Mineral dissolution kinetics at grain boundaries

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Mass transport of dissolved components in the shallow subsurface may often occur via a dissolution-reprecipitation mechanism, a process for which two decades of experimental study have provided substantial support. However, these studies were conducted in autoclaves at elevated temperatures and pressures. Direct observations of the mineral surfaces that constitute these reacting systems were prohibited, and thus kinetic mechanisms were not understood in any detail.

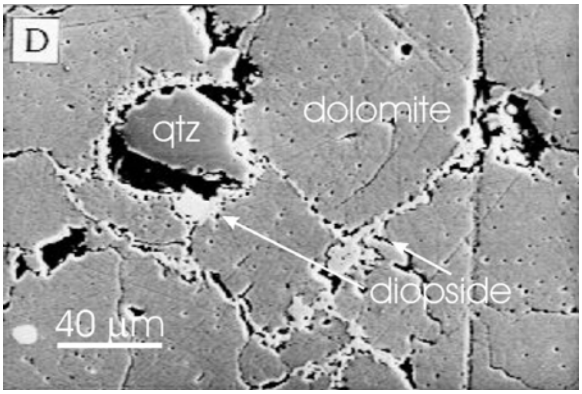

Figure 1: SEM photomicrograph of a dolomite quartz rock reacting to form dioside and CO_2 at 500 MPa and 680 °C (Luttge, 1995).

Recently, several researchers, e.g., Putnis (2004) and Baumgartner (2004), have revived interest in this research topic. While revisiting the mechanistic concepts they have highlighted in particular the importance of coupled mineral dissolution-precipitation kinetics.

In this context, our studies of crystal dissolution kinetics at lower temperatures (10 - 180°C) may help to shed some more light on this important problem. We employ a combination of direct observational techniques, i.e., atomic force microscopy (AFM) and vertical scanning interferometry (VSI) and computer simulations. Our research has led to a new model that emphasizes the importance of full incorporation of the three-dimensional crystal lattice into a fundamental kinetic treatment. Our stochastic approach is based on parameterized Monte Carlo techniques. *Ab initio/DFT* calculations are used for the parameterization.

Grain and phase boundaries and viscoelastic mechanical response

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The phenomenologies of creep and of seismic-frequency wave attenuation are intimately associated with the spatial distribution and structure & chemistry of grain and (solid-state) phase boundaries. My students and I pursue experimental research to quantify the relationships; the studies emphasize (i) state-variable analysis/description of dislocation-effected plasticity, (ii) phase- and grain-boundary effects on wave attenuation, and (iii) plastic-strain-effected phase separation in polyphase aggregates.

(i) Stress-relaxation experiments suggest that the dislocation rheology can be predicted in a strain-insensitive manner through use of a *single* microstructural state variable. It is the distribution of low-angle grain boundaries that corresponds to this state variable, and thus the physics of deformation is dependent on dislocation dynamics within those boundaries.

(ii) The power-law Q^{-1} v. f spectrum ("attenuation band") associated with the damping of seismic waves can result from a *single* loss mechanism having a non-exponential relaxation—specifically, one associated with chemical diffusion to relieve gradients in grain-boundary traction. Experiments scrutinizing the small anelastic strains involved in attenuation suggest that a threshold phenomenon related to electrochemical segregation to grain boundaries may be prevalent. Solid-state phase boundaries have been demonstrated as particularly strong mechanical absorbers, with implications, e.g., that hydrous-phase breakdown reactions in nature could produce rocks that *combine* high stiffness (fast velocities) with high attenuation.

(iii) Large-scale plastic strain in polyphase aggregates requires components of grain- and phase-boundary sliding. The relative sliding viscosities *must* result in solid-state phase separation (mineralogical layering) accompanying deformation. Discerning experimentally the scaling relationships could allow correlation of such natural structures with the thermodynamic conditions (σ,T) that produced them.

The energetics of grain/phase boundaries, modeled as arrays of lattice dislocations (for low-angle boundaries) or disclinations (for high-angle boundaries) are applied to understand the physical relationships uniting these observations.