



Garnet growth after overstepping

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ABSTRACT

Overstepping of metamorphic reactions is required to provide the driving force necessary for porphyroblast nucleation and growth. Forward models of garnet nucleation and growth are presented assuming an affinity for nucleation that corresponds to several tens of degrees or several kilobars of overstepping. The composition of garnet that nucleates and grows is assumed to be that which provides the largest decrease in free energy. With these assumptions, the zoning predicted for a garnet grown under isothermal, isobaric conditions is revealed to be sufficiently similar to the zoning predicted for garnet grown under continuous near-equilibrium conditions that distinction based on the shape of zoning profiles alone does not appear to be possible. Furthermore, the growth of an initial garnet crystal following nucleation after overstepping depletes the affinity for subsequent nucleation by sequestration of Mn into the existing garnet crystal. Progressive nucleation, therefore, requires additional energy input, most likely through changes in pressure and temperature, to replenish the affinity. The predicted zoning in garnets nucleated following substantial growth of the first nucleated garnet does not match the typical bell-shaped profile of Rayleigh fraction but rather displays distinctly diagnostic zoning depending on the assumed rate limiting step for growth. Diffusion controlled growth results in relatively broader and flattened profiles whereas interface controlled growth results in later garnets having a peaked core Mn profile. This latter profile would relax by diffusion in relatively short times (less than 1 Ma) and would thus not likely to be preserved, but appears to have been observed in garnet zone samples from central Vermont. Calculations for this sample also indicate that garnet ceased growing when chlorite was exhausted, at which point considerable affinity remained indicating that equilibrium was not achieved. Tectonic interpretations based on P–T paths calculated assuming near-equilibrium nucleation and growth of garnet are thus likely to require reevaluation in light of the magnitude of overstepping needed for nucleation and the possibility that equilibrium was not attained at the metamorphic peak.

1. Introduction

A number of recent papers have concluded that equilibrium isograd reactions may be overstepped by a considerable amount before nucleation of a new porphyroblast occurs (e.g. Waters and Lovegrove, 2002; Wilbur and Ague, 2006; Pattison and Tinkham, 2009; Pattison et al., 2011; Spear et al., 2014). Values of affinity estimated for the nucleation of garnet range from 166 to 2200 J/mol oxygen, representing overstepping of up to 80° or 4–5 kbar (Waters and Lovegrove, 2002; Wilbur and Ague, 2006; Pattison et al., 2011; Spear et al., 2014; Castro and Spear, 2016). Implications for the interpretation of pseudosections in light of this degree of overstepping are discussed in Spear and Pattison (2017).

If a porphyroblast such as garnet does not nucleate until there has been enough overstepping to build these levels of affinity, then it cannot have grown continuously at near-equilibrium conditions as it traverses along the rock's P–T path. Rather, the above studies suggest

that, once nucleated, garnet may grow at near isobaric-isothermal conditions (e.g. Hollister, 1969; Spear et al., 2014). If so, the chemical zoning recorded by the garnet cannot reflect a succession of near-equilibrium growth stages, as has been so commonly assumed (e.g. Spear and Selverstone, 1983; Gaidies et al., 2008). This in turn calls to question the practice of using the chemical zoning in garnet to infer the P–T path based on the assumption of near-equilibrium.

The question arises: if garnet nucleates at conditions considerably above the equilibrium isograd reaction, then what controls the chemical zoning of the garnet? Hollister (1966) attributed the zoning of Mn in garnet from the Kwoiek area, British Columbia to Rayleigh fractionation, a process by which the growing garnet sequesters Mn (and other elements) as it grows, depleting the reservoir from which garnet is growing in this component. In addition, Hollister (1966) demonstrated that the classic bell-shaped zoning profiles commonly exhibited by Mn in garnet could be achieved by an isothermal, isobaric process (i.e. Rayleigh fractionation with a constant partition coefficient). Whereas

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Rayleigh fractionation undoubtedly plays a major role in the development of Mn zoning, it is essentially an equilibrium fractionation between the garnet and the reservoir. It is still necessary to maintain a driving force for growth (i.e. affinity).

Subsequent investigations employed more comprehensive sets of equilibrium relations between garnet and matrix phases and arrived at essentially the same conclusions as Hollister (1966) (e.g. Spear et al., 1990; Symmes and Ferry, 1992). Significantly, these latter models assumed a continuum of near-equilibrium conditions along a P–T path to achieve representative garnet zoning, with no role for Rayleigh processes at constant temperature and pressure such as proposed by Hollister (1966). Frost and Tracy (1991) examined this topic and concluded that observed Ca zoning in garnet could be achieved by isothermal, isobaric processes through Rayleigh fractionation.

The purpose of the present communication is to present the theoretical framework within which the chemical zoning of garnet can be calculated following nucleation after considerable overstepping. Model zoning profiles will be presented for a rock containing a single or multiple garnets, and compared to model zoning profiles assuming equilibrium. Criteria for identifying a garnet that has grown out of equilibrium from its zoning pattern will be discussed. Finally, the question of whether equilibrium is ever achieved in a rock undergoing metamorphism will be addressed.

2. Theory

Affinity is the energy available to drive nucleation or chemical reaction and may be defined as either the partial derivative of Gibbs energy with reaction progress at constant temperature and pressure:

$$A = - \left(\frac{\partial G}{\partial \xi} \right)_{P,T}$$

or the change in Gibbs energy in going from reactants to products of a chemical reaction ($-\Delta G$). The second definition is most appropriate for the consideration of nucleation as was utilized by Spear and Pattison (2017) and the first definition is most appropriate for consideration of garnet growth under isothermal, isobaric conditions, as discussed here.

Following Gaidies et al. (2011), Pattison et al. (2011) and Spear et al. (2014), the affinity for nucleation of a porphyroblast such as garnet may be calculated as the difference between the G of the nucleated garnet and the fictive G of a compound of the same composition as the nucleated garnet calculated from the chemical potentials of the garnet-free matrix phases (Fig. 1a). Inasmuch as Gibbs free energy (G) changes with pressure and temperature, the affinity available for nucleation will also vary with P and T as a function of the ΔV and ΔS of reaction, respectively. The G of garnet is a function of composition so the affinity for nucleation is also a function of the garnet composition. Following the treatment in Thompson and Spaepen (1983) it was

assumed by the above authors that the most likely composition of garnet to nucleate would be that with the greatest affinity (Fig. 1a), the reason being that this composition generates the most available energy to overcome the activation energy barrier for nucleation (see also discussion in Spear and Pattison, 2017).

Following nucleation out of equilibrium, garnet will grow such that the compositions of the garnet and matrix phases evolve along their respective free energy surfaces until eventually equilibrium is closely attained (Fig. 1b, c). It is proposed that the composition of garnet formed during this continuous evolution is also that which provides the largest change in free energy: that is, the same criteria used to ascertain the composition of garnet that would form upon nucleation. Although the affinity required to drive the continuous reaction is most likely considerably smaller than the affinity required for nucleation, growth of garnet in steps that maximizes the decrease in free energy at each increment is consistent with the general trend of the system towards minimizing G. Furthermore, maintaining this assumption results in a continuum of compositional changes. This assumption also requires that the garnet is completely unreactive, such that every growth step is essentially the same as nucleating a new garnet, which is assumed to grow on the old garnet.

It is also implicit that the composition of garnet is not controlled by kinetic factors (e.g. rates and mechanisms of dissolution/precipitation at mineral surfaces, or of intergranular transport of nutrients), and that the composition is rather being only determined by this maximum free energy decrease. The validity of this assumption requires that the availability of Mg, Fe, Mn and Ca is not limited at the growing garnet interface. Additionally, the rate of garnet growth must be controlled by kinetic factors such as diffusion of Si or Al or surface attachment or detachment kinetics, otherwise, once nucleated, the garnet would grow instantaneously. In other words, the diffusivities of Mg, Fe, Mn and Ca are assumed to be rapid relative to the rate of garnet growth.

Calculating the composition of garnet requires finding the garnet composition such that the tangent to the garnet G surface is parallel to the tangent defined by the matrix phases. The equations needed to calculate this most likely garnet composition are as follows. Equations that constrain the slope of the tangent to the garnet G surface ($\mu_i^{\text{Grt}} - \mu_j^{\text{Grt}}$) are, according to the above assumptions, equal to those that constrain the slope of tangent to the matrix assemblage ($\mu_i^{\text{Matrix}} - \mu_j^{\text{Matrix}}$). There are three such independent equations:

$$\begin{aligned} \mu_{\text{alm}}^{\text{Grt}} - \mu_{\text{prp}}^{\text{Grt}} &= \mu_{\text{alm}}^{\text{Matrix}} - \mu_{\text{prp}}^{\text{Matrix}} \\ \mu_{\text{sps}}^{\text{Grt}} - \mu_{\text{prp}}^{\text{Grt}} &= \mu_{\text{sps}}^{\text{Matrix}} - \mu_{\text{prp}}^{\text{Matrix}} \\ \mu_{\text{grs}}^{\text{Grt}} - \mu_{\text{prp}}^{\text{Grt}} &= \mu_{\text{grs}}^{\text{Matrix}} - \mu_{\text{prp}}^{\text{Matrix}} \end{aligned} \quad (1)$$

The chemical potentials of the garnet components in the matrix assemblage are calculated as linear combinations of matrix phase components, for example:

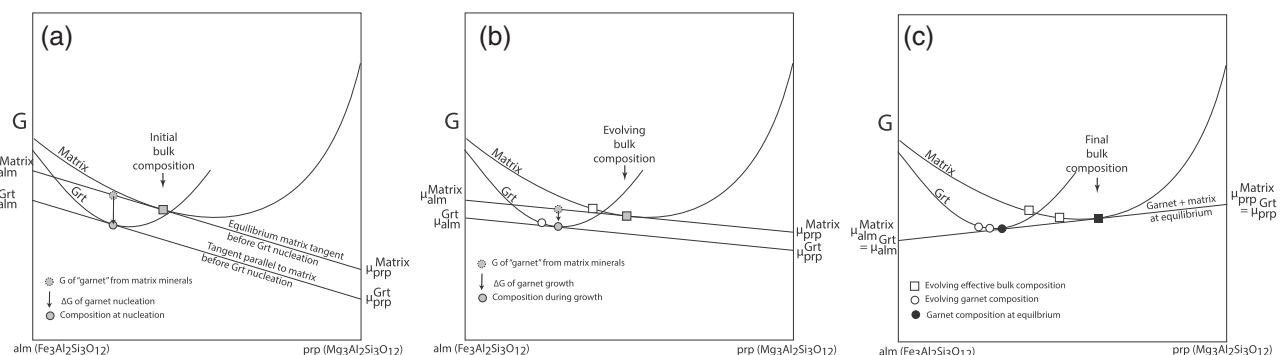


Fig. 1. Schematic G–X diagrams for matrix + garnet showing the evolution of garnet and matrix compositions during garnet growth following overstepping. (a) Configuration at garnet nucleation. (b) Configuration during growth. (c) Configuration at equilibrium. The composition of garnet is that which provides the maximum decrease in free energy (arrow in (a) and (b)). Note that the figure assumes complete equilibrium among the matrix phases.

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