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Quantifying Silica Reactivity in Subsurface Environments: Controls of Reaction Affinity and Solute Matrix 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 compositional baseline 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, silicate minerals and materials are significant because compositionally complex silicate glasses will become the front line of defense in containing radioactive wastes in the nation's long term and interim storage strategies (Dove and Icenhower, 1997). To date, the behavior of SiO₂(am) is largely inferred from studies of the better known crystalline polymorphs (e.g. α-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 NaCl 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

This report outlines our first year's progress and the resulting publications to date. In this experimental investigation, the dissolution kinetics of SiO₂(am) (fused and flame pyrolysis silica) were measured in solutions over the pH range of 4 to 10 containing 0.0 (deionized water, DIW) to 0.15 M NaCl at 40° to 275°C. Dissolution rates were determined in low temperature (40° to 80°C) and hydrothermal (120° to 275°C) reactor systems, using flow-through reactors that are broadly similar in design. Rate data collected from these two reactor designs are consistent with each other and yield the first comprehensive model of amorphous silica reactivity in deionized water and electrolyte solutions (Icenhower and Dove, 1998).

Measurements of rates show important similarities and differences between the corrosion behavior of SiO₂(am) and α-quartz. We find that the experimental energy of activation, $E_{a, xp}$, for the dissolution of SiO₂(am) is 75 ± 5 kJ mol⁻¹ in DIW. The introduction of up to 0.05 M NaCl yields similar $E_{a, xp}$ values of 80 ± 5 kJ mol⁻¹. These values are ~ 10 kJ mol⁻¹ higher than previous estimates of $E_{a, xp}$ for SiO₂(am) but are consistent with reported values of $E_{a, xp}$ for α-quartz. Dissolution rates measured at 200°C in DIW show that SiO₂(am) dissolves ~ 3 to $30\times$ faster than α-quartz. A possible explanation for this difference is that SiO₂(am) has a fraction of Si-O-Si bonds (angles up to 180°) that have a greater ionic character, and are therefore more reactive than α-quartz constituents (mean angle of 152°) (Icenhower and Dove, in prep.). Measurements of SiO₂(am) dissolution rates versus NaCl concentrations at 200°C show that sodium enhances rates by a factor of ~ 10 to $30\times$ compared to rates measured in DIW, which are less than rates for α-quartz under identical experimental conditions. In addition, we find that the dissolution rates of the two forms of SiO₂(am) (fused and flame pyrolysis silica) are similar within the experimental error of the early experiments. Results of this study suggest that the role of physical (structural) properties (e.g., Si-O-Si bonds) in governing reactivities of crystalline versus amorphous SiO₂ polymorphs is significant.

Planned Activities

Using these baseline findings, we will determine the rate-enhancing effects of cations, Li^+ , K^+ , Ca^{2+} , Mg^{2+} , and Ba^{2+} , that are often important rate-modifying constituents in natural subsurface waters. We will also determine the role of reaction affinity on the dissolution kinetics, and investigate the kinetics and mechanisms of Al^{3+} interactions with $\text{SiO}_2(\text{am})$ as a possible reaction inhibitor. Combining these studies with spectroscopic investigations of relationships between glass structure (as modified by water content) and measured reactivity, we will complete the project with a experimentally-based, comprehensive model of amorphous silica reactivity.

Other Access To Information

Dove, P.M. and Icenhower, J. (1997) *Kinetic and Thermodynamic Controls on Silica Reactivity: An Analog for Waste Disposal Media*; Invited chapter. Commissariat à l'Énergie 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).

Manuscripts in Advanced Preparation:

Dove, P.M. and Icenhower, J. (in prep.) *Water Behavior at Silica Surfaces*; Invited Chapter. In: *Adsorption on Silica Surfaces* (E. Papirer, editor).

Icenhower, J. and Dove, D.M. (in prep.) *The Dissolution Kinetics of Silica Glass Into Aqueous Solutions as a Function of Temperature, pH, and Ionic Strength*. For: *Geochimica et Cosmochimica Acta*.