



## Chemical zonation in garnet: kinetics or chemical equilibrium?

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Chemical zonation in garnet is widely used to reconstruct the pressure ( $P$ ), temperature ( $T$ ), time ( $t$ ), and fluid ( $f$ ) histories of mountain belts. Zonation is thought to result largely from changing  $P - T - t - f$  conditions during growth as well as post-growth intracrystalline diffusion. Chemical zonation is conventionally interpreted to mean that at least some of the garnet interior was out of chemical equilibrium with the matrix during metamorphism. In this case, thermally-activated diffusion in garnet is too slow to equalize chemical potentials. However, in their groundbreaking paper, Tajčmanová et al. (2014) postulate that in high-grade rocks, chemical zonation may actually reflect attainment of equilibrium. In this scenario, diffusion is fast but viscous relaxation is slow such that the zonation patterns directly mirror internal pressure gradients within garnet. Such zoning would likely be very different than typical concentric growth zonation.

Furthermore, Baumgartner et al. (2010) hypothesize that given significant variations in the molar volumes of garnet endmembers, diffusional relaxation may produce internal pressure gradients if the garnet behaves as a near constant-volume system. Consequently, growth zoning could be preserved by pressure variations within the garnet that equalize chemical potentials and slow or stop diffusion (i.e., the garnet is chemically heterogeneous but maintains internal chemical equilibrium due to the pressure variations). This mechanism predicts that areas of garnet with small compositional contrasts would undergo more diffusional relaxation than areas with large contrasts. Moreover, generation of large internal pressure gradients approaching 1 GPa would be expected to induce deformation (e.g., fracturing) in regions of large compositional gradients. Strongly growth-zoned amphibolite facies garnet from the Barrovian zones, Scotland (Ague and Baxter, 2007) shows neither of these features. The sharp compositional gradients are instead interpreted to reflect short residence times at peak- $T$  conditions. Existing diffusion coefficient calibrations predict shockingly short peak- $T$  residence times  $< 200,000$  years. Recent work (Chu and Ague, 2014) suggests that these calibrations predict coefficients that are too large; our new coefficients suggest residence times of  $\sim 10^6$  years which are longer but still indicate very rapid peak thermal pulsing superimposed on the total metamorphic timescale of ca.  $10^7$  years. Even with these new coefficients, however, extremely sharp compositional zoning from other settings (e.g., subduction complex garnet) can suggest peak- $T$  timescales of 100,000 years or less which defy easy explanation using conventional diffusion modeling.

In addition to diffusion, mineral compositions can be modified by coupled dissolution-reprecipitation (D-R). Although rarely reported, chemical mapping of slowly-diffusing trace elements like Ti, P, and Na reveals that D-R can affect garnet compositions in high-grade rocks (e.g., high-pressure Saxony granulite) and track burial and exhumation histories. Chemical equilibrium, at least with respect to the trace elements, was clearly not maintained between garnet interiors and their surroundings. Little or none of this record is preserved in major element zonation due to rapid diffusion at high or ultrahigh temperatures. D-R produces a fluid-filled porosity behind the dissolution front, which could strongly impact diffusion and grain-scale pressure variations. D-R is another mechanism by which stressed crystals could attempt to equilibrate with their surroundings.