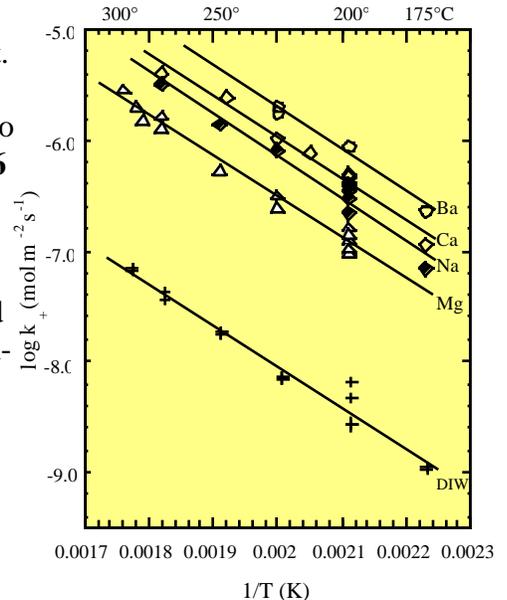


Fig. 5 Qtz dissolution in a IA- IIA mixture yields significant clue to mechanism

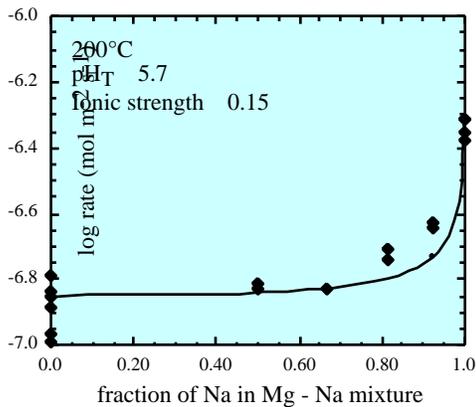
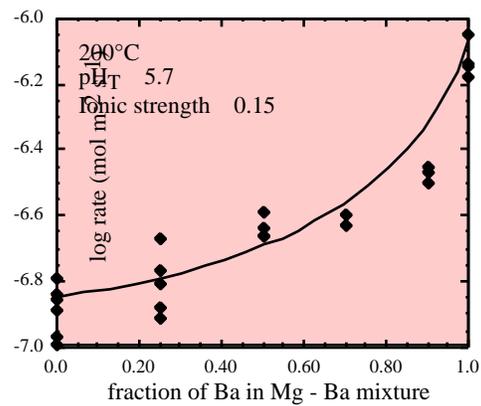


Fig. 6 Qtz dissolution in a IIA- IIA mixture

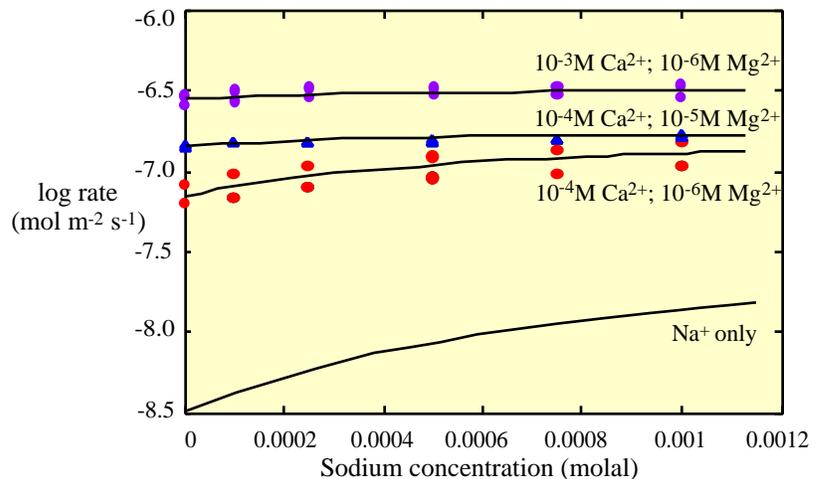


model to data from the rate versus concentration experiments conducted in single salt solutions. The resulting kinetic expression gives good predictions of rates measured in salt mixtures and is consistent with previous models of cation-enhanced dissolution kinetics of quartz. The model predicts that magnesium and calcium have greater roles in regulating quartz dissolution rates despite lower concentrations in natural waters than sodium and potassium because of their larger surface interaction strengths.

1.3.3. Kinetics of quartz and amorphous silica dissolution in solute mixtures. (Lorier, M.S. Thesis, Georgia Institute of Technology, Atlanta; Lorier and Dove, in prep., *Geochim. Cosmochim. Acta*).

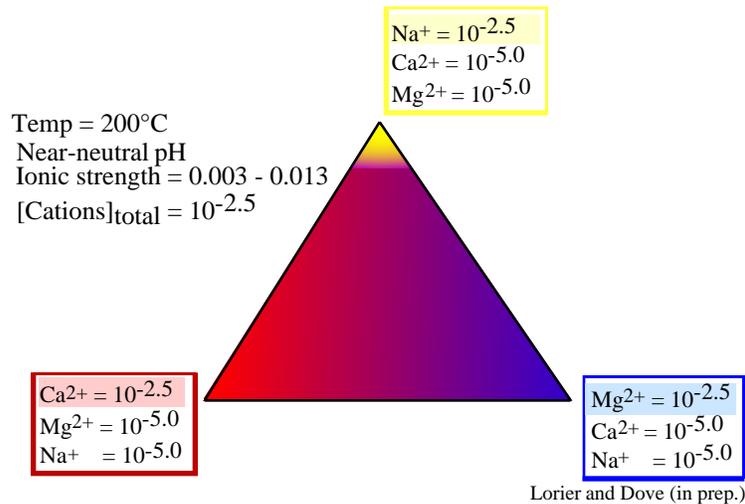
Troy Lorier will successfully complete a M.S. thesis this spring semester (May 2000). As a step towards quantifying silica behavior in the complex solution compositions of natural systems, this study determines the influence of major solutes found in subsurface waters on the dissolution kinetics of quartz and amorphous silica. Dissolution rates were measured using mixed flow-through reactor (MFR) systems as a function of solute concentration for the individual cations sodium, potassium, calcium, and magnesium, at 200°C and pH 5.7. Each of the major solutes increases the dissolution rate of amorphous silica and quartz by 60 to 100 times, as compared to deionized water (no cations present), to an extent that is dependent upon the identity of the cation, *i*, and dissolved concentration. These were the first experiments of their kind and showed that the behavior of amorphous silica is similar to what we had observed for quartz (e.g. Fig 3). At the cation concentration range relevant to the composition of terrestrial waters, rate measurements show that calcium and magnesium have the greatest control on net rates

Fig. 7 Findings suggest that major solutes calcium and/or magnesium may control rates despite low concentrations in most environm.



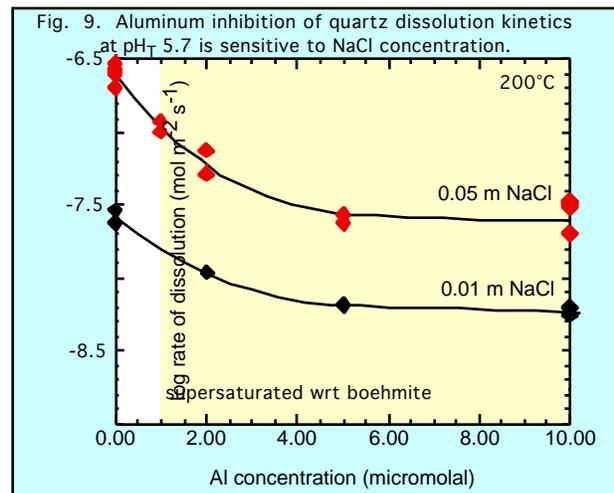
(Fig 7). The controls of mixed-cation solutions on dissolution rates are quantified by an empirical competitive surface interaction model. This model has a physical basis that is founded in the competitive interaction of each type of cation with the silica surface. Magnesium and calcium have the greatest influence on net rates of dissolution because of their relatively large cation-surface interaction constants, compared to lower values for the weakly interacting sodium and potassium. These findings have allowed Troy to make an important step toward understanding silica reactivity in the more complex natural and waste-modified subsurface fluids by designing several simple solution compositions to simulate a small range of groundwater chemistries in higher temperature environments. Fig 8 shows that the results of these first-of-kind experiments support the hypothesis that calcium and magnesium dominate net rates.

Fig. 8. Though sodium is most abundant solute, stronger interactions of Ca and Mg may control rates of silica dissolution



1.3.4. Counteracting solute effects- inhibiting dissolution by aluminum oxyhydroxides (Dove, 1997, ISHR; Dove and Grantham, in adv. Prep. *Geochim. Cosmochim. Acta*)

In stepping towards the comprehensive model of silica reactivity, we are determining how higher valence ions inhibit dissolution rates and hence, counteract the rate-enhancing effects of major solutes. We have quantified the influence of aluminum (IIIB) on quartz and amorphous silica dissolution rates in parallel kinetic and microscopic studies. Sorbed aluminum is qualitatively known to affect the surface properties, apparent solubility, and inhibit the dissolution kinetics of silica polymorphs (Iler, 1973). These studies (Hurd, 1973; Iler, 1973) are sometimes cited as evidence that aluminum inhibits the dissolution rate of silica by three to five orders of magnitude. However, our hydrothermal and low temperature studies (Dove et al., 1995; Dove and



Grantham, in adv. prep; Icenhower and Dove, in adv. prep.) determined that quartz and amorphous silica dissolution rates are inhibited by a factor of less than 10 when solutions contain as much as 50 μmolar Al (as AlCl_3) (e.g. **Fig. 9**). These rate-inhibiting effects are observed across the 30 - 300°C temperature range: from low temperatures where gibbsite formation is stabilized to hydrothermal solutions (e.g. **Fig. 10**) supersaturated with respect to boehmite (e.g. Wesolowski, 1992). The energetics of dissolution are significantly modified in the presence of aluminum. Measurements of the temperature dependence show that experimental activation energies increase from 80 ± 2 to 95 ± 4 kJ mol^{-1} when 10 μmol Al is introduced to DIW or salt solutions.

Because our observations of the modest rate-inhibiting effect conflicted with widely accepted notions, we were initially skeptical of these findings. To ensure that these results were not due to an experimental artifact caused by minute surface abrasion of the $\text{Al}(\text{OH})_3$ precipitates, we conducted crosschecks using recirculating reactors designed to avoid all possibilities of surface disturbances. Rate data collected by this method (Dove and Grantham, in adv. prep.) confirmed the relatively small rate-inhibiting effect of aluminum.

We also found that the extent of rate inhibition is dependent upon NaCl concentration as shown in **Fig. 10**. This cannot be explained by aqueous complexation (Dove and Grantham, in adv. prep.). This was another unexpected result because the aluminum-silica surface interaction strength is well known to be 10^4 to 10^9 greater than for sodium-silica (Iler, 1979). This suggests that sodium boosts *net* rate of silica dissolution independent of aluminum inhibition or sodium reduces the effectiveness of aluminum as an inhibitor.

Though the rate-inhibiting effect of aluminum is small, microscopic observations by *in situ* Atomic Force Microscopy document extensive accumulation of aluminum oxyhydroxide coatings on silica surfaces. The data are consistent with studies using other methods (e.g. Hem et al., 1973; Brown and Hem, 1975). **Fig. 11** illustrates the rapid accumulation of aluminum oxyhydroxide sorbates/precipitates in

sequential *in situ* AFM images of a (110) quartz surface after 30 (left) and 90 minutes of exposure

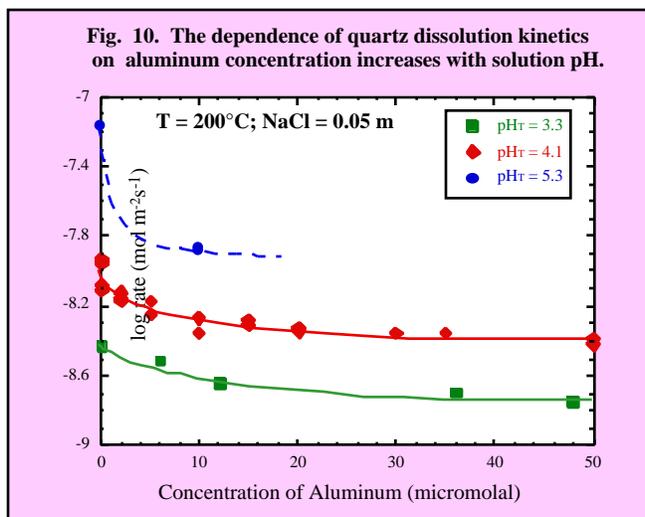
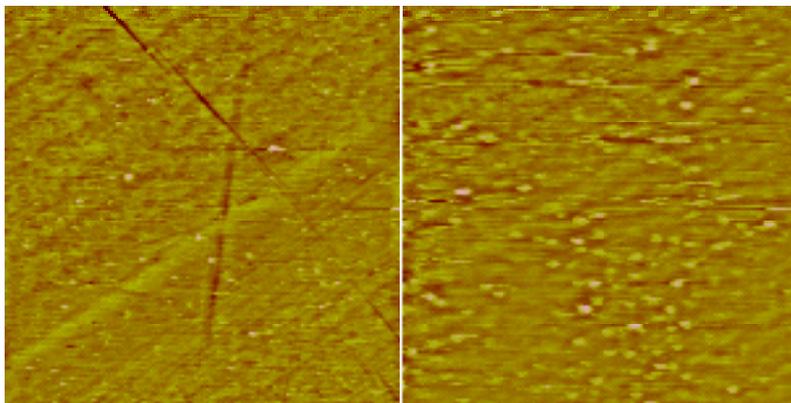


Fig. 11 *In situ* AFM images show 7 Angstrom steps on quartz (110) surface and precip nuclei w/exposure to 5 micromol Al



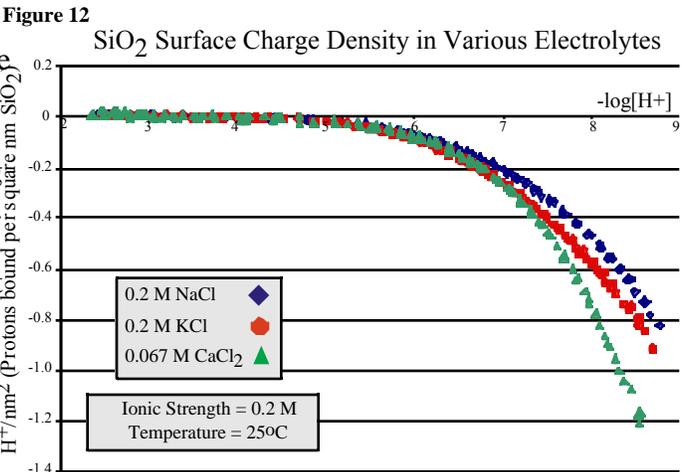
to 10 μmolar AlCl_3 solutions at pH 5.6. As surface begin to form with initial heights of 20-50 \AA and diameters of 50-200 \AA , the underlying silica surfaces becomes quickly physically isolated from contacting solutions. Surfaces exposed to aluminum-bearing solutions from low temperature experiments as well as surfaces from hydrothermal studies show that sorbates/precipitates soon become coatings with thicknesses on the order of 100's of nanometers. XRD and SEM analyses are unable to detect the presence or crystallinity of a coating on Al-treated quartz surfaces, but mas-NMR spectra of ^{27}Al indicate that the coating contains Al in VI coordination which is consistent with an amorphous and aluminum coordination chemistry at these conditions (Merino et al., 1989).

Our quantitative findings that aluminum has a relatively small rate-inhibiting effect have received considerable interest because of the ongoing controversy regarding probable mechanisms by which aluminum inhibits dissolution of amorphous silica. The 'silica problem' revolves around discussions of whether aluminum reduces H_4SiO_4 concentrations in natural waters by reducing silica solubility or by slowing rates of reaction (Lewin, 1961; Hurd, 1973; Wollast, 1974, 1983; Van Bennekom and van der Gaast, 1976; Van Bennekom, 1981; Van Bennekom, 1988; Van Bennekom et al., 1989; Van Bennekom et al., 1991). Explanations for the mechanism are still being evaluated. Our findings cannot yet entirely resolve the solubility question but clearly indicate that aluminum affects the kinetics of dissolution. Measurements of higher energies of activation indicate that Al-O-Si interactions lower the reactivity of silica surface structures. This is supported by theoretical studies (Lasaga and Gibbs, 1990; Xiao and Lasaga, 1996; Koretsky et al., 1998).

1.3.5. Silica surface charge in IA and IIA electrolyte solution (Craven, M.S. Thesis, Georgia Institute of Technology, Atlanta; Karlsson et al., submitted, *Geochem. Trans.*; Craven et al., in prep., *Geochim. Cosmochim. Acta*).

The mechanisms by which major solutes enhance rates of silica dissolution continue to be controversial (see later discussion). One hypothesis to explain this behavior proposes that the hydrated cations play an indirect role by forming outer-sphere complexes that affect the capacitance of the mineral-water interface (Karlsson et al, submitted). In this model, the protons and hydroxyls perform the dissolution mechanisms while the cations alter the state of surface protonation. To test this hypothesis and to develop a quantitative understanding of controls on silica surface charge development, new work by Karlsson et al. (submitted) and Craven (2000) are

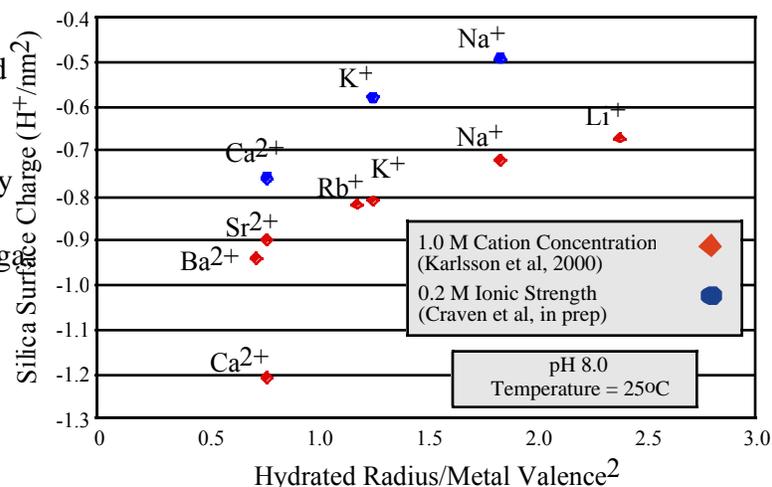
acquiring very high quality surface charge measurements (e.g. section 1.3.5). This new expertise promises to build an unprecedented quantitative understanding of charge development on silica surfaces. If the model is correct, silica surface charge and dissolution rates, with respect to solution electrolytes, should be dependent upon the hydrated radius, valence and concentration of the counterion at the interface. Preliminary potentiometric titration experiments have



measured the dependence of silica surface charge development in a suite of metal chloride solutions (NaCl, KCl, CaCl₂, SrCl₂) (Fig 12). The data are showing that cation-specific changes in surface charge may partially account for variation in macroscopic dissolution (Fig 13). This correlation of aqua ion chemistry to the surface charge density of silica could

possibly explain the rate-enhancing effects of cations by linking surface charge to rate equations of the form proposed by other authors for various silicate and oxide minerals (Wirth and Gieskes, 1979; Guy and Schott, 1989; Furrer and Stumm, 1986; Blum and Lasaga, 1988).

Figure 13
Correlating Cation Chemistry to Silica Surface Charge Density



INFORMATION ACCESS:

Published Manuscripts & Abstracts

Icenhower, J.P. and **P.M. Dove** (in press) The dissolution kinetics of amorphous silica into sodium chloride solutions: Effects of temperature and ionic strength. *Geochim. Cosmochim. Acta*.

Dove, P.M. (1999) The dissolution kinetics of quartz in dilute salt mixtures. *Geochimica Cosmochimica Acta*. **63**. 3715-3727.

Dove, P.M. and J.P. Icenhower (in press) Water Behavior Near Silica Surfaces. In: *Adsorption on Silica Surfaces*. Ed. E. Papirer, Dekker Publishing, New York.

Dove, P.M. and Icenhower, J. (1997) *Kinetic and Thermodynamic Controls on Silica Reactivity: An Analog for Waste Disposal Media*; Invited chapter. Commissariat a L'Energie Atomique - Valrho, École D'été. In: *Glass: Scientific Research for High Performance Containment* (S. Gin, editor).

Icenhower, J. and **Dove, P.M.** (1998) *The Dissolution Kinetics of Amorphous Silica: Structural Controls on Reactivity* (Abstract). International Mineralogical Association Conference, Toronto (in press).

Dove, P.M. and J.P. Icenhower (1998) Quantifying waste form reactivity in subsurface environments: Kinetics and mechanisms of SiO₂ glass dissolution as a baseline for multicomponent silicates. 1st Annual DOE Environmental Management Science Program Workshop, Chicago, July.

Dove, P.M. and Nix, C. (1997) Role of solvent-surface interactions in the electrolyte catalyzed kinetics of quartz dissolution. *Geochimica Cosmochim. Acta* **61**, p. 3329-3340.

Dove, P.M. and M.C. Grantham (1997) Influence of aluminum on the dissolution kinetics of quartz at hydrothermal conditions. *Fifth Internat. Symposium on Hydrothermal Reactions*, p. 69-72.

Grantham, M.C. and **Dove, P.M.** and T.J. DiChristina (1997) Biogeochemistry of subsurface environments: Investigation of bacterial effects on iron and aluminum oxyhydroxide coatings of silica. *Geochimica et Cosmochimica Acta*. **61**, p.4467-4477.

Dove, P.M. and J.P. Icenhower (1997) Kinetic and thermodynamic controls on silica reactivity: An analog for nuclear waste disposal media. in *Glass: Scientific Research Towards High Performance Confinement*. Commissariat a l'Energie Atomique, France.

Publications Submitted or in Advanced Preparation

Craven, C.M., M. Karlsson, W.H. Casey, and **P.M. Dove** (in review) Surface charge of amorphous silica in electrolyte solutions and implications for dissolution. *Geochemical Transactions*. (new web-based ACS journal)

Dove, P.M. and M.C. Grantham (in advanced prep.) The dissolution kinetics of quartz in aluminum-bearing solutions in hydrothermal solutions. for *Geochimica et Cosmochimica Acta*.

Craven, C.M., M. Karlsson, W.H. Casey, and **P.M. Dove** (in advanced prep.) Silica surface charge in IA and IIA electrolyte solutions: Resolving the controls of ionic strength on charge development. For *Geochim. Cosmochim. Acta*.

Lorier, T. and **P.M. Dove** (in advanced prep.) Kinetics of quartz and amorphous silica dissolution: Effects of IA, IIA and aluminum in low temperature and hydrothermal solutions. for *Geochim. Cosmochim. Acta*.

Theses Accepted for M.S. Degree, May 2000

Lorier, T.H. (2000) Kinetics of quartz and amorphous silica dissolution in solute mixtures. M.S. Thesis, Georgia Institute of Technology, Atlanta.

Craven, C.M. (2000) Silica surface charge in IA and IIA electrolyte solutions M.S. Thesis, Georgia Institute of Technology, Atlanta.

Other Activities

- 1999 Invited speaker, Gordon Research Conference:
*Surfaces, Interfaces, and Grain Boundaries in Rocks:
Structure, Properties, and Processes*
- 1999 Invited speaker, Gordon Research Conference: *Chemical Oceanography*
- 1999 Invited participant, NSF Workshop: *Future Directions in Mineral Physics*
- 1999 DOE BES, Geosciences Best University Research Award,
Interfacial Processes Symposium
- 1998 Mineralogical Society of America, Best Paper Award
(BES-funded project)
- 1999-04 US Department of Energy, Basic Energy Sciences Advisory Council
- 1998-99 US Department of Energy, Basic Energy Sciences Geosciences Council
- 1998 Invited participant, US DOE Workshop, *Climate Change Technology Initiative in
Terrestrial CO₂ Sequestration*.

Junior and Senior Scientists Supported by EMSP 96-10

Undergraduates:	Ms. Bridget Bruton
	Mr. Troy Lorier (became M.S. student in my group)
	Ms. Micki Cook
Graduate Students:	Ms. Meg Grantham
	Mr. Troy Lorier
	Mr. Colin Craven
Postdoctoral Scientist:	Dr. Jonathan Icenhower
Research Scientist:	Ms. Meg Grantham

Assistant Professor:

(continued project after J.Icenhower moved to PNNL)
Dr. Patricia Dove (now Associate)