

## Origins of Deviations From Transition-State Theory: Affects of Ion-Exchange Kinetics in Glass

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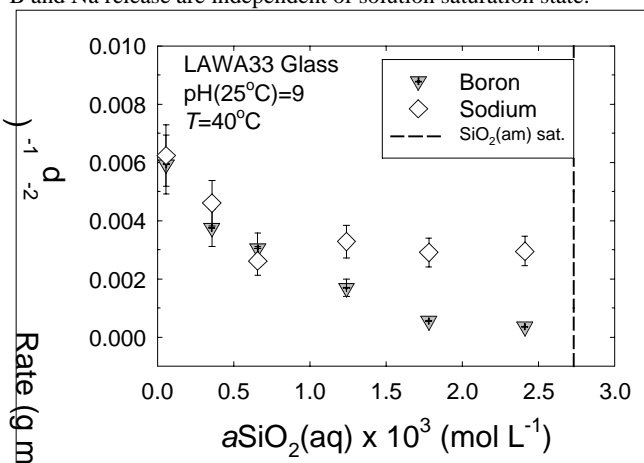
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### Introduction

Experimental investigations of glass dissolution kinetics have highlighted deviations from Transition-State Theory (1) (TST) as solution compositions approach equilibrium with rate-limiting secondary solids. These deviations from expectations are especially prominent in alkali borosilicate glass compositions that are proposed matrices for radioactive waste disposal. To date, a satisfactory explanation for such deviations has not been advanced.

### Experimental Results

Single-Pass Flow-Through (SPFT) experiments were conducted to evaluate the reaction kinetics of sodium aluminoborosilicate glasses. Solutions were doped in dissolved Si up to saturation with respect to amorphous silica. For glasses containing molar  $\text{Na} > (\text{Al} + \text{B})$ , the results are illustrated in below. Rates of boron and sodium release become independent of solution composition at high activities of  $\text{SiO}_2(\text{aq})$ , which is not predicted by TST-based models (2). The ion exchange (IEX) reaction,  $\text{Na}^+ = \text{H}_3\text{O}^+$ , explains not only the relatively fast release of sodium compared to boron, but the catalysis of Si—O rupture as well. Therefore, rates of B and Na release are independent of solution saturation state.



### Conclusions

Our experiments indicate the importance of IEX reactions in exerting a governing influence on element release in solutions approaching saturation. Therefore, TST models must be modified to accommodate the existing database.

### References

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2. B. E. Grambow, *Mat. Res. Soc. Symp. Proc.* **44**, 15-27 (1985).

## Kinetics of silica nanocolloid formation from supersaturated solutions

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The mechanisms by which silica colloids grow and precipitate are critical to understanding a host of geological and industrial processes, including silica diagenesis, fossilization by silicification, and the deposition of silica scale during the extraction of geothermal energy. However, rate laws reported for the precipitation of silica in natural environments are often contradictory, and the kinetics of monosilicic acid condensation are poorly understood. Here we examine the evolution of silica colloids in simulated brine solutions (ionic strength = 0.25 M) ranging in pH from 3 to 7.

Changes in monosilicic acid, nanocolloidal silica (<0.1  $\mu\text{m}$  effective diameter), and silica precipitate concentrations were monitored in batch reactions. The experiments were conducted with initial silica concentrations of 750 and 1250 mg/L. Monosilicic acid concentrations were measured using the colorimetric silicomolybdate assay. We analysed the total dissolved silica [ $\text{SiO}_2$ ] in 0.1  $\mu\text{m}$ -filtered solutions using ICP-AES and calculated nanocolloid concentrations by difference. The precipitate produced in a given run was defined as the difference between the starting silica concentration and [ $\text{SiO}_2$ ] measured in the 0.1  $\mu\text{m}$ -filtered solutions.

Previous experiments have shown that in solutions supersaturated with respect to amorphous silica, monomeric silica first condenses to nanoscale colloids with particle sizes of  $\sim 3$  nm. This population persists metastably until the nanocolloids coalesce and precipitate as silica gel. In this study, we explored the first step of this reaction in a simulated brine solution. Our analysis of the reaction kinetics that govern the initial stages of transformation from monosilicic acid to nanocolloids reveals that the rate of decrease of dissolved monomeric silica with time,  $R$ , has a fourth order rate dependence:  $R = k [\text{SiO}_2]^4$ . Here,  $k$  ( $\text{mM}^{-1} \text{sec}^{-1}$ ), the rate constant, varies with pH according to  $k = k_o [H^+]^{0.89}$ , and  $k_o$  is the rate constant at pH 0 (Figure 1). Data at lower concentrations and ionic strength currently are being fit to a similar fourth order model.

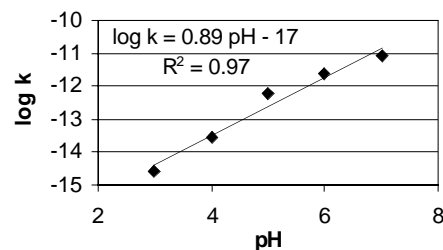


Figure 1. pH dependence of the transformation from monosilicic acid to nanocolloids.