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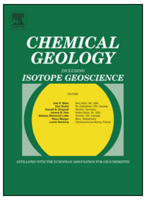

The implications of overstepping for metamorphic assemblage diagrams (MADs)

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ABSTRACT

Metamorphic assemblage diagrams (MADs, also known as pseudosections) are based on the assumption of chemical equilibrium throughout. Nucleation of a porphyroblast, however, requires a driving force that is achieved through overstepping of the isograd reaction. By making an assumption about the degree of overstepping required to nucleate garnet, aluminosilicate, staurolite, and cordierite, a modified MAD can be constructed that offers insights into metamorphic parageneses beyond those provided by an equilibrium phase diagram.

Assuming a representative value of 300 J/mol oxygen of affinity for the nucleation of a porphyroblast, modified MADs have been constructed for a typical pelitic bulk rock composition. The resulting diagrams show a displacement of the garnet isograd to higher temperature (T), a shrinking of the stability field for garnet + chlorite, an expansion of the field for aluminosilicate, and a shrinking of the stability field for cordierite. Furthermore, the size of the stability field for staurolite + garnet depends on which reaction produces aluminosilicate: if aluminosilicate nucleates from an assemblage of garnet + staurolite the field of staurolite + garnet is greatly expanded; if aluminosilicate nucleates from an assemblage of chlorite + muscovite, the field shrinks dramatically and may be eliminated entirely. If garnet is a reactive phase, then kyanite is predicted to nucleate prior to or nearly simultaneously with staurolite in typical Barrovian metamorphic trajectories. Finally, certain equilibrium assemblages present in only small regions of P–T space may not be realized unless sufficient driving force for nucleation or progressive reaction can occur over limited changes in P and T. The key consideration is the amount of affinity required to drive the reaction at the P–T conditions of interest.

1. Introduction

Equilibrium isochemical phase assemblage diagrams ("pseudosections" in the terminology of Hensen, 1971 and Powell et al., 1998), or, more simply, "metamorphic assemblage diagrams" (MADs), have been used extensively in recent years to infer conditions of metamorphism and metamorphic P–T paths (e.g. Powell et al., 1998). An informal survey of 2015 issues of the Journal of Metamorphic Geology reveals that about half of the articles contain MADs and typically more than just a single diagram. Subject to the chemical system chosen and the validity of the thermodynamic data and a-x models used to calculate them, MADs provide a representation of the P–T stabilities of metamorphic assemblages for a specified bulk rock composition.

Fundamental to the construction of such diagrams is the assumption of equilibrium among the phases, as is specified by Duhem's theorem (Prigogine and Defay, 1954). However, it is also well known that in the absence of an energetic driving force reactions will not proceed and porphyroblasts will not nucleate (e.g. Ridley and Thompson, 1986). There have been a number of papers in recent years that have presented compelling evidence for the role that overstepping of isograd reactions must play in metamorphic parageneses (see summary in Pattison et al., 2011). Hollister (1969) presents several lines of evidence for overstepping of common reactions found in pelites from rocks of the Kwoiek area, British Columbia, Waters and Lovegrove (2002) identified out-of-sequence porphyroblast growth in the contact aureole of the Bushveld Complex, Zeh and Holness (2003) presented textural and chemical evidence for overstepping of the garnet isograd, and Pattison and Tinkham (2009) described displaced and compressed isograds in the contact aureole of the Nelson batholith, B. C. that they attributed to overstepping. Spear et al. (2014) and Castro and Spear (2016) compared quartz-inclusion-in-garnet barometry (QuiG) to equilibrium isograd P–T conditions and concluded that considerable overstepping was required for the nucleation of garnet.

Overstepping displaces the P–T conditions of an assemblage boundary (isograd) relative to the location of that assemblage boundary on a

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MAD. Several studies have argued that delay of nucleation may cause the greatest degree of overstepping (Rubie, 1998; Waters and Lovegrove, 2002; Pattison and Tinkham, 2009; Gaidies et al., 2011; Kelly et al., 2013; Spear et al., 2014; Carlson et al., 2015). The purpose of this contribution is to explore some of the effects that nucleation-related overstepping may have on a typical MAD for metapelites, and some potential implications of this modified MAD for the interpretation of metamorphic parageneses. Whereas the extent of overstepping required to nucleate porphyroblasts will vary with porphyroblast type, strain history, and matrix assemblage (Waters and Lovegrove, 2002), we adopt a simplified model that allows us to focus on some of the more general implications.

1.1. Theoretical background

Nucleation of a porphyroblast requires overcoming the activation energy barrier. Classical nucleation theory predicts the nucleation rate (R) to be an exponential function of this activation energy (ΔG^*):

$$R = C\exp\left(\frac{-\Delta G^*}{RT}\right)$$

where C is a constant that is a function of the number of nucleation sites and a probability factor, R is the gas constant and T is temperature. The energy of the system (proto nucleus and immediate environment) is comprised of a competition between three terms: a volumetric energy (ΔG_v – always negative) that is the difference between the free energy of a metastable matrix assemblage and the free energy of the nucleated phase at the same conditions (Fig. 1), a strain energy (ΔG_s – always positive), and a surface energy of the nucleus (σ — always positive):

$$\Delta G = \frac{4}{3}\pi r^3(\Delta G_v + \Delta G_s) + 4\pi r^2\sigma$$

The activation energy (ΔG^*) is the energy barrier that must be overcome for nucleation to occur and is the energy at the critical radius, which occurs at the maximum of the plot of ΔG versus r:

$$\frac{d\Delta G}{dr} = 0$$

so

$$r^* = -\frac{2\sigma}{(\Delta G_v + \Delta G_s)}$$

Substituting r* into the equation for ΔG yields the activation energy:

$$\Delta G^* = \frac{16\pi\sigma^3}{3(\Delta G_v + \Delta G_s)^2}$$

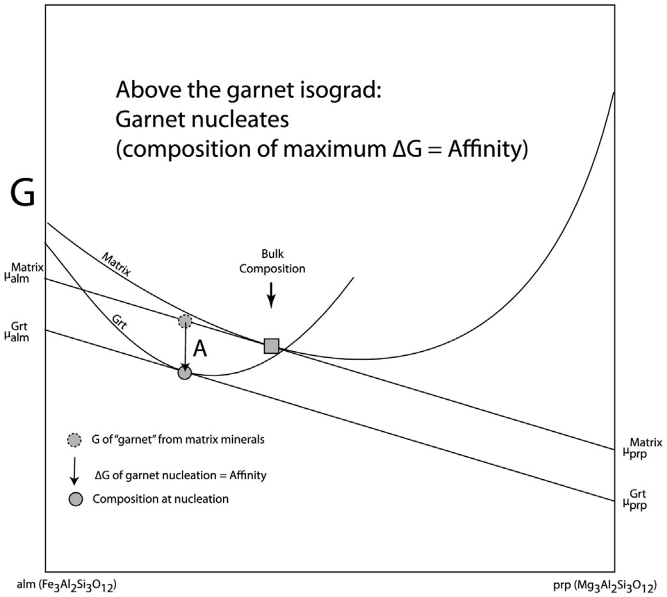

Fig. 1. Schematic G–X diagram showing the method for calculating affinity (A) for the nucleation of garnet. The composition of the garnet that nucleates is that which gives the largest decrease in free energy. The graphical constraint on this condition is that the tangent to the matrix assemblage and garnet free energy curves must be parallel. The mathematical solution is given in Spear et al. (2014).

Quantification of the strain (ΔG_s) and surface energies (σ) is difficult but neither is likely to be a strong function of the degree of overstepping. On the other hand, ΔGv is a first order function of overstepping due to the relationship between G, T and P:

$$dG = -\Delta SdT + \Delta VdP$$

Therefore, the activation energy barrier (ΔG^*) will, to a first order, be an inverse function of the square of the volumetric free energy as it varies with P and T. The nucleation rate, being an exponential function of this squared volumetric free energy term, will therefore increase extremely rapidly with the degree of overstepping.

In this paper, we follow the derivation of Thompson and Spaepen (1983) and Gaidies et al. (2011) (equations detailed in Spear et al., 2014) and calculate the volumetric free energy change as the difference in free energy between (1) a fictive, or virtual, nucleus whose free energy is defined by the chemical potentials of the phase-absent reactant matrix assemblage, and (2) the free energy of the nucleus that actually forms (Fig. 1). We call this quantity the affinity for nucleation, or simply affinity, following Gaidies et al. (2011), Pattison et al. (2011), and Spear et al. (2014). It is assumed that the most likely composition for the newly nucleated phase is that which provides the largest decrease in free energy or largest affinity (Fig. 1).

The extremely rapid increase in nucleation rate after a certain degree of overstepping provides a rationale to consider initial nucleation to occur at a specific value of overstepping. That is, the probability that a nucleus will form after a prescribed degree of overstepping increases abruptly from 0 to nearly 1. Whereas this is clearly an oversimplification and there are other factors, as noted above, that will influence nucleation, it permits exploration of some potentially important differences between the P-T conditions of isograd reactions on equilibrium phase diagrams and what might occur in a rock undergoing metamorphism. In this paper, we adopt the estimated value of A = 300 J/mol oxygen reported in Pattison et al. (2011).

The rate at which affinity builds with overstepping varies from reaction to reaction (Waters and Lovegrove, 2002; Pattison et al., 2011) and is a function of the assumed reactive assemblage and the porphyroblast to be nucleated. The porphyroblasts under consideration in this paper are those typical of pelitic schists: garnet (Grt), staurolite (St), aluminosilicate (Als: kyanite, sillimanite, andalusite), and cordierite (Crd). The concept of reactive assemblage is central to the following development. There is considerable evidence from numerous studies that not all phases present in a rock are involved in all reactions. That is, some phases may be entirely reactive (continuously equilibrating as conditions change), others may be partially reactive and some may be completely unreactive. Additionally, some phases may be unreactive during part of the metamorphic history and become partially or totally reactive at other parts. For example, Hollister (1969) argued that garnet, once formed, was largely unreactive and ilmenite was unreactive until staurolite appeared, at which point it became reactive. The mere existence of zoned minerals (e.g. garnet) proves that some phases are not totally reactive under certain conditions. In this paper, the term

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"reactive assemblage" is the assumed assemblage of phases that react completely at the specified conditions. Albeit a simplification, the designation of an assemblage as reactive permits calculation of a limiting case in the metamorphic process.

An example is the nucleation of garnet from the assumed reactive assemblage chlorite + biotite + muscovite + quartz + plagioclase + H_2O by the reaction (abbreviations after Kretz, 1983 and Whitney and Evans, 2010):

$$\mathrm{Chl + Ms + Pl + Qtz = Grt + Bt + H_2O} \tag{1}$$

or, at higher pressure where clinozoisite is part of the reactive assemblage, by the reaction:

$$\mathrm{Chl + Ms + Czo + Qtz = Grt + Bt + H_2O} \tag{1a}$$

The affinity (A) for garnet nucleation that builds with overstepping of these reactions is illustrated in Fig. 2 for the MnNCKFMASH system and the bulk composition listed in Table 2. Following Waters and Lovegrove (2002) and Pattison et al. (2011), all affinities reported here are in units of joules/mol of oxygen in the nucleating porphyroblast.

All thermodynamic calculations presented in this paper were calculated for the system MnNCKFMASH with the bulk compositions listed in Table 2 using modules written for Program Gibbs (Spear et al., 1991 and unpublished) and the thermodynamic data of Spear and Pyle (2010). Post processing (contouring, etc.) was done using Program MADPlotter (Spear, unpublished). These and subsequent affinity calculations were performed with the following procedure. First, the bulk composition, range of P–T conditions, and reactive assemblages to consider are selected (Chl + Ms + Pl + Qtz + Bt + H_2O ± Czo in Fig. 2). A grid of P–T conditions is created (in these figures the grid was ΔT = 2 °C, ΔP = 100 bars) and the equilibrium MAD for the reactive assemblage calculated at every grid point (e.g. around 15,000 calculations for each diagram; total execution time was typically less than 2 min. The affinity for the nucleation of the porphyroblast of interest (garnet in Fig. 2) was calculated following the method of Thompson and Spaepen (1983) adapted for multi-component, multi-phase equilibria by de Capitani and Brown (1987) and Spear et al. (2014) and depicted graphically in Fig. 1. The output from these calculations is a reaction affinity map (Pattison et al., 2011), contoured for affinity with the equilibrium isograd drawn at A = 0.

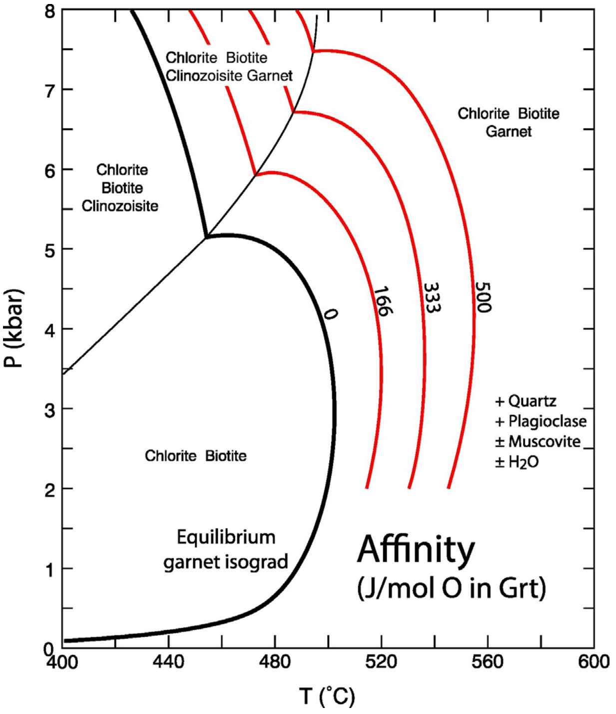

Fig. 2. P–T diagram illustrating how the affinity for nucleation of garnet varies with degree of overstepping of the garnet isograd reaction (Chl + Ms + Qtz ± Pl ± Czo = Grt + Bt + H_2O) for the bulk composition listed in Table 1.

As pointed out by Waters and Lovegrove (2002) and Pattison et al. (2011), the rate at which affinity is generated as a function of overstepping is a function of the ΔS reaction and ΔV reaction for overstepping in temperature and pressure, respectively. Hence, the rate at which affinity builds up depends on the matrix assemblage and the porphyroblast to be nucleated. Assuming the reactive assemblage is chlorite + muscovite + biotite + quartz, the reactions that produce staurolite, aluminosilicate, and cordierite may be written

$$\mathrm{Chl + Ms + Qtz = St + Bt + H_2O} \tag{2}$$

$$\mathrm{Chl + Ms + Qtz = Als\ (Ky, And, Sil) + Bt + H_2O} \tag{3}$$

$$\mathrm{Chl + Ms + Qtz = Crd + Bt + H_2O} \tag{4}$$

Fig. 3 shows plots of reaction affinity versus temperature of overstepping for each of these reactions, similar to Fig. 2 of Pattison et al. (2011).

Although the generation of affinity with respect to overstepping, according to the above assumptions, is well-constrained because the volumes and entropies of reactions are fairly well known, there is no general consensus in the literature as to the magnitude of affinity required to nucleate a new phase. Published suggestions range from 166 (J/mol O) (Wilbur and Ague, 2006) to 2400 (J/mol O) (Castro and Spear, 2016) (Table 1). It is expected that the magnitude of affinity required to nucleate will vary between porphyroblasts owing to differences in surface energies, as demonstrated by Waters and Lovegrove (2002). There is also indication that strain energy may contribute to reducing the affinity required for nucleation of porphyroblasts (Waters and Lovegrove, 2002; Pattison et al., 2011; Spear et al., 2014), as well as the presence of fluid (Rubie, 1986; Pattison and Tinkham, 2009). Nevertheless, from their study of the Nelson aureole, Pattison et al. (2011) estimated a value of 300 J/mol O, and in order to explore the generalized

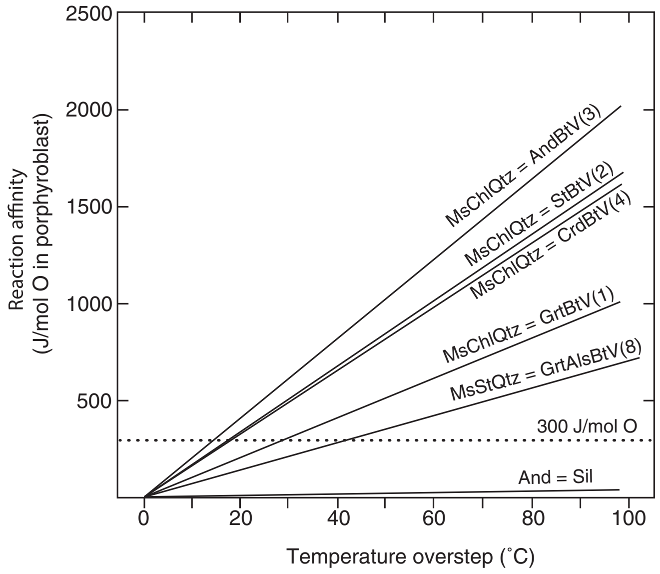

Fig. 3. Plot of reaction affinity versus temperature of overstepping for selected porphyroblast producing reactions (Reactions 1–4 and 8). The reaction andalusite = sillimanite is also shown for comparison.
Modified after Pattison et al. (2011).

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Table 1
Suggested affinity for nucleation of selected porphyroblasts.

Waters and Lovegrove (2002)	
• Cordierite	200 J/mol
• Staurolite	400 J/mol
• Andalusite	1000 J/mol
Wilbur and Ague (2006)	
• Garnet	166 J/mol
Pattison et al. (2011)	
• Mean value (any phase)	300 J/mol
Kelly et al. (2013)	
• Garnet	58–483 J/mol
Spear et al. (2014)	
• Garnet (strained)	200 J/mol
• Garnet (unstrained)	800–1500 J/mol
• Garnet (blueschist)	500 J/mol
Castro and Spear (2016)	
• Garnet (blueschist)	2000–2400 J/mol

Table 2
Bulk compositions for samples BC1 and TM-549 used in the calculation of MADs. Units are weight % oxides.

	BC1 (Fig. 2)	TM-549
SiO_2	54.09	55.71
Al_2O_3	25.53	20.84
MgO	3.58	3.61
FeO	6.94	6.38
MnO	0.32	0.17
CaO	1.55	0.97
Na_2O	0.78	1.80
K_2O	5.87	5.81
H_2O^*	5.33	4.72

* Sufficient H_2O was added to each bulk composition to ensure excess fluid at all P-T conditions.

effects of overstepping on MADs, that is the value that will be adopted in this paper.

A rock that contains chlorite + muscovite + biotite + quartz at low grade will generate 300 J/mol of affinity with approximately 13, 17, 18, or 28 degrees of overstepping, depending on whether the nucleating porphyroblast is andalusite, staurolite, cordierite, or garnet, respectively. The order is the same as the entropy change of the reactions forming each of the porphyroblasts (normalized per mole of O in each porphyroblast), which in turn is the same order as the amount of H_2O (normalized) that is released in each reaction. These temperatures of overstepping are calculated relative to the equilibrium isograd reaction so it is necessary to first calculate the equilibrium phase diagram.

1.2. Reactive assemblage chlorite + muscovite

To illustrate how overstepping will impact the location of phase boundaries on a MAD, a diagram is presented in Fig. 4 for a representative pelitic bulk composition (Table 2). The reactive assemblage is assumed to be chlorite + muscovite + biotite + plagioclase + quartz + H_2O ± clinozoisite. Affinities were calculated for the nucleation of garnet, staurolite, kyanite, andalusite, sillimanite, and cordierite over the entire diagram from Reactions 1–4 and the contour for the value of 300 J/mol O was drawn for each porphyroblast (heavy line).

The diagrams in Fig. 4 are combined into a composite MAD in Fig. 5. In constructing this diagram, it was assumed that each respective porphyroblast would nucleate upon reaching the 300 J/mol O threshold. Fig. 5 demonstrates that the specific porphyroblast to nucleate will depend on the pressure, similar to the equilibrium MAD. As noted above, more affinity is produced per degree of overstepping for aluminosilicate than for cordierite or garnet (Fig. 3). Hence, the boundary for the nucleation of aluminosilicate is not displaced as much as that for these other phases, and the P–T field over which aluminosilicate (andalusite or sillimanite) will nucleate is larger than in the equilibrium MAD. As a result, the field for aluminosilicate expands relative to that of staurolite, cordierite, and especially garnet. Note also that the curve for staurolite (Reaction 2) falls at higher temperature than those for Reactions 1, 3, and 4, as shown by the dashed line in Fig. 5, and so is not predicted to occur according to the above assumptions. Of course, it is important to note that the results in Figs. 4 and 5 are valid only for a specific bulk composition with the assumption that the nucleation of all porphyroblasts requires an affinity of exactly 300 J/mol O. It is likely that different porphyroblasts will require different affinities to nucleate so these results are illustrative only.

1.3. Reactive assemblage chlorite + muscovite ± garnet

In classical Barrovian metamorphism the next porphyroblast to appear after garnet is staurolite or kyanite (or both). Equilibrium petrogenetic grids in KFMASH predict that, in typical low-Al pelites (pelites that plot below the garnet + chlorite join on an AFM diagram), the following two reactions are traversed in sequence, leading to the development of staurolite and then kyanite:

$$\text{garnet + chlorite + muscovite = staurolite + biotite + quartz + } H_2O \quad (5)$$

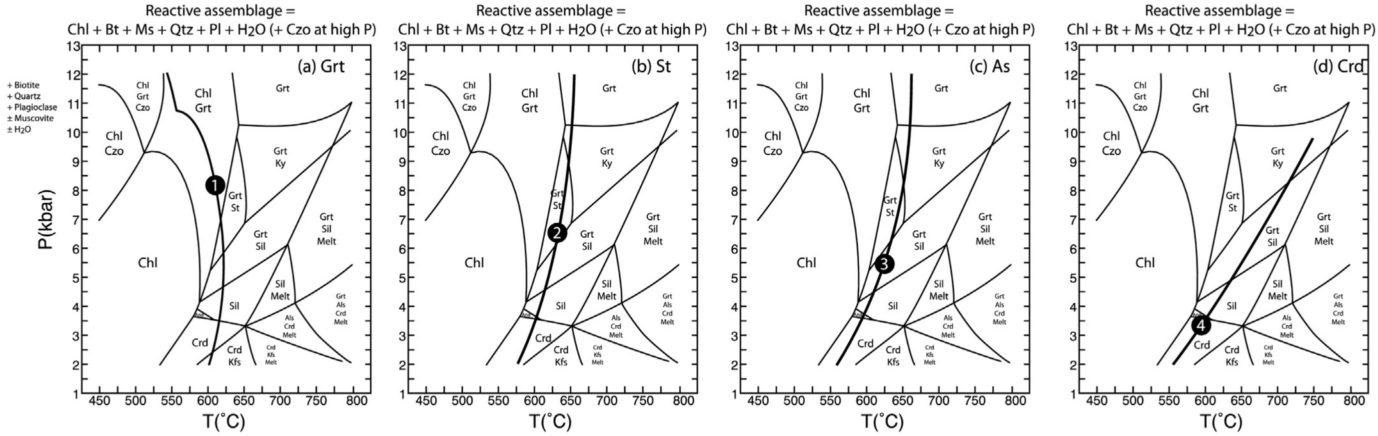

Fig. 4. Equilibrium MAD for bulk composition TM-549 (Table 2). Heavy lines are the 300 J/mol O affinity curves. (a) Reaction 1; (b) Reaction 2; (c) Reaction 3; (d) Reaction 4. Note that in these and subsequent diagrams, the melting reactions in the equilibrium MADs are schematic only.

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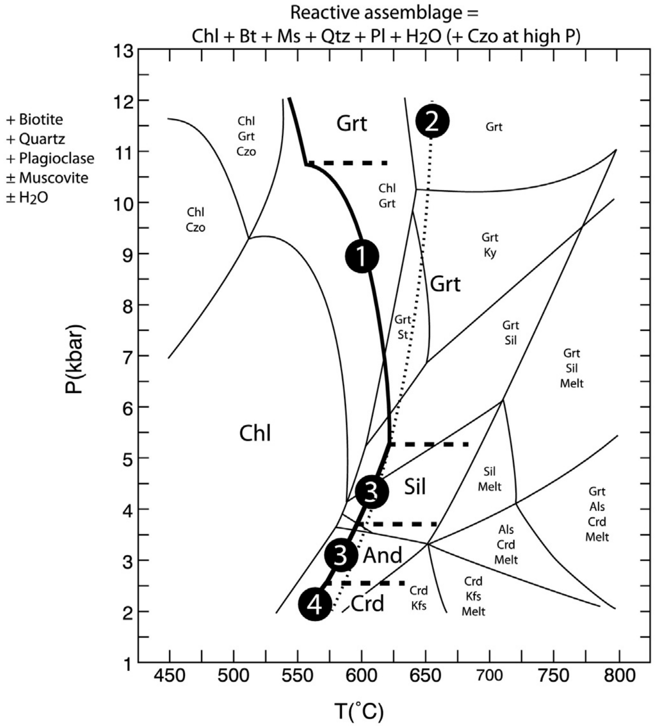

Fig. 5. P–T diagram showing displaced nucleation boundaries for garnet (Reaction 1), aluminosilicate (Reaction 3), and cordierite (Reaction 4) from Fig. 4. The equilibrium MAD (thin lines) is also shown for reference. The dotted line is the position of Reaction 2 from Fig. 4.

$$\text{staurolite} + \text{chlorite} + \text{muscovite} = \text{aluminosilicate} + \text{biotite} + \text{quartz} + H_2O \quad (6)$$

Reaction 5 will only occur if chlorite has not been consumed in the production of garnet and Reaction 6 will only occur if chlorite has not been consumed in the production of garnet and then staurolite. The P–T conditions at which chlorite will be consumed can be inferred from the equilibrium MADs in Fig. 4. At high pressures and around 625 °C the equilibrium assemblage changes from Chl + Grt to just Grt: the line separating these fields is the chlorite-out curve. Extrapolating to lower pressure, it may be inferred that chlorite will be available for the production of staurolite via Reaction 5 and hence a field for staurolite + garnet is shown on the equilibrium MAD. There is also a small pressure range (around 10 kbar: Fig. 5) over which kyanite will be produced via the reaction:

$$\text{garnet} + \text{chlorite} + \text{muscovite} = \text{kyanite} + \text{biotite} + \text{quartz} + H_2O \quad (7)$$

In the calculation of affinity for nucleation, it is necessary to know the reactive assemblage from which the porphyroblast nucleates. Reaction (5) assumes the reactive assemblage includes garnet and Reaction (6) assumes the reactive assemblage includes staurolite. Hollister (1969) and Pattison and Tinkham (2009) argued on textural grounds that garnet and staurolite were not reactive in the Kwoiek and Nelson aureoles, respectively, at least up to where staurolite begins to break down by the reaction

$$\text{staurolite} + \text{muscovite} + \text{quartz} = \text{aluminosilicate} + \text{garnet} + \text{biotite} + H_2O \quad (8)$$

Another argument advanced by Hollister is that the mere existence of chemical zoning in a porphyroblast proves that it is unreactive. However, it is possible for the rim of a porphyroblast to react while still preserving chemical zoning in its interior.

Evidence exists for both the participation and non-participation of garnet in reactions that produce staurolite (e.g. either Reaction (5) or Reaction (2)). For example, the garnet crystal described in detail by Spear (2014) shows textural and chemical evidence for some degree of resorption. Additionally, there are kyanite and staurolite porphyroblasts in the reaction zone surrounding garnet in this sample, suggesting Reactions (5) and (7) have both operated (see Fig. 3 of Spear, 2014). However, there is considerable textural evidence from other samples that this is typically not the case. Two examples are the big staurolite nappe of New Hampshire (Spear et al., 2007) and the Nelson aureole, British Columbia (Pattison and Tinkham, 2009), where porphyroblasts of staurolite typically include idioblastic crystals of garnet. Examination of the chemical zoning of garnet crystals inside staurolite and in the matrix reveals that matrix garnets have not been consumed relative to the included garnets (e.g. Fig. 6; see also Figs. 2–7 of Pattison and Tinkham, 2009). For rocks in which garnet is not reactive, then the production of staurolite in the New Hampshire and Nelson rocks must have occurred via reactions such as Reaction 2. Similarly, for rocks in which garnet and staurolite are not reactive, then the production of andalusite in the Nelson aureole must have occurred via reactions such as Reaction 3. Both possibilities (garnet reactive and garnet non-reactive) will be examined in the next sections.

To assess the implications of overstepping on the appearance of staurolite and/or kyanite in a rock in which garnet is or is not reactive, calculations of reaction affinity versus temperature are plotted in Fig. 7 against temperature at 7 kbar for Reactions 2, 3, 5 and 7. For reactions in which garnet is reactive (5 and 7), Reaction 5 occurs at lower temperature (618 °C) than Reaction 7 (623 °C) at a value of affinity = 0 (i.e. the equilibrium calculation), consistent with the first appearance of staurolite before kyanite in typical Barrovian sequences. However, Reaction (7), with larger ΔS reaction, generates affinity more rapidly with increasing T than does Reaction (5). Therefore, at a value of affinity just below 300 J/mol O, the curves cross and the affinity for kyanite nucleation exceeds that for staurolite nucleation. Consequently, if it is assumed that both porphyroblasts require similar amounts of energy to nucleate, and that this value exceeds about 300 J/mol O, the prediction is that kyanite should nucleate before staurolite.

If garnet is unreactive, then staurolite and kyanite grow via Reactions (2) and (3). The difference in affinities for these reactions at 7 kbar (Fig. 7) reveals that staurolite should nucleate before kyanite unless the affinity for nucleation exceeds around 750 J/mol O where the curves cross.

This calculation demonstrates that the initial nucleation of staurolite or kyanite is governed by very small differences in affinity. This small energetic variation may explain the common observation of staurolite and kyanite intergrown with no obvious textural evidence as to which nucleated first and which phase is replacing the other (e.g. Fig. 15d of Pattison et al., 2011). Additionally, it offers an explanation for the texture in Fig. 3 of Spear (2014) in which kyanite has grown in the reaction zone where garnet has been resorbed. It may also explain why rocks that contain kyanite + staurolite with no obvious evidence for staurolite dissolution (e.g. Reaction 6) are common in Barrovian terranes.

These small energetic differences, as well as the uncertainty in the actual affinity required for nucleation of a porphyroblast, indicate that it is unwise to attempt to construct a single modified MAD to incorporate these calculations. Rather, two sets of diagrams are presented (Fig. 8) that assume that either aluminosilicate (kyanite, sillimanite, or andalusite) appear first (Fig. 8a and b) or that staurolite appears first (Fig. 8c and d). Fig. 8b and d are identical to Fig. 8a and c, respectively, with the exception that the low-T equilibrium reactions producing garnet, aluminosilicate and cordierite have been removed.

The situation in which aluminosilicate forms first (Fig. 8a and b) is illustrated by extension of Reaction 3 (in which garnet is non-reactive) into the field where the assemblage is garnet + chlorite. Reaction 7 (in which garnet is reactive) could also have been used with a very similar

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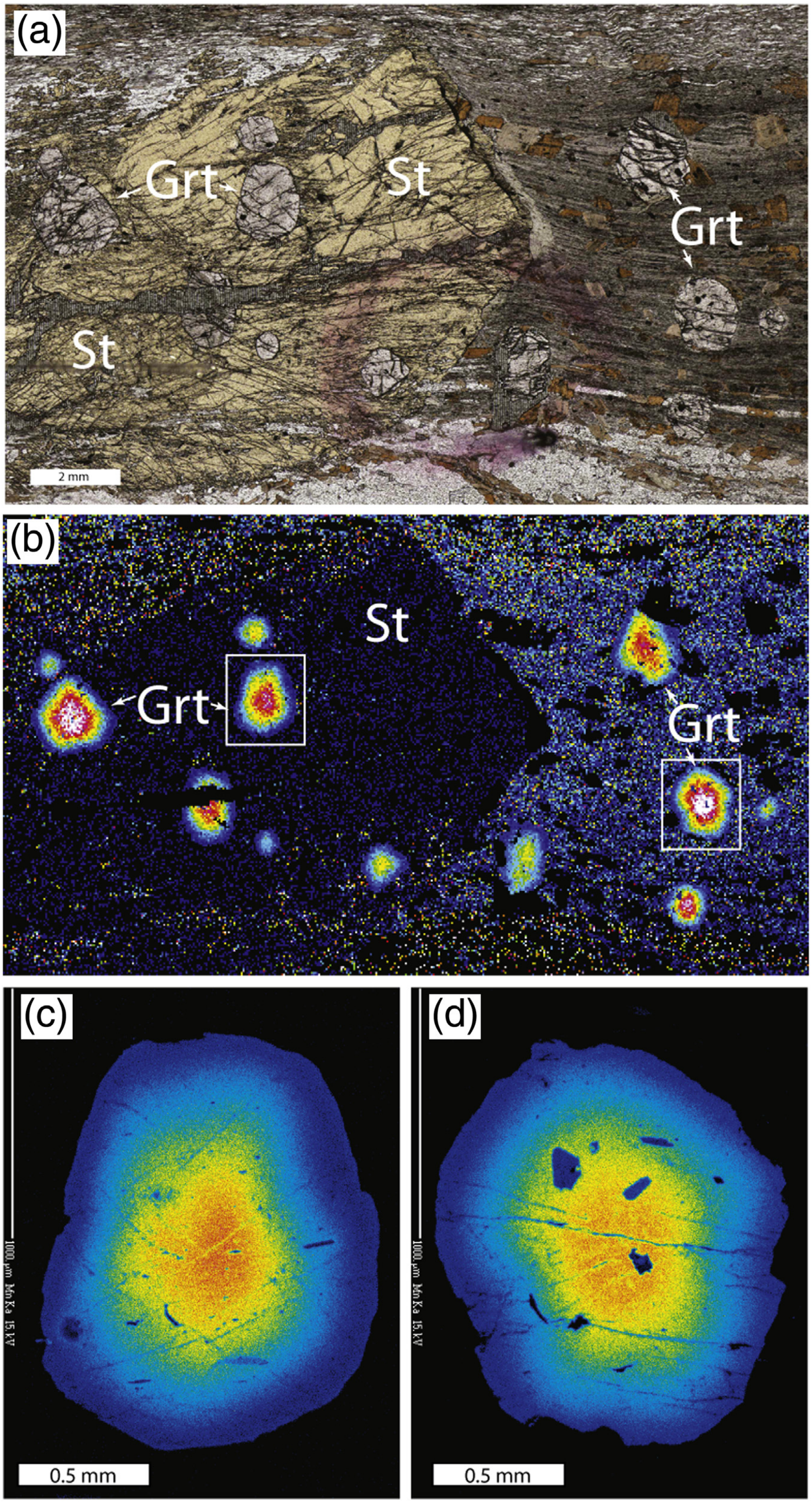

Fig. 6. Sample 92-57a from near Putney, VT with garnets included in staurolite and in the matrix. (a) Photomicrograph in plane light. (b) Low-resolution Mn X-ray map of entire area of (a). (c) Mn X-ray map of garnet included in staurolite. (d) Mn X-ray map of garnet in matrix. Note the Mn zoning of garnets included in staurolite shows no significant difference from the zoning in garnets in the matrix.

result. For aluminosilicate to form from either Reactions 3 or 7, it is required that chlorite not be exhausted by the growth of garnet via Reaction 1, so the chlorite-out curve is extended down to where it interests Reaction 3. Once aluminosilicate nucleates, both Reactions 3 and 1 may operate in parallel and all remaining chlorite should be quickly consumed. In this scenario, Reactions 2 or 5 will be superseded and staurolite will not nucleate; thus the modified MAD does not show a field for staurolite (Fig. 8b).

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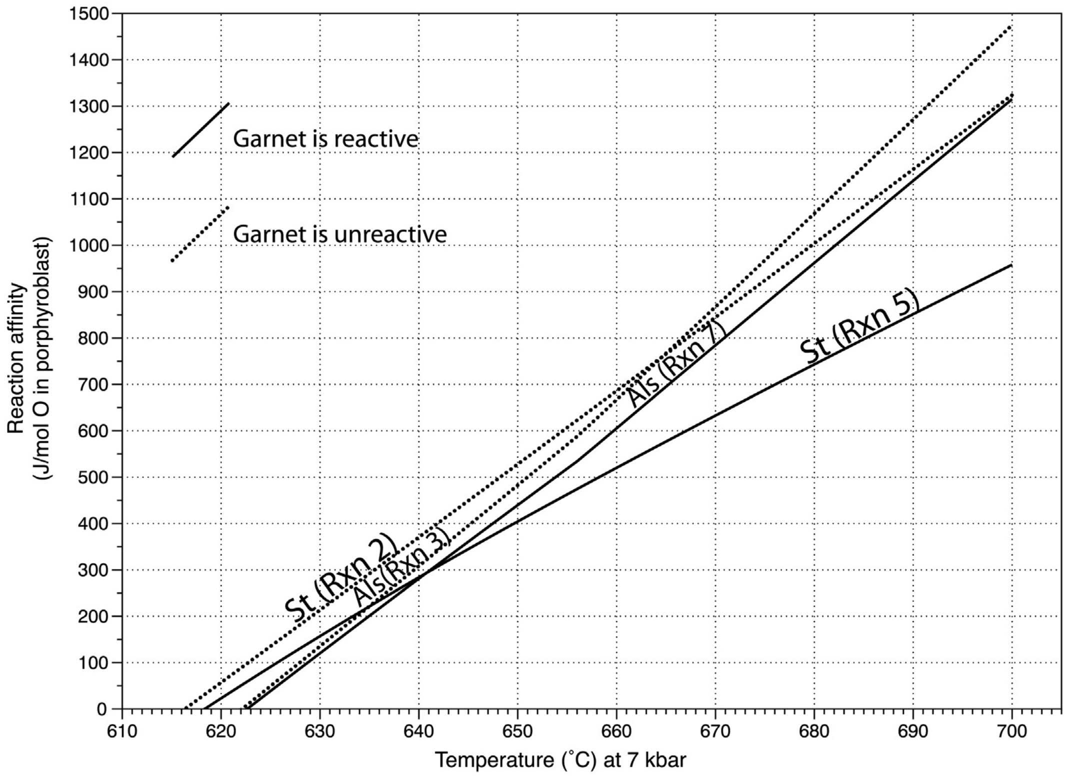

Fig. 7. Plot of reaction affinity versus temperature at 7 kbar for bulk composition TM-549. Solid lines are affinities for Reactions (5) and (7). Dotted lines are affinities for Reactions (2) and (3). The kink in Reactions 3 and 7 is due to change from Ky to Sil.

For the situation in which staurolite nucleates first (Fig. 8c and d), Reaction 2 (Reaction 5 would provide a very similar result) is shown in Fig. 8c and d. Again, it is likely that the production of staurolite (along with the production of garnet via Reaction 1 if garnet is unreactive) will quickly consume all remaining chlorite, so Reaction 6 is not likely to ever operate. Of course, it is also possible that both staurolite and aluminosilicate will nucleate from Reactions 2 and 3, in which case a large field for the assemblage garnet + staurolite + aluminosilicate will be observed.

The stability field for the assemblage staurolite + garnet + biotite is small on the equilibrium MAD (e.g., Fig. 5), and there is ample textural evidence from numerous studies (e.g. Hollister, 1969; Pattison and Tinkham, 2009) that eventually staurolite breaks down to aluminosilicate, generally sillimanite, via Reaction 8. The affinity for Reaction 8 has been calculated (Fig. 3) and the 300 J/mol O affinity contour is shown in Fig. 8d. This reaction is displaced up-temperature, relative to its equilibrium position, more substantially than the several chlorite-consuming reactions discussed above because it is a lower-entropy (more weakly H_2O-producing) reaction. The curve is solid over the part of the subsolidus region where staurolite has formed, resulting in a small field where garnet + aluminosilicate (sillimanite in Fig. 8d) would be found.

2. Discussion

2.1. Modified MADs

The diagrams in Fig. 8b and d have been modified from the equilibrium MAD to reflect the development of porphyroblasts assuming that around 300 J/mol O affinity is required for nucleation, and are herein described as modified MADs or MMADs. Reactions that produce melt, which are not the focus of this paper, are shown schematically in their equilibrium positions in Fig. 8, recognizing that they too may be affected by overstepping. However, it is suspected that unless melting requires the nucleation of a new phase other than melt, the amount of overstepping of melting reactions will be minimal.

The resulting MMADs (Fig. 8b and d) display expanded fields for the stability of chlorite owing to the suppression of nucleation of the respective porphyroblasts. The greater displacement of the reaction forming garnet from chlorite (Reaction 1) relative to those forming cordierite, staurolite, and aluminosilicate (Reactions 2, 3 and 4) results in a diminished stability field for Grt + Chl. In situations where staurolite nucleates first following nucleation of garnet and exhausts all reactive chlorite (Fig. 8d), the field for garnet + staurolite (without aluminosilicate) is greatly expanded relative to the equilibrium stability field, owing to the delay of nucleation and growth of aluminosilicate from a precursor assemblage of Ms + St + Grt by Reaction 8. Both of the above predictions closely match observations in the Nelson aureole (Pattison and Tinkham, 2009). Alternately, if aluminosilicate nucleates first and for some reason the nucleation of staurolite is suppressed until all chlorite is exhausted (Fig. 8b), then there is predicted to be a large field for garnet + aluminosilicate without staurolite. Of course, it is also possible that both staurolite and kyanite can nucleate more or less simultaneously by Reactions 2 and 3.

There is no unique way to be more predictive about the reactive assemblage without invoking a specific P–T path, so the reaction boundaries between fields once porphyroblasts nucleate are simply shown as horizontal (constant pressure) dashed lines. It should also be pointed out that the assumption of non-reactivity for garnet and possibly staurolite has the consequence of modifying the bulk composition, which will change the location of curves involving these phases relative to what is shown in Fig. 8. Again, there is no unique way to model this unless a P–T path is specified, which is beyond the scope of this paper.

A broader implication of these modified MADs is that the assumption of equilibrium crystallization may result in erroneous interpretations of the metamorphic P–T conditions. Specifically, the displaced stability fields for several mineral assemblages in Fig. 8 differ quite substantially from those in the equilibrium phase diagram, as also found by

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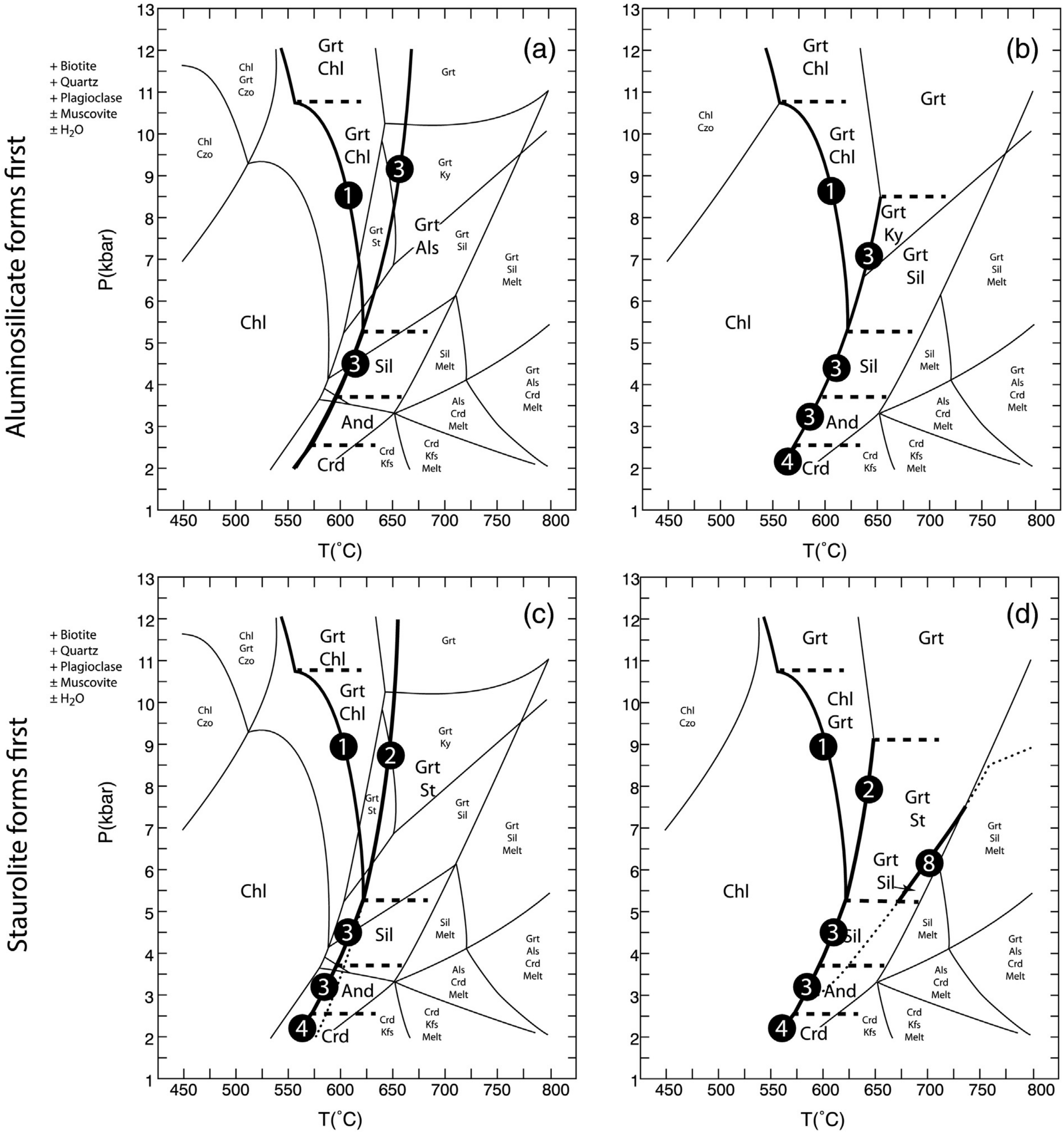

Fig. 8. Equilibrium and modified MADs for bulk composition TM-549 showing reaction positions for the first appearance of aluminosilicate by Reaction 3 (a and b) or staurolite by Reaction 2 (c and d). (d) also shows the breakdown of staurolite to aluminosilicate by Reaction 8 (dotted where garnet is not present and in the melt field).

Pattison et al., 2011). Consideration of overstepping also carries the implication that assemblages predicted to occur in very small P–T regions in equilibrium phase diagrams, and especially ones that involve nucleation of a new phase, are not likely to be realized in any natural samples unless the generation of affinity for the nucleation reaction is great. The ostensibly tight P-T constraints implied by mineral assemblages that fall in such small fields therefore need to be viewed critically.

Overstepping is required not only for the nucleation of a new phase but also to drive continuous reactions, although the magnitude of affinity to drive a continuous reaction is not likely to be as large as that required for nucleation (cf. Pattison et al., 2011). Nevertheless, the compositional changes of a mineral such as garnet, once nucleated, are not likely to follow equilibrium values but should lag somewhat behind the equilibrium values.

Interestingly, the thermodynamic framework that allows for the calculation of isochemical phase diagrams has also provided the tools to model the energetic consequences of delayed nucleation and to determine the degree to which metamorphic assemblages develop away from equilibrium. Estimates of the magnitude of affinity required for nucleation vary considerably, as indicated in Table 1. Methods to determine the actual P and T of nucleation that do not require assumptions about chemical equilibrium are needed in order to calculate the affinity for nucleation in natural samples. For example, Raman spectroscopy has been used to determine the pressure on quartz inclusions in garnet from which an isomeke can be calculated that constrains the conditions of entrapment (e.g. Thermoba-Raman-try: Kohn, 2014). This approach has been employed by Spear et al. (2014) and Castro and Spear (2016) to estimate the conditions of garnet nucleation and thus the amount of overstepping of the garnet isograd in Barrovian and subduction settings. The development of more rigorous textural, chemical, and mechanical criteria will also be needed for quantification of the degree of overstepping. For example, it is probable that strain energy and fluid

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presence or absence affects nucleation (see Table 1), although the magnitude is difficult to assess. Theoretical models for heterogeneous nucleation are probably not the same as for homogeneous nucleation and will need to be developed. Finally, because the processes of nucleation and growth occur along grain boundaries in metamorphic rocks, development of models of grain boundaries at the nanoscale will be needed for future progress.

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