Barite dissolution: Computer simulations and experimental results

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A combination of Monte Carlo simulations and atomic force microscopy (AFM) studies explored barite dissolution kinetics at the molecular scale. This study shows that the barite (001) face undergoing dissolution develops two sets of oppositely-oriented triangular etch pits. The morphological evolution of the pits was successfully simulated using a kinetic model that incorporates the full 3-dimensional barite structure (Figure 1).
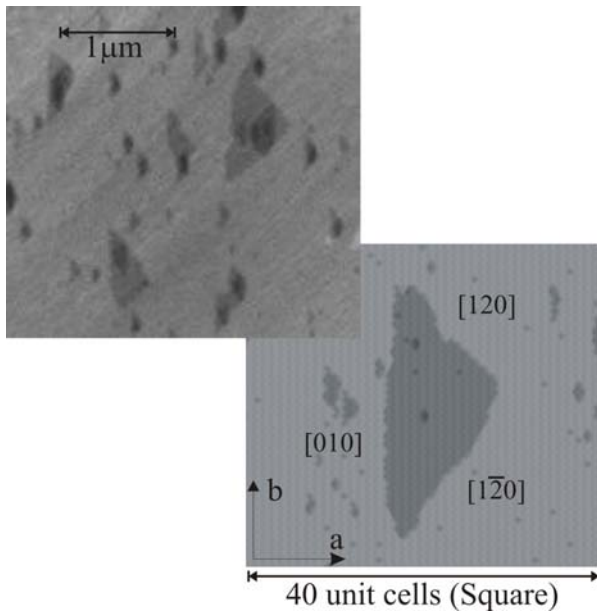

Figure 1. <u>Top</u>: AFM generated height map of the (001) barite surface after exposure to pure water for 37 minutes. Triangular shaped etch pits, one half unit cell deep, expand laterally as the crystal dissolves. <u>Bottom</u>: Monte Carlo simulation of the same crystal surface. The etch pits in the simulation are very similar to the real ones observed with AFM. The dimension of the simulated surface is 40x40 unit cells using crystallographic coordinates.

The relationship between cation/anion ratio, step velocities and bulk dissolution rate in calcite

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A growing body of experimental data and theoretical arguments suggests that the ratio of mineral lattice ions in solution may exert a unique control on both dissolution and growth kinetics, and thus that the ion activity product does not offer a unique description of the rate. Zhang and Nancollas (1998) have demonstrated that the dissolution rate of a spiral dislocation in an AB crystal can be described as

$$R = -k_d \frac{(1-S)\ln S}{\sqrt{2-S}} q_d(r_i, S)$$

where r_i is proportional to the solution ratio of A and B ions, S is the saturation ratio, and q_d is a correction function describing the differences in kink nucleation and propagation
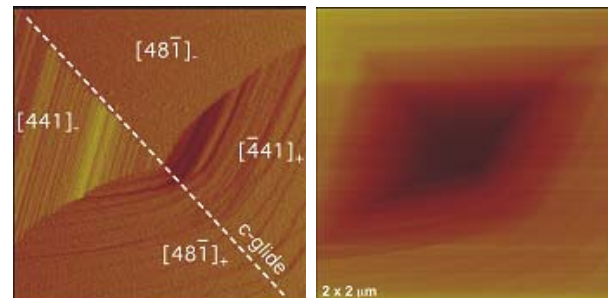
Dissolution spirals, AFM (L) and VSI (R) data.

rates between an AB and Kossel crystal lattice. We have used the native anisotropy of the calcite (104) surface as a means of exploring the sensitivity of step velocities (AFM) to changes in Ca^{2+} / CO_3^{2-} ratio at various degrees of undersaturation. Our results confirm a strong sensitivity of the obtuse (+) step direction to changes in ionic ratio. From coupled experiments, we also discuss the relationship between ionic ratio and the overall dissolution rate (VSI). Our results imply considerable complexity in the relationship between solution composition, thermodynamic driving force, step-specific interaction, and dissolution rate. They also suggest variation in the rate as a function of the interaction between ionic ratio, saturation state, and impurity burden.

Reference

Zhang J, Nancollas GH, *J. Coll. Interf. Sci.* **200**:131-145 (1998).