

Project Number:
DE-FG07-01ER63295

Project Title: Origins of Deviations from Transition-State Theory: Formulating a New Kinetic Rate Law for Dissolution of Silicates

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Number of Graduate Students Involved: 2

Number of Undergraduate Students Involved: 2

RESEARCH OBJECTIVES

Present models for dissolution of silicate minerals and glasses, based on Transition-State Theory (TST), overestimate the reaction rate as solution compositions approach saturation with respect to the rate-governing solid. Therefore, the reactivity of key materials in the environment, such as feldspar, mica, and borosilicate glass, is uncertain and any prediction of future aqueous susceptibility to dissolution is suspect. The core objective of this investigation was to determine the origin of these discrepancies and to fashion a quantitative model that reliably predicts the reactivity of silicate materials in realistic environmental conditions. This was accomplished using newly developed experimental techniques. Results of these experiments were verified against computer simulations based upon first-principle theory.

RESEARCH PROGRESS AND IMPLICATIONS

Please, note that a final report was submitted by the PNNL group (Dr. J. Icenhower) in 2004. This additional final report repeats and summarizes progress and results only for the Rice group working under the same joint proposal but with a separate budget and an additional one year no-cost extension.

Determining Dissolution Rates Near Saturation Using Vertical Scanning Interferometry (VSI)

Accurate rate measurements are difficult to determine near or at saturation. Because reaction rates diminish in response to saturation, the dissolution process is typically very slow. Accordingly, concentrations of key elements in a dissolution experiment may be near or at the lower limit of detection of most analytical devices. Therefore, we have used Vertical Scanning Interferometry (VSI) techniques to accurately quantify dissolution rates over a range of solution saturation states by measuring minute height differences between a reacted and a reference surface. Based on the height difference between the reacted and the reference surface over the duration of the experiment, the rate of dissolution can be calculated from the specimen density. Further details of the VSI method can be found in articles by Lüttge and coworkers (e.g., LÜTTGE et al., 1999; LÜTTGE, 2004a).

Figure 1 displays the results of a comparison of glass dissolution rates obtained by element release to solution *on the same test specimens* with dissolution rates determined using VSI measurements. The data shown in Fig. 1 demonstrate that VSI is a reliable means of quantifying (slow) dissolution rates with high precision. Although in subsequent work the PNNL group (e.g., ICENHOWER et al., 2003, 2004) focused on glass dissolution rates, the Rice group focused on the

ΔG dependence of the dissolution rate of natural minerals, e.g., feldspar endmembers: albite and anorthite.

Mineral dissolution kinetics

In our investigation, we have utilized a combined approach of experimental techniques, e.g., VSI, AFM, and XPS and computer calculations based on Monte Carlo (MC) techniques in combination with *ab initio* and Density Functional Theory (DFT) calculations to simulate atomistic behavior at the mineral—fluid interface. This approach allowed us to account for the 3-dimensional structure of the solid surface and its different reactive sites. This is important, since the bonding characteristics and therefore the reactivity of the first ~nanometer of surface materials are different than molecular arrangements away from the surface (bulk crystal) (BANFIELD and ZHANG, 2001; LASAGA, 1998). Our objective was to define, quantify, and model the likely motion of molecular units at the surface (LASAGA and LÜTTGE, 2001; LASAGA and LÜTTGE, 2004a, b; 2005; LÜTTGE, 2004a, b; 2005b); etch pit and kink site development are only a small subset of the possible processes that can occur.

The results of our investigations (e.g., Arvidson et al., 2003; 2004; 2005; BEIG and LÜTTGE, 2005; and VINSON and LÜTTGE, 2005) have demonstrated the importance and interplay of several so-called basic processes that occur at the fluid-solid interface. These results have provided experimental support for the stepwave model presented by LASAGA and LÜTTGE (2001, 2003). We have illustrated that the overall crystal dissolution rate will depend critically on the three-dimensional structure of the crystal surface. Therefore, the surface structure must be included in any molecular treatment of crystal dissolution kinetics, or conversely, crystal growth kinetics. Dissolution can occur at a given surface reactivity only as fast as key molecular units arrive at and depart from the surface. Under conditions of increasing saturation ($\Delta\mu/kT$) and otherwise identical conditions (e.g., cation-anion bond strength, Φ/kT , energy of adsorption on the surface, E_{ad}/kT), the velocity of arrival of the rate-determining species may control the overall reaction. A faster arrival rate of a molecular unit at the surface of the mineral will result in a decrease in the dissolution rate (LASAGA and LÜTTGE, 2003; LASAGA and LÜTTGE, 2004a, b).

We compared the dissolution rates of two albite crystals (Na-feldspar); one that had previously been etched to produce extensive surface roughness, and one that was pristine (BEIG and LÜTTGE, 2005; LÜTTGE, 2005). We tested the two crystals simultaneously in our titanium flow reactor (ARVIDSON et al., 2005) and measured the extent of surface-normal retreat, and therefore reaction rate, of the specimens using VSI. Dissolution rates were measured as a function of solution saturation state. In previously published work, the ΔG dependence of mineral dissolution rates was studied by using mineral powders and focusing on the changes in solution chemistry. Comparison of these datasets shows inconsistencies between different laboratories even for the same mineral. Our study employing single crystals and direct

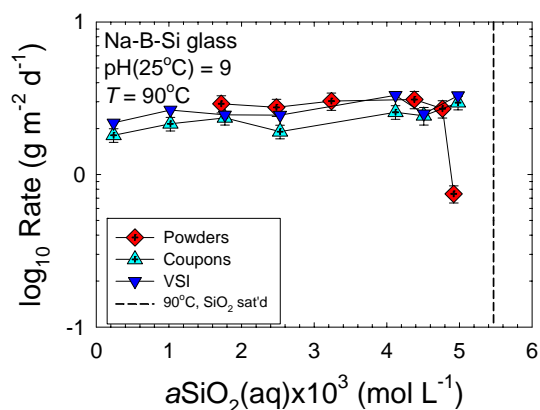


Figure 1. Plot of \log_{10} dissolution rate versus activity of silicic acid in solution nearly up to saturation with amorphous silica at 90°C, pH=9. The plot shows that rates based on solution analyses from tests with coupons or powders and from VSI measurements yield identical rate values (ICENHOWER et al., 2003).

observations of the dynamics of surface topography was able to explain the apparent discrepancy. Our results suggest a two-mechanism model to explain the dissolution behavior and the measured overall bulk rates. This model includes a “switch”, i.e., a bifurcation between the two mechanisms. When the second mechanism is active it is always dominant. For near-equilibrium conditions within the ΔG range where etch pits driven by screw dislocations are usually absent, the dissolution rate depends on the history of the sample. In contrast, the dissolution rate can be orders of magnitude faster if the equilibrium is approached from the far-from-equilibrium side, i.e., the dissolution plateau. In this case deep etch pits are already present and serve as the source for the continuous formation of stepwaves. Conversely, if the mineral-water system deviates from equilibrium, these pits cannot open up and the stepwave mechanism is not available - with dramatic consequences for the overall dissolution rate. Therefore, we have to consider the possibility of two distinctly different dissolution rates at otherwise identical temperature, pH and saturation state conditions.

This result is expected to have important implications for natural systems. The history of the soil or rock system will thus determine weathering rates. If the system maintained close-to-equilibrium conditions at all times, or larger deviations from equilibrium were short enough to prevent screw dislocation pits from opening, the dissolution rates will be eventually orders of magnitude slower than in a setting that allowed for the opening of such pits. Also, if samples with different histories are mixed, all intermediate rates would be possible depending on the ratio of pitted and unpitted material. If these conclusions are correct, kinetic models of reactive-flow and nuclear waste deposits must accommodate a far larger variability in rate than that expected from end-member-type laboratory studies. This result also puts constraints on our “hunt” for a “single” dissolution rate for any specific mineral.

Finally, we have reviewed the use and applicability of transition state theory (TST) to mineral dissolution. The results foster a skeptical view of this approach. Simple surface adsorption models can most likely not explain the complexity of the 3-dimensional lattice and its participation in the dissolution process. Current laboratory data of bulk dissolution rates are not precise enough to permit derivation of a specific dissolution mechanism by simply fitting a rate law to the data.

In contrast, the use of a stochastic approach that treats crystal dissolution as a many-body problem has led to the development of the stepwave model and some in-depth exploration of the dissolution mechanism. This new approach, in combination with analytical techniques like atomic force microscopy and vertical scanning interferometry, in addition to bulk dissolution experiments, shows promise of the development of a fundamental understanding and comprehensive theory of crystal dissolution.

Our findings can be explored in more detail in the following list of peer-reviewed publications resulting from the original proposal. The project publications do not include the numerous conference abstracts that the Rice group has presented during the lifetime of the project.

INFORMATION ACCESS

- Arvidson R.S., Collier M., Davis K.J., Vinson M.D., Amonette J.E., Lüttge A. (2005) The role of magnesium in calcite dissolution. *Geochimica et Cosmochimica Acta*. (in press).
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