Plenary Address by the Dana Medalist

Rates and mechanisms of metamorphic processes from natural occurrences

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Quantitative analysis of chemical and microstructural features of metamorphic rocks is a powerful and essential tool for kinetic studies. Natural occurrences can be exploited to provide data under conditions inaccessible to laboratory methods, and should be used to validate experimental measurements. The advantage of approaches based on natural rocks stems from the fact that with rare exceptions, direct laboratory replication of the kinetics of metamorphic processes is impossible, because the timescales of nearly all such processes exceed the duration of laboratory experiments by many orders of magnitude. As a result, application of kinetic data determined by experiment commonly requires long extrapolations in temperature or time or both. This problem is particulary acute for the fundamental mechanisms that transform one mineral assemblage to another and that establish chemical equilibrium among coexisting phases and within individual minerals, because rates of these thermally activated processes vary exponentially with temperature.

Extraction of quantitative kinetic data from natural occurrences demands careful identification and verification of the underlying physical mechanisms; creation of a tractable mathematical or numerical model that captures the essential kinetics of the physical mechanisms; diligent efforts to constrain the values of the model's input parameters; and sensitivity analysis to establish the resulting ranges of uncertainty in the output variables.

Examples from the author's past and present research that illustrate the value of kinetic studies based on natural occurrences include: (1) determination of the kinetics of the transformation in nature of aragonite to calcite from analysis of growth-limited replacement microstructures; (2) determination of intergranular diffusion kinetics — from which estimates of rates of equilibration and scales of disequilibrium follow — from diffusion-controlled reaction textures; (3) determination of nucleation-and-growth kinetics from statistical analysis of sizes and locations of crystal arrays; and (4) determination of intracrystalline diffusion kinetics in garnet from modeling of stranded diffusion profiles in partially resorbed crystals.

Yb and Y diffusion in grossular garnet

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Diffusion of ytterbium and yttrium has been measured in natural grossularite (~93% grossular component) under dry, oxygen- buffered conditions. The sources of diffusants for the experiments were microcrystalline Yb and Y aluminate garnets. Experiments were performed by placing the source material and polished garnet slabs in AgPd capsules, and sealing them, along with a solid buffer, under vacuum in silica glass capsules. Prepared capsules were annealed in 1-atmosphere furnaces for times ranging from a few months to 30 minutes at temperatures from 700-1100°C. The Yb and Y distributions in the garnet were profiled with Rutherford Backscattering Spectrometry (RBS). For experiments buffered at QFM, the following Arrhenius relations are obtained:

$$D_{Yb} = 7 \times 10^{-7} \exp(-312 \text{ kJmol}^{-1}/RT) \text{ m}^2\text{s}^{-1}$$
$$D_Y = 1 \times 10^{-6} \exp(-312 \text{ kJmol}^{-1}/RT) \text{ m}^2\text{s}^{-1}$$

Diffusion coefficients for Y and Yb from experiments buffered at IW are about an order of magnitude slower than under QFM-buffered conditions.

The similar diffusivities found for Y and Yb are consistent with earlier observations by Van Orman et al. (2002) that show little variation in diffusivities among the REE in pyrope. The slower diffusivities under IW buffered conditions are also consistent with earlier work showing a positive dependence of cation diffusion on fO_2.

We are exploring REE diffusion for other garnet compositions, and considering these and previously reported data (van Orman et al., 2002; Tirone et al., 2005) in light of the dependence of diffusivities on garnet unit cell dimensions that has been noted for major element diffusion in garnet (Carlson, 2003).

Reference

Carlson (2003) GSA Meeting Abstracts with Programs 35, 95.
Tirone et al. (2005) GCA (in press).
Van Orman et al. (2002) CMP 142, 416-424.