Rates and mechanism of Y, REE, and Cr diffusion in garnet

WILLIAM D. CARLSON*

Department of Geological Sciences, University of Texas at Austin, Austin, Texas 78712, U.S.A.

ABSTRACT

Numerical simulation of the evolution of stranded diffusion profiles in partially resorbed garnet crystals from the aureole of the Makhavinekh Lake Pluton, Labrador, yields quantitative determinations of rates of diffusion of Y, rare earth elements (REEs), and Cr at ∼700–900 °C, 0.53 GPa. Diffusion coefficients for these trivalent cations are 0.5–1.5 log$_{10}$ units smaller than those for major divalent cations measured in the same crystals, but diffusivities for trivalent cations are all equal to one another to within ±0.25 log$_{10}$ unit. Integration of these new data with previously published results resolves some prior inconsistencies, and defines the dependence of diffusivities for Y, the REEs, and Cr on temperature, pressure, and oxygen fugacity, while accounting for minor effects of ionic radius and host-crystal composition. Nd, Sm, and Eu—elements that are strongly depleted in rims of relict garnet crystals due to preferential partitioning out of garnet during resorption—evolve small but distinct maxima from initially nearly flat profiles; this “uphill diffusion” results from cross-coupling with Y and the other REEs, which are strongly concentrated in relict garnet rims by resorption. The weak dependence of diffusivity on ionic radius and host-crystal composition, the near-equivalence of diffusivities of Y+REEs with that of Cr, and the strong positive cross-coupling among Y+REEs are all explained by a diffusion mechanism that links the mobility of Y+REEs with that of Cr; this is likely a consequence of the dominance of the menzerite-(Y) component as a means of incorporating Y+REEs in the garnet structure. However, the variety of possible substitution mechanisms that may enable Y+REE incorporation into garnet, and the degree to which each may be favored in different regimes of temperature, pressure, and oxygen fugacity, imply a potential for great complexity, as the net diffusional flux may result from the superposed effect of multiple diffusion mechanisms, each with different kinetics.

Keywords: Diffusion, garnet, rare earth elements, yttrium, chromium

INTRODUCTION

Garnet is unmatched in its ability to record temperature-time histories in the form of diffusionally modified compositional zoning, across a range of geologic conditions and lithologies that encompasses much of the Earth’s deep crust and upper mantle. This ability has led to extremely fruitful application of quantitative models for the diffusion of the major divalent cations in garnet to studies of tectonometamorphic evolution; the reviews by Kohn (2005) and by Ganguly (2010) provide excellent examples. But in contrast to the comparatively well-constrained kinetics of diffusion for Mg, Fe, Mn, and Ca, only sparse knowledge exists of the rates and mechanisms that govern diffusion in garnet of geologically important trace elements, such as Y, the rare-earth elements (REEs), and Cr. Because it is now feasible to measure concentrations of most of these trace elements rapidly and accurately at the scale of a few tens of micrometers or less, their potential for generating breakthroughs in geological applications is growing rapidly.

The need for full knowledge of diffusion rates and mechanisms for trivalent cations in garnet stems from both geochronological and petrological objectives. Uptake and diffusional redistribution of the REEs are first-order controls on the interpretation of Sm-Nd and Lu-Hf garnet ages (e.g., Skora et al. 2006, 2009; Kohn 2009; Kelly et al. 2011), and on petrologic inferences regarding magma generation and metasomatism in the mantle (e.g., Tirone et al. 2005). Similarly, the distribution of Y in garnet is an important monitor of the evolution of accessory mineral assemblages that are vital to geochronology and to thermobarometric determinations in deep crustal orogenic systems (e.g., Pyle and Spear 2000, 2003; Foster et al. 2002; Hermann and Rubatto 2003; Tomkins and Pattison 2007; Corrie and Kohn 2008). Perhaps most importantly, if it is true that trivalent cations diffuse significantly more slowly than do the principal divalent cations—as observations in nature and some experiments suggest—then diffusion data on trivalent trace elements are an essential high-temperature complement to existing data on divalent cations. Because diffusional homogenization typically occurs for the major divalent cations over geological timescales at or above temperatures characteristic of upper amphibolite-facies metamorphism, i.e., ∼650–700 °C (e.g., Yardley 1977; Carlson and Schwarze 1997; Caddick et al. 2010), slower rates of trace-element diffusion would allow them to preserve records of higher-temperature processes, which would expand greatly the role of garnet diffusion kinetics in the analysis of lower crustal and upper mantle dynamics. Numerous geologic applications therefore require precise knowledge of Y+REE diffusion kinet-