Near-equilibrium albite dissolution kinetics

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Many kinetic processes of critical environmental importance occur close to thermodynamic equilibrium and derive their driving force from relatively small free energy differences.
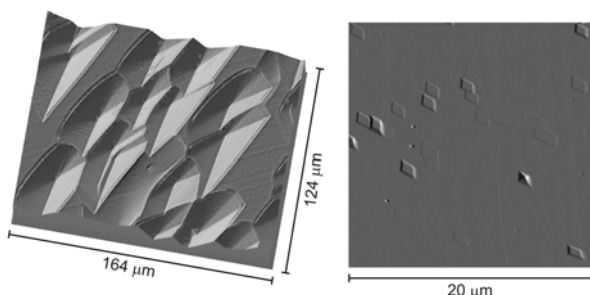

Figure: Left – 3D VSI map of treated albite (001) surface covered by coalescing, pyramidal etch pits. Right – AFM deflection map of untreated albite (001) surface dominated by smooth terraces containing flat-bottomed etch pits.

In order to generate a better understanding of the reaction kinetics of these systems we conducted dissolution experiments at pH 9 and 185ºC. Combining vertical scanning interferometry (VSI) and atomic force microscopy (AFM) allowed us to identify the dissolution mechanisms and quantify the rates of albite single crystals over a range of Gibbs free energy. During our experiments both a "treated" (exhibiting etch pits) and "untreated" (pristine) crystal were dissolved simultaneously within the same reactor. We observed a difference of up to 100 times in dissolution rate between both samples. Examination of reacted crystals at the micron- and nanoscale revealed evidence of two different dissolution mechanisms dominating the dissolution of the different crystals (see Figure). The rate difference persists over a range of solution saturation state and indicates that the dissolution mechanisms obey different Gibbs free energy dependencies. As a consequence, a mineral's history can have a major impact on its subsequent dissolution rate. With these results in mind, we examined existing kinetic datasets measured to determine the relationship between dissolution rate and Gibbs free energy. We suggest that existing discrepancies between experimental studies can be explained by differences in experimental methods. Finally, results from our albite dissolution study will be compared to similar experiments using single crystals of the other plagioclase endmember, i.e., anorthite and discussed within the context of an existing model for mineral/fluid interaction.

Feldspar dissolution rates and the Gibbs free energy of reaction

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This experimental study is an investigation of the relation between the dissolution rate of albite feldspar and the Gibbs free energy of reaction, ΔG_r. The experiments were carried out in a continuously stirred flow-through reactor at 150 °C and $pH_{(150°)}$ 9.2. The dissolution rates R are based on steady-state Si and Al concentrations and sample mass loss. The overall relation between ΔG_r and R was determined over a free energy range of $-150 < \Delta G_r < -15$ kJ mol^{-1}. The data define a highly non-linear, sigmoidal relation between R and ΔG_r that is characterized by 3 distinct free energy regions. The region furthest from equilibrium ($-150 < \Delta G_r < -70$ kJ mol^{-1}) represents an extensive rate plateau. In the sigmoidal 'transition equilibrium' region ($-70 \leq \Delta G_r \leq -25$ kJ mol^{-1}) the rates are strongly dependent on ΔG_r. Dissolution nearest equilibrium ($\Delta G_r > -25$ kJ mol^{-1}) is characterized by a weak dependence of the rates on ΔG_r. The data have been fitted to a rate equation (adapted from Burch et al., 1993) that represents the sum of two parallel reactions. A comparison of the R-ΔG_r data with transition state theory (TST) reveals a complete incompatibility.

Reference

Burch T.E., Nagy K.L. and Lasaga A.C. (1993), Chem. Geol. **105**, 137-162.