

FINAL REPORT
Submitted to the
Department of Energy
Office of Basic Energy Sciences

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

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I. Summary of Major Findings from EMSP 96-10 Activities

During the three years of this project, Professor Dove's laboratory made tremendous progress in understanding controls on amorphous silica dissolution kinetics in aqueous solutions. Our findings have already received considerable attention. In hydrothermal and low temperature studies, the work focused on determining quantitative and mechanistic controls on the most abundant silica polymorphs in Earth environments- quartz and amorphous silica. Our studies achieved goals set forth in the original proposal to establish a new quantitative understanding of amorphous silica dissolution. This support has already resulted in the following journal and peer reviewed publications:

Publications to-date:

- Karlsson, M. C.M. Craven, **P.M. Dove** and W.H Casey (2001) Surface charge concentrations on silica in different 1.0 M metal chloride background electrolytes and implications for dissolution rates. In press for *Aquatic Geochemistry*.
- Icenhower, J.P. and **P.M. Dove** (2000) The dissolution kinetics of amorphous silica into sodium chloride solutions: The effects of temperature and ionic strength. *Geochimica et Cosmochimica Acta*, **64**, 24, p. 4193-4203.
- Dove, P.M.** (1999) The dissolution kinetics of quartz in aqueous mixed cation solutions. **63**, p. 3715-3727. *Geochimica et Cosmochimica Acta*.
- Dove, P.M.** and J.P. Icenhower (1999) Water Near Silica Surfaces. *Silica*. Ed. E. Papirer, Dekker Pub. Pg. 277-295.
- 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.

Publications submitted or in advanced preparation:

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

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*.

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 *Nature*.

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.

Extended abstracts and special conferences:

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.

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.

Conference Abstracts

Craven, C.M. and **P.M. Dove** (2000) Quantifying Solute Controls on the Surface Charge of Colloidal Silica in Aquatic Systems. *American Geophysical Union*, San Francisco, December.

Lorier, T.H., and **P.M. Dove** (1999) The dissolution kinetics of quartz in terrestrial waters. Geological Society of America Annual Conference, Denver, October.

Craven, C.M., M. Karlsson, W.H. Casey, and **P.M. Dove** (1999) Why solution composition affects oxide dissolution rates: Surface charge of oxide minerals as a function of solution electrolytes. Geological Society of America Annual Conference, Denver, October.

Icenhower, J.P. and **P.M. Dove** (1998) Kinetics of amorphous silica dissolution: Constructing a general model of SiO₂ polymorphs reactivity. *Geological Soc. of America National Meeting*, Toronto, October.

Icenhower, J. and **P.M. Dove** (1998) The dissolution kinetics of amorphous silica: Structural controls on reactivity. *International Mineralogical Association Meeting*, Toronto, August.

- Dove, P.M.** and M.C. Grantham (1997) Influence of aluminum on the dissolution kinetics of quartz in hydrothermal solutions. *Fifth International Symposium on Hydrothermal Reactions*, Gatlinburg, Tennessee.
- Dove, P.M.**, M.C. Grantham, and T.J. DiChristina (1997) Influence of iron-reducing microbes on iron oxyhydroxide coatings on silica in aerobic and anerobic environments. *Geological Society of America National Meeting*, October, Salt Lake City.
- Grantham, and **Dove, P.M.** and T.J. DiChristina (1997) Influence of iron-reducing microbes on iron oxyhydroxide coatings in aerobic and anaerobic environments. Symposium in honor George A. Parks, *American Chemical Society*, San Francisco.
- Kumar, A. and **Dove, P.M.** (1996) Adsorption of aluminum onto quartz and the evolution of quartz dissolution rates. Fall Meeting of the *American Geophysical Union*, San Francisco.
- Kumar, A. and **Dove, P.M.** (1996) Surface coating induced evolution of microscale geochemical heterogeneity and quartz surface reactivity. *Geological Soc. of America National Meeting*, October.

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

Statement of funds that remained at the end of EM 96-10:

Our research activities expended all of the funds in this project.

III. Awards and Honors

Patricia Dove

Spring 1996. Geochemical Society.
Clarke Medal
Fall 1996. Teaching Excellence Award.
Georgia Institute of Technology
Spring 1998 Best University Research Award,
'Interfacial Processes' Symposium
Department of Energy
Fall 1998 Best Paper Award
Mineralogical Society of America
Fall 2000 Elected Fellow
Mineralogical Society of America

Colin Craven

Fall 2000. American Geophysical Union, Hydrology Section.
Outstanding Student Paper Award
San Francisco

II. Interactions with Users:

Tanks 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 'users' having specific needs for the findings of our EMSP project related to the urgency of problems in the **Tanks Focus Area (TFA)**. Since that time, our working relations developed as Dove interacted with TFA scientists and engineers on the problems of waste glass properties. These interactions refined our experimental objectives to better meet their needs. 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. The travel costs to attend this unanticipated opportunity were paid from EMSP project funds. In January 2000, Dove also attended a similar meeting in Atlanta with PNNL, SRL and BNF scientists/engineers to discuss new issues and make another level of decisions on the Product Acceptance goals.

Our EMSP-funded research interfaced very well with the ongoing studies of Dr. Pete McGrail and colleagues in the Applied Geochemistry Group at PNNL. The value of our work to 'users' was further demonstrated when Dove's EMSP-funded Postdoc, Dr. Jonathan Icenhower was hired by the same PNNL group. With the Icenhower move from postdoc in the Dove lab to a senior scientist position at PNNL, we directly facilitated information transfer from the 'university to user' environment. Icenhower brought experience in silica-water reactivity and the experimental expertise in high-quality methods of mineral-water reaction kinetics to the PNNL waste clean-up effort. In a further interaction, M.S. student Troy Lorier was hired at the Savannah River Laboratory for a staff position with

the Bill Holtzcheiter glass group. His research meshed well with on-going efforts at SRL. In short, our EMSP project went well-beyond the academic goals of producing high quality scientific knowledge to establish connections with on-site users to solve problems in TFA. This project also produced new talent for the waste immobilization effort.

III. Highlights of Research Findings

1. The dissolution kinetics of amorphous silica into sodium chloride solutions: Effects of temperature and ionic strength.

(Icenhower and Dove, 2000, 64, 4193-4203, *Geochim. Cosmochim. Acta*). The kinetics of amorphous silica, SiO₂ (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 SiO₂ glass (fused purified quartz and pyrolyzed SiCl₄), dissolution rates were measured in our lab by applying three types of reactor systems. This allowed us to assess

Figure 2 a,b.

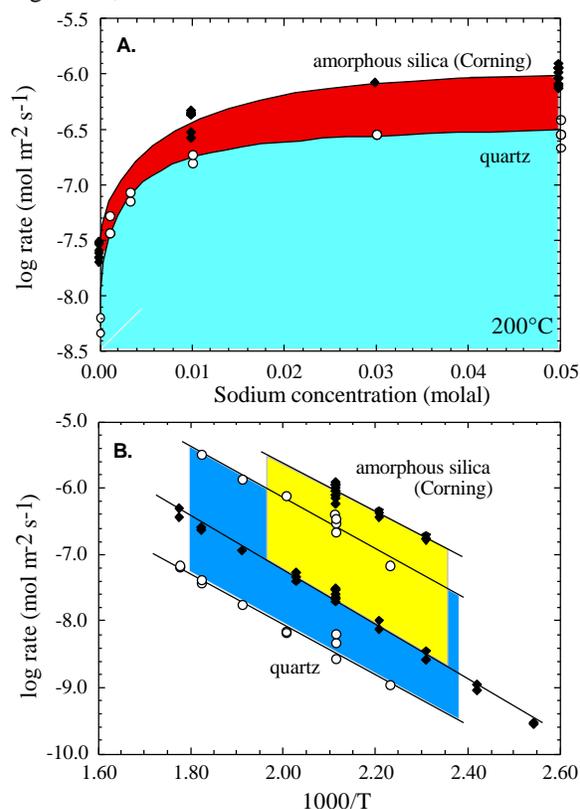
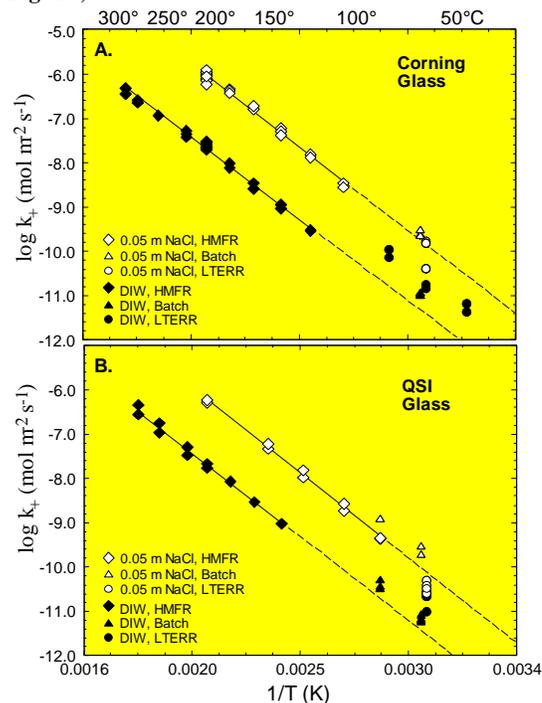


Fig. 1 a,b



kinetic

behavior over the full temperature range while also improving our understanding of factors that contribute to the general problem of inter-laboratory variability. Dissolution rates of the two materials are similar within experimental error. Absolute rates of amorphous silica dissolution exhibit an experimental activation energy, $E_{a, xp}$, 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 ~10X 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.

2. Dissolution kinetics of quartz in aqueous mixed cation solutions. (Dove, 1999, *Geochim. Cosmochim. Acta*).

The dissolution kinetics of quartz are 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 cations increase 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 (Fig. 5). 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+}).

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

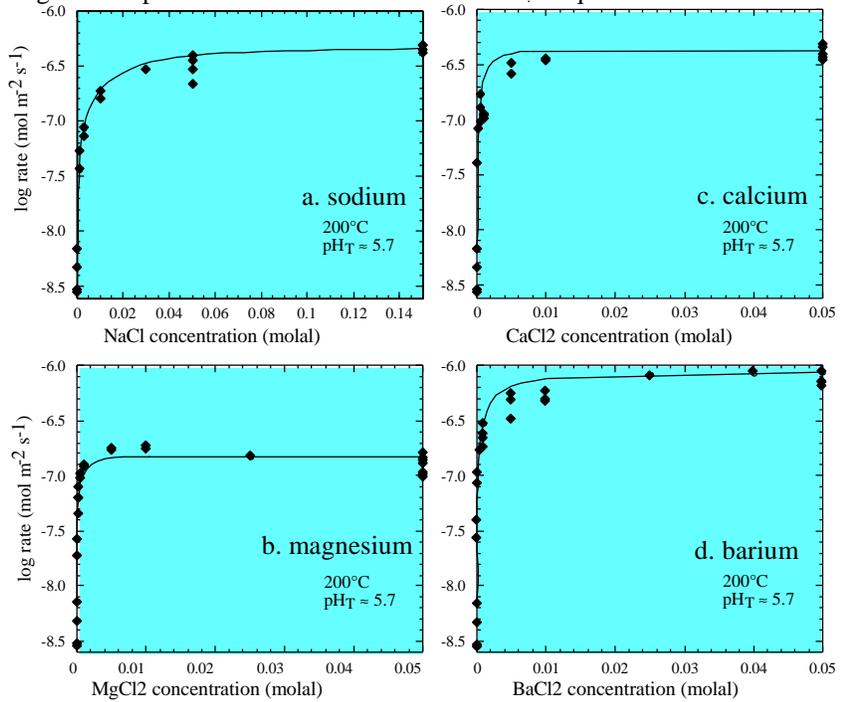


Fig. 4 Temperature dependence of quartz dissolution in deionized water and 0.05 M chloride salts.

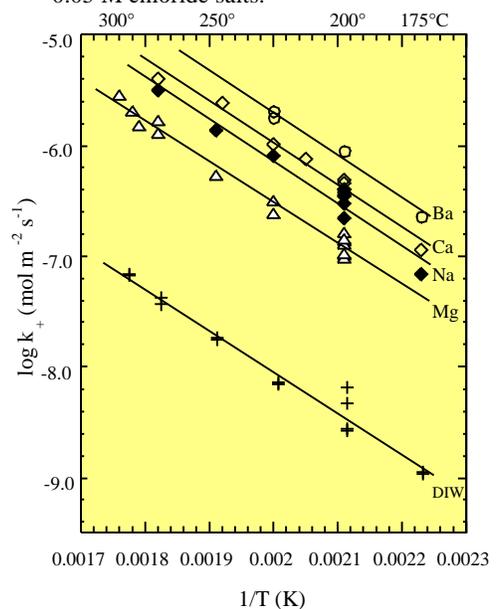
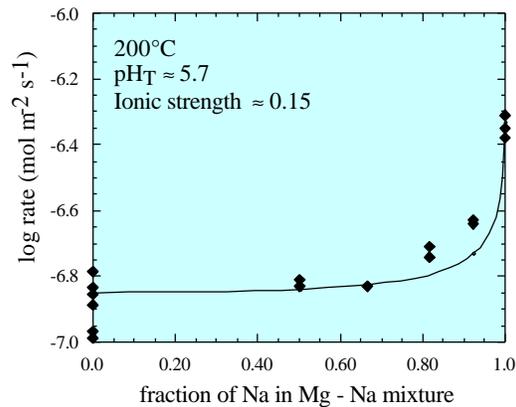


Fig. 5 Qtz dissolution in a IA- IIA mixture yields significant clue to mechanism



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 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.

3. Kinetics of quartz and amorphous silica dissolution in solute mixtures. (Lorier, M.S. Thesis, 2000, Georgia Institute of Technology, Atlanta; Lorier and Dove, in prep., for Nature). 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.

Fig. 6 Qtz dissolution in a IIA- IIA mixture

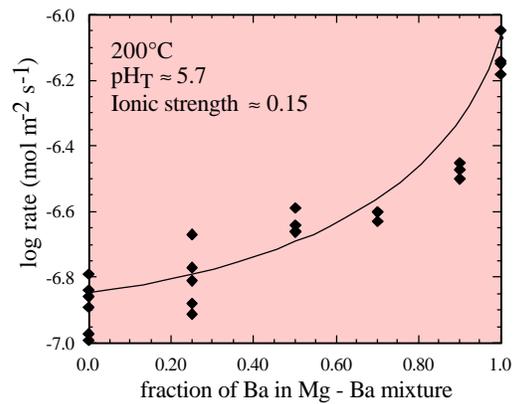
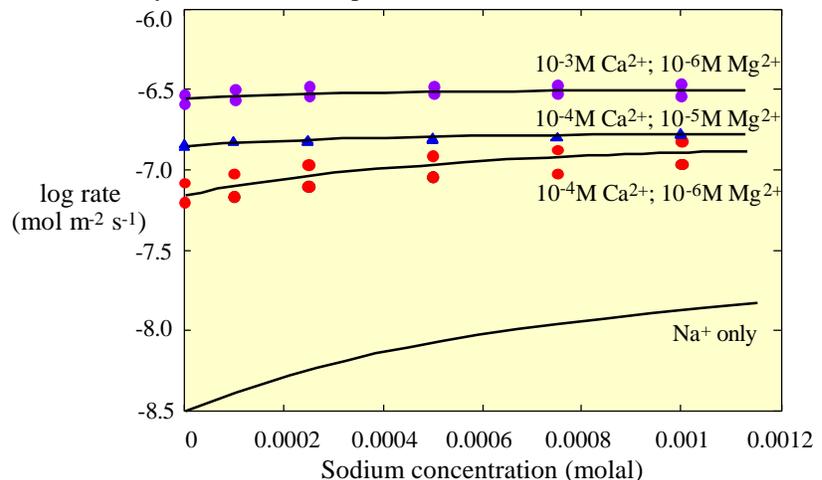


Fig. 7 Findings suggest that major solutes calcium and/or magnesium may control rates despite low concentrations in most environm.



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 are the first experiments of their kind and show 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**). 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

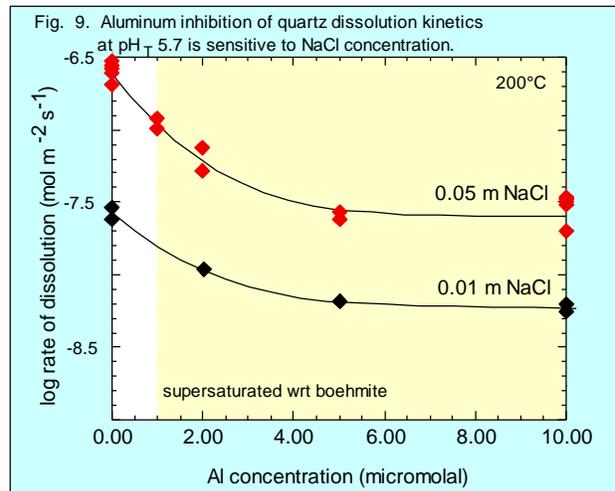
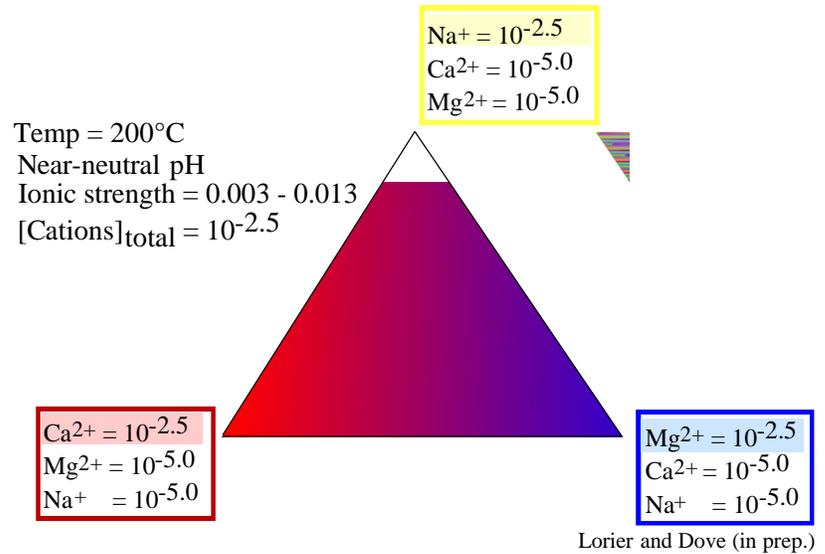
subsurface fluids by designing several simple solution compositions to simulate a small range of groundwater chemistries in higher temperature environments.

Fig 8 summarizes the results of these novel experiments and the findings support the hypothesis that calcium and magnesium dominate net rates.

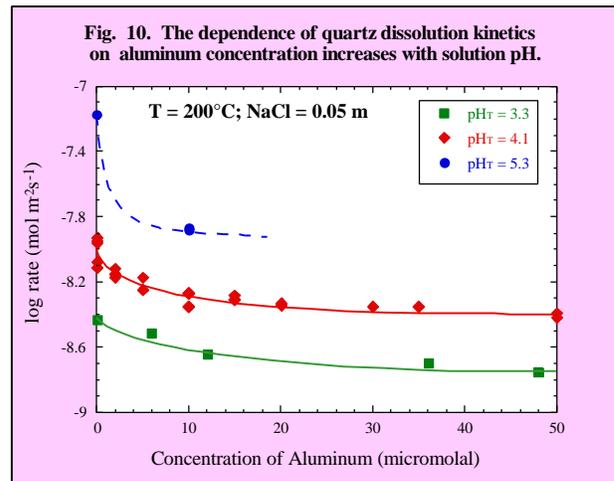
4. Counteracting solute effects-inhibiting dissolution by aluminum oxyhydroxides (Dove, 1997, ISHR; Dove and Grantham, in adv. Prep. *Geochim. Cosmochim. Acta*)

In stepping towards the comprehensive model of silica reactivity, we are determining how higher valence ions inhibit

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



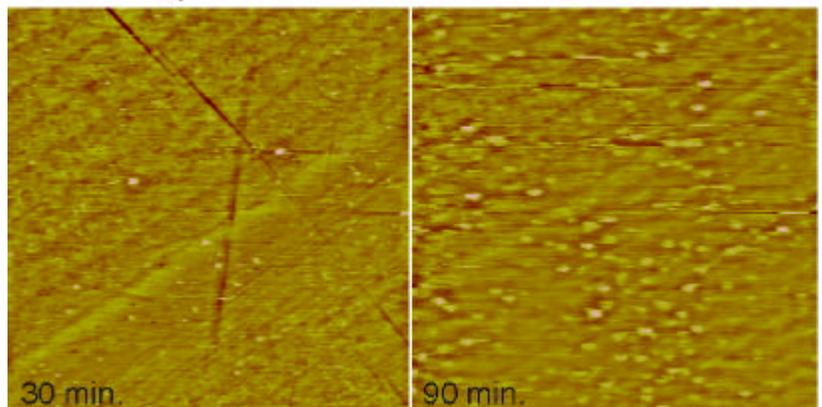
dissolution rates and hence, counteract the rate-enhancing effects of major solutes. We have quantified the influence of aluminum (IIIB) on quartz and amorphous silica dissolution rates in parallel kinetic and microscopic studies. Sorbed aluminum is qualitatively known to affect the surface properties, 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 press) determined that quartz and amorphous silica dissolution rates were inhibited by a factor of <10X. Solutions that contained as much as 50 μ molar Al (as AlCl_3) had little effect (e.g. **Fig. 9**). We also showed that the inhibiting effect of Al has a complex dependence upon NaCl concentration. **Fig 10** shows that the rate-inhibiting effect of aluminum is particularly sensitive to solution pH. These rate-inhibiting effects are observed across the 30 - 300°C temperature range- from the low temperatures where gibbsite formation is stabilized to the hydrothermal solutions that are 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 10μ mol 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.

As noted earlier, we also found that the extent of rate inhibition is dependent upon NaCl concentration as shown in **Fig. 9**. This cannot be explained by aqueous complexation (Dove and Grantham, in adv. prep.). This was another unexpected result

Fig. 11. In situ AFM images show 7Å steps on a quartz (110) surface and the formation of precipitation nuclei with exposure to a 5 micromolar Al solution.



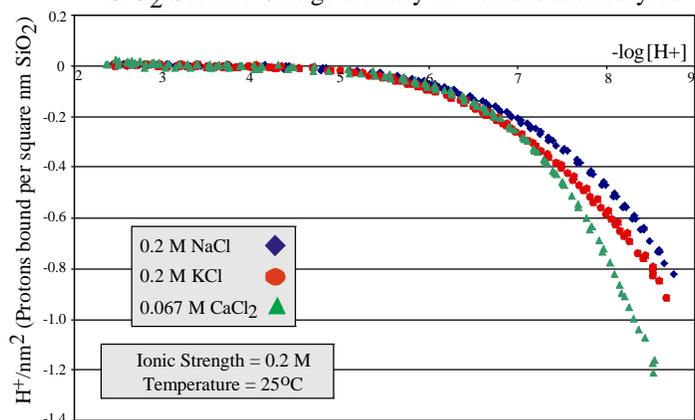
because the aluminum-silica surface interaction strength is well known to be 10^4 to 10^9 greater than for sodium-silica (Iler, 1979). This suggests that sodium boosts *net* rate of silica dissolution independent of aluminum inhibition or sodium reduces the effectiveness of aluminum as an inhibitor.

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 to 10^{-2} molar AlCl_3 solutions at pH 5.6. As surface precipitates of nuclei begin to form with initial heights of 20-50 Å and diameters of 50-200 Å, 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).

5. Silica surface charge in IA and IIA electrolyte solutions (Craven, M.S. Thesis, 2000, Georgia Institute of Technology, Atlanta; Karlsson et al., 2001, *Geochem.*

Figure 12
SiO₂ Surface Charge Density in Various Electrolytes



Trans.; Craven et al., submitted, *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, 2001). 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 as a function of solution composition. 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) (**Fig 12**). The data are showing that cation-specific changes in surface charge may partially account for variation in macroscopic dissolution (**Fig 13**) and suggest that EM-relevant ions such as Sr and Cs also have important effects. 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).

IV. Summary

This EMSP project has been highly successful and we thank our sponsors for the opportunity to advance scientific knowledge in this important area of research.

Figure 13

Correlating Cation Chemistry to Silica Surface Charge Density

