The interfacial energy penalty to crystal growth close to equilibrium

Fred Gaidies¹ and Freya R. George²
¹Department of Earth Sciences, Carleton University, 1125 Colonel By Drive, Ottawa, ON K1S 5B6, Canada
²Department of Earth and Planetary Sciences, Johns Hopkins University, 3400 N Charles Street, Baltimore, Maryland 21218, USA

ABSTRACT
Understanding the origin of rock microstructure is critical for refining models of the geodynamics of the Earth. We use the geometry of compositional growth zoning of a population of garnet porphyroblasts in a mica schist to gain quantitative insight into (1) the relative growth rates of individual crystals, (2) the departure from equilibrium during their growth, and (3) the mobility of the porphyroblast-matrix interface. The driving force for garnet growth in the studied sample was exceedingly small and is comparable in magnitude to the interfacial energy associated with the garnet-matrix interface. This resulted in size-dependent garnet growth at macroscopic length scales, with a decrease in radial growth rates for smaller crystals caused by the penalty effect of the interfacial energy. The difference in growth rate between the largest and the smallest crystal is ~45%, and the interface mobility for garnet growth from ~535°C, 480 MPa to 565°C, 560 MPa in the phyllosilicate-dominated rock matrix ranged between ~10^{-11} and 10^{-20} m^2 s^{-1}. This is the first estimation of interface mobility in natural rock samples. In addition to the complex structural and chemical reorganization associated with the formation of dodecahedral coordination polyhedra in garnet, the presence of abundant graphite may have exerted drag on the garnet-matrix interface, further decreasing its mobility.

INTRODUCTION
The microstructure of a rock is defined by the three-dimensional distribution of the sizes, shapes, and abundances of its grains and the spatial arrangement of the grain-boundary network separating them. Rock microstructure has been shown to fundamentally influence large-scale geodynamic processes. For example, grain size controls the yield strength of a rock during plastic deformation (e.g., Kumamoto et al., 2017), with important implications for the strength of Earth’s lithosphere (Hansen et al., 2019) and its influence on the uplift of mountain belts (e.g., England and Molnar, 2015), the geometry of subduction zones (e.g., Buffett and Becker, 2012), and the development of plate boundaries (Thiellmann and Kaus, 2012). Grain size has also been related to the convection regimes of terrestrial planets (Rozel, 2012), and the interpretation of seismic data can be dependent on the crystallographic alignment of minerals (e.g., Miyazaki et al., 2013; Ji et al., 2015). While it is known that the microstructure of a rock results from nucleation and crystal growth, our quantitative understanding of these fundamental processes and their specific impact on microstructure development in geological materials is still limited.

Integral to the evolution of rock microstructure—and, hence, the interpretation of its geodynamic implications—are the rates and mechanisms by which minerals grow. Size-dependent growth (SDG) of crystals is commonly associated with transport-controlled mineral reactions, with faster radial growth for crystals of smaller size and relatively slow growth of larger crystals (e.g., Zener, 1949; Carlson, 1989; Balluffi et al., 2005). Transport-controlled SDG has been observed in rocks at macroscopic to submicroscopic length scales (e.g., Gaidies et al., 2017, and references therein). SDG has also been postulated to be associated with interface-controlled reactions, albeit only for microscopic or even smaller crystal sizes where the interfacial energy associated with the surfaces of the crystals is assumed to be sufficiently large compared to the bulk energy of the crystals, acting as a penalty to growth (e.g., McCabe, 1929; Christian, 2002). In such a case, SDG can be expected to yield a systematic decrease in radial growth rates with a decrease in crystal size.

We present evidence for SDG caused by the interfacial energy penalty to the growth of metamorphic crystals up to 1.5 mm in diameter. To our knowledge, this is the first documentation of this mechanism at such length scales in metamorphic rocks. We postulate that this growth mechanism commonly operates at the millimeter scale in metamorphic as well as in igneous systems when reactions take place close to equilibrium. Hence, this process may be more common in the microstructural evolution of rocks than previously assumed. Furthermore, we propose a method for estimating the departure from equilibrium as well as the interface mobility associated with the growth of porphyroblasts in metamorphic rocks. This method avoids the uncertainties inherent to thermodynamic data sets commonly used in crystal growth models.

SAMPLE AND METHODS
The rock studied is sample 24-99, a garnet-zone mica schist that has been repeatedly investigated in studies focusing on the tectono-metamorphic evolution of the Sikkim Himalaya (Dasgupta et al., 2009; Anzcziwicz et al., 2014; Gaidies et al., 2015; George and Gaidies, 2017, 2020; George et al., 2018). Petrographic and phase equilibrium constraints (Gaidies et al., 2015; George and Gaidies, 2017) indicate that garnet of this rock crystallized in an assemblage containing chlorite, white mica, quartz, plagioclase, ilmenite, and graphite, yielding porphyroblasts ranging in radius between ~0.75 mm and 0.04 mm (Fig. 1). Garnet crystallized over a pressure-temperature (P-T) range of ~50°C and 120 MPa and was succeeded by biotite growth close to the maximum P-T conditions experienced by the rock at ~565°C and 560 MPa. Lu-Hf garnet whole-rock geochronology points to garnet growth at ca. 11.1–10.5 Ma (Anzcziwicz et al., 2014).

Both the centers and the sizes of the garnet crystals are randomly distributed across the rock.

CITATION: Gaidies, F., and George, F.R., 2021, The interfacial energy penalty to crystal growth close to equilibrium: Geology, v. 49, p. 988–992, https://doi.org/10.1130/G48715.1
volume (Gaidies et al., 2015), providing microstructural evidence for interface-controlled nucleation and growth kinetics (e.g., Carlson, 1989; Daniel and Spear, 1998; Kelly et al., 2013; Kretz, 1974, 1993; Petley-Ragan et al., 2016). This is supported by geochemical analyses (George and Gaidies, 2017), which indicate the quasi-equilibrium of major components over macroscopic length scales during garnet growth. Significant chemical disequilibrium of these components developed only across the garnet crystals, resulting in their compositional growth zoning (Fig. 2; George and Gaidies, 2017, their figure 4).

To reduce geometric artifacts in the interpretation of the geochemical analyses, each garnet crystal was cut along a plane containing the geometric center of the crystal, as identified by high-resolution X-ray micro-computed tomography, and parallel to one of its (110) faces. Compositional data were collected with the electron probe microanalyzer along a line parallel to the longest dimension of each garnet. Because diffusion of the major components has been negligible even in the smallest garnet crystals (George and Gaidies, 2017), increments of different crystals with identical component concentrations can be interpreted to have formed simultaneously (e.g., Kretz, 1974). Hence, major-component concentrations in garnet may be used as relative time lines.

Average growth rates of each crystal can be estimated using the heating rate determined from diffusion geospeedometry and the temperature range over which growth occurred. Using the kinetic data set of intracrystalline diffusion obtained by Chakraborty and Ganguly (1992), the estimated heating rate is \( \sim 100°C \text{ m.y.}^{-1} \) (George and Gaidies, 2017), so that the growth rates range between \( \sim 1.6 \text{ mm m.y.}^{-1} \) for the largest crystal and \( \sim 0.65 \text{ mm m.y.}^{-1} \) for crystals of size class 16 (as defined in Fig. 1). Slower growth would have resulted in the diffusional modification of the compositional growth zoning of garnet, particularly in the smallest crystals. This also implies that these growth rates reflect minimum values, given that faster growth cannot be excluded when using this diffusion geospeedometry method.

![Figure 1. Crystal size frequency distribution of the garnet population in the studied sample, and size class notation used in this study. Star marks crystal sizes used for growth rate analysis.](image1)

![Figure 2. (A–D) Compositional profiles from rim to rim of representative crystals of the garnet population in the studied sample. Also shown are quadratic fits (red lines) of compositional gradients developed during radial growth, concomitant to growth of the smallest crystal analyzed (size class 16, Fig. 1). xsps, xgrs, xprp, and xalm correspond to the mol-fractions of spessartine, grossular, pyrope, and almandine, respectively. (E) Schematic derivation of relative radial growth rate for two differently sized crystals.](image2)
Here, we compare relative radial growth rates of the different garnet crystals by using the average gradients of their pyrope, spessartine, and almandine contents developed across equivalent radial growth segments (Fig. 2). Average compositional gradients are calculated using quadratic fits of the zoning and a data point spacing of 20 μm and are compared to the average gradients developed in the largest crystal. These relative gradients are used as proxy for the relative radial growth rates. The growth interval chosen for this analysis reflects almost all of the growth history of garnet of size class 16 as well as the concomitant rim growth of crystals that nucleated earlier than this size class (Fig. 2). According to crystallization simulations by George and Gaidies (2017), that portion of the total growth history of garnet started at ~534°C, 480 MPa and finished at the peak metamorphic conditions.

RESULTS AND DISCUSSION
Size-Dependent Growth

Figure 3 illustrates a systematic decrease in the relative radial growth rate with a decrease in the size of the crystals. The reduction in growth rate from the largest to the smallest crystals is ~45%. Even though the overall steepening of the compositional gradients with decreasing crystal size can be observed in the zoning of all four garnet end members (Fig. 2), the gradients in the grossular content have not been quantified given its comparatively irregular zoning at the micrometer scale, affecting the gradient approximation. These compositional fluctuations are interpreted to reflect the local disequilibrium of this component at the garnet surface during growth, resulting from relatively slow interface reactions associated with its incorporation into garnet. The compositional sector zoning developed in the grossular distribution in this sample (George and Gaidies, 2017) supports the inference of relatively slow interface reactions.

Included in Figure 3 is the relative driving force for crystal growth, \( \frac{\Delta G}{\nu} - \frac{2\sigma}{r} \), acting on the surface of garnet as a function of its crystal size, according to the growth law for interface-controlled SDG (e.g., Christian, 2002; Gaidies et al., 2017):

\[
dr = \frac{dM}{dt} \left( \frac{\Delta G}{\sigma} - \frac{2\sigma}{r} \right),
\]

where \( \frac{dr}{dt} \) is the radial growth rate, \( M \) is the interface mobility, \( \sigma \) is the interfacial energy, \( v \) is the molar volume of garnet, and \( r \) is the radius of its surface curvature assuming a spherical garnet geometry. \( \Delta G \) is the chemical driving force for garnet growth, defined as the difference of the molar Gibbs energies of an equilibrated system containing garnet and an equilibrated system in which garnet is not present (for further details, see the Supplemental Material).

The observed trend in the growth rate–crystal size relationship can be predicted using Equation 1 for a \( \Delta G/\sigma \) ratio ranging between ~1 and 4 m² mol⁻¹ and clustering around ~2 m² mol⁻¹ (Fig. 3). For this fit, the growth rate of the largest crystal is decreased by 8% relative to a crystal that was too large to experience the \( \sigma \) penalty to growth. It is important to note that other driving forces for growth such as elastic and plastic strains as well as the energy of deformation potentially contained in precursor phases cannot be considered here but may also have influenced the kinetics of crystal growth.

Alternatively, SDG may have been the result of size-related imperfections in the lattices of the crystals. However, because the model of \( \sigma \) penalty to growth predicts the observed reduction in radial growth for smaller crystals, we argue that it may reflect the underlying physics of the growth processes. SDG can be inferred for the estimated \( \Delta G/\sigma \) ratio in the analyzed garnet population. However, SDG may be difficult to identify in crystals with significantly larger radii and a similar \( \Delta G/\sigma \) ratio (Fig. 3). The critical radius may be defined as the size of a crystal below which radial growth slows down significantly, and may be obtained from the largest curvature in the \( \Delta G/\sigma \) trend lines. Accordingly, the critical radii are ~570 μm, 410 μm, 260 μm, and 100 μm for \( \Delta G/\sigma \) ratios of 2 m² mol⁻¹, 4 m² mol⁻¹, 10 m² mol⁻¹, and 100 m² mol⁻¹, respectively (Fig. 3). In cases where the \( \Delta G/\sigma \) ratio approaches unity, i.e., for relatively small chemical driving forces or large interfacial energies, this growth mechanism may also operate in populations with crystals as large as 1 mm in radius. In cases where crystal growth occurred far from equilibrium, \( \Delta G/\sigma \) ratios would have been several orders of magnitude larger, and thus SDG is likely to be detectable only at micrometer or nanometer scales (Fig. 3).

**Departure from Equilibrium, \( \Delta G \)**

Using proposed values for \( \sigma \) associated with interfaces between garnet and a metapelitic mineral assemblage typical of the Barrovian garnet zone (0.007–0.255 J m⁻²; Gaidies et al., 2011; Kelly et al., 2013), our results imply exceedingly small driving forces for garnet growth in the order of 0.01–0.5 J mol⁻¹, as may be expected for metamorphism close to equilibrium. Figure 4 illustrates the relationship between \( \Delta G \) and the departure from the
equilibrium conditions of the garnet-forming reaction at the onset of growth of garnet of size class 16 (Fig. 1). ΔG has been calculated at each P-T point using the G-minimization algorithm THERIAK (https://serc.carleton.edu/details/files/29426.html; de Capitani and Brown, 1987) and the thermodynamic data of Holland and Powell (1998) (for details regarding the activity models used, see Gaidies et al. [2015]). The modification of the thermodynamically effective system composition during previous garnet growth steps has also been considered. As can be seen, a departure from equilibrium of ~5°C corresponds to a ΔG of several hundred joules per mole (Fig. 4), confirming that SDG in the studied sample took place close to equilibrium.

Interface Mobility, M

The mobility of an interface reflects the structural and chemical reorganization associated with its propagation into the reactant during growth and, hence, is of key importance for the rates of mineral reactions and the rock microstructures that result from them. Estimates of M have been proposed for metals (e.g., Janssens et al., 2006), alloys (e.g., Santofimia et al., 2009), and ceramics (e.g., Chen, 1993) but are rare for systems relevant for metamorphic and igneous processes (Kuleci et al., 2016).

Using Equation 1 and the proposed σ values discussed above, as well as the estimated range of radial growth rates and the inferred ΔG/σ ratio, M ranges between 10^{-19} and 10^{-26} m^2 J^{-1} s^{-1}. A potential variation of M over the growth interval presented in Figure 3 is not considered in these calculations but is deemed negligible given the relatively small P-T range of garnet growth considered. Note that growth rates twice to three times as large as those obtained here would not change these M values, which are three to four orders of magnitude smaller than what has been obtained for the formation of brucite by the hydration of periclase (Kuleci et al., 2016), at a T similar to the conditions of garnet growth studied here.

A possible reason for the larger M of the periclase-to-brucite transformation compared to the garnet-forming reaction is the similar crystal structures of periclase and brucite, with the cations in octahedral coordination in both phases. The structural reorganization associated with the formation of garnet from a phyllosilicate precursor is more complicated, involving the formation of dodecahedral coordination polyhedra, likely substantially decreasing M.

Impurities such as graphite crystals, which are common in the sample studied and possibly accumulated in grain boundaries during garnet growth, may have exerted additional drag on the interface, further decreasing M. It is important to note that regardless of this comparatively small M, growth of garnet in this sample took place close to equilibrium, as outlined above. For the inferred growth rates and using the proposed σ values, M would have been as small as 10^{-23} m^2 J^{-1} s^{-1} to generate a driving force of ~600 J mol^{-1} corresponding to 10°C overstep of the equilibrium conditions (Fig. 4). In such a case, the ΔG/σ ratio would have been ~10^{10}–10^{14} m^2 mol^{-1}, and SDG would have operated only at the nanometer scale (Fig. 3).

CONCLUSIONS

Our research highlights the fundamental importance of interface properties for microstructural evolution during metamorphism close to equilibrium. It challenges the long-standing hypothesis that the curvature of an interface can only influence the growth rate of nanometer-sized particles. Instead, it suggests that interface properties can cause a growth rate divergence of nearly 50% even at the millimeter scale during chemical reactions close to equilibrium, such as in high-T metamorphic systems. Given the general applicability of the kinetic theory used here, it can be expected that our results are equally relevant for high-T igneous systems, impacting existing models of grain growth and size distribution and, consequently, the interpretation of rock microstructure.

ACKNOWLEDGMENTS

This research was supported by Natural Sciences and Engineering Research Council of Canada research grant 315857 to Gaidies. We thank three anonymous reviewers for constructive comments, and C. Clark for editorial support.

REFERENCES CITED

Anzcikiewicz, R., Chakraborty, S., Dasgupta, S., Mukhopadhyay, D., and Koltonik, K., 2014, Timing, duration and inversion of prograde Barrovian metamorphism constrained by high resolution Lu-Hf garnet dating: A case study from the Sikkim Himalaya, NE India: Earth and Planetary Science Letters, v. 407, p. 70–81, https://doi.org/10.1016/j.epsl.2014.09.035.

Balluffi, R.W., Allen, S.M., and Carter, W.C., 2005. Kinetics of Materials: Hoboken, New Jersey, John Wiley & Sons, Inc., https://doi.org/10.1002/0471749311.

Buffett, B.A., and Becker, T.W., 2012, Bending stress and dissipation in subducted lithosphere: Journal of Geophysical Research, v. 117, B05413, https://doi.org/10.1029/2012JB009025.

Carlson, W.D., 1989, The significance of intergranular fusion in aluminosilicate garnets: Experimental determination in spessartine-almandine diffusion.
couples, evaluation of effective binary diffusion coefficients, and applications: Contributions to Mineralogy and Petrology, v. 111, p. 74–86, https://doi.org/10.1007/BF00296579.

Chen, I.-W., 1993, Mobility control of ceramic grain boundaries and interfaces: Materials Science and Engineering A, v. 166, p. 51–58, https://doi.org/10.1016/0921-5093(93)00309-3.

Christian, J.W., 2002, The Theory of Transformations in Metals and Alloys: Amsterdam, Pergamon, 1200 p., https://doi.org/10.1016/B978-0-08-044019-4.X5000-4.

Daniel, C.G., and Spear, F.S., 1998, Three-dimensional patterns of garnet nucleation and growth: Geology, v. 26, p. 503–506, https://doi.org/10.1130/0955-0953(1998)26<503:TPGONN>2.3.CO;2.

Dasgupta, S., Chakraborty, S., and Neogi, S., 2009, Population-wide garnet growth zoning revealed by LA-ICP-MS mapping: Implications for trace element equilibration and synkinematic deformation during crystallisation: Contributions to Mineralogy and Petrology, v. 173, 74, https://doi.org/10.1007/s00410-009-0503-8.

George, F.R., and Gaidies, F., 2018, Population-wide garnet growth zoning revealed by LA-ICP-MS mapping: Implications for trace element equilibration and synkinematic deformation during crystallisation: Contributions to Mineralogy and Petrology, v. 173, 74, https://doi.org/10.1007/s00410-018-1503-0.

Hansen, L.N., Kumamoto, K.M., Thom, C.A., Wallis, D., Hansen, L.N., Armstrong, D.E.J., Warren, J.M., Goldsby, D.L., and Wilkinson, A.J., 2017, Size effects resolve discrepancies in 40 years of work on low-temperature plasticity in olivine: Science Advances, v. 3, e1701338, https://doi.org/10.1126/sciadv.1701338.