QUANTIFYING WASTE FORM REACTIVITY IN SUBSURFACE ENVIRONMENTS: KINETICS AND MECHANISMS OF SiO2 GLASS DISSOLUTION AS BASELINE FOR MULTICOMPONENT SILICATES

This on-line presentation describes work in progress.

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INTRODUCTION

The international community has selected multicomponent silicate glasses to host high-level radioactive wastes. Although these materials will be the front line of defense in interim and long-term storage strategies, there are few quantitative models to predict their durability in the complex fluids of subsurface environments. As we began this project, four problems had limited advances:

1. Lack of standardized reactor systems to measure the kinetics of dissolution (corrosion) and yield reproducible inter-laboratory data.

2. Absence of comprehensive studies establishing the dissolution kinetics of the endmember silicate glass: SiO2(am).

3. Inability to interpret the dissolution rates of complex multicomponent glasses. (up to 18 components!)

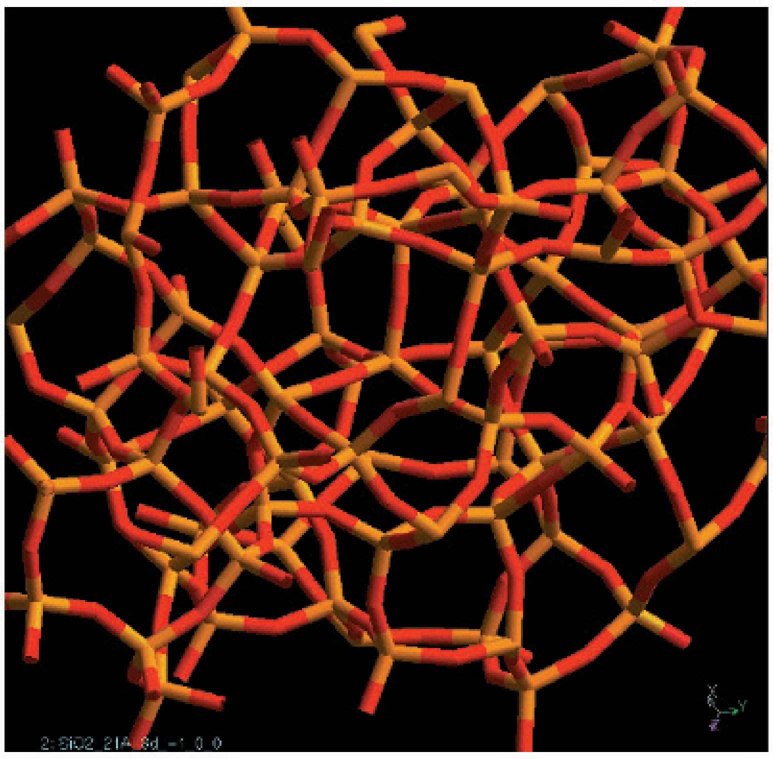
4. Absence of predictive model that quantifies possible rate-modifying effects of solutes in natural and engineered systems.

This EMSP project addresses each problem in a multi-phase investigation.

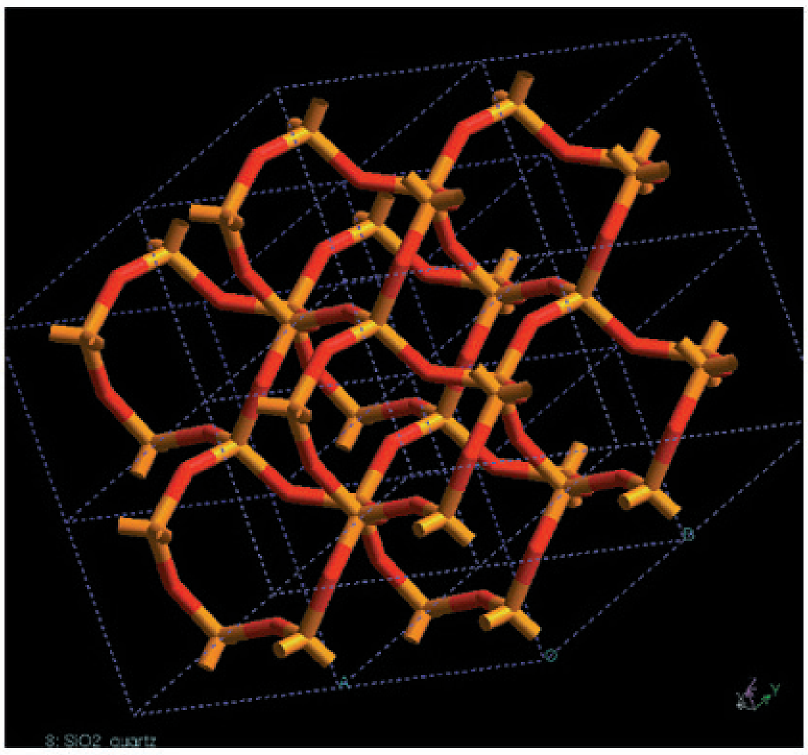
MATERIAL/MINERAL-WATER SYSTEM

- Structures of endmember SiO2 polymorphs

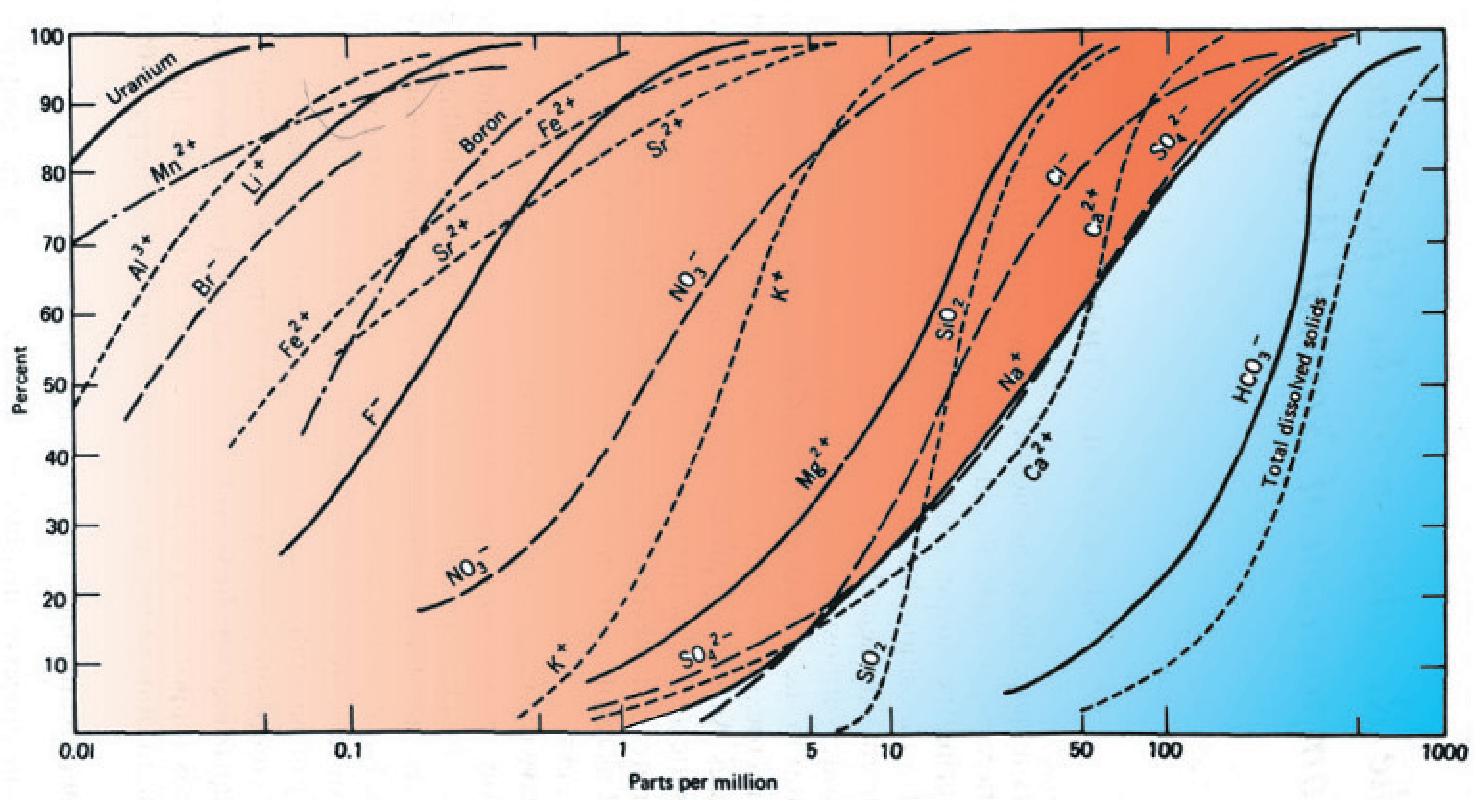
Silica Glass



Quartz



- Predominant solutes in terrestrial waters (Davies and DeWiest, 1966)



STRATEGY

1. Develop reactor system(s) to measure glass dissolution kinetics at 30 - 300°C.

2. Establish baseline: Dissolution kinetics of high purity SiO_2 glass
   - temperature dependence in distilled-deionized water
   - rate-enhancing and -inhibiting effects of solutes, Na^+ and Al^{3+}
   - net reactivity in solutions that approximate natural water compositions
   - solution pH

3. With SiO_2 baseline, introduce new component(s)
   - determine controls of important structural solutes on reactivity
   - construct a progressively complex predictive model for multicomponent glasses

4. Quantify relationships between durability and structure.
   - use baseline data to develop general model for SiO_2 polymorph reactivity
   - quantify role of hydration in long-term durability

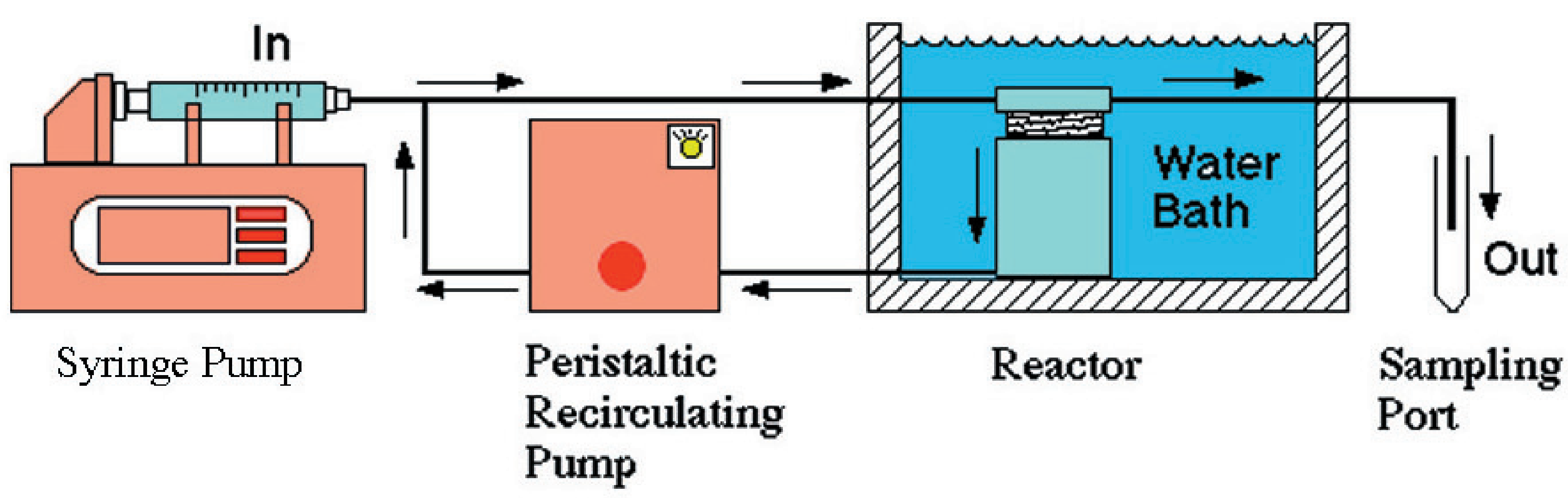
PHASE 1:
Methods Development

Two sources of high purity silica glass were used:

- Fused quartz from Quartz Scientific, Inc.™
- Amorphous silica produced by flame pyrolysis of $SiCl_4$ from Corning, Inc.™

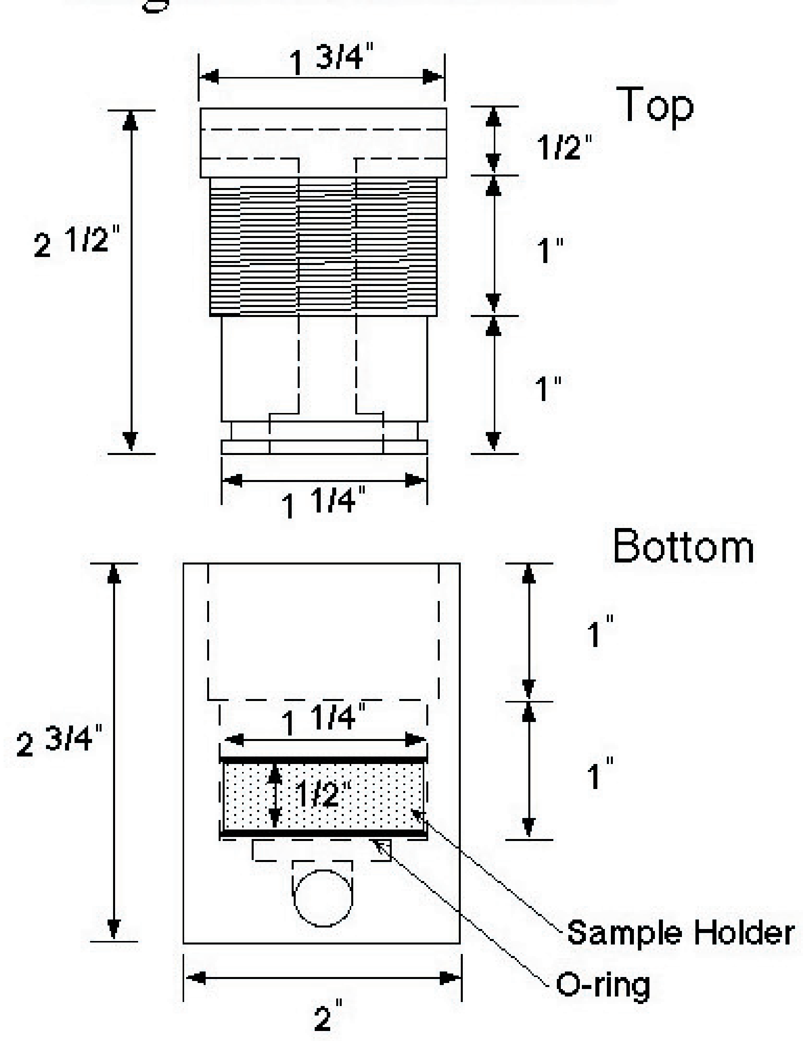
These materials were ground sieved to obtain the 200-300 micron fraction. Samp

Recirculating Flow-Through System
(30 - 80°C)

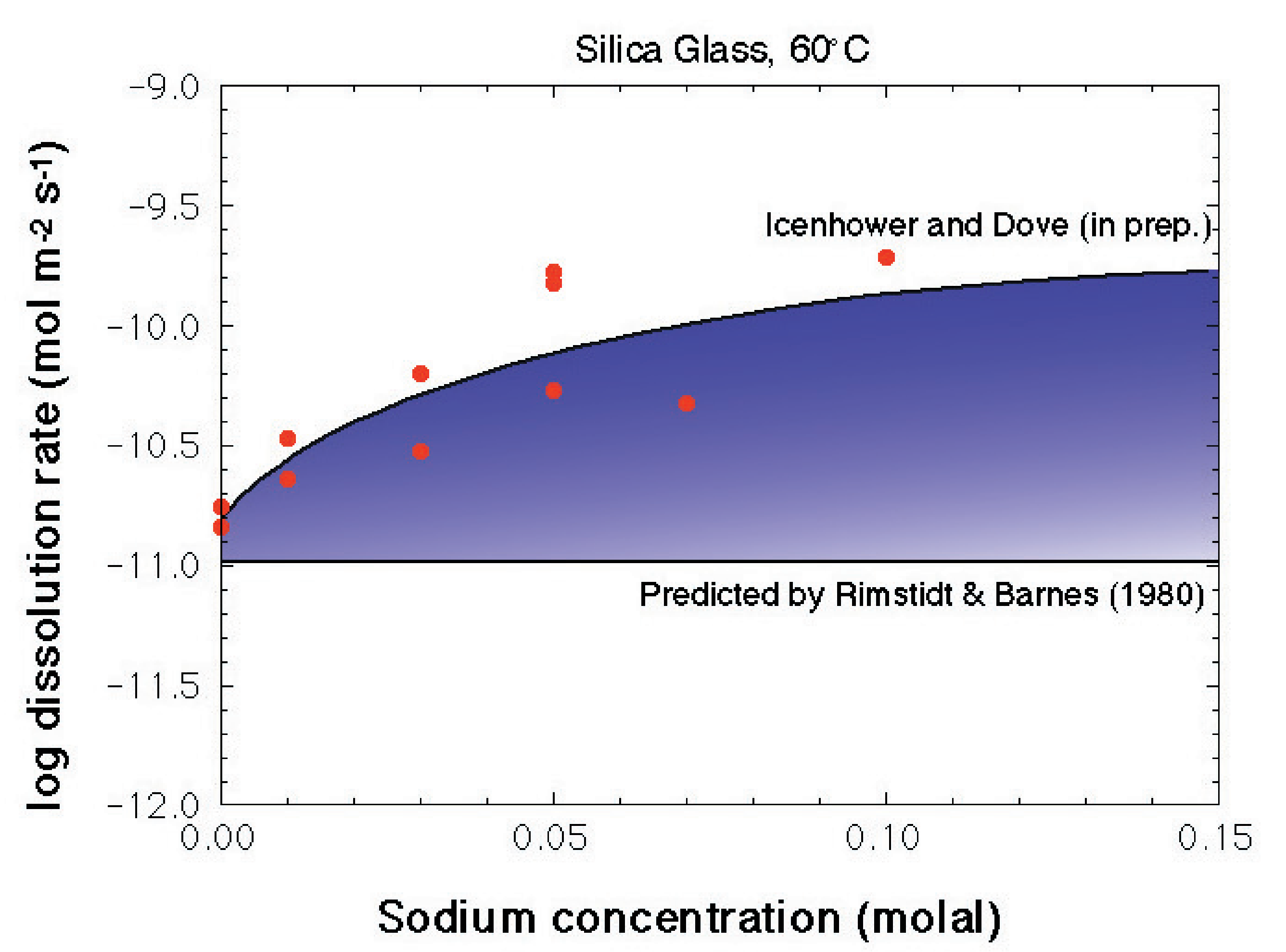


Flow through rates are controlled by the syringe pump (2 to 12 microliters/min) while peristaltic pump governs recirculation rate (10 mlL/min). Reactors have CSTR behavior when recirculation rates exceed injection rates by ≥17X.

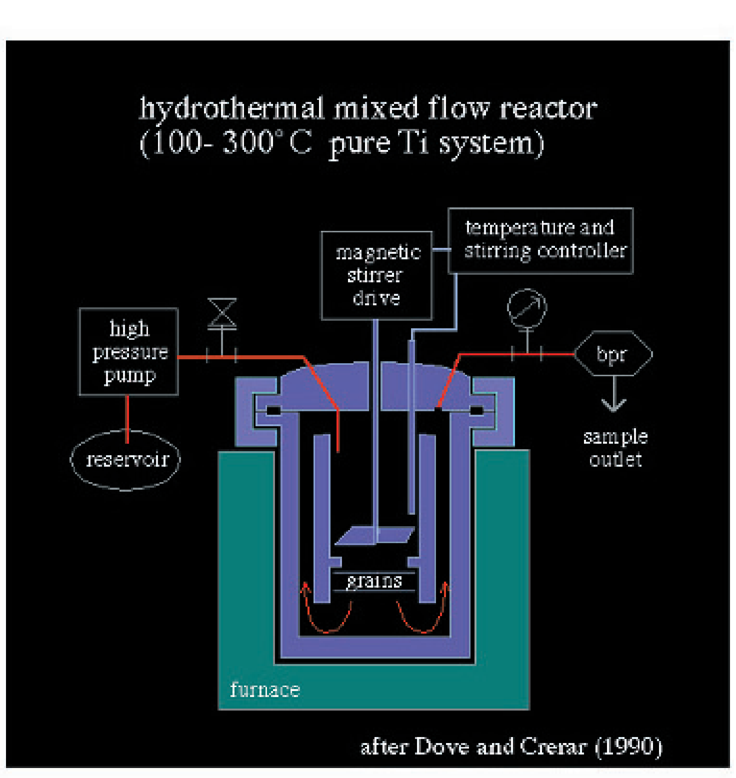
Cross-section View of
Virginia Tech Reactor



after Rimstidt (1998)



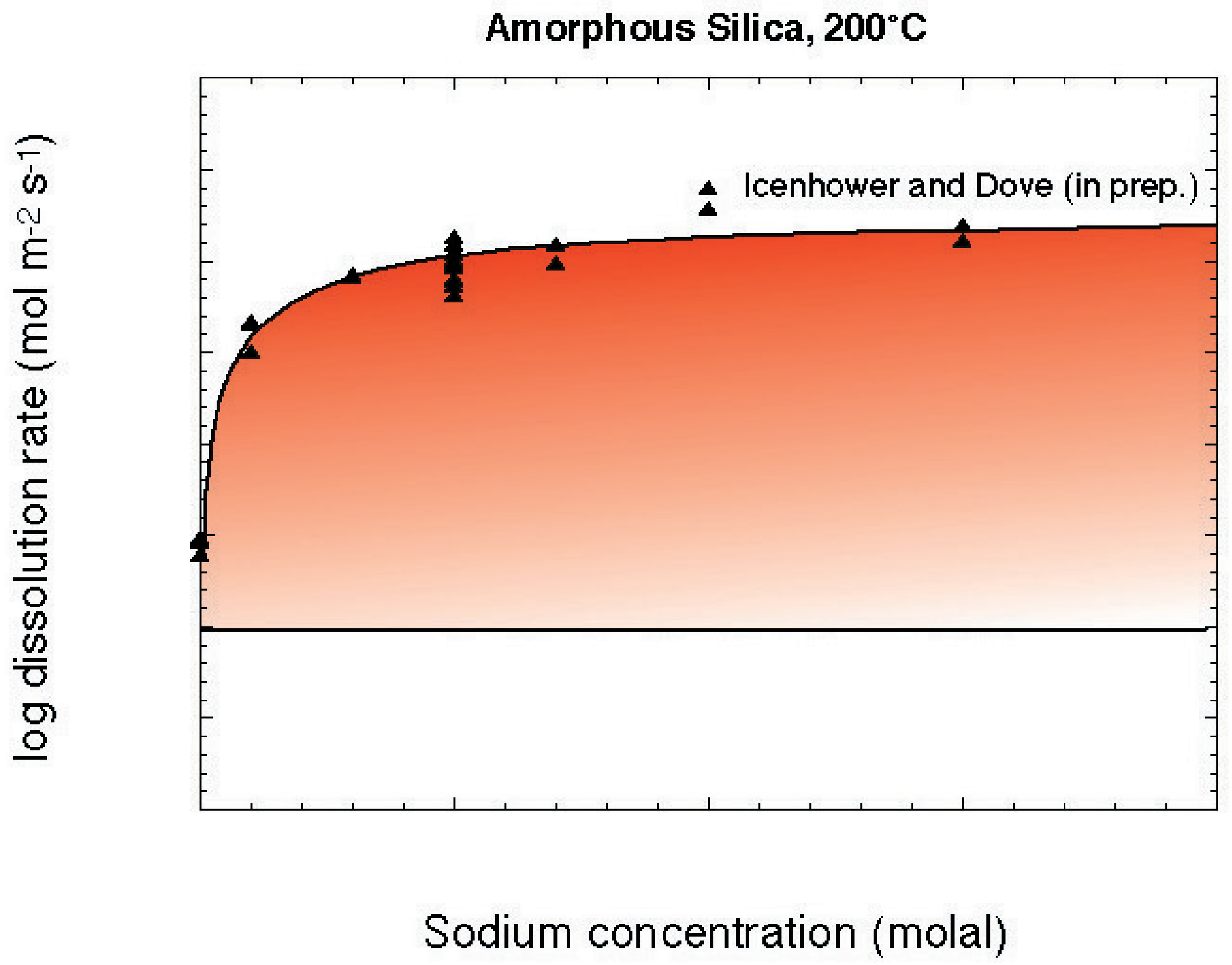
Dependence of silica glass dissolution kinetics at 60°C on sodium concentration. Rates increase by ~8X in 0.05 m NaCl compared to deionized water and contrast with previous predictions.

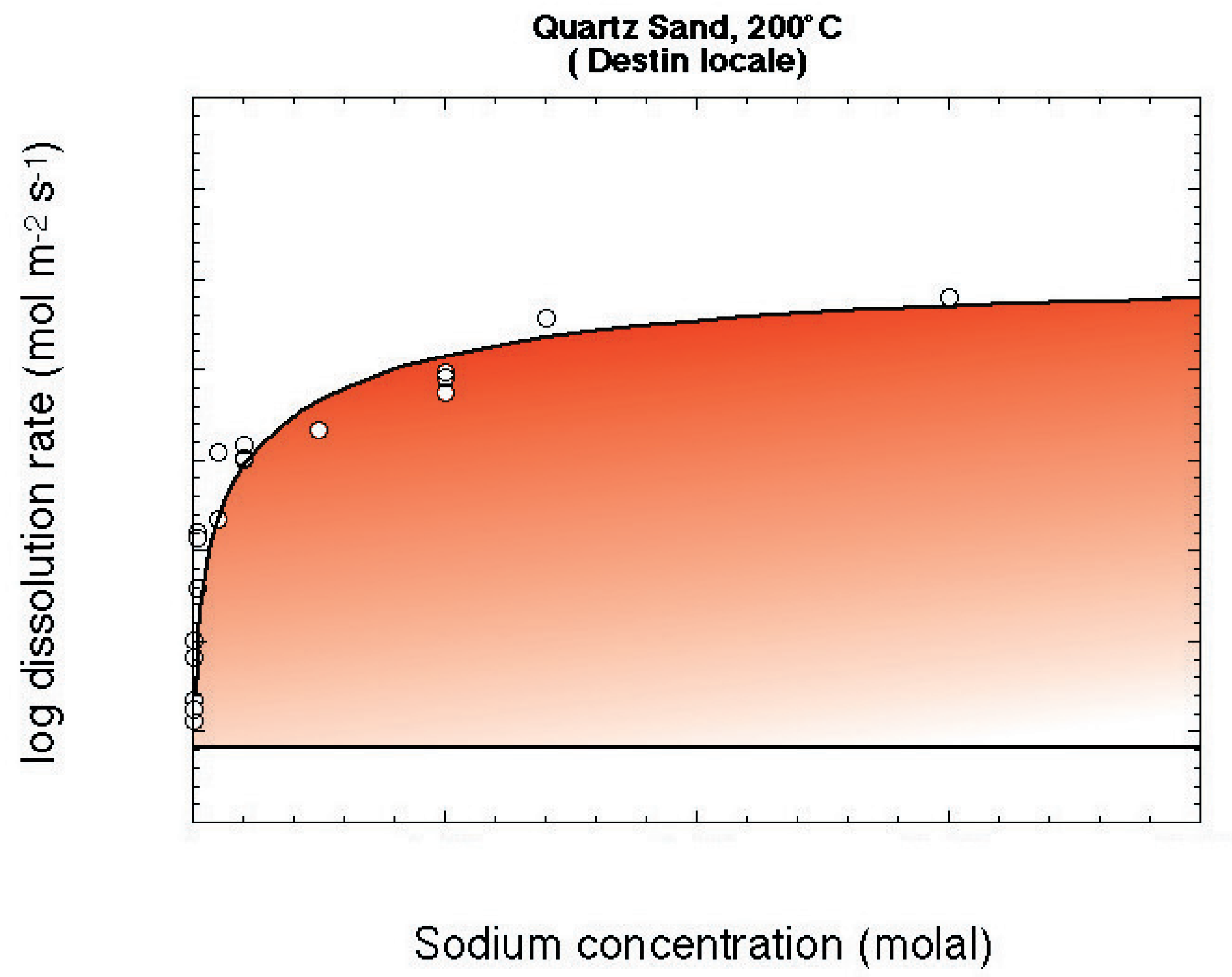


Flow-through hydrothermal mixed flow reactors were used to measure dissolution rates at 140 - 295°C.

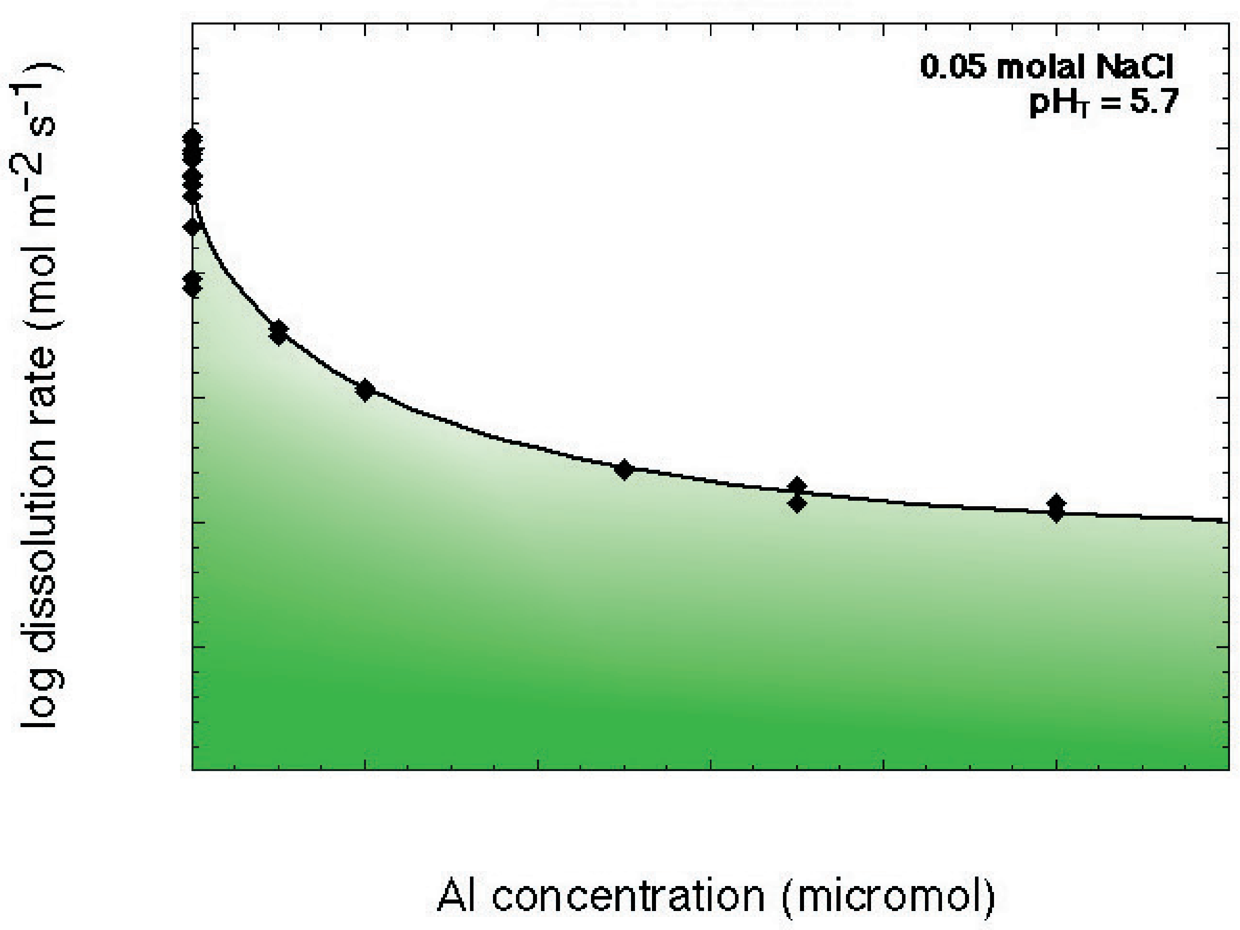
PHASE 2:
Constructing a Baseline for Silica Glass and Comparisons to Quartz

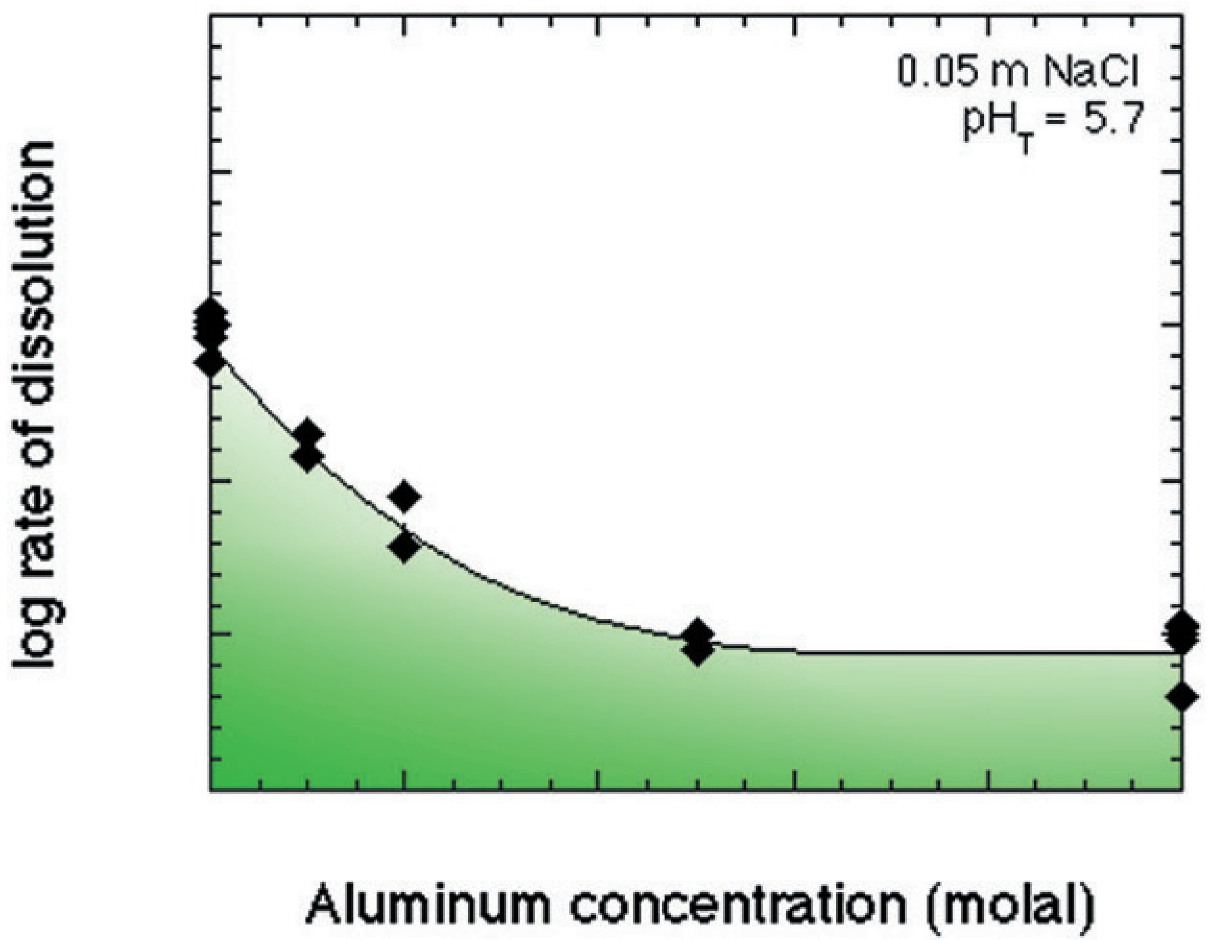
The first reported measurements for silica glass dissolution kinetics at 200°C show dependence on sodium concentration (left). Sodium (0.05 m NaCl) increases rates by ~50X compared to those measured in deionized water. Behavior is similar to quartz (right).



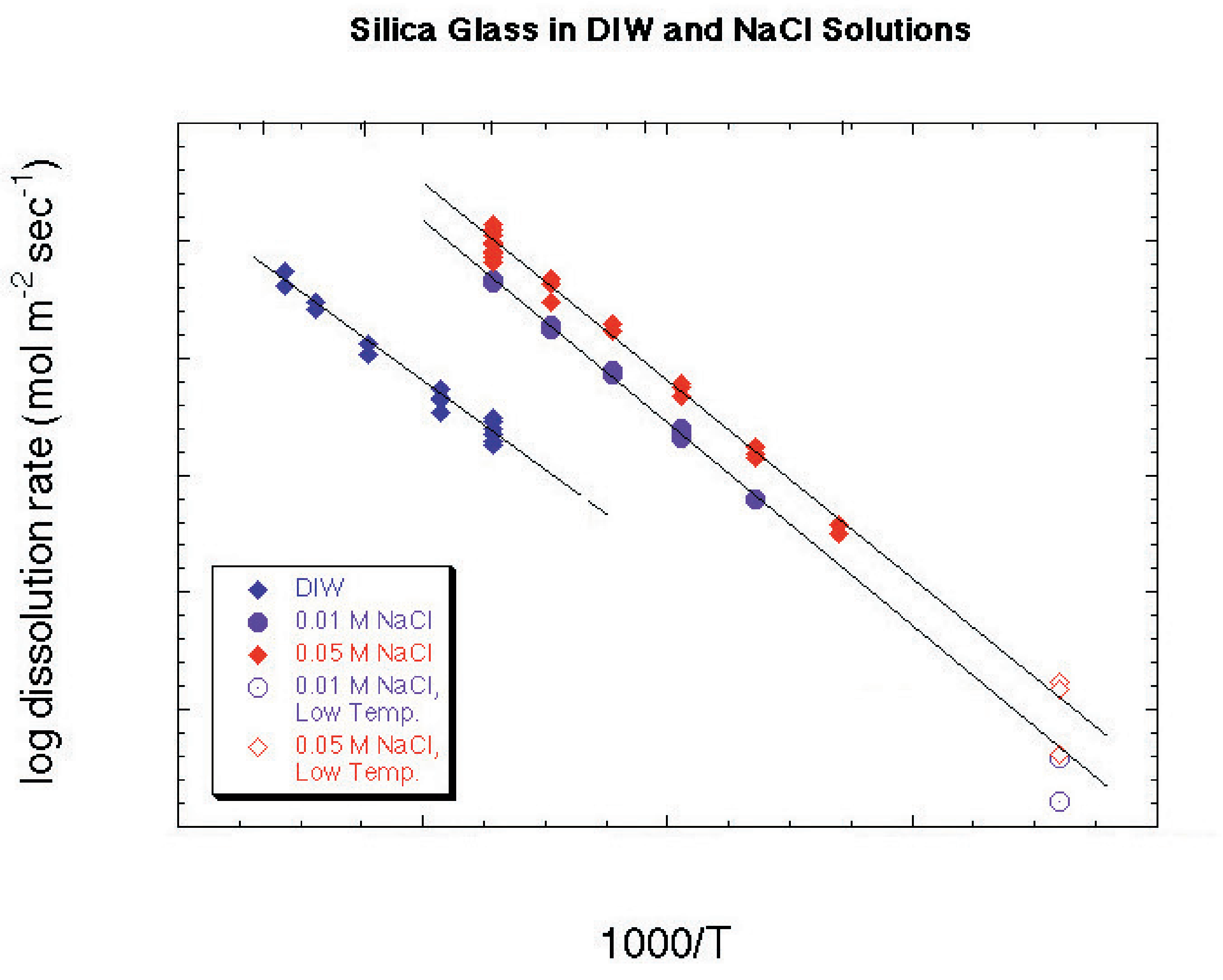


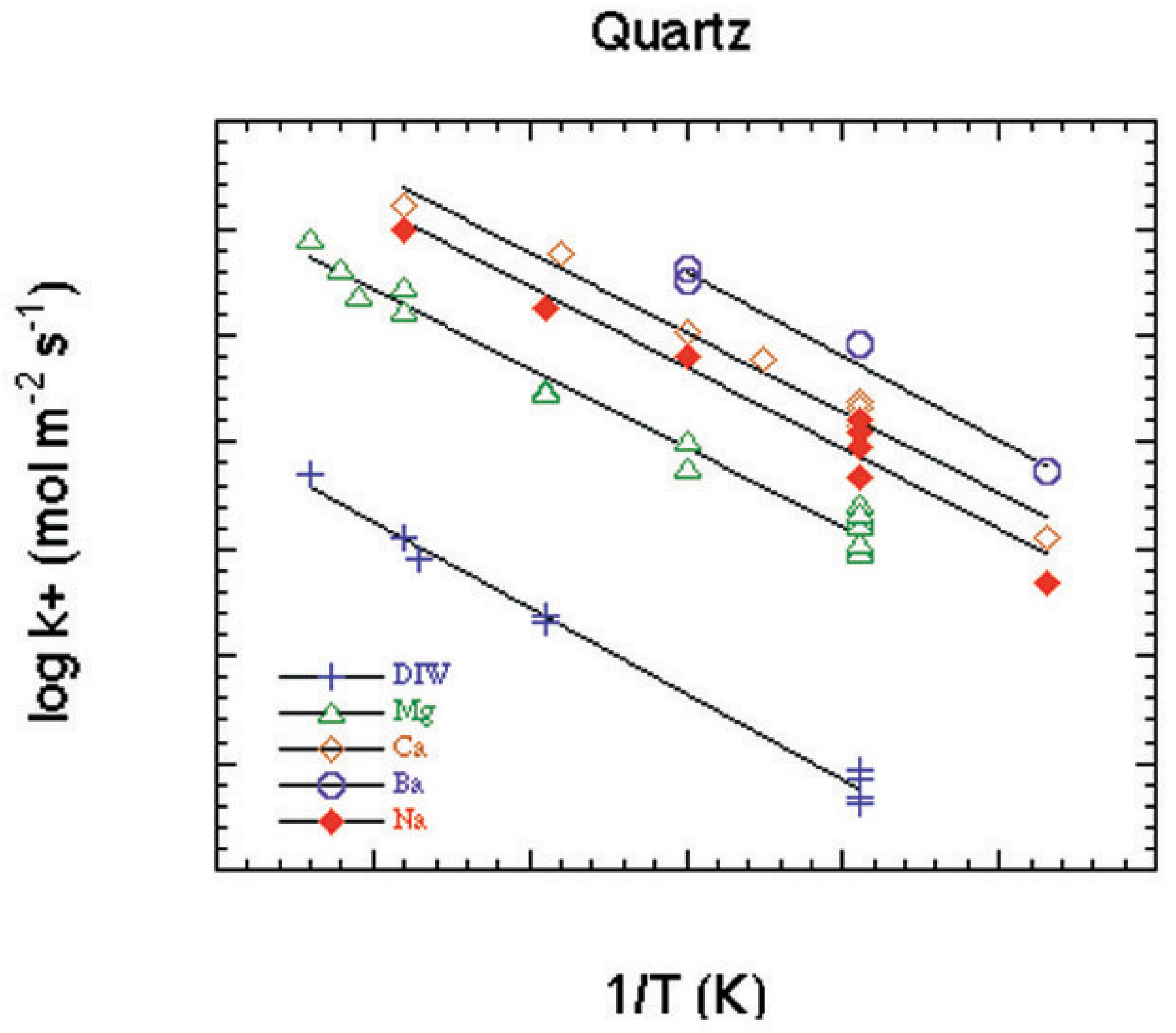
The dependence of dissolution rate on Al concentration (left) shows inhibition by a factor of only ≤10 in solutions containing 0.05 m NaCl. At these conditions, boehmite solubility is exceeded at approximately 5 micromoles Al at these conditions but the extent of inhibition appears continuous without inflection. Quartz exhibits similar behavior (right).



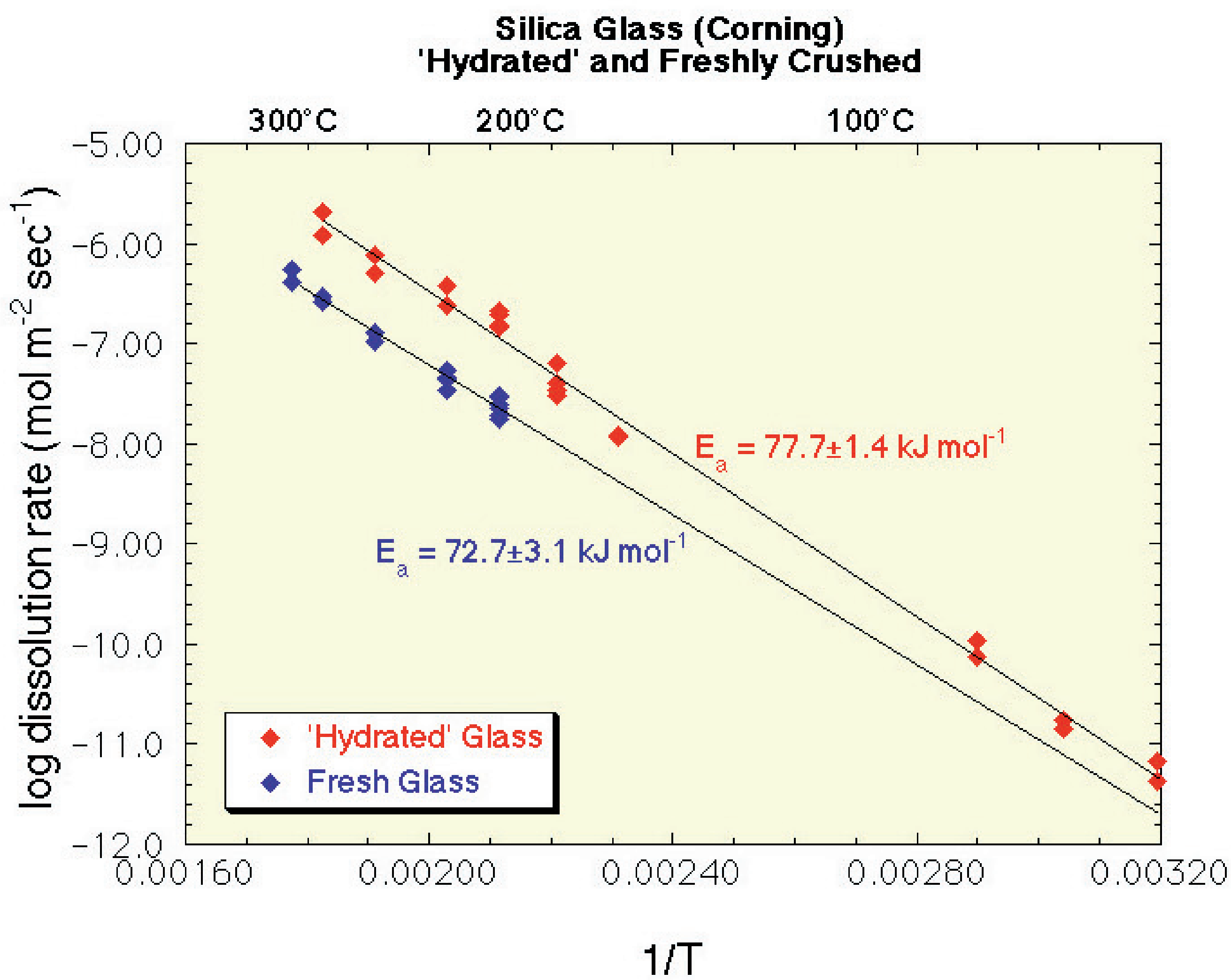


Arrhenius diagrams illustrate the temperature dependence of silica glass (left) for three solution compositions. Data are the first measurements of silica glass dissolution kinetics at ≥100°C.
Best-fit experimental activation energies, Ea, are similar to those measured for quartz (right). We predict that dissolution rates of silica glass and quartz in solutions containing IA and IIA cations will exhibit similar reactivity trends (e.g. Dove and Nix, 1997).





PHASE 3:
Role of Hydration in Glass Durability



Arrhenius diagram shows the faster rates observed when silica glass is pretreated by subjecting the starting materials (from Corning, Inc.) to 60°C solutions for approximately 1,000 hours. Work is underway to characterize OH contents for a suite of pretreated materials and correlate with dissolution properties.

WORK IN PROGRESS

- Develop comprehensive model of silica glass dissolution kinetics
- Correlate dissolution rates with estimates of OH content in glass using spectroscopic methods.
- Construct predictive model that describes relationships between dissolution rates and glass structures modified from SiO2(am) compositions by Na, Ca, B, and Al.
- Develop dissolution rate model for reactivity in solutions that simulate fluid compositions of subsurface environments.

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ACKNOWLEDGMENTS

This work is supported by the Department of Energy EMSP project DE-FG07-96ER14699. We thank Corning, Inc. and Quartz Scientific, Inc. for their contributions of silica glass materials. Professor Don Rimstidt generously shared the unpublished design of the low temperature reactor vessels. We also thank Troy Lorier, Meg Grantham, and Kevin Davis for contributions to important aspects of this project.