## MECHANISMS OF CLASSICAL CRYSTAL GROWTH THEORY EXPLAIN QUARTZ AND SILICATE DISSOLUTION BEHAVIOR

Aqueous fluids play a crucial role in mineral weathering and transport in sediments, as well as in fluid-rock interaction deeper in the Earth's crust. For decades researchers have sought general descriptions of mineral dissolution kinetics as a means to quantify and predict behavior over time spans greatly exceeding those accessible in the laboratory. However, a relationship incorporating thermodynamic variables and time that "works" over a range in saturation level and temperature has been elusiveeven for a single mineral under laboratory conditions.

In a study published recently in the *Proceedings of the National Academy of Sciences*, Patricia Dove and Nizhou Han at Virginia Tech and their colleague Jim De Yoreo at Lawrence Livermore National Laboratory have shown that mineral *dissolution* can be understood through the same mecha-

b а -21.0 -30.0 Dissolution homogeneous nucleation Ln {|-R<sub>d</sub>| / [(Ω-1)<sup>2/3</sup>|σ|<sup>1/6</sup>]} [(Ω-1)<sup>2/3</sup>|σ|<sup>1/6</sup>]] -22.0 -31.0 -23.0 Ln {|-R\_|/ -32.0 dislocation defects -24 ( -28.0 -33.0 -25.0 25.0 20.0 15.0 10.0 step propagation from dislocation defects 2.0 0.0 5.0 10.0 15.0 20.0 25.0 5.0 0.0 2.0 40 6.0 8.0 2.5 1.5 1.0  $|1/\sigma|$  $|1/\sigma|$ -33.0 -27.0 impurity defects -32.0 -26.0 25.0 -31.0 eous nucleatio -24.0 -30.0

nistic theory of nucleation developed previously to describe mineral *growth*. By viewing dissolution as the formation of "negative crystals," the researchers were able to generalize the nucleation-rate equations to obtain a model that predicts progressive changes in the dissolution mechanism with degree of undersaturation—from step retreat to defect-controlled

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1000 North Division Street – Peekskill, NY 10566-1830 Tel: (914)739-1134 Fax: (914)739-1257 www.excaliburmineral.com - www.diamondcrystals.net E-mail: info@excaliburmineral.com to homogeneous nucleation of etch pits. The underlying reason for the transitions is that the rate at which a crystal dissolves is controlled by the density of steps on the surface. Whichever process creates the greatest step density dominates the dissolution process.

Prof. Dove and her colleagues tested the model using a new set of experiments performed on pure quartz sand, in which they measured the dependence of dissolution rate on undersaturation. Complementary AFM observations of the steady state surfaces that developed on natural faces showed that rates conform to model predictions over a wide range of thermodynamic conditions. They also showed that the "salt effect," recognized almost 100 years ago, results from a transition in the dominant mechanism from dislocation- to nucleation-driven dissolution.

It turns out that the model (see figure) also explains dissolution behavior previously reported for feldspar. It also reconciles apparently conflicting data sets for kaolinite dissolution at two different temperatures by showing the basis for a temperature-activated transition in the dissolution process. These differences suggest that the practice of extrapolating hightemperature data to ambient temperatures may over-predict rates of dissolution when the extrapolation comes from rates driven by etch-pit nucleation.

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A mechanistic model that takes into account the competition between step creation at dislocations and by nucleation highlights the analogy between growth and dissolution and explains apparent discrepancies in measured growth and dissolution rates. A) Rates measured at  $80^{\circ}$ C by Nagy et al. 1991, *AJS*, are explained by the dislocation model; whereas B) the dependence of rate on chemical driving force at the higher temperature of  $150^{\circ}$ C by Devidal et al. 1997, *GCA*, is predicted by the nucleation model.

The researchers believe that their nucleation model may also predict dissolution rates of sparingly soluble salts, perhaps opening up the possibility to understand "demineralization" of biological materials under certain conditions.

Dove PM, Han N, De Yoreo JJ (2005) **Mechanisms of classical crystal growth theory explain quartz and silicate dissolution behavior**. Proceeding of the National Academy of Sciences 102: 15357-15362

This article was picked by **Bruce Watson**.