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Beyond the Equilibrium Paradigm:
How Consideration of Kinetics Enhances Metamorphic Interpretation

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ABSTRACT

The equilibrium model of prograde metamorphism, in which rocks are regarded as departing only negligibly from equilibrium states as they recrystallize, has generated a wealth of petrologic insights. But mounting evidence from diverse approaches and observations over a range of scales has revealed that kinetic impediments to reaction may prevent metamorphic rocks from attaining rock-wide chemical equilibrium along their prograde crystallization paths. To illustrate the resulting potential for inaccurate interpretation if kinetic factors are disregarded, we briefly review several case studies, including: out-of-sequence, metastable, and displaced isograds in contact aureoles; paragenetic sequences documenting overstepped, disequilibrium reaction paths; patterns of compositional zoning in garnet demonstrating partial chemical equilibrium; petrologic incongruities between observation and thermodynamic prediction; and inhibited reaction progress revealed by petrologically constrained numerical simulations of garnet crystallization. While the equilibrium model provides an indispensable framework for the study of metamorphic systems, these examples emphasize that all reactions require departures from rock-wide equilibrium, so all rocks must traverse kinetically sensitive reaction paths during recrystallization. Mindfulness of the potential significance of kinetic influences opens new avenues for petrologic investigation, thereby enhancing both analysis and interpretation.

Keywords: kinetics, disequilibrium, crystallization, metamorphism

INTRODUCTION

The equilibrium paradigm—the concept that metamorphic rocks pass progressively through sequential states of minimum free energy until they reach their thermal peak, remaining steadily at equilibrium as they transform—has met with great success. It has allowed petrologists to synthesize an abundance of accumulated observations into a coherent first-order picture of the responses of earth materials to the heating and compression they experience in Earth's crust and upper mantle. Increasingly, however, that view of metamorphism is being recognized as incomplete, and in some cases misleading: it neglects the facts that reactions cannot proceed at equilibrium and that metamorphic recrystallization involves passage through transient disequilibrium states along a rock's reaction path.

Experiments have yielded significant insights into rate-limiting metamorphic processes (e.g., Greenwood 1963; Walther and Wood 1984; review by Kerrick et al. 1991), and a rich literature describes kinetically controlled processes due to retrogression or polymetamorphism. In this article, we focus on the interpretation of natural samples traversing prograde paths, emphasizing the ways in which kinetic impediments to reaction can produce crystallization under conditions removed from the equilibrium state. We present observations spanning a range of scales, diverse metamorphic environments, and varied analytical approaches (field and petrographic studies, microchemical analysis, and thermodynamic and numerical modeling), with the aim of highlighting the intrinsic value of considering from the outset the role of kinetics in metamorphic interpretation.

RATIONALE FOR THE EQUILIBRIUM VIEW OF METAMORPHISM

The equilibrium model for prograde metamorphism has evolved as our understanding of metamorphism has advanced. It originally focused on the idea that rocks attain their minimum free-energy configuration at the maximum temperature they experience, giving rise to 'peak'

mineral assemblages and compositions. This interpretation is based on the metamorphic-facies principle, which embodies predictable relationships between mineral assemblages and bulk compositions, systematic associations of mineral assemblages in rocks of different bulk composition metamorphosed together, and the repeatability of mineral assemblage sequences in regional and contact settings the world over. Such regularity would be difficult to explain if rocks did not approach their equilibrium configuration at their metamorphic peak.

This equilibrium model of metamorphism has permitted the full power of chemical thermodynamics to be brought to bear on quantifying the conditions of metamorphism, resulting in the development and widespread application of geothermobarometry. The subsequent emergence of comprehensive thermodynamic databases and activity-composition models for minerals, accompanied by phase-equilibrium modeling software, has permitted rock-composition-specific phase diagrams to be calculated. These predict mineral modes and compositions against which natural observations and measurements can be quantitatively interpreted. Our current understanding of the range of metamorphic conditions in the crust and mantle derives almost entirely from successful application of these methods.

The 'peak-*T*' view of metamorphism is independent of both the tectonic path and recrystallization mechanisms by which a given peak metamorphic mineral assemblage is attained. Emphasis has increasingly moved to analysis of the pressure-temperature-time evolution of metamorphic conditions, because it provides deeper insight into tectonic processes and rates. In this context, an extension of the 'peak-*T*' equilibrium model is that as rocks progress along a path of changing pressure and temperature, they pass continuously through a series of equilibrium states until peak temperature is reached. The implication is that the rate of

reaction is faster than the rate at which the *P*-*T* conditions change, so the rock is never far from equilibrium at any point on its *P*-*T* path.

This version of the equilibrium model of metamorphism is more contentious. It ascribes the modes and textures of mineral assemblages only to equilibrium reactions, even if achieved by a series of interconnected local equilibria (e.g., Carmichael 1969), implying that kinetic barriers to reaction are never significant. It neglects the specific mechanisms by which rocks recrystallize and the rates at which that recrystallization occurs. On a *P*–*T* phase-diagram section, the magnitude of the free-energy difference between competing phase configurations for a given *P*-*T* condition, or between two different *P*-*T* conditions on either side of a modal-change line, is not apparent. This energy difference is irrelevant to a purely equilibrium approach to metamorphism. In natural processes, however, any equilibrium boundary must be overstepped to some degree to proceed, and competing phase configurations might differ only slightly in free energy; consequently, energetic barriers to recrystallization may potentially impede or delay the attainment of the equilibrium configuration. In such cases, kinetically controlled processes may then dominate the evolution of mineral assemblage and texture.

The petrologic community has widely adopted the calculation and description of *P*-*T* paths of metamorphism, implying acceptance that certain rocks must contain stranded textural or compositional remnants of their history. Recognition of preserved departure from rock-wide equilibrium leads to two key petrological questions: What magnitude of departure from equilibrium is possible, in terms of temperature and/or pressure, and more generally, free energy? Does the possibility of kinetically controlled processes influence the way one interprets a rock's textural and modal features in terms of its *P*-*T* path?

EVIDENCE FOR THE IMPORTANCE OF KINETICS TO PETROLOGIC INTERPRETATION

Petrological evidence

Classic examples of kinetic controls on metamorphic reaction progress include the widespread co-existence of the Al_2SiO_5 polymorphs andalusite and sillimanite, and the occurrence of locally eclogitized granulites in the Bergen Arcs in Norway, in which the conversion of granulite to eclogite is restricted to localized zones of ingress of hydrous fluid that catalyzed the reaction (Austrheim 1987). Of broader interest is whether kinetic barriers can give rise to significant departures from equilibrium during prograde metamorphism of pelitic and basic lithologies involving devolatilization reactions. There is increasing evidence suggesting that they do, and below we discuss several examples, ranging from the map scale to the microscale.

Nelson aureole, British Columbia. Figure 1a shows the distribution of mapped isograds in carbonaceous argillaceous host rocks in the Nelson aureole in southeastern British Columbia, whereas Figure 1b shows the predicted position of reaction isograds based upon an equilibrium thermodynamic model (details provided in Pattison and Tinkham 2009). The two most conspicuous differences are (1) the exceedingly narrow mapped garnet zone, compared to the ~900 m-wide garnet zone that is predicted assuming equilibrium, and (2) the >1000 m-wide mapped zone of co-existence of staurolite-only and staurolite+andalusite-bearing mineral assemblages, compared to the <100 m-wide staurolite+andalusite zone predicted assuming equilibrium. The estimated thermal overstepping of initial garnet growth was 30 °C, and of staurolite consumption, 60-70 °C. Other differences include (3) the predicted consumption of garnet downgrade of the first occurrence of sillimanite vs. the persistence and indeed growth of garnet upgrade of the consumption of staurolite in the natural rocks, and (4) the persistence of andalusite upgrade of the first appearance of sillimanite.

A simple explanation for these disparities relates to differences in the rate at which the macroscopic driving force for reaction builds up as the equilibrium boundaries are overstepped (Waters and Lovegrove 2002; Pattison and Tinkham 2009). This energy is needed to overcome kinetic barriers to nucleation and growth. The macroscopic driving force for reaction is termed reaction affinity (A), and is defined as the negative of the free energy difference between the equilibrium state, where $A = 0$, and any other state of the system that is not in equilibrium, where $A \neq 0$ (de Donder 1936; Prigogine and Defay 1954). In the specific situation involving overstepping caused by lack of nucleation, reaction affinity can be taken as the Gibbs free energy difference between the thermodynamically stable (but not-yet-crystallized) products and the metastable reactants, either in the form of the precursor mineral assemblage (Pattison et al. 2011), or in the form of dissolved components in a supersaturated intergranular fluid (Carlson 2011). The rate of build-up of reaction affinity with respect to temperature overstep is a function of the entropy change of the reaction (for overstep in pressure, it is the volume change). Figure 2 illustrates the rate of rise of reaction affinity with temperature overstep for some common reactions in metapelites, with the slope of each line being the entropy change for the reaction, which is strongly controlled by how much H_2O is released in the reaction. The reactions in the Nelson aureole for which there is petrological evidence of overstepping are the low-entropy, chlorite-free staurolite-to-andalusite reaction in the middle part of the aureole and, at lower absolute temperatures at the outer edge of the aureole, the moderate-entropy chlorite-to-garnet reaction.

An additional factor that likely played a role at this locality was the catalytic effect of fluid (Rubie 1986). The clustering of the garnet, staurolite and andalusite isograds (Fig. 1a), combined with textural evidence suggesting that all three porphyroblasts grew from reaction of fine-grained

matrix minerals, rather than involving the other porphyroblasts as predicted by equilibrium thermodynamics, was interpreted by Pattison and Tinkham (2009) as a fluid-catalyzed cascade effect triggered by introduction of H_2O to the grain-boundary network in response to the initial, overstepped production of garnet within the stability field of staurolite and andalusite. A second example of a fluid-catalyzing effect in the aureole is the local and patchy reaction of staurolite to andalusite within a broad domain in which many rocks contain andalusite-free staurolite-bearing assemblages, implying the existence of kinetic barriers to the conversion of staurolite to andalusite that were locally lowered by fluid presence.

Bushveld aureole, South Africa. Metapelitic rocks in the Bushveld aureole, South Africa, preserve a detailed microstructural record of an overlapping sequence of growth and consumption of porphyroblasts of staurolite, andalusite, biotite and cordierite from a chloritoid+chlorite-bearing precursor rock (Waters and Lovegrove 2002). The qualitative paragenetic sequence the authors deduced from the microstructures is shown in Figure 3a. By contrast, the predicted sequence of mineral growth and consumption, based on an equilibrium phase diagram specific to the rock composition of interest, bears no resemblance to the observed sequence whatsoever (Fig. 3b). The authors inferred that the reactions responsible for the observed growth of the porphyroblasts were high-entropy muscovite+chlorite-consuming devolatilization reactions that occurred in a narrow temperature interval up to 80 °C higher than the low-entropy, weakly H_2O-producing chloritoid-consuming reactions predicted to initially develop andalusite and staurolite (Fig. 3c). They concluded that the low-entropy reactions were overstepped and ultimately overtaken in terms of reaction affinity by the high-entropy reactions, at which point several reactions, both stable and metastable, occurred simultaneously, consuming the chloritoid and producing the andalusite, staurolite and biotite now present in the rock.

A significant observation in this study was the recognition of the growth and consumption of metastable cordierite within the reaction interval. Cordierite, stable at low pressures, should not be present at the higher pressures of staurolite stability. Waters and Lovegrove (2002) ascribed its development to its greater ease of nucleation compared to staurolite and andalusite. A purely equilibrium interpretation of these rocks would require an implausible *P-T* path of abruptly varying pressure. This example demonstrates that when *P-T* paths of metamorphism are inferred from the sequence of growth and consumption of minerals, it may be necessary to consider reactions other than those predicted in an equilibrium phase diagram, as also found in experimental studies (e.g., Greenwood 1963). Whereas the final (peak) mineral assemblage in the Bushveld rocks is consistent with that predicted assuming equilibrium, the path by which it arrived at that assemblage was influenced by both the *P-T* path and the kinetically controlled reaction path.

Synthesis. Pattison et al. (2011) provided other examples, mainly in metapelites, of regional and contact localities showing thermal overstepping of reaction boundaries or a lack of continuous equilibration during prograde metamorphism. Patterns emerge that can broadly be grouped according to the entropy change of the reactions involved. The least amount of demonstrable overstepping (5-30 °C) is observed for high-entropy devolatilization reactions, especially chlorite-consuming reactions that occur over narrow multivariant intervals; the greatest amount of overstepping (60-90 °C) is observed for low-entropy reactions, an observation that pertains to reactions in both the greenschist and amphibolite facies; and intermediate degrees of overstepping (30-70 °C) are inferred for moderate-entropy reactions, such as the chlorite-to-garnet reaction (for which the upper end of the range is for Mn and/or Al-rich bulk compositions

in which the garnet-in reaction is predicted to occur at especially low temperatures, e.g., < ~450 °C).

Additional factors. Absolute temperature and heating rate influence some, but not all, kinetically controlled processes, with lower temperatures and higher heating rates in general favouring disequilibrium when reaction rates are controlled by surface and transport processes (e.g., Putnis and McConnell 1980, section 6.2). However, in situations where disequilibrium is due to delays in nucleation (e.g., Rubie 1998), heating rate is not the primary control on the magnitude of the departure from equilibrium (Ridley and Thompson 1986; Waters and Lovegrove 2002; Gaidies et al. 2011; Ketcham and Carlson 2012). The more important factor is the magnitude of the temperature overstep, owing to the initial exponential dependence of nucleation rate on reaction affinity (e.g., Ridley 1986). Other factors include the catalytic effects of fluids (Rubie, 1986; see examples above) and the effects of deformation (e.g., Bell and Hayward 1991), although the latter are less well understood.

Implications for the metamorphic facies principle. Whereas the above examples demonstrate that the continuous-equilibrium model of prograde metamorphism may not always pertain, do they constitute violations of the metamorphic-facies concept? In localities where kinetic inhibitions to reaction have impeded crystallization of the thermodynamically stable equilibrium assemblage, the answer must be yes. Nonetheless, they may not compromise the broader principle. The examples noted in this article preferentially occur within individual facies (e.g., greenschist faces, amphibolite facies), or between major reaction isograds (e.g., between staurolite-in and K-feldspar-in isograds), rather than at the facies boundaries or major reaction isograds themselves. The latter are typically marked by high-entropy devolatilization reactions involving consumption of common hydrous minerals like chlorite and muscovite, in which the

amount of overstepping is expected to be minimal, or at least not sufficiently large to disrupt the repeated patterns noted earlier. It may be that the metamorphic-facies principle succeeds because it reflects major mineral-assemblage changes that occur at a few relatively discrete intervals where significant reaction, recrystallization and chemical equilibration occur (Pattison et al. 2011). Whereas the broad features of a metamorphic sequence may be accounted for by an equilibrium model, full understanding of the details of isograd patterns, mineral textures, mineral modes, mineral compositions, and chemical zoning will likely require consideration of both equilibrium and kinetics.

Evidence from Mineral Zoning

Metamorphic minerals that develop and preserve chemical zoning during growth can record differences among elements in their length scales for chemical equilibration, signaling departures from rock-wide equilibrium during prograde reaction. Achievement of chemical equilibrium requires the elimination of all chemical potential gradients between reactants and products. The length scales over which chemical equilibration can be established therefore depend on the required transport distances and on the rates of diffusion through the intergranular medium. Both may be expected to differ among chemical components involved in a reaction. When the length scale for equilibration—that is, when the scale of *local equilibrium* in the sense of Thompson (1959 and references therein)—varies significantly for different components, crystallization will occur under conditions of *partial chemical equilibrium*, meaning system-wide equilibration for some components, but not for others. Such conditions, imposed by the limitations of transport kinetics in the intergranular medium, may be made particularly evident by growth zoning in garnet.

For garnet and other aluminous porphyroblasts, the intergranular flux of Al is commonly inferred to be rate-limiting for crystal growth (Carlson 2011), but all other garnet constituents must also diffuse to the growing crystal from potentially different distal sources. Those elements that diffuse more rapidly than Al will keep pace with growth, and the crystal's zoning will reflect their negligible chemical-potential gradients in the form of near-equilibrium compositions at the growth surface. Preservation of those compositions in the crystal's interior as reaction progresses generates typical equilibrium growth zoning; an example would be bell-shaped profiles for Mn in garnet. But elements that diffuse more slowly than Al cannot equilibrate over the required length scale. As a result, their concentrations at the surface of growing garnet will be kinetically controlled, and will be subject to a variety of influences that reflect the details of the reaction path and mechanism.

A vivid example of partial chemical equilibrium in the form of 'overprint zoning' comes from the study of Yang and Rivers (2001). The garnet crystal shown in Figure 4 exhibits smooth concentric zoning for Mn, but a strongly banded distribution for Cr. Rapid intergranular diffusion of Mn allowed equilibration over a length scale sufficient to flatten its chemical-potential gradient, so that its zoning reflects progressive depletion of a spatially uniform, rock-wide reservoir; in contrast, very restricted intergranular diffusion of Cr impeded its redistribution, so that its zoning reflects *in situ* incorporation of the heterogeneous distribution present in the precursor matrix. Figure 4 illustrates schematically the character of the chemical-potential gradients involved, which reflect the relative rates of intergranular diffusion. Other examples are less obvious, but no less profound in their consequences. Varied examples of partial chemical equilibrium during prograde metamorphism are discussed in Carlson (2002) and in Ague and Carlson (2013); here we sample just two more to illustrate the point.

The zoning of porphyroblasts in the garnet-zone metapelites of Harpswell Neck, Maine (cf. Spear and Daniel 1998) highlights another instance in which a purely equilibrium-based interpretation would be in error (Carlson et al. 2015, and references therein). As seen in Figure 5, porphyroblasts that grew in locally quartz-rich, mica-poor environments (crystals A, B, C, with quartz-rich layers identified by black zones in the Mg map) exhibit patchy overprint zoning for Mn, Fe, and Mg, incorporating layering from the precursor; but for Ca and Y, these same crystals display smooth concentric zoning, reflecting rock-wide equilibration. Equilibrium-based interpretations, which require each isolated Mn high to originate in a separate nucleation event, cannot be reconciled with the discrete central maxima for Y. In this instance, Ca and Y achieved rock-wide equilibration, but Mn, Fe, and Mg did not. Raman spectroscopy of fluid inclusions reveals that fluids attending early garnet growth were CO_2-rich; the difference in equilibration for the various elements can be explained by their differential solubilities in such fluids. Immediately adjacent crystals that grew in locally mica-rich environments (D) exhibit zoning patterns little different from those expected from equilibrium prograde zoning, providing no clue to the large variation in sizes of equilibration domains for different elements during their growth. Such porphyroblasts falsely appear to mimic large-scale equilibrium crystallization, highlighting the need for vigilance in interpretation.

Concentrations of trace elements, especially Y and the REEs, exhibit variability in garnet as great or greater than that shown by major-element zoning. The data and recent synthesis of Moore et al. (2013) revealed that Y+REEs may sometimes exhibit smooth zoning with pronounced central peaks, demonstrating equilibration over long length scales with an unchanging matrix assemblage (e.g. Otamendi et al. 2002), or they may exhibit a variety of annular maxima, demonstrating equilibration, over similarly long length scales, with changing

accessory- or major-phase assemblages that are modulated by reactions occurring within the matrix (e.g. Pyle and Spear 1999; Konrad-Schmolke et al. 2008). But Moore et al. (2013) stressed that in other circumstances, these elements may express disequilibrium during garnet growth, in the form of overprint zoning (Martin 2009), diffusion-limited uptake (e.g. Skora et al. 2006), or control by external fluids that did not equilibrate with the matrix mineral assemblage (Moore et al. 2013). In all cases, the principal factor that determines the length scale for equilibration is the rate of intergranular transport.

Incongruities between calculated and observed phase equilibria

Forward-modeled predictions of changing mineral composition with *P* and *T* commonly yield detailed evidence of metamorphic peak conditions and of mineral growth along segments of *P*-*T* paths (e.g. Konrad-Schmolke et al. 2007; Groppo et al. 2009). Set against this success in recovering metamorphic conditions from mineral compositions, however, is a troubling observation: zoned mineral compositions (most typically of garnet) may appear to track equilibrium thermodynamic predictions of growth during burial and heating, but the compositions of garnet calculated at the lowermost pressures and temperatures of its stability are rarely seen in nature. Specifically, calculations that feature very low-*T* garnet stability suggest that its Mn and Ca components should reach, or sometimes significantly exceed, 50 molar percent (e.g., Caddick et al. 2010; Caddick and Kohn 2013). A rock-wide equilibrium response would mandate the growth of Mn- and Ca-rich garnet (presumably to subsequently be preserved as crystal cores), but natural crystals from mafic and pelitic lithologies are invariably far more Fe- and Mg-rich. Scarce reports of extremely Mn- and Ca-rich low-temperature metamorphic garnet (e.g., Tsujimori et al. 2006) imply that these compositions are indeed possible, countering potential arguments that the available thermodynamic data are simply in error and leaving two

316 plausible interpretations: that early growth compositions are subsequently lost by
317 recrystallization or intracrystalline diffusion, or that garnet simply does not begin to grow at or
318 near the 'garnet-in' boundary in many cases.

319 An example of apparently delayed crystal growth comes from blueschist-facies rocks on
320 the Aegean island of Sifnos. Dragovic et al. (2012) isotopically dated multiple points from the
321 core to the rim of large garnet crystals, chosen to represent as much of the prograde metamorphic
322 history as possible. An equilibrium thermodynamic model constructed for the rock suggests that
323 the earliest-formed garnet preserves a composition appropriate for growth more than 1 GPa
324 deeper and/or 80 ˚C hotter than the interpreted point at which the 'garnet-in' reaction was
325 crossed (Fig. 6). Recent reinterpretation based upon an alternate model (Spear et al. 2014) also
326 yielded apparent garnet nucleation 70–90 ˚C hotter than the equilibrium garnet isograd, and
327 although the pre-garnet growth history is poorly constrained, any possible path to the point at
328 which garnet eventually grew reflects a similarly large overstepping of equilibrium garnet-
329 growth reactions. The large crystal size and relatively low maximum temperature of the sample
330 suggest that primary growth compositions are preserved without significant diffusive
331 modification, and repeatability of the observation in different Sifnos lithologies, including
332 samples that underwent 3-D tomographic analysis prior to thin sectioning (e.g., Dragovic et al. in
333 review), limits the chances of systematically failing to expose the true garnet core. It remains
334 most likely that initiation of garnet growth was delayed and that the total duration of crystal
335 growth was then brief (< 1 Myrs). In terms of free energy, the implied overstepping is similar in
336 magnitude to that inferred in other localities and lithologies, as described in the section that
337 follows. Recalculating the phase equilibria, but without permitting garnet stability, yields the
338 free-energy excess associated with deviation from equilibrium (Fig. 6), suggesting a reaction

affinity of ~ 0.5 kJ/mol of oxygen in garnet (6 kJ/mol of 12-oxygen garnet) at the *P*-*T* of inferred initial garnet growth. The wide spacing of the affinity contours at low temperatures and pressures reflects the fact that the reaction entropy and volume are small when close to equilibrium, so that the driving force for metamorphic recrystallization remains insufficient to overcome barriers to nucleation until a relatively large overstep in *T* and *P* is achieved.

As discussed previously, the phase diagram from which Figure 6 was constructed would typically show only the state of minimum free energy. Quantifying the magnitude of the free-energy departure associated with alternative configurations might prove to be a useful way in the future of estimating the driving force for metamorphic recrystallization, and thus the likelihood and magnitude of significant reaction overstepping (Pattison et al. 2011).

Petrologically constrained numerical simulations of crystallization

Numerical simulations—when carefully constrained by petrological observations and measurements—can couple the kinetics of specific reaction mechanisms to the thermodynamic driving forces for reaction in ways that permit quantitative estimation of the magnitudes of departures from equilibrium during metamorphism. Depending upon which of the processes essential to crystallization is regarded as rate-limiting, such models make qualitatively different predictions for the reaction path: recent examples are those of Schwarz et al. (2011), Gaidies et al. (2011), and Ketcham and Carlson (2012), for which the rate-limiting processes are, respectively, reactant dissolution, product precipitation, and intergranular diffusional transport. These models also differ in more subtle ways that influence their predicted departures from equilibrium, and they have been assessed against different types of natural observations. The first two models, those with no diffusional impediment to crystallization, predict smaller departures

361 from equilibrium than the third. Yet all of them highlight the importance to metamorphic
362 crystallization of a variety of kinetic factors and diverse potential reaction mechanisms.

363 Here we focus upon the diffusion-controlled model, because it has been applied by Kelly et
364 al. (2013a, 2013b) to garnet nucleation and growth in multiple samples that span a broad range of
365 *P-T* conditions, heating rates, and bulk compositions, as well as syn- to post-deformational
366 crystallization. This forward model provides a quantitative link between measureable textural
367 features in porphyroblastic rocks and the length scales of diffusion—and corresponding
368 departures from equilibrium—that generate them. For each sample, data from field, petrological
369 and microchemical analyses constrain a model *P-T-t* crystallization path, and thermodynamic
370 data yield the evolution of the free energy of reaction $\Delta_r G$ along it. Numerical simulation of
371 diffusion-controlled nucleation and growth then computes the sizes, locations, nucleation times,
372 and time-varying growth rates of porphyroblasts across the crystallization interval; factors
373 controlling nucleation rates and diffusional fluxes are adjusted to achieve quantitative
374 congruence with measured textural features in the modeled sample.

375 A typical outcome is shown in Figure 7. Key aspects are appreciable thermal overstepping
376 (27 °C) before the first nucleation event occurs, and a large departure from equilibrium (an
377 accumulation of 52 $J \cdot cm^{-3}$ of stored latent energy) before reaction rates accelerate sufficiently to
378 begin to reduce the reaction affinity. Nucleation is not restricted to a narrow interval barely
379 above the equilibrium temperature, as equilibrium-based models would require; instead, it
380 extends across nearly the entire crystallization interval, although it is concentrated around the
381 peak of overall metastability, as indicated by the maximum value of the latent energy of reaction.
382 This is confirmed by the observed variability of central Mn contents and their systematic relation
383 to crystal size, with cores of smaller crystals matching in composition the outer mantles of larger

crystals. Whereas the equilibrium model would require that all crystals nucleate on or near the reaction boundary and thus acquire identical central compositions, the systematic variation in measured central Mn contents instead documents that nucleation continues late into the crystallization interval, so that many crystals nucleate well after the equilibrium boundary has been crossed, and after much of the reaction has already taken place. The interval over which reaction occurs spans a significant range of temperature and time: most crystallization (10-90% of the total) takes place several tens of degrees (50-80 °C) above the equilibrium temperature, and the bulk of the reaction occurs nearly ten million years after the equilibrium boundary is first crossed. The modal proportion of garnet at any point in time and temperature is less—and in the early stages of reaction, much less—than predicted by equilibrium phase diagrams, so changes in effective bulk compositions are significantly delayed by the retardation of reaction progress.

The application by Kelly et al. (2013b) of such models to a suite of 13 diverse rocks yielded consistent findings, paralleling those for the single example just described. The implication from this modeling approach is that garnet crystallization may occur at conditions significantly removed in temperature, time, and energy from the equilibrium state.

CENTRAL CONCEPTS

From the foregoing, four key concepts emerge.

First, in petrologic interpretation, the assumption of potentially significant kinetic influence is less restrictive than the assumption of rock-wide equilibrium crystallization. The equilibrium paradigm implies that one is justified in assuming that departures from the equilibrium state were negligible during crystallization, unless and until evidence comes to light that requires otherwise. But this assumption carries risk. As documented above, petrologically significant departures from rock-wide equilibrium may occur during reaction, yet leave behind only subtle or cryptic

traces in the rock as the length scales for equilibration expand near the metamorphic peak. There exists a continuum between obvious and cryptic instances of petrologically significant departures from equilibrium during metamorphism; in the synthesis above, this is true regardless of the scale of features examined, the environment of interest, or the investigative approach employed. In terms of the processes involved, the clear-cut examples are not anomalous, nor substantively different, from the examples in which only subtle indicators of disequilibrium survive. It may therefore be limiting, and potentially misleading, to start from the expectation that equilibrium has pertained throughout the metamorphic episode, and to abandon or modify that assumption only when forced by some observation to do so. A less confining approach is to acknowledge from the outset that all reactions require departures from equilibrium. Observations made with this recognition in mind are more likely to capture the full range of features in the rock important to petrologic interpretation.

Second, the *P*-*T*-*t* history and reaction path inferred from a rock on the basis of an equilibrium model may be displaced substantially from the actual history and path. The onset of reaction may be delayed, and eventual recrystallization may proceed too slowly for rock-wide mineral assemblages, modes, and compositions to keep pace with changes in physical conditions. Thus rocks may traverse reaction paths that are not predictable or interpretable from equilibrium considerations alone.

Third, length scales for equilibration during metamorphic reaction may be decidedly different for different elements under the same conditions, leading to partial chemical equilibrium. That is, although local equilibrium may exist in systems that support large-scale chemical-potential gradients, the length scale for such 'local' equilibrium may be different for each chemical species. This requires explicit consideration of difficult questions: How do length

scales of equilibration differ among the major constituents of the minerals involved in a reaction, and among minor/trace constituents? Which length scales are relevant and which are irrelevant to any chosen petrologic interpretation?

Fourth, *P-T* paths inferred from mineral zoning, mineral modes, and even mineral assemblages are vulnerable to error unless they are considered in the context of the potential for partial chemical equilibrium and for kinetic impacts on reaction progress. Kinetic impediments to equilibration may be more commonplace than is evident from the most obvious examples that are readily accepted as indicative of metastability (e.g., the coexistence of polymorphs over ranges of *P* and *T*), and these impediments can be of sufficient magnitude to alter zoning, modes, and assemblages in ways that can compromise petrologic interpretation based on the equilibrium model.

LOOKING FORWARD

It is a tribute to the power of the equilibrium paradigm that petrologists can now identify and begin to quantify the departures from equilibrium that necessarily accompany metamorphic crystallization. A pressing question, therefore, is how prevalent and how significant kinetic controls on prograde metamorphic processes and products will prove to be. Are they important yet often overlooked? The petrological community can address that issue by remaining mindful of the possibility of kinetically influenced crystallization, in order to recognize evidence for it, to capture the nuanced view of metamorphism that it provides, and to gain the enhanced insights that it produces.

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563
564

FIGURE CAPTIONS

FIGURE 1. (a) Sample locations (*dots*) and mapped isograds in the aureole of the Nelson Batholith, British Columbia. *Solid lines*: mineral-in isograds. *Dashed lines*: mineral-out isograds. **(b)** Predicted isograds from the same locality as (a), based on equilibrium thermodynamic predictions and a modeled thermal profile. Diagrams and interpretations from Pattison and Tinkham (2009).

FIGURE 2. Estimates of rate of build-up of macroscopic reaction affinity, due to thermal overstepping of the equilibrium reaction position, for reactions of differing entropy. The uniform energetic threshold for nucleation (*dotted line*) is used for comparative purposes only; in reality, this will vary with the nature of mineral reactants/products and other factors. Diagram from Pattison et al. (2011).

FIGURE 3. (a) Interpretation, based on microstructures, of the sequence of mineral growth and consumption in porphyroblastic metapelites from the aureole of the Bushveld Intrusive Complex, South Africa. **(b)** Predicted sequence of mineral growth and consumption in the same rock as in (a), based on equilibrium thermodynamic predictions. **(c)** Interpreted overstepped reaction interval involving several stable and metastable reactions occurring in parallel over a narrow temperature range (cascade effect). The reaction sequence in (c) is the same as in (a), the latter compressed into the estimated 540-560 °C thermal interval. Diagrams and interpretations from, or based on, Waters and Lovegrove (2002).

FIGURE 4. Partial chemical equilibrium during garnet growth. (*left and center*) X-ray maps of Mn and Cr concentrations, contrasting equilibrium drawdown of uniform Mn reservoir with overprinting of Cr heterogeneities in matrix. After Yang and Rivers (2001). (*right*) Schematic chemical-potential gradients in intergranular medium during growth of porphyroblast

588 (*rectangle*), for elements with fast (Mn), moderate (Al), and very slow (Cr) intergranular
589 diffusion.

590 **FIGURE 5.** Partial chemical equilibrium during garnet growth. X-ray maps of zoning
591 patterns in crystals *A*, *B*, and *C* display patchy overprint zoning of layered distributions of Mn,
592 Fe, and Mg, but smooth concentric zoning for Ca and Y. An immediately adjacent crystal *D*,
593 which grew in a mica-rich layer, exhibits smooth concentric zoning for all elements.

594 **FIGURE 6.** *P-T* diagram calculated for a blueschist-facies rock from Sifnos, Greece (rock
595 composition, thermodynamic data and mineral solution models as in Dragovic et al., 2012,
596 supplemented with an ideal solution model for Fe-Mg-Mn stilpnomelane). Color shading and
597 contours show increase in system free energy if garnet is excluded from the calculation, relative
598 to free energy if garnet is included. Contour interval is 100 J/mol of oxygen in garnet. *P-T*
599 regions in which an alternative porphyroblast-forming phase grows in place of garnet are shaded.
600 First recorded garnet compositions imply growth at *P-T* conditions significantly above
601 equilibrium stability for garnet-in. System free energy is lowered by ~ 0.5 kJ/mol of oxygen in
602 garnet if ~ 1 volume % garnet is grown at these *P-T* conditions.

603 **FIGURE 7.** Departures from equilibrium as computed by petrologically constrained
604 numerical simulation of diffusion-controlled nucleation and growth (details of calculations
605 appear in Kelly et al., 2013b). Along gray *P-T-t* path (*top*), initial nucleation of garnet is delayed
606 by 3 Ma to 27 °C above equilibrium *T*; bulk of garnet crystallization occurs 8-14 Ma after
607 reactants become unstable (*center, bottom*), and 50-80 °C above equilibrium boundary.
608 Computed delay in modal accumulation of garnet is consistent with measured systematic
609 correlations of crystal size with central composition (*insets at top*); last crystals to nucleate have
610 core compositions matching outer mantles of early-nucleating crystals, documenting that

611 nucleation persisted late into the crystallization interval, rather than being restricted to conditions
612 at or near the reaction boundary, as the equilibrium model requires.

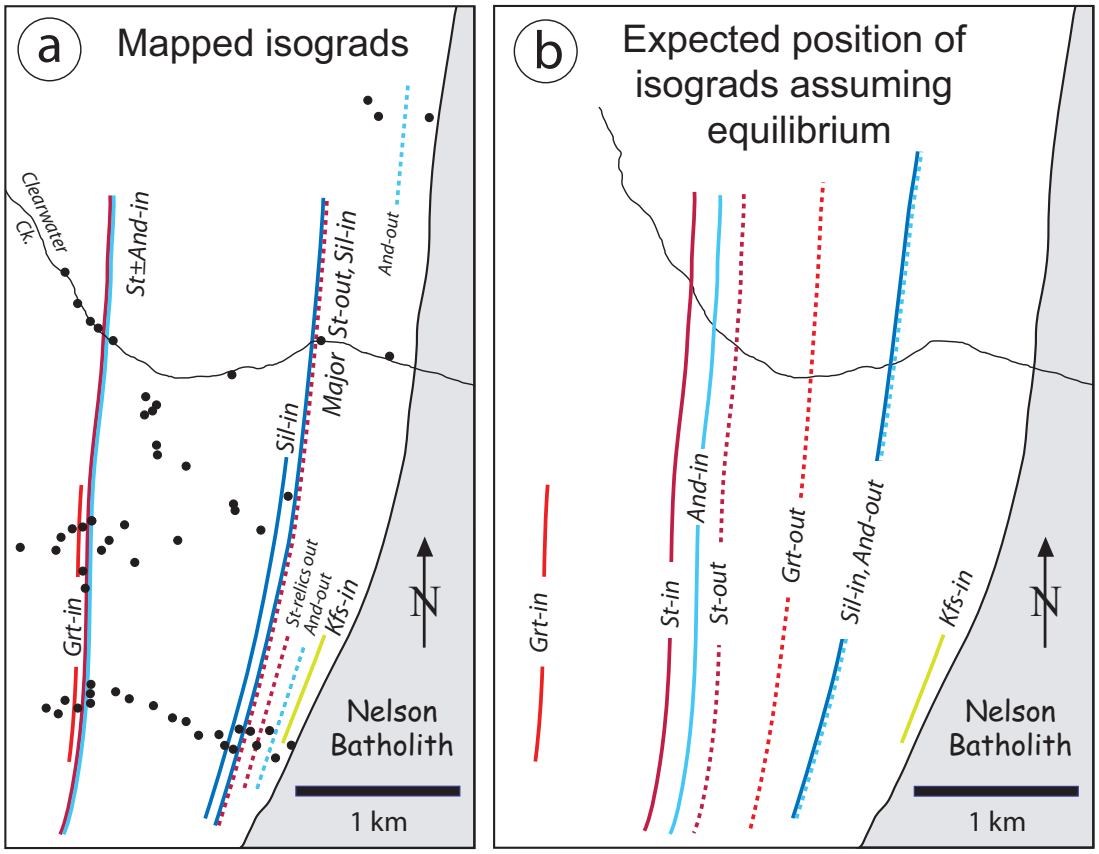
a
Mapped isograds
Clearwater Ck.
St±And-in
St-out, Sil-in
And-out
Major
Sil-in
Grt-in
St-relics out
And-out
Kfs-in
N
Nelson Batholith
1 km
b
Expected position of isograds assuming equilibrium
Grt-in
St-in
And-in
St-out
Grt-out
Sil-in, And-out
Kfs-in
N
Nelson Batholith
1 km

FIGURE 1

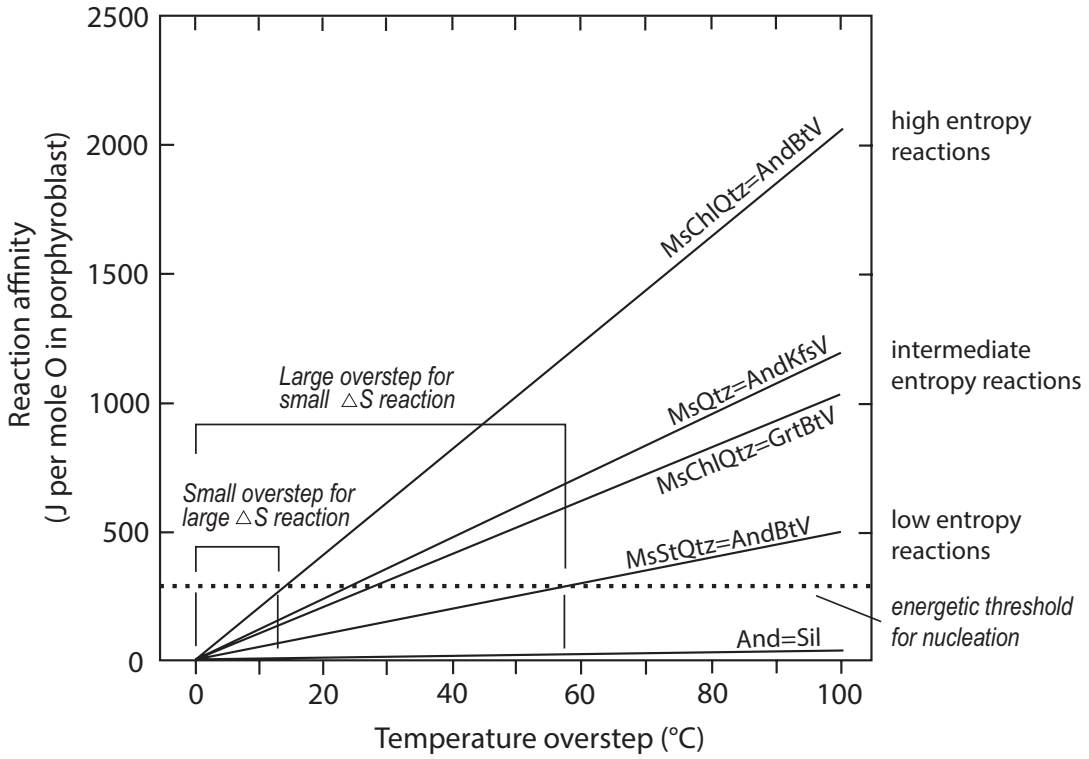
2500
2000
1500
1000
500
0
Reaction affinity
(J per mole O in porphyroblast)
0
20
40
60
80
100
Temperature overstep (°C)
MsChlQtz=AndBtV
MsQtz=AndKfsV
MsChlQtz=GrtBtV
MsStQtz=AndBtV
And=Sil
high entropy reactions
intermediate entropy reactions
low entropy reactions
energetic threshold for nucleation
Large overstep for small △S reaction
Small overstep for large △S reaction

FIGURE 2

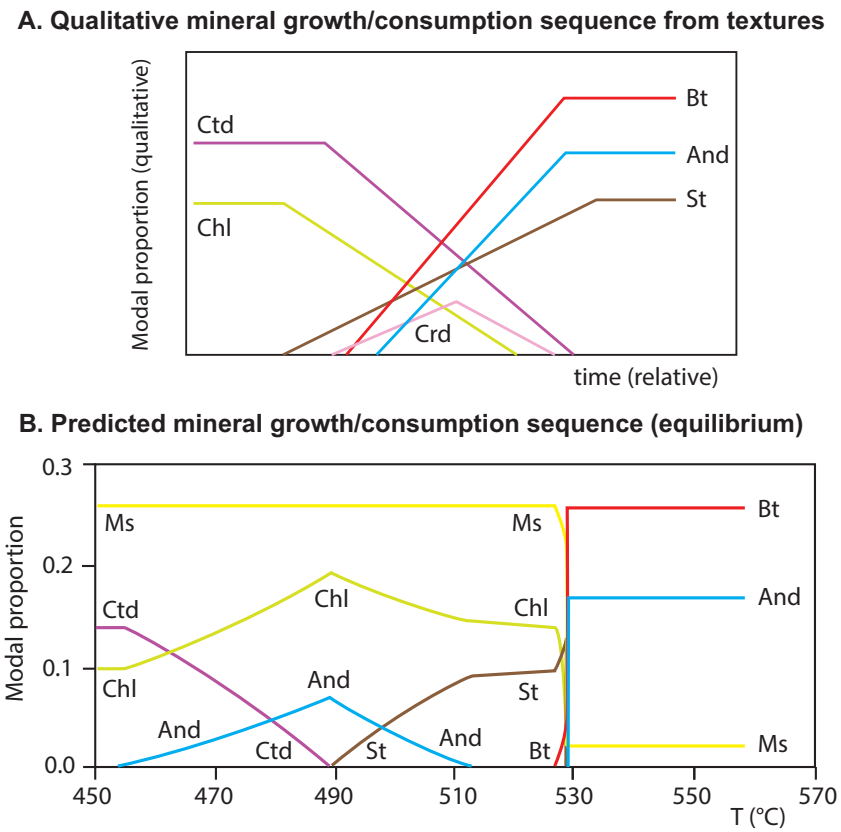
A. Qualitative mineral growth/consumption sequence from textures
Modal proportion (qualitative)
Ctd
Chl
Crd
Bt
And
St
time (relative)
B. Predicted mineral growth/consumption sequence (equilibrium)
Modal proportion
0.3
0.2
0.1
0.0
Ms
Ctd
Chl
And
Ctd
St
And
Chl
Ms
Chl
St
And
Bt
Bt
And
Ms
450
470
490
510
530
550
570
T (°C)
C. Interpreted interval of overstepped mineral/growth consumption
Modal proportion (qualitative)
Ctd
Chl
Crd
Bt
And
St
450
470
490
510
530
550
570
T (°C)

FIGURE 3

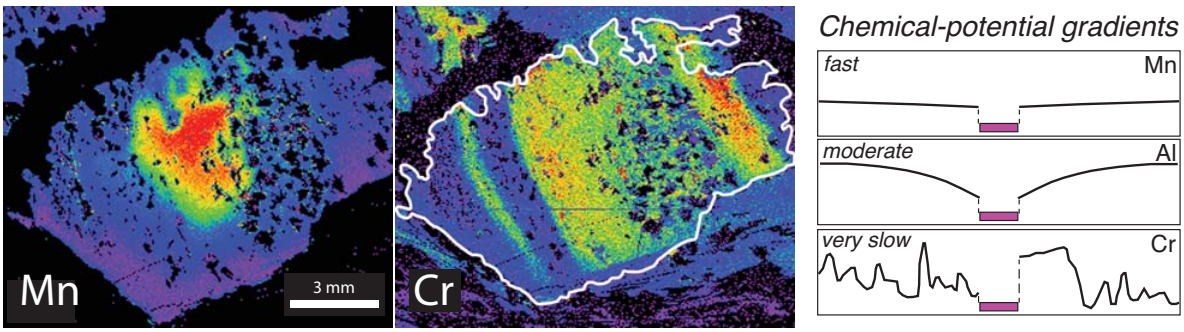
Mn
3 mm
Cr
Chemical-potential gradients
fast
Mn
moderate
Al
very slow
Cr

FIGURE 4

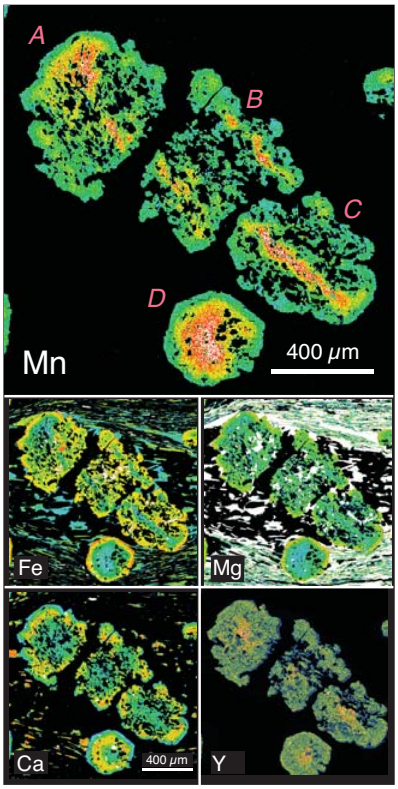

FIGURE 5

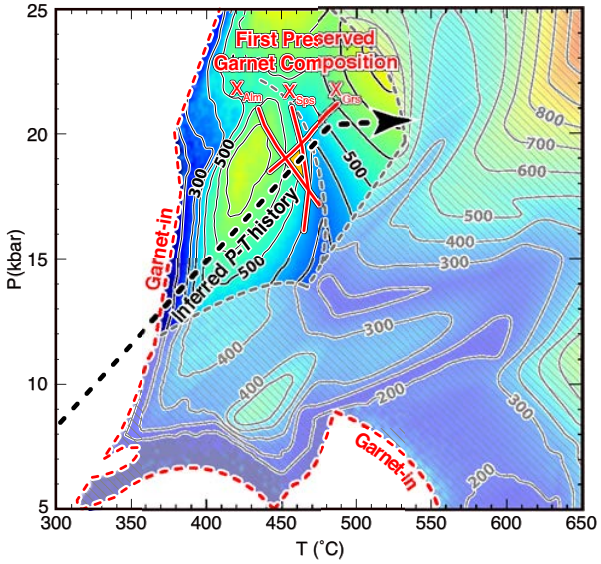
First Preserved
Garnet Composition
X_{Alm}
X_{Sps}
X_{Grs}
Garnet-in
Inferred P-T history
Garnet-in
P(kbar)
T (°C)
25
20
15
10
5
300
350
400
450
500
550
600
650
800
700
600
500
400
300
200

FIGURE 6

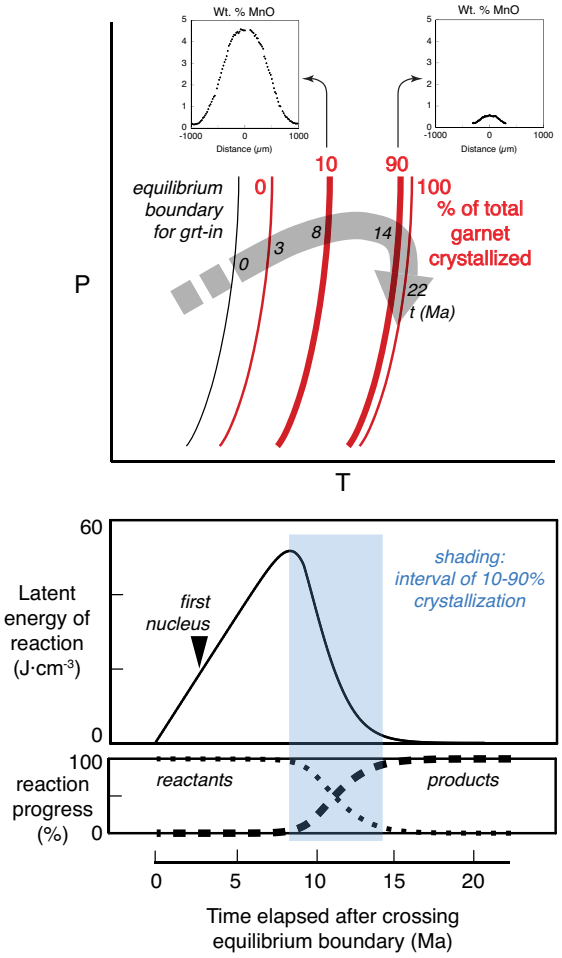
Wt. % MnO
Distance (μm)
Wt. % MnO
Distance (μm)
10
90
equilibrium boundary for grt-in
0
100
% of total garnet crystallized
8
14
3
0
22
t (Ma)
P
T
60
Latent energy of reaction (J·cm-3)
first nucleus
shading: interval of 10-90% crystallization
0
100
reaction progress (%)
reactants
products
0
0
5
10
15
20
Time elapsed after crossing equilibrium boundary (Ma)

FIGURE 7