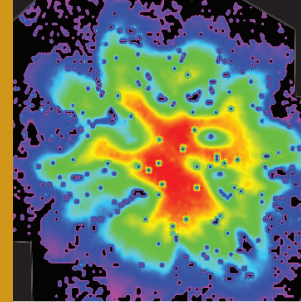# Metamorphism as Garnet Sees It: The Kinetics of Nucleation and Growth, Equilibration, and Diffusional Relaxation

## Jay J. Ague[1,2] and William D. Carlson[3]

**G**arnet bears witness to the importance of kinetics during metamorphism in its microstructural features, compositional zoning, and diffusional response to thermal events. Porphyroblastic textures carry quantitative signals of protracted nucleation and sluggish intergranular diffusion, key impediments to reaction progress that may result in crystallization under conditions well removed from equilibrium. Growth zoning in garnet reveals partial chemical equilibration with matrix minerals: intergranular transport keeps pace with garnet growth for some elements but not for others, leading to variable degrees and length scales of chemical equilibration. Partial relaxation of compositional zoning by intracrystalline diffusion is a sensitive and quantitative indicator of thermal history, constraining rates and timescales of peak metamorphic heating, processes of burial and exhumation, and retrogression on cooling.

KEYWORDS: kinetics, reaction mechanisms, nucleation, diffusion, rates, timescales

## INTRODUCTION

The presumption that metamorphic rocks remain steadily at equilibrium as they transform—the "equilibrium paradigm"—is central to the analysis of metamorphic systems. It underlies everything from the concept of metamorphic facies to the tracing of complex pressure–temperature–time (*P–T–t*) paths on isochemical phase diagrams. But reactions cannot proceed in systems at thermodynamic equilibrium. Metamorphic recrystallization therefore requires passage through transient nonequilibrium states.

Garnet provides special insights into these transient states and into the reaction mechanisms needed to surmount the associated kinetic barriers to equilibration. Other minerals carry such information as well (cf Waters and Lovegrove 2002; Pattison et al. 2011), but in their microstructural relationships and their chemical and isotopic zonation, garnet crystals encode an unparalleled record of metamorphic processes and rates. They yield unique information about nucleation and growth phenomena, rates of intergranular element transport, degree of chemical equilibration, fluid-infiltration events, and timescales of peak metamorphic heating, burial/exhumation, and retrogression.

1 Department of Geology and Geophysics, Yale University
P.O. Box 208109, New Haven, Connecticut 06520-8109, USA
E-mail: jay.ague@yale.edu

2 Peabody Museum of Natural History, Yale University
New Haven, Connecticut 06511, USA

3 Department of Geological Sciences, University of Texas at Austin
Austin, Texas 78712, USA
E-mail: wcarlson@jsg.utexas.edu

## GARNET CRYSTALLIZATION AS A KEY TO METAMORPHIC PROCESSES

Garnet commonly forms porphyroblasts, metamorphic crystals substantially larger than those in the surrounding matrix. The sizes and locations of these crystals are the macroscopic expression of nanoscale processes that operate during crystallization. Thus the microstructural and microchemical analysis of porphyroblastic textures taps an extraordinarily rich source of information on metamorphic processes, as reviewed in Carlson (2011), to which the reader is referred for both further background and treatment in greater depth.

### Porphyroblastic Microstructures: Nanoscale Processes Revealed

Most garnet porphyroblasts form via dehydration reactions that produce a fluid-saturated intergranular medium. In these circumstances, garnet crystallization requires: dissolution of reactant minerals to supersaturate the intergranular fluid; garnet nucleation from that fluid, typically on a mineral substrate; transport of nutrients through the fluid from reactants to products; and precipitation of nutrients onto the growing crystal. In analyses of natural textures, the processes most commonly considered as rate-limiting for garnet growth are intergranular diffusional transport and precipitation onto the surface of the growing crystal. These contrasting growth-limiting processes produce different feedbacks into rates and locations of nucleation events, giving rise to two end-member crystallization mechanisms, conventionally termed diffusion-controlled and interface-controlled nucleation and growth (DCNG and ICNG, respectively). We can test for the operation of these mechanisms in natural systems because they yield distinctly different macroscopic textures.

In the case of ICNG, rapid intergranular transport makes the fluid a spatially uniform reservoir of garnet nutrients. In such a reservoir, earlier nucleation events do not influence the location of later events, so nucleation is spatially random to the extent that the precursor is homogeneous. (Of course, locations of nucleation may still be influenced by protolith layering or by inhomogeneous distributions of favorable substrates, strained reactant crystals, etc.) The equal availability of nutrients throughout the reservoir yields uniform growth rates, so all crystals that nucleate simultaneously grow to the same final size.

In the case of DCNG, however, gradients in fluid saturation develop between unreacted and reacted regions of the rock (FIG. 1). Diffusionally depleted zones expand around growing crystals, and within these zones the driving force for nucleation is reduced, so crystal separations are on average greater than for equivalent systems undergoing ICNG. Diffusionally transported nutrients are sourced locally, so growth rates and sizes of proximal crystals are reduced by competition; in the case of garnet, the supply of Al is commonly rate-limiting for growth. Local sourcing of nutrients also means that crystals are larger and more numerous in regions originally richer in reactants.

Tests for DCNG versus ICNG require 3-D information on the sizes and locations of porphyroblasts, now readily available via high-resolution X-ray computed tomography. Although histograms of crystal sizes (crystal size distributions or CSDs) are time-integrated records of nucleation and growth, they are nonunique: nearly identical CSDs can arise from multiple mechanisms. A far more robust discriminant is quantitative textural analysis (QTA), a statistical evaluation of crystal sizes and locations that tests for evidence of the nucleation suppression and growth suppression shown in FIGURE 1. Over a range of length scales, QTA assesses the departure from randomness of an array of crystal centers and quantifies the degree of correlation between crystal sizes and their proximity to one another; it is most effective when used to analyze growth from a uniform, fine-grained matrix of precursors. The QTA studies reviewed in Carlson (2011, pages 432–433) reach the conclusion that DCNG governs the crystallization of aluminous porphyroblasts (especially garnet) across a wide range of metamorphic conditions in both pelitic and mafic compositions.

## Numerical Modeling of Garnet-Porphyroblast Microstructures

Three numerical models of garnet crystallization have recently appeared that can be used to discriminate among potential mechanisms. In the model of Schwarz et al. (2011), reactant dissolution is rate-limiting; in the model of Gaidies et al. (2011), product precipitation is rate-limiting; and in the model of Ketcham and Carlson (2012), intergranular diffusion is rate-limiting.

One key example of the several quantitative predictions made by such models is the size of the thermal interval over which nucleation takes place. The two models of interface-controlled processes both predict extremely narrow intervals: a maximum of 6 °C in Schwarz et al. (2011) and 1–2 °C in Gaidies et al. (2011). In stark contrast, fits of the Ketcham and Carlson (2012) model to the textures of 13 diverse, natural rocks require nucleation that continues in each case throughout nearly the entire crystallization event, yielding thermal intervals for nucleation spanning 50 to 100 °C (Kelly et al. 2013).

Assuming rock-wide equilibration of the divalent cations in garnet (i.e. Mg, Fe, Mn, Ca) in an intergranular fluid, narrow thermal intervals for nucleation require essentially uniform central compositions for all garnet porphyroblasts in the rock (reflecting nucleation at or near the equilibrium temperature); the preponderance of garnet growth must then occur in the absence of further nucleation. But most available data from natural occurrences appear to conflict with that notion: when core compositions are preserved and measured (e.g. Chernoff and Carlson 1997), they are not uniform; instead, they range widely, and their systematic variation commonly demonstrates protracted, continual nucleation that spans nearly the entire interval of time and temperature during crystallization, consistent with DCNG.

All numerical models require considerable simplifications and multiple assumptions, so none of them can claim to replicate the complex processes of nucleation and growth in their entirety. The mechanisms and kinetics of crystallization remain active areas of investigation, with much still to be learned; numerical simulations of the crystallization of garnet (along with other porphyroblasts) will continue to reveal vital aspects of these key metamorphic processes.

## Nucleation and Diffusion: Impediments to Reaction and Equilibration

Observations rooted in QTA, as well as numerical models, reveal that the two dominant controls on crystallization of garnet porphyroblasts are the rates of nucleation and intergranular diffusion of Al. These processes, of course, are not specific to garnet, but instead are common aspects of metamorphic crystallization. When recognized as general impediments to chemical transport and reaction progress, they carry broader petrologic significance: their kinetics imply potential for significant thermal overstepping of reactions, crystallization under conditions well removed from equilibrium, reactions spanning extended intervals of time and temperature, and limited length scales for chemical equilibration. These kinetic impediments remind us that although metamorphic rocks may reach final states that approximate chemical equilibrium, they must take nonequilibrium paths to get there.
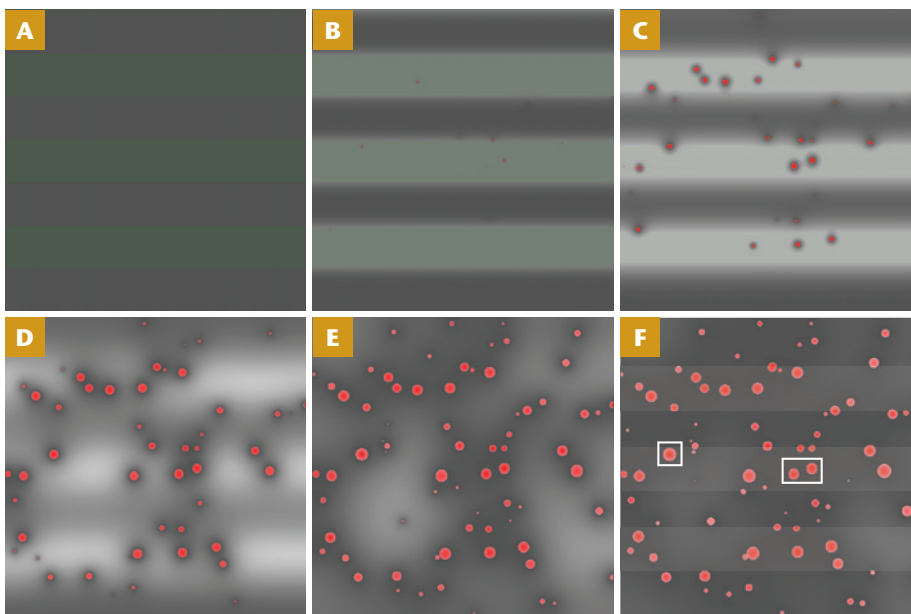


FIGURE 1 Simulation of prograde diffusion-controlled nucleation and growth (DCNG) in a layered precursor; model of Ketcham and Carlson (2012). The greyscale indicates the degree of supersaturation of intergranular fluid with Al; the green tint depicts the presence of reactant; porphyroblasts are red, with deeper colors for earlier-accreted material. The boxes in (F) identify three crystals that nucleated nearly simultaneously [panel (C)]; the large crystal at left grew largely in isolation, whereas the pair at right are smaller due to competition for nutrients. The locations of originally reactant-rich layers are indicated in (F) by a faint grey overlay, which allows one to discern that those regions contain larger and more numerous porphyroblasts, a fact otherwise not evident in the final microstructure. From Carlson (2011)

## HOW GARNET ZONING MONITORS CHEMICAL EQUILIBRATION

Intracrystalline diffusion in garnet is slow enough that growth zoning is commonly preserved in crustal rocks, for major or trace elements, or both. If rock-wide equilibration was achieved during growth, this zoning can be used to track the evolution of $P$–$T$ conditions. But garnet zoning can also reveal failure to achieve chemical equilibrium during metamorphism.

### The Potential for Partial Chemical Equilibrium

Among the major constituents of garnet, Al is commonly found to be the component whose intergranular diffusional flux determines the overall rate of reaction, so Al supersaturation is the quantity tracked by the gradients and depleted zones shown in FIGURE 1. But all other constituents must also diffuse from distal sources through the intergranular fluid to the growing crystal. Elements that diffuse faster than Al can keep pace with growth, and rock-wide elimination of gradients in their chemical potentials will be recorded by their zoning in garnet; but elements that diffuse slower than Al cannot equilibrate over comparable length scales, and this too will be reflected in garnet zoning. Rock-wide equilibration for some elements, but not for others, is *partial chemical equilibrium*.

A striking example is shown in FIGURE 2A (after Yang and Rivers 2001). Concentric zoning for Mn reflects progressive depletion of a spatially uniform reservoir and thus documents rapid intergranular diffusion of Mn. But Cr exhibits overprint zoning: the garnet crystal incorporated heterogeneities present in the precursor, reproducing the original layering (FIG. 2A, lower panel). This is partial chemical equilibrium: although Mn achieved chemical equilibration over distances much greater than the scale of individual grains, Cr did not. In this way, garnet zoning serves as a monitor of the length scales of intergranular diffusion and of the degree of chemical equilibrium achieved during crystallization.

### Good Rocks Gone Bad? Examples of Partial Chemical Equilibrium

Examples of partial chemical equilibrium during garnet crystallization are commonplace (cf Carlson 2002), and their prevalence highlights the importance of kinetic impediments to rock-wide equilibration. Below we describe a few such instances to illustrate this vital notion.

*Solubility-Limited Transport*  FIGURE 2B illustrates patchy overprint zoning for Mn in the three upper crystals, which contrasts with normal zoning in the crystal below them. In an equilibrium interpretation, each of the patchy crystals would require multiple, separate nucleation events, one for each separate region of high Mn concentration. But typically only one crystallographic orientation, and thus a single nucleation event, is revealed by orientation-contrast imaging (Hirsch et al. 2003). Fluid inclusion evidence shows that the restricted Mn diffusion reflects garnet growth amidst a $CO_2$-rich fluid with limited Mn solubility; rock-wide equilibrium was established only after a transition occurred to an $H_2O$-rich fluid, which accompanied nucleation and growth of the normally zoned crystal and growth of the smoothly zoned outer rims on the others.

*Interfacial Controls on Growth Rate at High Thermal Overstepping*  The striking garnet-zone and staurolite–kyanite-zone garnets studied by Wilbur and Ague (2006) feature zoning that reveals initial dendritic to branched crystal morphologies (FIG. 2C). These morphologies are indicative of interface-controlled growth from a highly supersaturated fluid. Models for their growth involve very steep gradients in concentrations at the tips of growing branches, akin to those in other interface-controlled processes. These crystals are thus an exception to the above generalization of diffusional control, but they likely represent nucleation and growth under conditions even further removed from equilibrium.

*Disequilibrium Due to Diffusional Impediments*  Garnet porphyroblasts with normal, well-equilibrated zoning for Mn, Fe, and Mg were found by Chernoff and Carlson
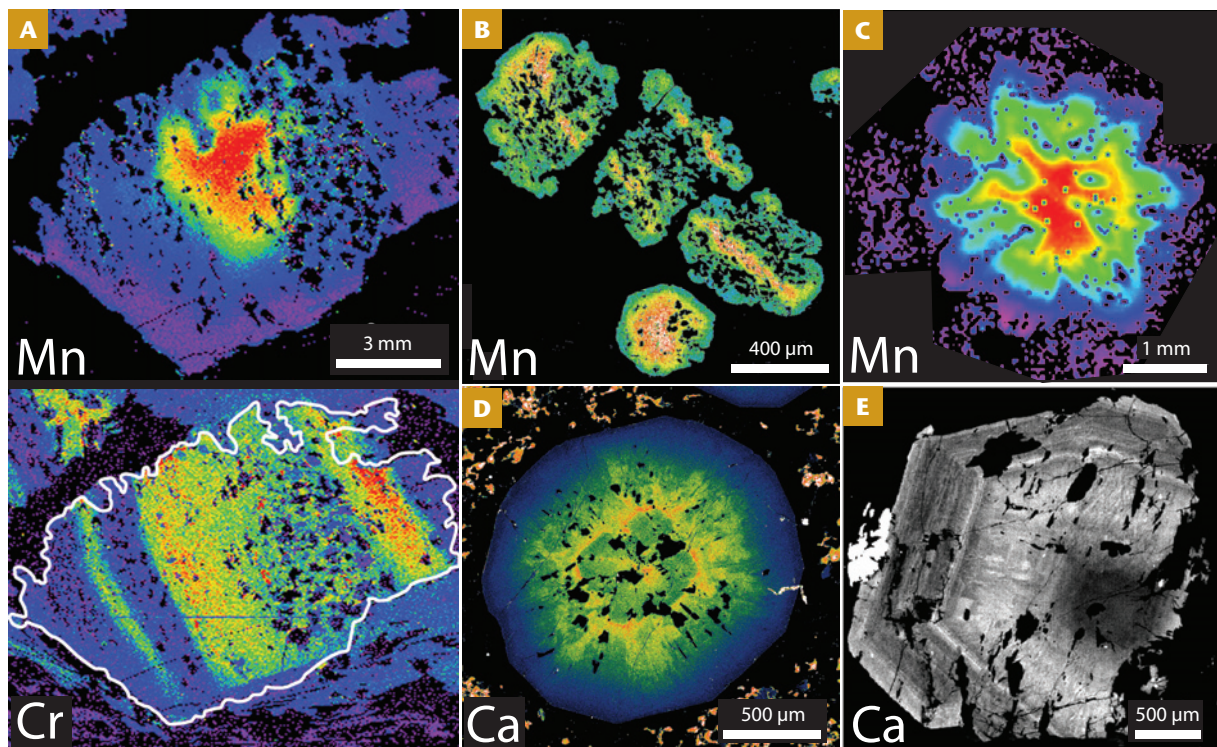


**FIGURE 2**  X-ray maps of garnet zoning, illustrating varying degrees and diverse causes of partial chemical equilib-rium during crystallization, as explained in the text. Warmer colors (or brighter grays) denote higher concentrations.

(1997) to contain internal spikes of high Ca concentration (Fig. 2D). In an equilibrium interpretation, the pressure fluctuations implied by the Ca spikes would require extremely rapid regional burial and rebound. But the Ca spikes appear at systematically different Mn/Fe/Mg contents, and thus different times, in crystals of different sizes. These asynchronous spikes resulted from slow intergranular diffusion of Ca, which altered the progressive evolution of the diffusionally depleted zone surrounding each porphyroblast; as Ca fluxes across each depleted zone waned, plagioclase in the zone—formerly a Ca sink—became a transitory, local Ca source. In this example of partial chemical equilibrium, Mn, Fe, and Mg equilibrated rock-wide, but Ca did not.

*Disequilibrium Due to Armoring or Zonation of Reactants*   The inability of intergranular transport to access the interiors of reactant grains may also be reflected in garnet zoning, as in the example described by Baxter and DePaolo (2002). In that case, the Ca contents of garnet record equilibration of the intergranular medium principally with the more calcic outer mantles of recrystallizing plagioclase crystals, not their less calcic interiors.

*Fluid-Driven Zoning*   The influx of fluids into a rock during crystallization may produce garnet zoning that reflects equilibration with that fluid, implying minimal influence, or none, from the coexisting mineral assemblage. Variations in fluid chemistry can produce rock-wide compositional fluctuations that serve as time markers (Fig. 2E): in the study by Berg et al. (2013), fluid-driven oscillations, combined with measured rotations of the crystals during the fluid-influx events, revealed twofold to fivefold increases in strain rate due to fluid-induced strain softening.

*Transport-Modulated Uptake of Trace Elements*   Trace elements, especially Y and the rare earth elements (REEs), display extraordinarily diverse zoning in garnet, encompassing all of the behaviors illustrated above for major elements (Moore et al. 2013). Mottled patterns reflect overprint zoning, and diffusion-controlled uptake generates systematic patterns of central peaks and annular maxima that vary with atomic number (Skora et al. 2006). Rock-wide equilibration is implied by single, broad central maxima that approximate Rayleigh fractionation, and by concentric chemical shifts that correlate with changes in accessory-phase assemblages (Pyle and Spear 1999) or major-phase assemblages (Konrad-Schmolke et al. 2008); concentric oscillatory zoning stems from fluid infiltration (e.g. Berg et al. 2013; Moore et al. 2013).

## INTRACRYSTALLINE DIFFUSION: A MONITOR OF TIMESCALES AND RATES

Intracrystalline (within-grain) diffusion will modify compositional zonation and reveal postgrowth thermal histories, including the timescales of peak heating, burial/exhumation, and retrogression. Diffusion follows an Arrhenius-type relationship, so rates increase with temperature; they decrease somewhat with pressure and increase slightly at higher oxygen fugacity (e.g. Ganguly 2010).

### Major Element Diffusion

In crustal settings, the major cations Mg, Fe, Ca, and Mn diffuse within the dodecahedral (eightfold) sublattice of garnet. This is *multicomponent* diffusion, in which all elements can undergo diffusion at the same time. Thus, diffusion of a single element cannot be treated independently of the others. For example, if Mg diffuses out of some domain in a garnet, some combination of Fe, Ca, and/or Mn must diffuse in to maintain stoichiometry. Multicomponent diffusion can lead to nonintuitive chemical evolution, including *uphill* diffusion of compo-

nents toward regions of higher concentration (e.g. Carlson 2006). The general theory for multicomponent diffusion was derived in the ceramics and physical chemistry literature. It was later applied to silicate minerals, incorporating the simplifications that the solutions were close to ideal and/or that gradients in activity coefficients were negligible (Lasaga 1979). This treatment is usually reasonable for common garnet compositions (Borinski et al. 2012).

Radial, multicomponent diffusion in a sphere is generally used to model measured diffusion profiles:

$$\begin{pmatrix} \dfrac{\partial X_1}{\partial t} \\ \dfrac{\partial X_2}{\partial t} \\ \dfrac{\partial X_3}{\partial t} \end{pmatrix} = \dfrac{1}{r^2}\dfrac{\partial}{\partial r}\left[ r^2 \begin{pmatrix} D_{11} & D_{12} & D_{13} \\ D_{21} & D_{22} & D_{23} \\ D_{31} & D_{32} & D_{33} \end{pmatrix} \begin{pmatrix} \dfrac{\partial X_1}{\partial r} \\ \dfrac{\partial X_2}{\partial r} \\ \dfrac{\partial X_3}{\partial r} \end{pmatrix}\right] \qquad (1)$$

where $X$ is mole fraction, $r$ is radial distance, $D_{ij}$ are diffusion coefficients, and $t$ is time. The subscripts 1, 2, and 3 refer to any three of the four major components of garnet (almandine, pyrope, grossular, spessartine); the fourth is not independent of the other three, as the mole fractions must sum to one.

The $D$ values in the diffusion coefficient matrix can be determined by a variety of means (e.g. Ganguly 2010), but a significant complication is that they are dependent on garnet composition. Available evidence indicates that, for example, smaller cations such as Mg are less sensitive to these compositional effects than larger ones such as Ca. Carlson (2006) provided an internally consistent formulation to compute self-diffusion coefficients in which unit cell dimension is used as a proxy for these compositional effects. Ca is normally the most slowly diffusing of the major eightfold cations.

### Trace Element Diffusion

Trace elements also diffuse through garnet. If their motion is not coupled to that of other elements, then their diffusion can be described simply by Fick's laws with a single diffusion coefficient. However, many important trace elements exhibit more complex behaviors.

The diffusion of rare earth elements on eightfold sites in garnet (e.g. Ganguly 2010) has important implications for Sm–Nd or Lu–Hf garnet whole-rock dating (see Baxter and Scherer 2013 this issue). A critical consideration, however, is that the REEs and Y are trivalent, but they substitute onto sites normally occupied by divalent cations. The dominant mechanism for maintaining local neutrality is likely to be cross-coupled substitution of divalent ions like Mg and Fe for trivalent Al (and Cr) on octahedral sites, simultaneously with substitution of trivalent REEs and Y for divalent ions on eightfold sites (Carlson 2012). In deep-crustal garnet, the rates of REE, Y, and Cr diffusion are 1.0 to 1.5 orders of magnitude slower than Mg and Fe rates (Carlson 2012).

Highly charged ions like $Ti^{4+}$, $Hf^{4+}$, and $P^{5+}$ probably diffuse even more slowly than the REEs. Significant diffusion of Ti to exsolving rutile and ilmenite precipitates in garnet has been documented for ultrahigh metamorphic temperatures (~1000°C; Ague and Eckert 2012; Ague et al. 2013). Phosphorus diffusion may be even more restricted; sharp gradients in composition can be preserved even in ~1000 °C rocks (Ague and Eckert 2012). The mechanisms by which such substitutions occur are actively debated. Cross-coupled substitutions involving $Na^+$, $^{IV}Si$, $^{VI}Si$, $^{VI}Al$, $Fe^{2+}$–$Fe^{3+}$, vacancies, and $OH^-$, among others, have been postulated (see Ague and Eckert 2012; Proyer et al. 2013; and references in these papers).

## Stranded Diffusion Profiles in Garnet and Timescales of Peak Heating

The longer a crystal is held at a given $T$, the more diffusional smoothing of internal zoning there will be. Thus, if $T$ is constrained petrologically and the diffusivity of an element or group of elements is also known, then the extent of diffusional smoothing constrains thermal timescales. A simple example is estimation of the maximum duration of the thermal peak of metamorphism. Scenarios involving coupled growth and diffusion require more complex models, as discussed by Gaidies et al. (2008) and Caddick et al. (2010).

Consider a garnet crystal that contains a preexisting compositional step function that undergoes diffusional relaxation during peak-$T$ metamorphism (FIG. 3A). The diffusion profiles are "frozen in" after the peak as the rock cools and diffusion slows. Forward modeling of the element profiles using equation (1) (for major elements) at known peak $T$ can then be used to find the time needed to match the measured profiles. This time represents the total time the garnet was at peak conditions. For example, a crystal could be held at 700 °C for 1 My, or there could have been four separate thermal pulses at 700 °C, each lasting 0.25 My; the diffusion profiles would be indistinguishable (Ague and Baxter 2007).

If the initial gradient was not a simple step function but rather involved multiple steps or was gradational, the profiles would be broader for the same $T$–$t$ history than those computed for a step function, as long as enough time had passed to eliminate any initial steps (FIG. 3B). Forward modeling assuming an initial step function would then *overestimate* the peak timescale.

The more diffusion there is, the more difficult it may be to define the initial composition. The diffusion profile in FIGURE 3C has propagated all the way to the crystal's center, and thus core concentrations have dropped below their initial value. Profile fitting using the observed value as an initial condition would underestimate the timescale. In addition, the profiles can resemble other zonation phenomena, such as Rayleigh fractionation, and, thus, the relative roles of growth and diffusion are obscured. For these reasons, the limited-diffusion cases, which are the most straightforward to model, are ideally suited for revealing rapid tectonometamorphic processes.

## Is Barrovian Metamorphism Barrovian?

Garnet in sillimanite-zone rocks of the classical Barrovian type locality, Glen Clova, Scotland, can preserve sharp compositional gradients (FIG. 4). Typical models of Barrovian metamorphism caused by conductive thermal relaxation of overthickened crust predict peak thermal timescales of about $10^7$ y (e.g. Lyubetskaya and Ague 2010). However, if the rocks were held at high temperatures (~670 °C) for this long, the compositional gradients for major divalent cations in garnet would be largely obliterated by diffusion. Consequently, even though the *total* timescale of garnet growth was ~8 My (Baxter et al. 2002), the timescale of *peak* heating events during this interval must have been considerably shorter—about $10^6$ y or less (Ague and Baxter 2007; Vorhies and Ague 2011). As the heating pulses were associated with bimodal synmetamorphic magmatism, metamorphism at the Barrovian type locality did not strictly follow the commonly accepted model of self-heating of overthickened crust; instead, it included a significant component of magmatic heat advection (Baxter et al. 2002; Ague and Baxter 2007; Lyubetskaya and Ague 2010; Vorhies and Ague 2011; Viete et al. 2013).

## Diffusion Reveals Rates of Tectonism

There will be some diffusion on the way to peak conditions, and some during cooling too. Consequently, the method outlined above estimates the *maximum* duration of the peak conditions (FIG. 3A). Nonetheless, the diffusion profiles are likely to be dominated by the thermal peak. For example, the total timescale of diffusion along common nonisothermal $P$–$T$ paths can be estimated by calculating diffusion at a constant characteristic $T$ given by $0.95T_{Peak}$, where $T_{Peak}$ (K) is the peak $T$ of metamorphism (Faryad and Chakraborty 2005). Faryad and Chakraborty showed that heating from 540 °C to 600 °C and cooling back to ~500 °C
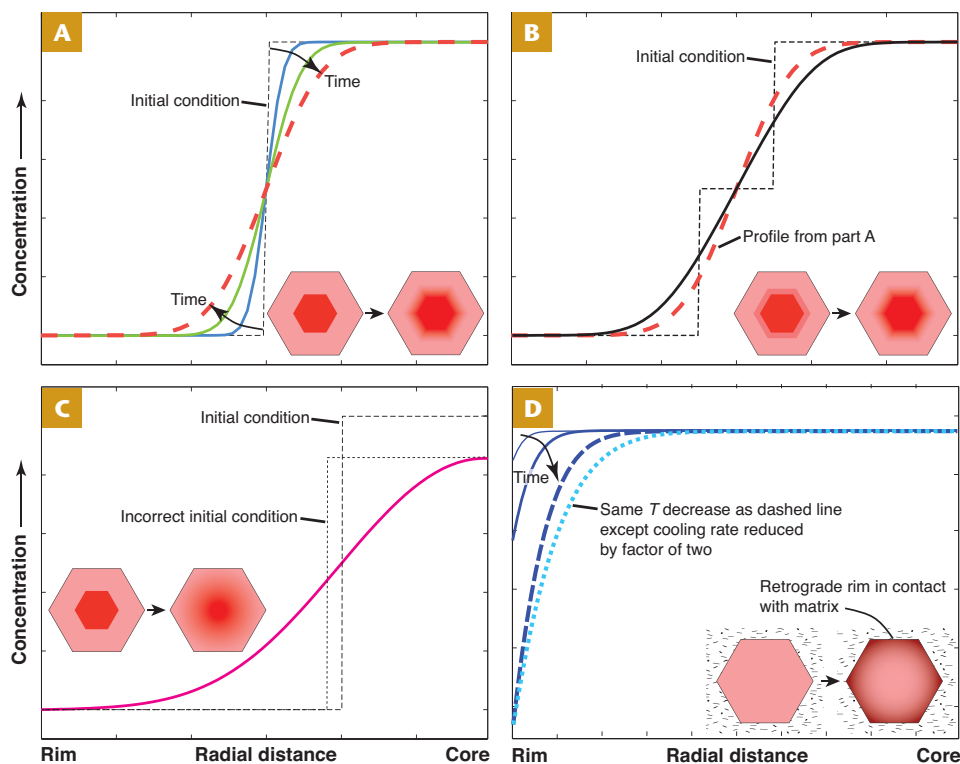


**FIGURE 3** Model diffusion profiles for a single trace or major element illustrating various relaxation scenarios described in the text. (**A**) Relaxation of a step function in concentration. (**B**) Relaxation of a multistep compositional gradient. The red dashed line is the same profile shown in (A). (**C**) Extensive diffusion that penetrates to the core of the grain. (**D**) Retrograde diffusion in a garnet rim. The profiles could represent Mg or Mg/Fe. Note the deeper penetration for a slower cooling rate across the same thermal interval.
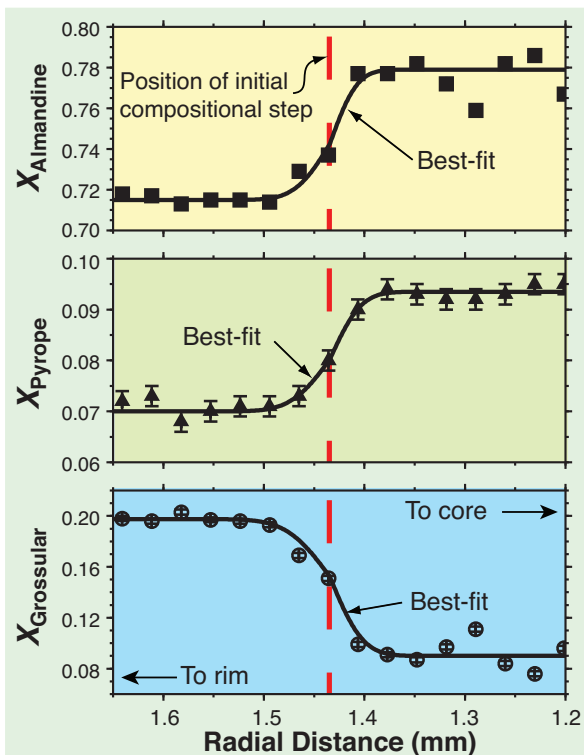
**FIGURE 4** Measured compositions for a garnet interior, Barrovian type locality, Scotland. *X* = mole fraction; solid lines denote best-fit diffusion profiles; error bars are two sigma. MODIFIED FROM AGUE AND BAXTER (2007)

The simplest initial condition is flat garnet profiles. These are usually produced at high grades by complete diffusional smoothing of growth zonation, so modeling of retrograde rim development is typically done on amphibolite to granulite facies rocks. If a fluid or melt is present to enhance transport in the intergranular medium, then the entire rim of the crystal may be affected. If not, then garnet Mg/Fe typically decreases only at contacts with biotite or other ferromagnesian phases (e.g. Pattison and Bégin 1994).

FIGURE 3D shows the development of a hypothetical retrograde rim with decreasing *T*. Importantly, fitting equation (1) to the measured profiles can yield estimates of the time needed for cooling, or the cooling rate, or both if independent information is available to constrain one or more points along the *T–t* path. The slower the cooling rate, the farther a diffusion profile will propagate into a crystal (FIG. 3D). Florence and Spear (1995) used retrograde profiles to estimate rapid cooling rates of >50 °C My⁻¹ in part of the southern Adirondack Highlands, New York, USA.

Diffusion modeling must account for the mass of rim lost if the rim was partially resorbed during retrogression. Resorption is typically marked by rimward increases in elements that garnet hosts but matrix minerals don't. Common examples include Mn (Kohn and Spear 2000), and REEs and Y (Carlson 2012). As the rim is resorbed, these elements partition preferentially into the garnet, raising their concentrations in the outermost rim of the crystal. Back-diffusion into the garnet then occurs, given sufficient temperature and time.

## CONCLUDING REMARKS

Because garnet commonly develops compositional variations that may be subject to partial diffusional relaxation, it can be key to understanding the timing and duration of metamorphic events. In its porphyroblastic microstructures and growth zoning, garnet also encodes a detailed record of crystallization mechanisms and kinetics, and monitors equilibration, often highlighting partial chemical equilibrium during crystallization. The prudent petrologist will avoid uncritical acceptance of the equilibrium paradigm and will seek out the more nuanced perspective on kinetic impediments to crystallization and equilibration that garnet provides.

(where diffusion of divalent cations effectively stops) took only 0.8–0.9 My in the Wölz Tauern (Eastern Alps). They then calculated subduction/exhumation rates of ~4 cm y⁻¹ and heating/cooling rates of 100–260°C My⁻¹. Such rapid rates are consistent with rates of plate motion and show that metamorphism can be geologically brief.

### *Retrograde Diffusion at Garnet Rims*

Garnet rims can exchange cations with matrix phases during cooling; the most common example is decreasing Mg/Fe due to retrograde exchange with biotite or cordierite. For modeling, common assumptions are that the matrix phase is so abundant that its composition is not modified significantly by loss of Mg from garnet and that diffusion through the matrix phase is essentially instantaneous. Biotite can fulfill these requirements, but does not if there is little or no intergranular fluid to facilitate grain- boundary transport (Florence and Spear 1995).

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