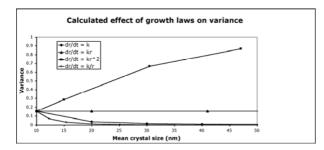
Crystal growth rate law identified from changes in variance of crystal size distributions

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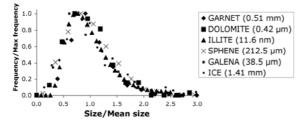
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Rate laws for crystal growth can be identified by the change in the natural log-based variance (β^2) of crystal size distributions (CSDs) during growth. Rate laws proposed for minerals include: dr/dt = k for polynuclear and spiral growth; dr/dt = k/r for diffusion-limited growth; dr/dt = kr² for mononuclear growth; and dr/dt = kr for proportionate growth, where r is crystal radius, t is time, and k is constant. Computer simulated growth (first figure below) indicates that the first three laws are unlikely: starting with a lognormal CSD having $\beta^2 = 0.16$, CSD variance either approaches zero or increases unrealistically.



Variances for most measured CSDs are small and relatively constant; therefore, the proportionate rate law is favored. For example, mean sizes measured for minerals in the reduced plot below vary widely, from 11.6 nm to 1.41 mm, whereas their variances have a narrow range, from 0.14 to 0.30. In addition, the shapes of these CSDs are approximately lognormal, and only proportionate growth can generate and maintain such lognormal shapes. The other growth mechanisms listed above may occur during crystallization while the overall rate law is proportionate. Experiments with K-alum and calcite crystals indicate that proportionate growth is favored by the advective supply of reactants, whereas constant growth appears when reactant supply is limited by diffusion.





Nucleation and growth mechanisms in phase transformations: Insights from dynamic experiments

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Phase transformations change material physical properties and are thus of fundamental importance to geodynamic models and to probing the Earth with geophysical techniques. Although thermodynamics can be used to predict equilibrium phase assemblages, it tells us nothing about reaction kinetics, the spatial distribution of nuclei, or the grain size distribution and crystallographic orientations of newly developed phases. It is these factors that will control physical properties and physical property anisotropies. In order to understand better phase transformation mechanisms and resultant microstructures, we have been developing and applying techniques for the analysis of microstructures, in an SEM, during high temperature experiments. Experiments on geologically important systems are very difficult. However experiments using metals as rock analogues are possible and give considerable mechanistic insight.

We have observed phase transformations in Ti metal. The structure of Ti transforms at ~882°C from hexagonal close packed (HCP - α) to body centred cubic (BCC - β). The BCC phase nucleates as both intracrystalline plates and grainboundary allotriomorphs. Electron backscatter diffraction analysis shows that intracrystalline plates have a Burgers orientation relationship with the parent HCP grain ({0001} // {110} and <11-20>//<111>). Boundary planes orientations and topography associated with plates suggest that plates nucleate and grow by a shear mechanism. Grain-boundary allotriomorphs have a Burgers orientation with one of their neighbouring HCP grains. The boundary plane orientations are arbitrary and have no associated topography suggesting that allotriomorphs grow by a diffusive process. Direct observations of boundary motion and textural analysis show that, during HCP to BCC transformation, BCC phase microstructure and texture are dominated by the growth of grain boundary allotriomorphs, rather than intracrystalline plates. We will explore the implications of these observations for the kinetics of phase transformations in the Earth.