

Dissolution of Borosilicate Glass Into Brine Solutions: Effects of Sodium and Magnesium

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Introduction

Brine solutions may be present in geologic repositories if: (1) the repository is sited in rock salt (e.g., Waste Isolation Pilot Plant, or **WIPP**, Carlsbad, NM), or (2) heat given off by high level waste drives repeated cycles of evaporation and condensation. **However, the dissolution of borosilicate glass into brine solution has not systematically been studied and, therefore, the kinetics of dissolution has not been satisfactorily quantified.**

Here, we present the results of experiments conducted using a flow-through apparatus at 90°C, pH (25°C) = 9, on a borosilicate glass (International Simple Glass, or **ISG**), over a NaCl (0 to 4.0 molal, or *m*) or MgCl₂ (0 to 1.5 *m*) concentration interval. In addition, experiments were carried out using a simplified brine (3.5 *m* NaCl and 1.0 *m* MgCl₂), similar in composition to those at WIPP.

One of the fundamental questions this project addresses is: **What controls the dissolution rate of borosilicate glass?** Is it the sum of the free energy contributions from each molecular group in the glass, or is it the rupture of the Si—O bond in the silicate network? If it is the latter, then we would expect that even multicomponent borosilicate glass will behave like the silica (SiO₂) polymorphs (β-quartz, amorphous silica or a SiO₂). Previous work has shown that dissolution rates of SiO₂ polymorphs are catalyzed by NaCl [1, 2]. Therefore, these experiments have the potential to yield important insights into the dissolution behavior of high-level waste glass in repository environments.

An additional area of inquiry surrounds the effects of Mg²⁺ on borosilicate glass dissolution kinetics. Magnesium is an important component in many brine solutions, but its effects remain ambiguous. In the literature, **both catalytic and inhibition effects** have been attributed to the presence of Mg²⁺ [3, 4]. These experiments specifically address this problem.

Methods

Experiments were conducted using a flow-through apparatus in which solution was pumped through Teflon reactors at rates of 30 or 60 mL/d. Reactors contained either glass powders (850 – 600 μm diameter) or monoliths (2 × 2 × 0.4 cm coupons). The surface area of the samples were determined either by B.E.T. (powders) or digital calipers (monoliths). Experiments were run at the same flow-rate (*q*) to surface area (*S*) to ensure a valid basis of comparison.

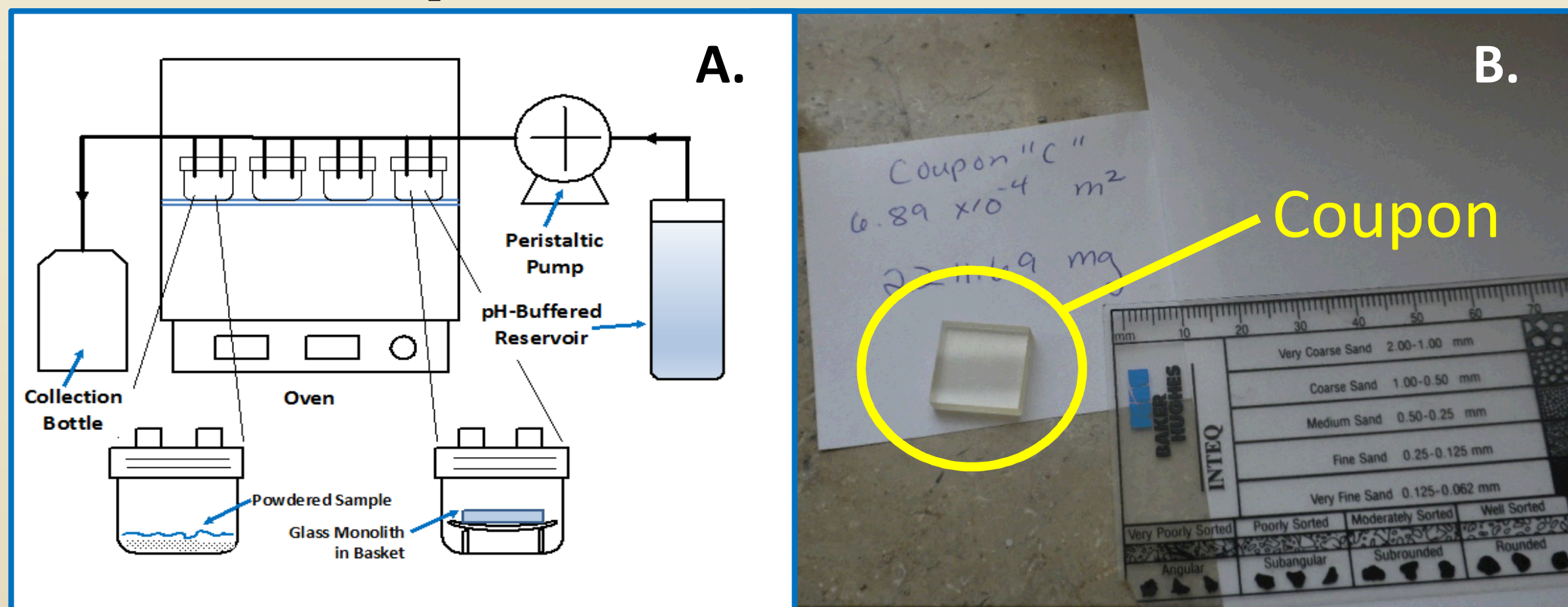


Figure 1: Schematic of flow-through system (1A.; left), and picture of typical glass monolith coupon (1B.; right).

1. Rate Determination—Effluent Assay

Dissolution rates were quantified by determining the release of Si to solution (ICP-AES). Aliquots of the effluent solution were collected weekly, until steady-state conditions (constant element concentrations) occurred. Rates were quantified using the following equation:

$$rate_i = \frac{(C_i^{out} - C_i^{bg})q}{f_i S} \quad \text{where } rate_i \text{ is the flux of element } i \text{ [g/(m}^2\text{·d)],}$$

C_i^{out} and C_i^{bg} are the concentrations of element *i* in the effluent and background, resp. (g/L), *q* is the flow-rate (L/d), f_i is the mass fraction of element *i* in glass (dimensionless) and *S* is the specific geometric surface area (m²). Under some experimental conditions, the glass dissolution rates were so low that the concentrations of elements in the effluent neared the analytical quantification limit. For these situations a method based on interferometry was used, as discussed next.

2. Rate Determination—Interferometry

For this technique, a small portion of a glass monolith was masked by applying a bead of silicone RTV cement to the surface. The coupon is then placed into the flow-through reactor. After a certain amount of elapsed time, the monoliths were removed from the reactor and the silicone mask removed. The silicone bead preserves a pristine reference surface whose relative height with respect to the reaction surface can be measured by white light interferometry. Height differences of approximately 20 nm can be accurately and repeatedly measured by the interferometer. The technique is summarized in the following cartoon and figure:

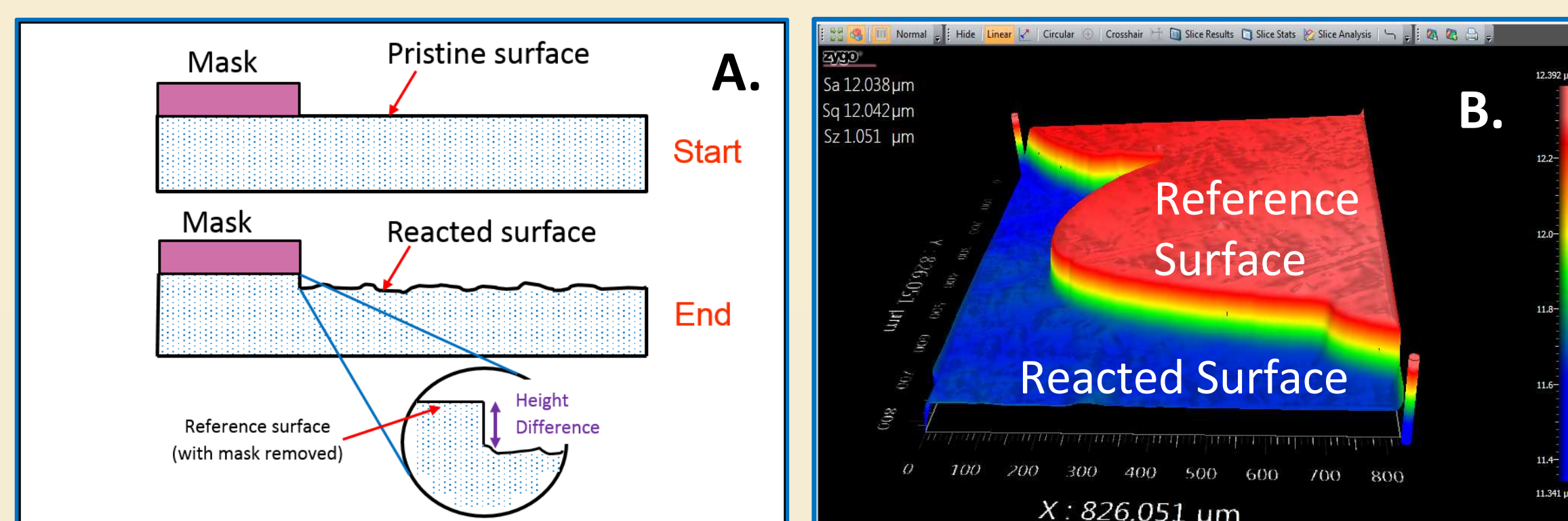


Figure 2: A cartoon illustrating the relationship between the masked, reference and reacted surfaces (2A.; left). A 3D height map (2B; right) of a portion of the reference and reacted surfaces of a ISG monolith (826 × 826 μm) exposed to solution at 90°C for two weeks (red = relative high, blue relative low “elevations”). The silicone mask has been removed, revealing the reference surface. The reacted surface is at a lower relative “elevation” due to surface retreat (dissolution).

The difference in height between the reference and reacted surfaces is proportional to the dissolution rate:

$$Rate = \rho \frac{\Delta h}{\Delta t} \quad \text{where the } Rate \text{ is dissolution rate [g/(m}^2\text{·d)], } \rho \text{ is the glass density (g/m}^3\text{), } \Delta h \text{ is the measured height difference between the reference and reacted surfaces (m), and } \Delta t \text{ is elapsed time (days).}$$

Results

1. NaCl Solutions

The figure below illustrates that glass comes to steady-state conditions in ~30 - 50 days in NaCl solutions.

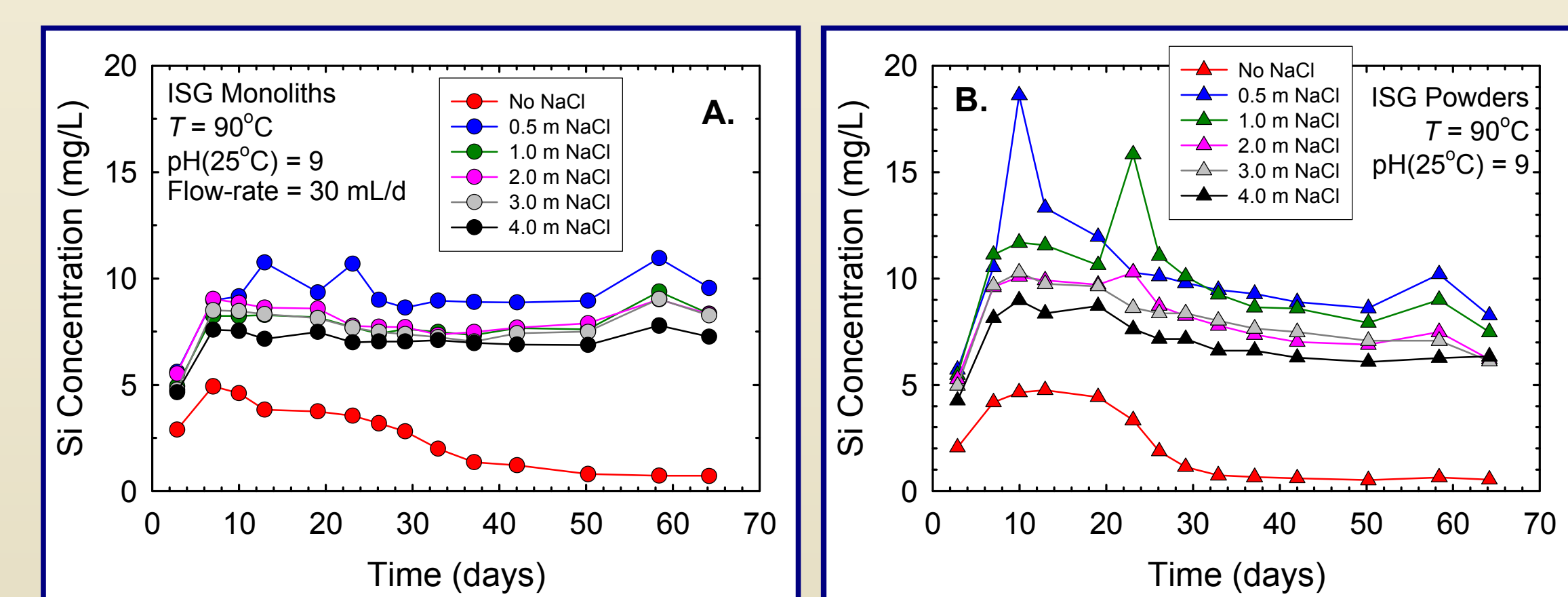


Figure 3: Figures illustrating the approach to steady-state conditions for monoliths (A; left) and powders (B; right). The figures show the release of Si from glass to solution.

Note that the figures indicate the release of Si from glass to solution is slowest for the solution that contains no NaCl, is fastest for the 0.5 molal NaCl solutions, then progressively decreases with increasing NaCl. Calculated dissolution rates (based on Si release) confirm that this is the case: **The presence of even low concentrations of NaCl increases the dissolution rate of borosilicate glass.**

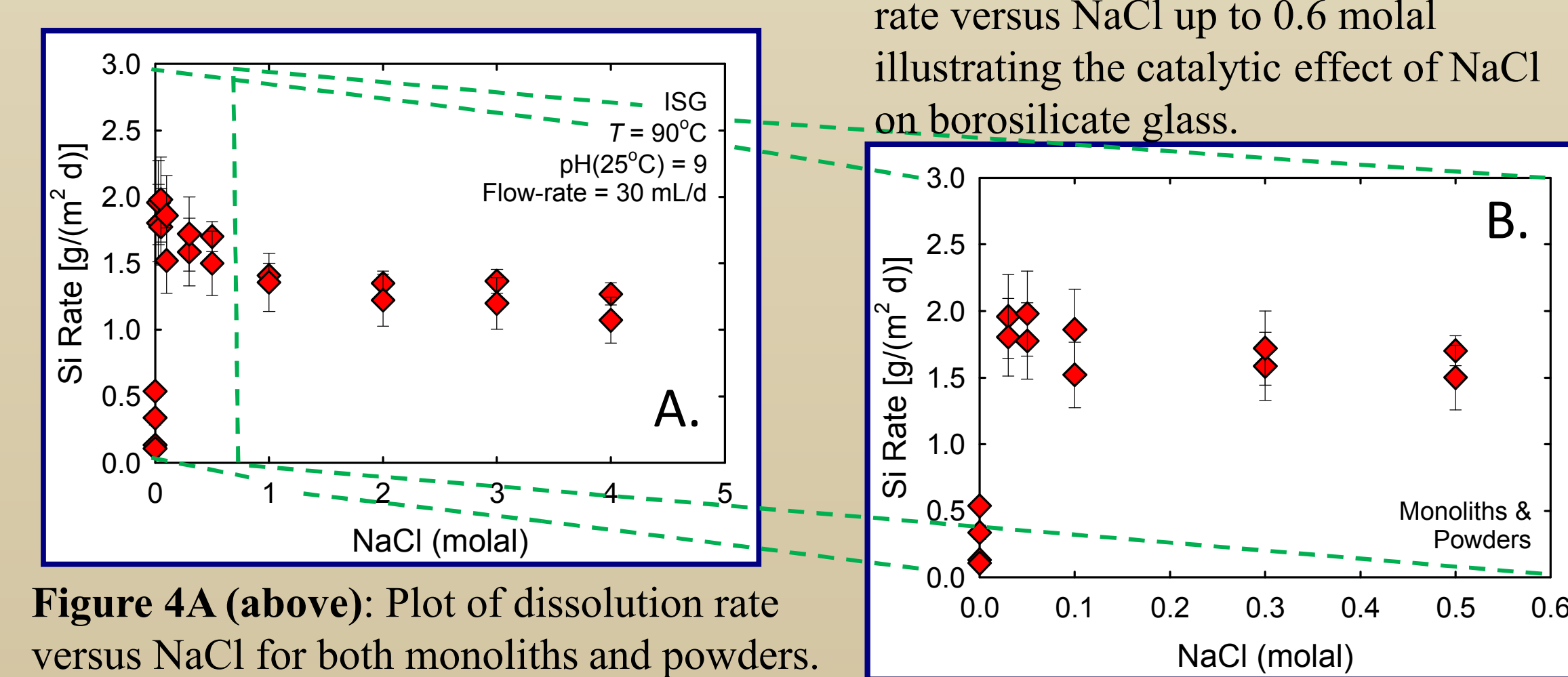


Figure 4A (above): Plot of dissolution rate versus NaCl for both monoliths and powders.

The data indicate that NaCl causes an increase in the rate of borosilicate glass dissolution, just as in the case of SiO₂ polymorphs. However, what does this increase look like?

To determine relationship between NaCl and the rate, we normalized the rates by dividing those in NaCl solutions to the average in NaCl-free solutions. In this way, we could compare rates between SiO₂ polymorphs and borosilicate glass on a more-or-less even basis:

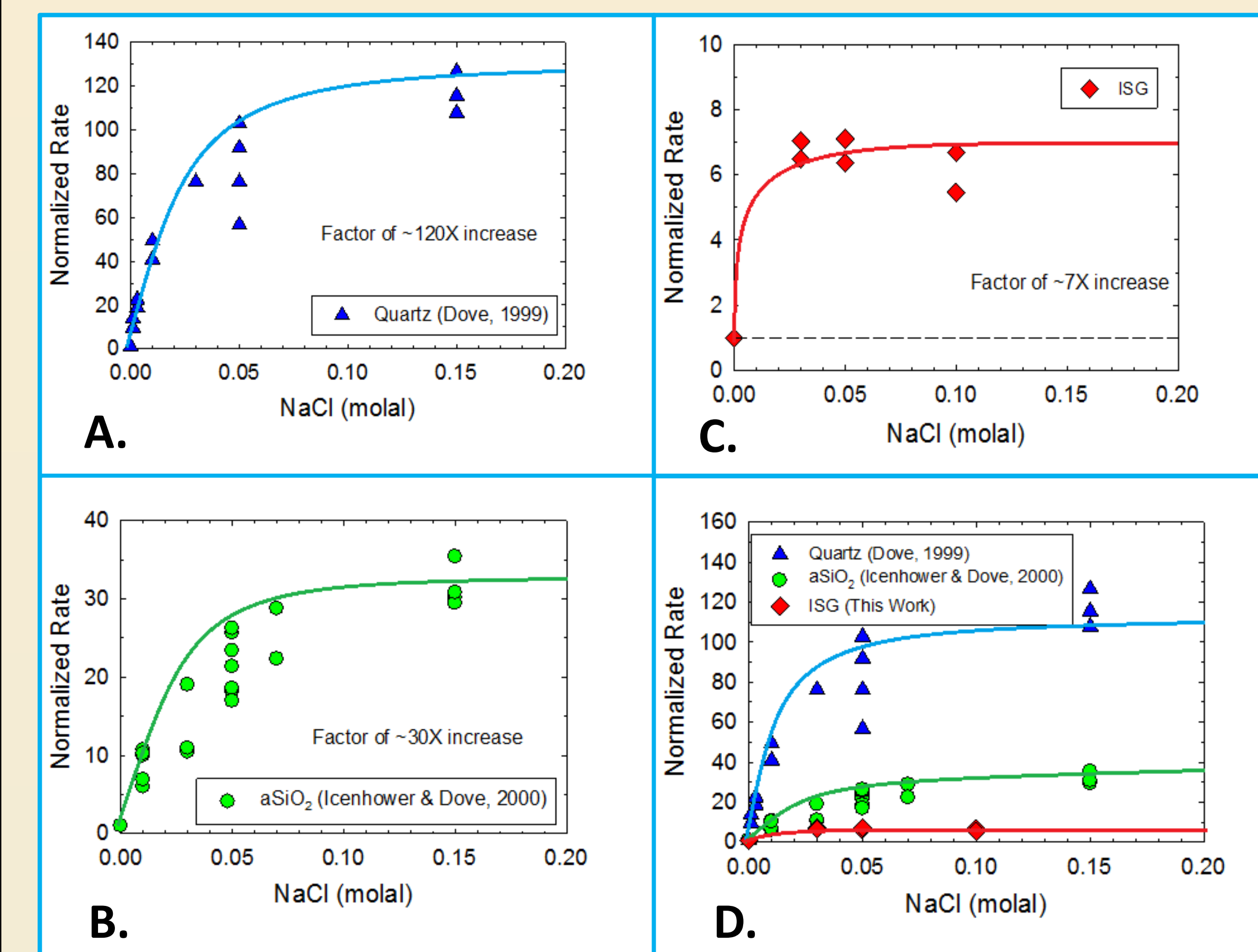


Figure 5: Plots of Normalized Rates (rates in NaCl solutions/average rates in NaCl-free solutions) versus NaCl for (5A) β-quartz [1], (5B) aSiO₂ (amorphous silica) [2], (5C) ISG borosilicate glass (this work), and (5D) all three solids on the same plot.

As the above figures makes clear, the dissolution behavior of ISG borosilicate glass is similar to that of the silica polymorphs, even though the magnitude of the rate catalysis is not as large. **These data indicate that silica polymorphs and borosilicate glass dissolution is governed by breaking of Si—O bonds.**

With increasing NaCl in solution, the rates decrease from peak values in a linear fashion:

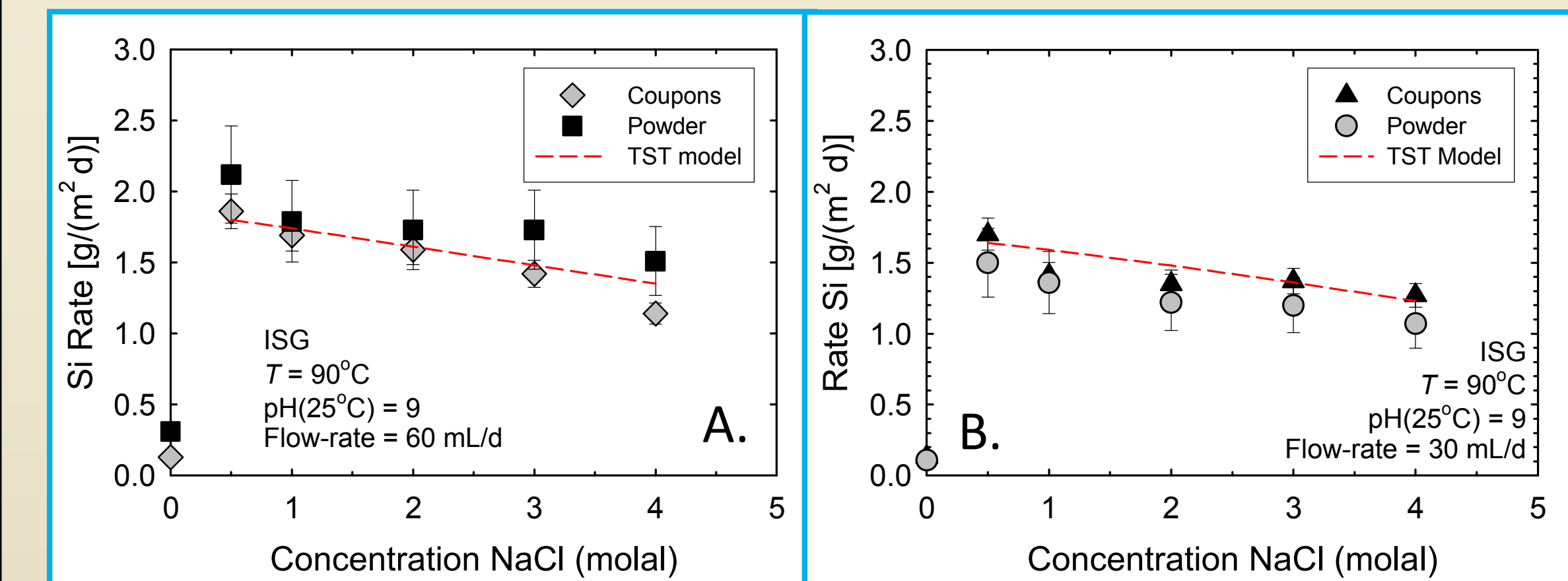


Figure 6: Plots of the rate of dissolution (based on Si release) versus NaCl concentration for solutions >0.5 molal. Rates for monoliths and powders are distinguished. The data indicate that the dissolution rate in concentrated brines is governed by the decrease in the activity of water.

These data can be understood in terms of the model for silica dissolution:

$$Rate = k_0 \cdot (a_{SiO_2}) \cdot (a_{H_2O})^2 \cdot \left(1 - \frac{Q}{K}\right)$$

This rate expression indicates that the rate is a product of k_0 , the rate constant [g/(m²·d)], the activity of silica in the glass (dimensionless), the activity of water (dimensionless) and a term describing the departure from equilibrium ($1 - Q/K$) (dimensionless). Thus, the decrease in the activity of water, occurring in response to the increase of NaCl in solution, results in a rate decrease. **This relationship can be understood in terms of Transition State Theory (TST); there are fewer free molecules of water available that can rupture the Si—O bond.**

References: [1] Dove, P. M. (1999). *Geochim. Cosmochim. Acta* **63**, 3715-3727. [2] Icenhower, J. P. and Dove, P. M. (2000) *Geochim. Cosmochim. Acta* **64**, 4193-4203. [3] Debur, M. De Windt, L., Frugier, P., Gin, S. and Viellard, P. (2016) *J. Nucl. Mater.* **475**, 255-265. [4] Harrison, M. T. (2014) *Procedia Mater. Sci.* **7**, 186-192.

2. MgCl₂ & Mixed (NaCl-MgCl₂) Solutions

Dissolution rates for ISG were determined by Si release. Because Si concentrations in the effluent approach the analytical quantification limit, rates were also determined using interferometry. The rates are very similar (~4× difference maximum). As the figure below demonstrates, **the rates of borosilicate glass dissolution decrease as Mg is added to solution.**

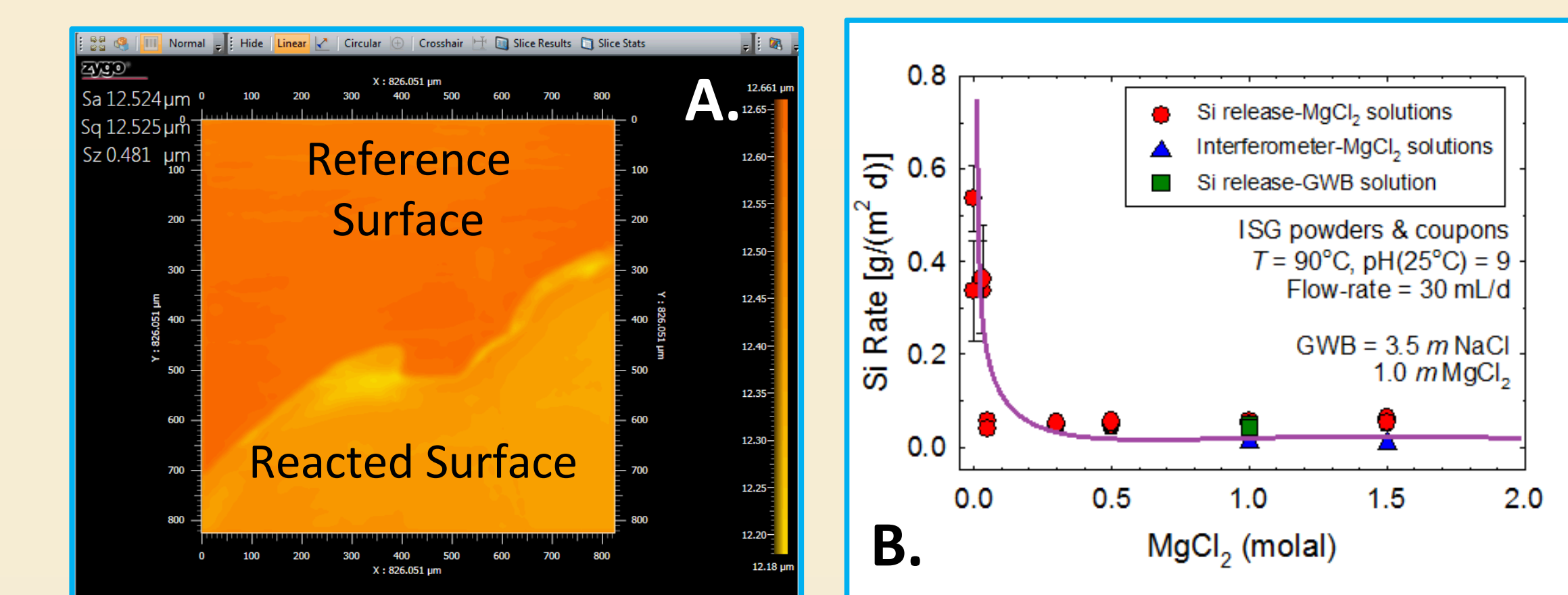


Figure 7: (A; left) Two-dimensional height map obtained on a 826 × 826 μm section of a glass coupon reacted in 1.0 m MgCl₂ solution for 40 days. The Δh between the reference and reacted surface is ~300 nm. (B; right) A plot of the dissolution rate versus MgCl₂ concentration. Rates were determined by Si assay in MgCl₂ (red circles), in simplified synthetic brine (GWB; green squares) and by interferometry (blue triangles). Powders and monoliths are not differentiated on this figure. Note that the dissolution rate of ISG in the synthetic GWB is indistinguishable from the rates in MgCl₂ only.

The difference in dissolution rates between glass reacted in NaCl versus MgCl₂ is shown below. The maximum and minimum differences are ~70 and 40×. In addition, note that the rate of the glass reacted in the simple brine (GWB; 3.5 *m* NaCl, 1.0 *m* MgCl₂) is indistinguishable from glass reacted in MgCl₂ only. **These data demonstrate that the effects of Mg²⁺ dominate over those of Na⁺.**

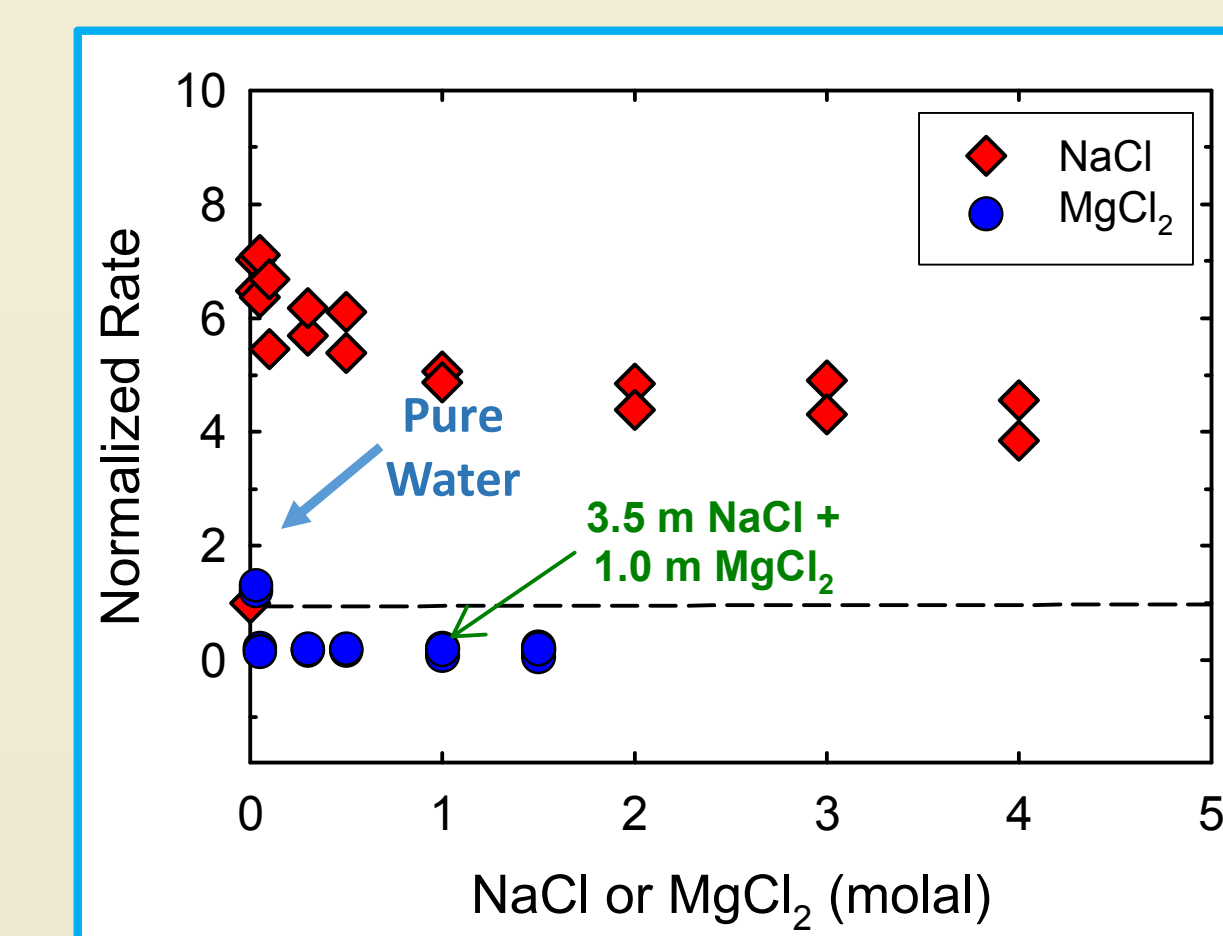
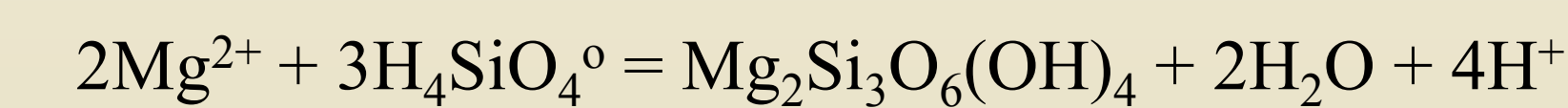


Figure 8: Plot of normalized rate versus concentration of either NaCl or MgCl₂.

A Caveat: In other experiments, especially those in static (rather than flow-through) reactors, the presence of magnesium correlates with rate *catalysis*, not *inhibition*. Rate catalysis is thought to occur due to precipitation of Mg-rich clays, which depletes solution in Si. The glass responds by dissolving faster so that Si will return to the former concentrations. Equilibrium between Mg²⁺, silica and Mg-rich clay can be written as:



It is therefore possible that because the experiments are conducted in flow-through reactors, the solution is too dilute with respect to silicic acid to become saturated with Mg-rich clay.

Conclusions

The major conclusions of this work in progress are:

- Dissolution rates of borosilicate glass are catalyzed by NaCl at low concentrations.
- This rate behavior is similar to that observed for silica polymorphs, suggesting that borosilicate glass behaves like SiO₂.
- At higher concentrations of NaCl, the rates decrease due to a decrease in the activity of water.
- The presence of MgCl₂ inhibits glass dissolution in flow-through reactors, but different behavior might be expected in static reactors, in which Mg-rich clay minerals are likely to form.

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