



A conceptual model for kinetically controlled isotope fractionation by fast growing minerals

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Isotope profiles in magmatic minerals are increasingly being used to constrain parental magma compositions or temperatures of crystal formation. An important assumption for their use is that equilibrium was reached at the scale of interest. However, an increasing number of studies document concentration and isotope profiles within single grains suggesting disequilibrium during crystal growth in various geological settings. These data emphasize the need to invoke kinetic effects during crystal growth.

We present a multi-component and multi-dimensional numerical modeling approach in which a spherical grain is growing in a surrounding spherical matrix of fixed size and known composition. The grain boundary is assumed to be in local equilibrium at any given time and the time-dependent ratio between mineral growth and diffusivity in the reservoir is parameterized as the growth Peclet-number (Pe) in order to describe the movement of the mineral surface with respect to the matrix. Corroborating earlier predictions for one dimension, it is shown that under conditions of fast mineral growth in a viscous magma ($Pe \geq 1$) — as it can be assumed for lava lakes or small igneous bodies, for example — highly incompatible elements ($k \ll 1$) will be accumulated near the growing mineral surface, forming a compositional boundary layer with a composition in apparent disequilibrium with the matrix. Equilibration between the boundary layer and the matrix will then depend on the diffusivity of an element, if the effect of free and forced convection on the grain and its surrounding boundary layer is sufficiently small. Diffusion rates of individual isotopes depend on their masses, and hence isotope fractionation is predicted to occur within the boundary layer during progressive crystal growth. As a result, local equilibrium on the grain boundary allows

the fast growing crystal to “record” this fractionation in its resulting isotope profile.

Preliminary modeling results reveal significant isotope fractionation above typical analytical uncertainties even for systems with relatively small mass differences (e.g. $^{87}\text{Sr}/^{86}\text{Sr}$). For example, an isotopic fractionation from core to rim of a plagioclase crystal of up to -0.015% for $\delta^{86}\text{Sr}$ is predicted for a cm-sized grain growing over 100 years (with $\text{Pe}=1$). However, the maximum amount of isotope fractionation and the shape of the isotope profile within the crystal is shown to be sensitive to the applied growth rate law (e.g. const. radius vs. const. mass). As a consequence, these profiles potentially provide an additional key tool to decipher crystallization processes and timescales.

In addition, this model potentially provides applications to a variety of geological settings, simply because it is the time-dependent ratio between mineral growth and near-surface diffusion in the growth medium that might control the uptake of an element into the crystal lattice and thus potentially preserves concentration and isotope profiles which are in disequilibrium with the bulk reservoir.