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Research Article

Revaluation of “equilibrium” P-T paths from zoned garnet in light of quartz inclusion in garnet (QuiG) barometry

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ABSTRACT

Metamorphic P–T paths provide valuable constraints on the tectonics of collisional orogens and many such paths have been deduced from analysis of chemical zoning in garnet. Inclusion barometry (e.g. quartz-in-garnet or QuiG) provides complementary and sometimes contradictory information regarding the interpretation of garnet zoning and the P–T paths derived therefrom. For example, QuiG barometry on several generations of garnet from well-characterized samples from Fall Mountain, New Hampshire, is consistent with the P–T path inferred from other methods. However, QuiG barometry is inconsistent with P–T paths inferred from garnet zoning from the Orfordville Belt (Vermont), Townshend Dam (Vermont), the Connecticut Valley Trough (Vermont), and Sifnos (Greece). New data from the Perry Mountain Formation, southeastern New Hampshire, suggests that QuiG may preserve a record of polymetamorphic events. Specifically, QuiG barometry in coticule samples is interpreted to record a previously unrecognized early medium pressure (ca. 0.9 GPa) metamorphism and a later low pressure (ca. 0.3 GPa) metamorphism.

1. Introduction

Garnet has served as a central focus of metamorphic studies for the discernment of P–T paths because it has the capability of storing a record of its history through the crust through inclusion suites, chemical zoning, and age zoning (e.g. Ague and Carlson, 2013; Baxter et al., 2013; Baxter and Scherer, 2013; Caddick and Kohn, 2013). Although it is generally acknowledged that metamorphic rocks cannot react if in equilibrium and a finite amount of overstepping is required to drive metamorphic processes, it is generally assumed that the degree to which metamorphic rocks are out of equilibrium is sufficiently small that utilization of equilibrium constraints does not introduce a substantial error in the calculation of metamorphic P–T paths (e.g. Caddick and Kohn, 2013).

However, a number of studies have presented observations that challenge this assumption of a close approach to equilibrium throughout the duration of garnet growth. As early as 1969, Hollister (1969) demonstrated that overstepping of equilibrium reaction boundaries was required to explain textural relations of aluminosilicate minerals (staurolite, kyanite, andalusite and sillimanite) from the Kwoiek contact aureole in British Columbia. More recently, a pioneering study by Waters and Lovegrove (2002) provided unambiguous textural data documenting the sequence of porphyroblast growth in the contact aureole of the Bushveld complex and demonstrated that it was not the sequence that was predicted from equilibrium calculations, and drew the conclusion that considerable overstepping of the equilibrium phase boundary was required for porphyroblast nucleation. Pattison and Tinkham (2009) reach similar a similar conclusion for porphyroblast growth in the Nelson contact aureole by comparing the spacing of isograds mapped in the field with the spacing of isograds that would be predicted from equilibrium calculations and thermal modeling. Pattison and Spear (2018) presented compelling evidence that not only might garnet nucleation be overstepped during regional metamorphism, but also staurolite and aluminosilicates.

The introduction of a new tool into the petrologist's arsenal — inclusion barometry — has provided a technique for evaluating the extent of overstepping required for porphyroblast nucleation. In particular, quartz-in-garnet barometry, or QuiG, has been applied to rocks from collisional orogenic belts in New England (Spear et al., 2014; Wolfe and Spear, 2018, in review), the Cyclades subduction complex of Greece (Ashley et al., 2014; Castro and Spear, 2016), and to high pressure gneisses and eclogites (Alvaro et al., 2020; Gonzalez et al., 2019). In several of these studies, it was found that when the results of QuiG barometry were compared to the calculated P–T conditions of the garnet isograd based on equilibrium modeling, garnet was concluded to have nucleated not near the equilibrium isograd but only after considerable overstepping .

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The extent to which the above results are true — that garnet only nucleates after considerable overstepping of the equilibrium phase boundary — raises a very important question as to the validity of previously published P–T paths that are based on the assumption of garnet having grown through a sequence of equilibrium states. If application of QuiG barometry reveals a P–T history for garnet growth that deviates from the P–T histories inferred from conventional chemical zoning analysis, then the nature and causes of this deviation urgently requires evaluation because of the numerous P–T paths that have been inferred from this latter approach. Inasmuch as metamorphic P–T paths, many of which have been constrained from garnet zoning studies, are a key constraint in the tectonic interpretation or orogenesis, evaluation of the accuracy of QuiG is of considerable importance.

The purpose of this paper is to summarize some of the recent results in which QuiG barometry has been applied to constrain metamorphic P–T conditions. In some of these studies, QuiG barometry reveals a different P–T history from that previously published whereas in others QuiG barometry reinforces published inferences about metamorphic P–T paths. Examples are also presented in which QuiG barometry provides new constraints on metamorphic histories in rocks for which traditional, equilibrium studies have seen only limited success.

2. Petrologic methods applied to garnet

Garnet has long enjoyed the status of an "uncommonly useful" mineral in petrologic studies (Baxter et al., 2013) and numerous approaches have been championed to deciphering P–T histories from garnet phase equilibria and compositional zoning (e.g. see Caddick and Kohn, 2013, for an excellent review). The earliest geothermometers utilized element partitioning between garnet and coexisting phases as a proxy for temperature of crystallization or equilibration (Kretz, 1959; Ramberg, 1952) and one of the most oft-cited geothermometers in the metamorphic literature is the garnet-biotite Fe—Mg exchange thermometer of Ferry and Spear (1978).

Chemical zoning in garnet was recognized as potential P–T recorder shortly following the earliest chemical zoning profiles were measured using the electron microprobe. Indeed, Hollister (1966) recognized that bell-shaped Mn zoning in garnet followed the predictions of Rayleigh fractionation. His model reproduced the observed zoning isothermally, although Hollister commented that the fractionation factor could change with temperature and produce similar results. Tracy et al. (1976) described growth zoning in garnet from central Massachusetts as a product of continuous Fe-Mg-Mn reactions. Although not explicitly stated, the underlying assumption in the application of continuous reactions in this way is that the garnets were growing close to equilibrium and the reactions were driven by changes in T and P, which fundamentally differs from isothermal growth via Rayleigh fractionation.

Over 35 years ago, Spear and co-workers (Spear et al., 1984; Spear and Selverstone, 1983) published a method by which the P–T path followed by a rock that was undergoing progressive metamorphism could be constrained by inversion of the chemical zoning preserved in garnet and coexisting phases into P–T–t (relative t) space. The method was based on expansion of the total differentials for temperature and pressure in terms of a set of independent compositional variables that could be measured in garnet and co-existing phases:

$$T = F(X_1, X_2, X_3, \ldots)$$

$$P = G(X_1, X_2, X_3, \ldots)$$

where the number of independent variables was the same as the Gibbs phase rule variance. The total differentials are

$$\Delta T = \left(\frac{\partial T}{\partial X_1}\right)_{X_2, X_3 \ldots} \Delta X_1 + \left(\frac{\partial T}{\partial X_2}\right)_{X_1, X_3 \ldots} \Delta X_2 + \left(\frac{\partial T}{\partial X_3}\right)_{X_1, X_2 \ldots} \Delta X_3 \ldots$$

$$\Delta P = \left(\frac{\partial P}{\partial X_1}\right)_{X_2, X_3 \ldots} \Delta X_1 + \left(\frac{\partial P}{\partial X_2}\right)_{X_1, X_3 \ldots} \Delta X_2 + \left(\frac{\partial P}{\partial X_3}\right)_{X_1, X_2 \ldots} \Delta X_3 \ldots$$

The partial derivatives constitute the Jacobian matrix, which can be derived by inverting a matrix consisting of the linearly independent heterogeneous reactions (see Spear, 1993, for a derivation). In trivariant systems, this meant that the observed garnet zoning could be inverted to produce changes in P and T. Initial applications were limited to rocks in which the thermodynamic variance was sufficiently small (ideally 3 but also possible with variance = 4 if zoned plagioclase was also monitored). Early applications of the method (e.g. Selverstone et al., 1984; Spear and Rumble III, 1986) revealed that garnet from Barrovian terranes (e.g. the eastern Alps and central New England) grew along generally clockwise P–T paths, consistent with predictions from thermal models of continental collision (England and Richardson, 1977; England and Thompson, 1984). Modification of the method that invoked the addition of mass balance constraints (e.g. Spear, 1988; Spear et al., 1991) permitted inversion of the chemical zoning signature using only two compositional parameters from garnet (called the method of intersecting isopleths), provided the effective rock bulk composition during garnet growth was known or could be modeled.

This approach enjoyed considerable expansion of application through the development of internally consistent thermodynamic databases for metamorphic phases (e.g. Berman, 1988; Holland and Powell, 1990, 1998, 2011) and software that permitted ready calculation of phase assemblages and mineral compositions over the entire range of crustal P–T conditions (e.g. THERMOCALC, Powell et al., 1998; Theriak-Domino, de Capitani and Petrakakis, 2010; Perple_X, Connolly and Petrini, 2002; Gibbs, Spear et al., 1991). The advantage of only needing the zoning of two garnet components to produce a P–T path was, obviously, enormous and in recent years, the application of this method to the calculation of metamorphic P–T paths based on garnet zoning has proliferated greatly and P–T paths from a large number of terranes have been calculated. Many of these studies have actually used three independent garnet components to verify closure but it is rare that all three intersect in a single point in P–T space, which could be the result in inaccuracies in the thermodynamic data or activity models, or knowledge of the effective bulk composition at the time of garnet growth. Indeed, several studies have been published on the difficulties in accurately assessing the effective bulk composition during metamorphic recrystallization and how it might evolve as metamorphism proceeds (e.g. Lanari and Duesterhoeft, 2019; Palin et al., 2016). Alternatively, the lack of internal consistency among P–T conditions inferred from the intersecting isopleth method could stem from the inappropriate application of equilibrium constraints.

3. Methods

3.1. The QuiG method

Inclusion barometry is based on the assumption that when a porphyroblast such as garnet overgrows another phase so that the phase becomes included in the host, the host-inclusion pair are initially in mechanical equilibrium such that the inclusion exactly fits inside of the hole in the host. Subsequent changes in P and T and eventual exhumation results in changes in the size of the host hole and inclusion so that at surface conditions the inclusion no longer fits perfectly inside the host and experiences strains imposed by the host under an external stress field (either positive or negative). Raman shifts for the inclusion mineral are sensitive to the strain on the inclusion and measuring the difference between the location of the Raman peak for the inclusion with that of a similar, unstrained grain of the same material provides an estimate of the strain on the inclusion which can be used to calculate the pressure on the inclusion. Additionally, the host mineral experiences elastic strain due to the trapped inclusion expanding or contracting. Application of a thermoelastic model (e.g. Guiraud and Powell, 2006) permits calculation of the pressure (at ambient T) at which there is zero strain on the host, from which an isomeke (the line in P–T space along which the inclusion just fits inside of the host hole) can be calculated. Detailed discussions of the approach to calculation of strains from Raman shifts and inclusion pressure from strains are given by Angel et al. (2017, 2019) and Gonzalez et al. (2019).

In the present study, Raman spectra were collected on quartz grains from several garnets in each sample from both the garnet cores and garnet rims. Shifts of the 464 cm^{-1} peak relative to unconstrained matrix quartz were used to infer inclusion pressures using the measurements of Schmidt and Ziemann (2000) and pressures of entrapment were calculated following the method described by Guiraud and Powell (2006) with modifications based on Angel et al. (2017) and the experimental calibration of Thomas and Spear (2018) and Bonazzi et al. (2019). The analytical procedure implemented here is the same as that described in Wolfe and Spear (2018) and readers are referred to that contribution for further details.

3.2. Graphite thermometry

Raman spectra were collected for thermometry following the procedure outlined in Beyssac et al. (2002) and Aoya et al. (2010) in which the ratio of the so-called “d2” and “G” peaks have shown to be dependent on the maximum temperature attained by a sample. Maximum temperatures were estimated using the calibration of Beyssac et al. (2002).

3.3. Graphite barometry

Shifts of the 1579 cm^{-1} peak of graphite inclusions inside of garnet were measured to determine the pressures of entrapment, similar to the approach used for QuiG barometry. Raman peak positions were measured for both included graphite and matrix graphite and shifts of the included graphite grains were calculated relative to the unconstrained peaks. These values of Raman shifts (Δw) were converted into inclusion pressures using a transform of the 25 °C pressure dependence of the 1579 cm^{-1} peak given by Hanfland et al. (1989), which yielded the linear equation (good up to 1 GPa) of:

$$P_{inclusion} = 2174.3\ \Delta w - 24.116$$

Graphite entrapment isomekes were then calculated using the EOS for graphite from the Holland and Powell (2011) thermodynamic dataset and the thermoelastic model of Guiraud and Powell (2006), similar to the approach used for QuiG barometry.

3.4. Garnet-biotite and garnet-plagioclase thermobarometry

Calculations of temperature and pressure were done on the measured extremes of garnet, plagioclase and biotite compositions using the calibrations of Hodges and Spear (1982) and Hodges and Crowley (1985).

4. Results

This section discusses the results of reevaluating P–T paths based on application of QuiG barometry to previously studied samples. Some examples reveal close consistencies between the originally published P–T path and the results of inclusion barometry whereas other examples show no consistency between the QuiG results and garnet zoning paths. Finally, two examples are discussed in which QuiG barometry places new constraints on the evolution of samples that were not previously accessible by garnet zoning analysis.

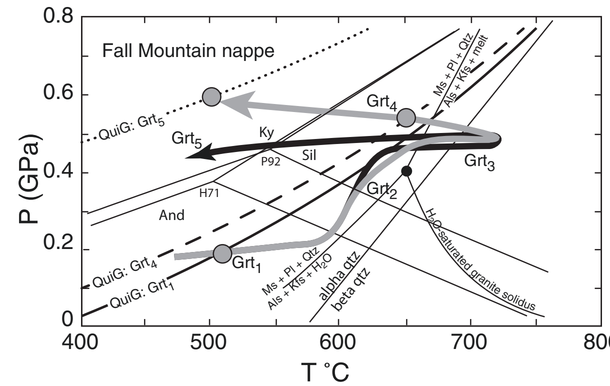

Fig. 1. P–T diagram modified from Spear et al. (2002; Fig 12a) to include the results of QuiG barometry. The black P–T path is from Spear et al. (2002) and is based on microstructural analysis, geothermobarometry, and thermodynamic modeling. QuiG barometry on quartz inclusions from three distinct garnet generations (Grt_1, Grt_4 and Grt_5) are shown as solid, dashed, and dotted lines, respectively. The intersection of QuiG isomekes with the P–T path for these inclusions is shown by grey circles. The grey P–T path is modified from Spear et al. (2002) to accommodate QuiG results for Grt_5. H71 and P92 are the Al_2SiO_5 triple points of Holdaway (1971) and Pattison (1992), respectively.

4.1. Fall Mountain, New Hampshire

Fig. 1 shows the P–T path that was inferred for garnet-sillimanite-biotite-muscovite-ilmenite-plagioclase-quartz migmatites of the Fall Mountain nappe based on a combination of thermodynamic modeling, geothermobarometry, garnet zoning (major and trace elements), and petrogenetic grids (black path; Spear et al., 1990; Spear et al., 2002). Five generations of garnet growth were documented and interpreted to reflect different stages of the thermotectonic evolution of the rocks including prograde growth at low pressure (Grt_1), growth during loading from overlying nappes (Grt_2), growth during anatectic melting (Grt_3), growth of secondary garnets during cooling and loading (Grt_4), and growth along the outer rims of some garnets that was poorly constrained but must have occurred at lower temperature based on exchange thermometry and garnet zoning (Grt_5).

Raman shifts of quartz inclusions in garnet were measured from two samples (BF-14p and BF-9 g) from the Connecticut River at Bellows Falls, VT. Because these samples had been previously well-characterized, it was possible to select quartz inclusions from three different garnet generations (Grt_1, Grt_4 and Grt_5). As can be seen in Fig. 1, the QuiG isomekes for these three generations of garnet (circles) are consistent with the previously inferred conditions for the growth of these garnets from other means. The one exception is Grt_5, which QuiG barometry indicates grew at around 0.6 GPa whereas the previous work placed it at around 0.45 GPa. However, as mentioned above, the pressure at which Grt_5 grew was not well constrained from the previous work and the new QuiG data are interpreted as providing a more reliable pressure. The P–T path inferred from the assembly of previous and new work is shown by the grey path. The increase in pressure for the formation of Grt_5 is of tectonic interest because it reflects the amount of loading experienced by the Fall Mountain nappe following anatexis and prior to exhumation.

4.2. Orfordville belt, Vermont

P–T paths based on garnet zoning for two garnet-biotite-muscovite-staurolite-kyanite-quartz-plagioclase-ilmenite samples from the Orfordville belt, Vermont and New Hampshire, were published by Spear and Rumble III (1986) (Fig. 2). The paths display a generally clockwise shape with an episode of isothermal pressure decrease and increase recorded in the core. The QuiG isomeke for on these samples are consistent with the inferred P–T conditions for the garnet core of

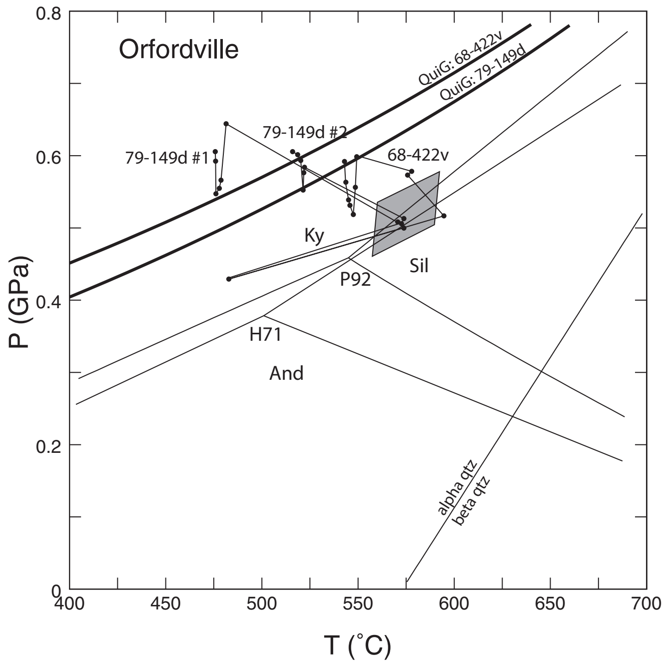

Fig. 2. P–T diagram modified from Spear and Rumble, 1986; Figs. 2 and 7) with the addition of QuiG barometry. Grey parallelogram shows peak P–T conditions inferred from garnet-biotite thermometry and garnet – plagioclase – aluminosilicate barometry. P–T paths were inferred from modeling chemical zoning in garnet (see Spear and Rumble, 1986, for details). Note that QuiG barometry reveals higher pressures than those inferred from thermobarometry but is more consistent with the presence of kyanite and absence of sillimanite. The consistency of QuiG barometry throughout the entire garnet argues for the growth of garnet at constant P and T rather than along the path indicated. H71 and P92 are the Al_2SiO_5 triple points of Holdaway (1971) and Pattison (1992), respectively.

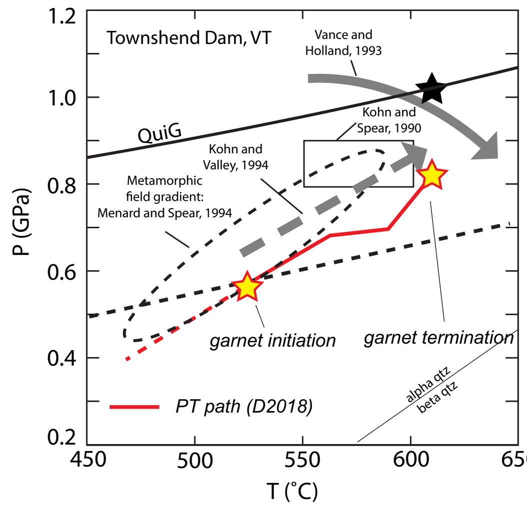

Fig. 3. P–T diagram showing the P–T path inferred from the method of intersecting isopleths for a sample from the Townshend Dam spillway, Vermont from Dragovic et al. (2018) (red line and yellow stars). The results of QuiG barometry (this study) indicate that the garnet grew under nearly isothermal, isobaric conditions at the black star. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

around 0.6 GPa. Furthermore, there is no variation in the Raman shifts of quartz inclusion with position in the garnet, which has been interpreted to indicate that garnet grew nearly isothermally and isobarically, similar to results detailed by Wolfe and Spear (2018). Spear and Rumble (1986) also published an estimate of the peak P–T conditions based on garnet-biotite thermometry and garnet-aluminosilicate-quartz-plagioclase (GASP) barometry (grey parallelogram), which falls around 0.15 GPa below the QuiG isomekes. There is no reason to suspect that the garnet-biotite thermometry is in error and the peak temperature is constrained to be at around 580 °C. However, the calibration of the GASP barometer used in this study was that of Hodges and Spear (1982), which was based on samples from near the Al_2SiO_5 triple point at Mt. Moosilauke, New Hampshire, and the assumption that the P–T conditions of the triple point were those determined by Holdaway (1971). Fig. 2 also shows the P–T conditions of the Holdaway (1971) triple point and those preferred by Pattison (1992). A qualitative reassessment of the P–T conditions at Mt. Moosilauke would suggest that pressures from the GASP barometer should be around 0.07 GPa higher, which would make the GASP barometry more consistent with QuiG barometry. Finally, it should be noted that the two samples examined contain kyanite and no sillimanite has been reported from any pelites in the vicinity. This observation also suggests that the QuiG barometry is probably closer to the true pressure experienced by these samples.

However, the results of QuiG barometry also differ from the P–T paths deduced from the chemical zoning in garnet. Rather, if the garnets really did grow under isothermal, isobaric conditions, there is no P–T path information contained in the zoning profiles.

4.3. Townshend Dam, Vermont

Dragovic et al. (2018) published a P–T path from a garnet-biotite-muscovite-paragonite–quartz-plagioclase±clinozoisite schist of the Pinney Hollow formation at Townshend Dam, Vermont, based on thermodynamic modeling and intersecting isopleths (Fig. 3). The path followed by this sample is of special interest because an earlier study by Gatewood et al. (2015) reported Sm/Nd ages of garnet rims, middle, and cores and these ages were used by Dragovic et al. (2018) to infer fluid production rates from the garnet producing reaction. This locality has also been the focus of a number of additional petrologic and isotopic studies because of the excellent exposures, the range of bulk compositions displayed, and the abundance of large mm-cm size garnet porphyroblasts (e.g. Christensen et al., 1989; Kohn and Spear, 1990; Kohn and Valley, 1994). The results of QuiG barometry on quartz inclusions from the garnet rim from a sample from the same locality of Pinney Hollow formation as examined by Gatewood et al. (2015) and Dragovic et al. (2018) suggests pressures of around 1.0 GPa at the inferred peak temperature of around 600 °C (black star in Fig. 3). Most importantly, the Raman shifts of quartz inclusions displayed no systematic variation from garnet core to rim, again implying that the garnet grew nearly isothermally and isobarically. In addition, the peak pressure implied by QuiG barometry is somewhat higher than that inferred from classical geobarometry or intersecting isopleths (yellow star and black box), perhaps because of inaccurate barometer calibration, as suggested for the Orfordville samples. Interestingly, the path suggested by Vance and Holland (1993, although for the Gassetts schist and not the Pinney Hollow formation) intersects the QuiG isomeke very close to the black star. Vance and Holland based their path on calculated phase relations and a petrogenetic grid, which may prove to be more robust than methods that utilize garnet zoning.

4.4. Sifnos, Greece

Castro and Spear (2016) presented the results of QuiG barometry for three samples from the northern eclogite-blueschist unit (EBU) on Sifnos, Greece. One discovery revealed by QuiG from that study is that that samples from different parts of the belt experienced at least two different peak pressures (ca. 1.5 GPa and ca. 2.0 GPa). This conclusion was not apparent from previous studies that employed classical thermobarometry and that concluded that the entire EBU experienced the same peak P–T conditions. Equally significant was the discovery that garnet did not nucleate until after overstepping of the nominal

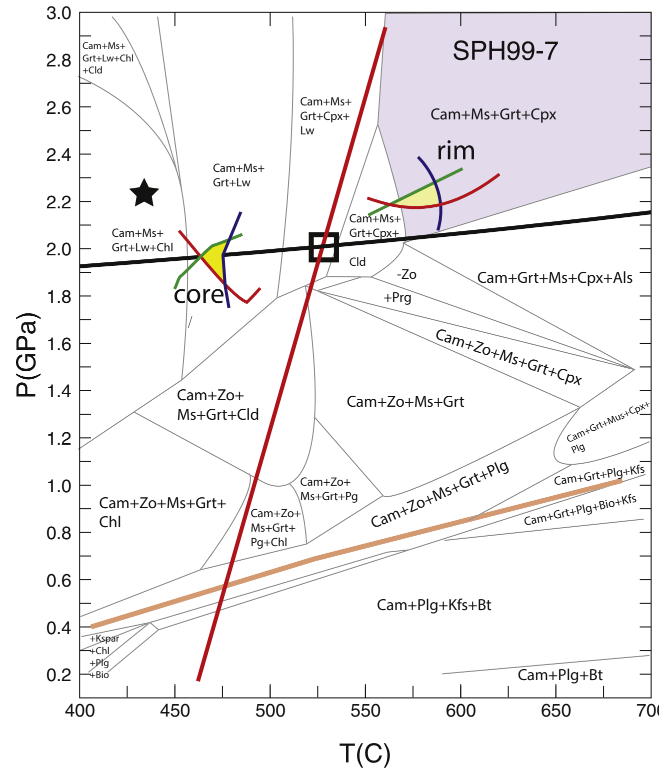

Fig. 4. P–T diagram modified from Castro and Spear (2016; Fig. 12). QuiG and ZiR values have been recalculated as outlined in the methods section (ZiR calibration of Tomkins et al., 2007: red line). Black box is the minimum temperature of garnet nucleation and growth based on ZiR temperatures. Black star is the P and T determined from intersecting isopleths in the garnet core. Light purple region is the peak metamorphic assemblage. Orange line is the location of the garnet isograd. Regions outlined with red, green and blue curves with yellow fill are the P–T conditions inferred for the garnet core and rim from intersecting garnet isopleths from Dragovic et al. (2012). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

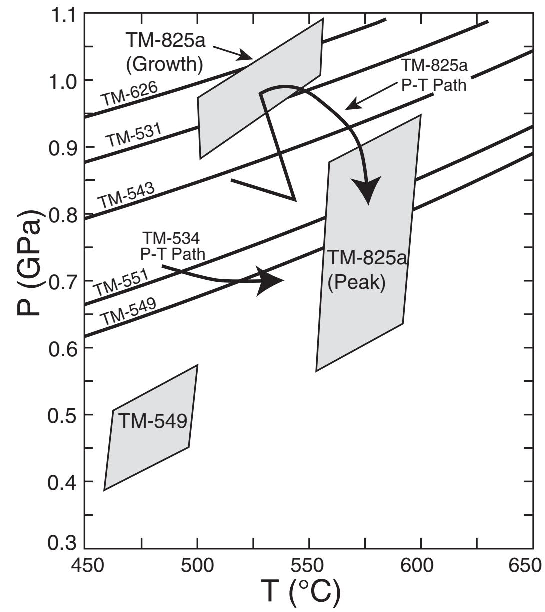

Fig. 5. P–T diagram showing peak metamorphic conditions and P–T paths inferred from garnet zoning from the east flank of the Strafford dome, Vermont from Menard and Spear (1994), Fig. 4) with the addition of QuiG barometry. P–T paths were inferred from both garnet zoning and core-rim geothermobarometry. QuiG barometry for sample TM-626 is consistent with the core P–T conditions for nearby sample TM-825a. However, the P–T path and rim P–T conditions for samples TM-825a and TM-534 are inconsistent with the uniformity of QuiG barometry throughout the garnet crystals. Peak thermobarometry for sample TM-549 underestimates the metamorphic pressure by 1.5 kbar compared with QuiG barometry and the P–T path for TM-543 is not supported by QuiG barometry on nearby samples.

isograd conditions by a considerable amount. The pressure determined from Raman shifts from a sample from this study (SPH99–7) were recalculated based on the experimental data of Thomas and Spear (2018) and is shown in Fig. 4. Rutile inclusions are common in garnet from this sample as reported by Spear et al. (2006) and provide a minimum temperature for garnet nucleation of around 525 °C, 2.0 GPa (Fig. 4). The calculated garnet isograd occurs at around 0.6–0.8 GPa (Fig. 4) indicating an overstepping of around 1.2–1.4 GPa. Equally significant, the garnet core and rim intersecting isopleths (colored lines with yellow fill in Fig. 4) imply garnet growth over a nearly isobaric heating path, a conclusion that is not supported by the QuiG data and rutile inclusion thermometry. The significance of this result is that it implies that the fluids produced during garnet growth may have been released suddenly following garnet nucleation rather than gradually as garnet grew along a subduction geotherm.

4.5. The Connecticut Valley Trough (CVT): prograde P–T paths

Menard and Spear (1994) published the results of thermobarometry and thermodynamic modeling based on garnet zoning for pelitic schists (quartz + plagioclase + muscovite + biotite + garnet ± staurolite ± kyanite) from the Connecticut Valley Trough (CVT) in central Vermont. Over fifteen samples from the same traverse examined by Menard and Spear (1994) have been examined using QuiG barometry by Wolfe and Spear, 2018 and Spear et al. (2014) and a comparison of results is shown in Fig. 5. It is important to note that in all of these samples, the maximum Raman shifts of quartz inclusions in garnet do not vary with position in the garnet and thus reflect a single isomeke, which again is interpreted as resulting from garnet having grown nearly isothermally and isobarically. The lowest grade, garnet-zone samples (TM-551 and TM-549) both record pressures from QuiG barometry that are 0.1–0.2 GPa higher than that reported by Menard and Spear from garnet-plagioclase-muscovite-biotite barometry (compare grey parallelogram for TM-549 with isomekes for TM-549 and TM-551, which is located near TM-549). This difference might be due, at least in part, to the calibration of the garnet-plagioclase-muscovite-biotite barometry used by Menard and Spear (1994) (i.e. Hodges and Crowley, 1985, based on Mt. Moosilauke samples and the Holdaway, 1971, triple point). Sample TM-531, which is located within a few tens of meters of sample TM-534, also records a higher pressure from QuiG barometry than that inferred from conventional thermobarometry. The other two samples (TM-543 and TM-626) are located along strike from TM-825a in the staurolite-kyanite zone. QuiG barometry for sample TM-626 is consistent with the inferred garnet core P–T conditions for sample TM-825a but the peak conditions for TM-825a are significantly lower pressure than the QuiG results. As mentioned above, there is no variation in maximum Raman shift from garnet core to rim in these samples, which is at odds with the P–T path for TM-825a calculated by Menard and Spear (1994) from zoning in garnet. This said, it was quite difficult to extract P–T paths from garnet zoning from the samples examined by Menard and Spear (1994) and several samples yielded no or very little paths at all (e.g. Figs. 5 and 6 of Menard and Spear, 1994).

4.6. The Connecticut Valley Trough (CVT): constraints on exhumation

QuiG barometry in principle has the ability to record various stages of garnet growth unhampered by assumptions regarding which phases are in chemical equilibrium. A recently published example is that of

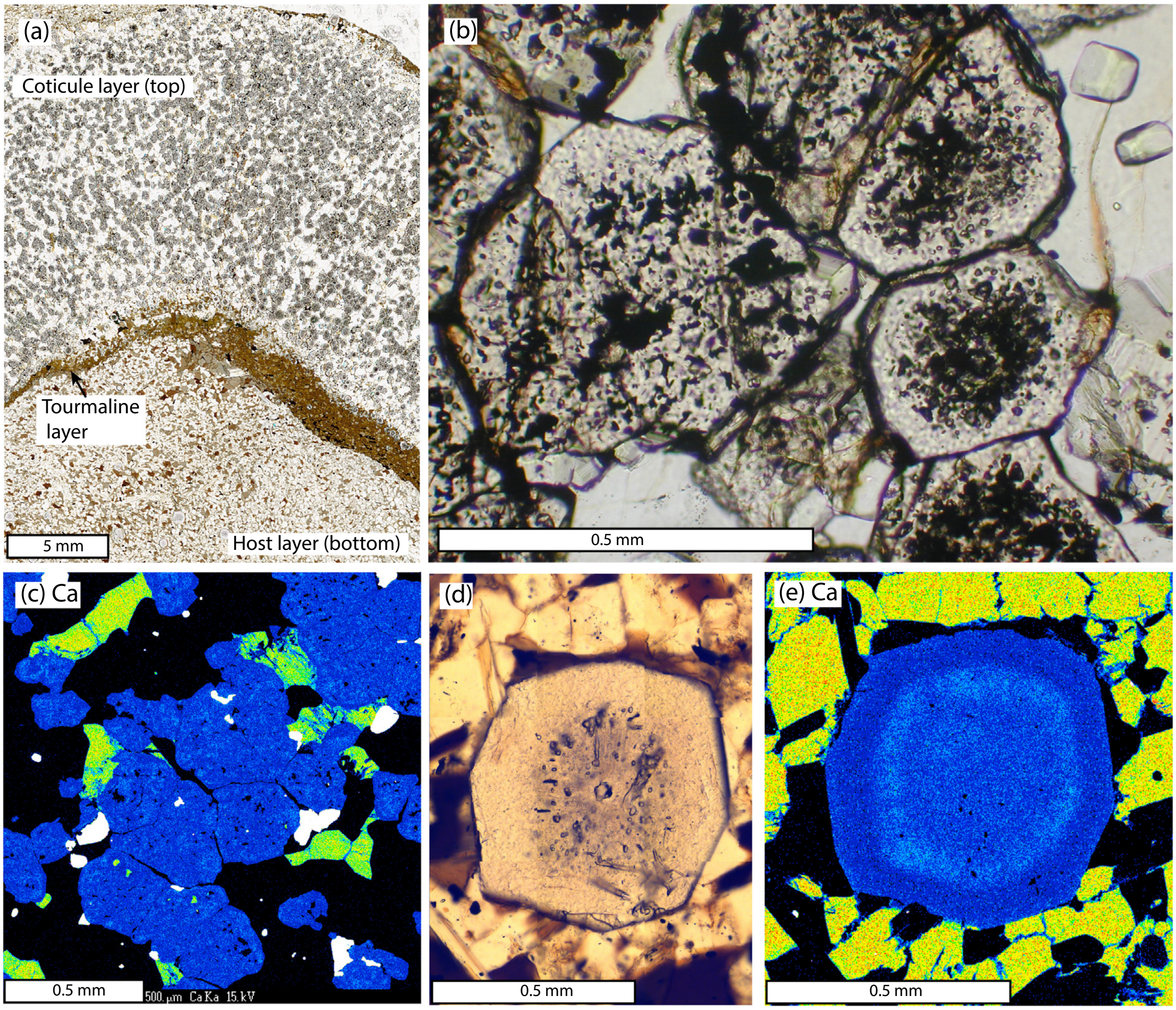

Fig. 6. (a) Photomicrograph of sample PMNN-3c showing strongly layered character. The coticule is the top layer, the host lithology is the bottom layer and the two are separated by a brown tourmaline-rich layer. (b) Photomicrograph of garnet with numerous inclusions of quartz and graphite from the top (coticule) layer. Note the inclusion-poor rims on some garnets. (c) Ca X-ray map of garnet from the coticule layer. Garnet is essentially unzoned. (d) Photomicrograph of garnet from the bottom (host) layer. Note the cloudy, quartz-rich core and the inclusion-poor rim. (e) Ca X-ray map of garnet from the bottom layer. Garnet is only weakly zoned in Ca. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Wolfe and Spear (2018) in which dissolution-reprecipitation reactions were interpreted to have occurred during exhumation and to have been catalyzed by infiltrating fluids. These reactions produced "cloudy" garnet rims characterized by numerous fluid inclusions and mantled by biotite ± muscovite ± plagioclase ± quartz that has partially replaced garnet. Quartz inclusions in garnet displayed positive Raman shifts in unaltered parts of the garnet and negative Raman shifts in the "cloudy" parts. The inclusions in the recrystallized garnet were interpreted to have initially formed during garnet growth at pressures of 0.85–1.0 GPa but were reset at pressures of around 0.3 GPa due to the recrystallization of garnet. Similar textures from the CVT had been studied previously (e.g. Hames and Menard, 1993) but the conditions of the dissolution-reprecipitation reaction were not constrained owing to the absence of suitable thermobarometers.

4.7. Polymetamorphism revealed in coticule, Perry Mtn. Formation, New Hampshire

The term coticule has been used to describe any garnet-quartz rock in which the garnet is abundant, fine-grained, and high in spessartine content (e.g. Herbosch et al., 2016). They are often small sedimentary units interbedded with more typical sedimentary or volcanogenic rocks. A sample from the Perry Mountain Formation in southeast New Hampshire has been examined using Raman spectroscopy and suggests a polymetamorphic history that was previously unknown in the area.

The sample discussed here (PMNN-3c) is from an outcrop of the Perry Mountain formation described in detail by Eusden (1988) and was part of a detailed geochemical study by Thomson (2001). The reader is referred to this latter paper for details of the geologic setting, outcrop appearance, and geochemistry of this and related samples. Thomson (2001) describes sample PMNN-3c as "type-3" (dark-colored, laterally extensive) and it is strongly layered and characterized by large variations in the ratio of garnet to other phases.

Sample PMNN-3c is composed of three distinct compositional bands (Fig. 6a). The top layer contains the phases garnet + quartz + plagioclase + apatite + graphite + chlorite ± biotite. Garnet in this layer is angular and up to 400 μm in diameter (although many garnets are less than 100 μm in diameter) with inclusion-rich cores and small inclusion-poor rims (Fig. 6b). Inclusions of quartz, graphite, apatite, and chlorite have been identified. Within the resolution of the electron microprobe, garnet is chemically homogeneous with spessartine content of approximately $X_{sps} = 0.25$. The bottom layer contains garnet

+ quartz + plagioclase + muscovite + biotite. Garnet in this layer is larger (400–600 μm diameter; Fig. 6d), much less abundant, contains a conspicuous inclusion-rich core and inclusion-poor rim, and is unzoned except in Ca (Fig. 6e). Between these two layers is a tourmaline-rich layer devoid of garnet (Fig. 6a).

4.7.1. P–T results

A summary of the P–T calculations is presented in Fig. 7. Both the upper (coticule) and lower (host) layers contain quartz inclusions in the inclusion-poor portions of the garnet rims that display negative Raman shifts of up to -1.9 cm^{-1}. Isomekes calculated from these shifts reveal pressures around 0.45 GPa at an assumed temperature of 550 °C. The bottom layer of sample PMNN-3c contains, in addition to garnet, the minerals biotite, muscovite, and plagioclase making it suitable for application of the garnet-biotite Fe—Mg exchange thermometer and the garnet-plagioclase-biotite-muscovite barometer. The P–T conditions recorded by these thermobarometers are slightly lower pressure than those recorded by QuiG barometry, as indicated by the grey polygon in Fig. 7b. The reason is likely similar to the issues with the calibration of the GPMB barometer as suggested for the discrepancy in conditions from the Orfordville belt.

Garnet from both layers also contain quartz inclusions in the vicinity of their cores that record positive Raman shifts on the order of 2 cm^{-1}. Isomekes calculated from these shifts record pressures of around 0.6 to 1.0 GPa, depending on the temperature (Fig. 7). Graphite barometry from graphite inclusions in garnet cores records pressures of 0.87–1.0 GPa. Maximum temperatures recorded by graphite thermometry on graphite inclusions in the cores of the upper (coticule) garnet are on the order of 600–625 °C. Combining this result with graphite and QuiG barometry on the cores of the garnet suggests that the garnet cores experienced metamorphic conditions on the order of 600–625 °C, 0.85–1.0 GPa.

A further observation supports the interpretation that this sample experienced two different metamorphic pressures. All of the garnet crystals in the coticule layer contain inclusions and nearly all garnet crystals have not experienced any cracking. However, there are a number of crystals, mostly near the tourmaline layer, that contain large inclusions of quartz and/or biotite and that display radial cracks (Fig. 8a), most of which are filled with chlorite. Assuming that the initial metamorphism (M1) occurred at 625 °C, 0.9 GPa and the second metamorphism (M2) occurred at 550 °C, 0.3 GPa, the pressure of a quartz inclusion at the temperature of M2 would have been around 0.78 GPa (Fig. 8b). An interpretation of this observation is that this internal pressure is insufficient for a small quartz inclusion generate a crack in the garnet host but for sufficiently large inclusions this amount of internal pressure did produce radial cracks in small garnets. It is not believed that simple decompression from the M1 conditions of around 0.9 GPa and 625 °C to the surface would have been sufficient to crack the garnets because there are numerous examples of large quartz inclusions in garnet from various Barrovian terranes (e.g. the Connecticut Valley Trough in Vermont) where the garnet has not cracked. For comparison, quartz inclusions formed at the conditions of M1 would record an internal pressure (Pinc) of only 0.27 GPa at 1 bar, 298 °C, which is apparently insufficient to crack a garnet. In other words, if the garnet crystals had not experienced both M1 and M2 events, they would not have cracked. The observation that the cracks are filled with chlorite supports the interpretation that the cracks occurred at the temperature of M2.

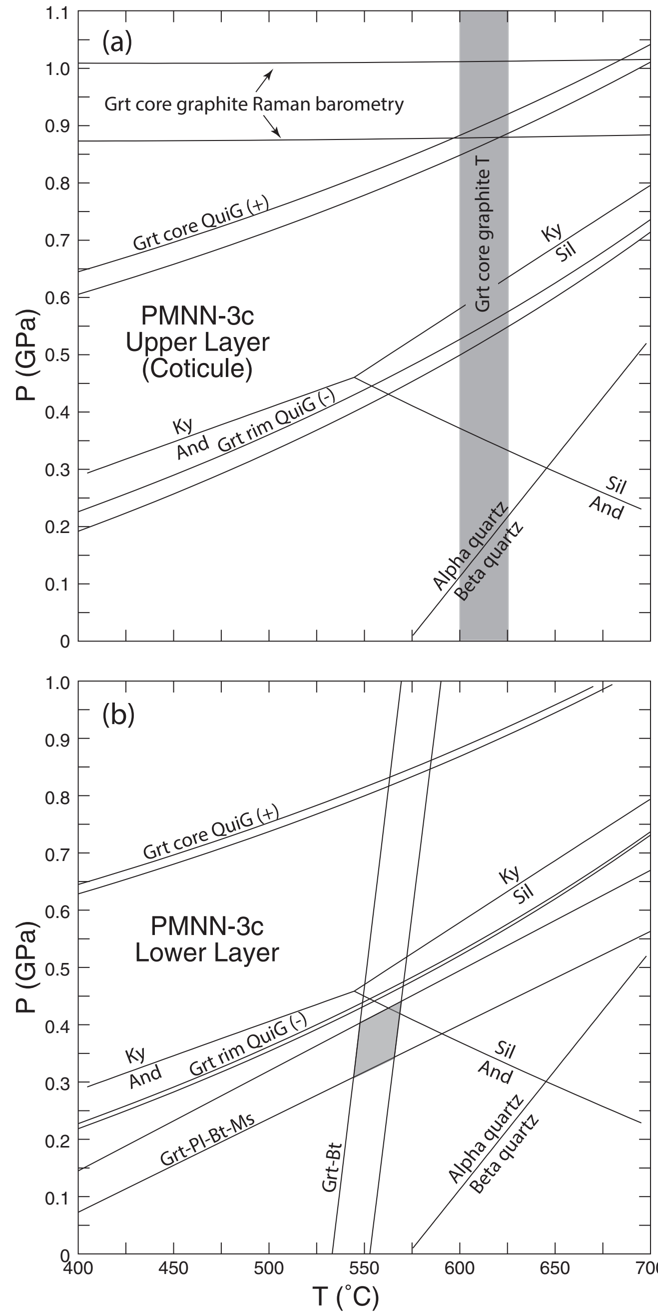

Fig. 7. P–T diagrams summarizing the results of quartz inclusion barometry (QuiG), graphite inclusion barometry, graphite thermometry (vertical grey band), garnet-biotite thermometry and garnet-plagioclase-biotite-muscovite barometry for sample PMNN-3c. (a) Results from the upper (coticule) layer. (b) Results from the lower (host) layer. Grey parallelogram shows the intersection of garnet – plagioclase – biotite – muscovite barometry and garnet – biotite thermometry and reflects the peak P–T conditions for the second metamorphism (M2). Note the approximately 4 kbar difference in QuiG barometry between core and rim of garnet from both layers. Ky = kyanite; Sil = sillimanite; And = andalusite; Grt = garnet, Bt = biotite; Pl = plagioclase; Ms. = muscovite.

4.7.2. Interpretation

The regional metamorphic P–T conditions for the Perry Mountain Formation in southeastern New Hampshire have been constrained by Eusden et al. (1984) and Eusden (1988) and are characterized by at least two low-pressure (andalusite facies series) metamorphic events, presumably associated with thermal aureoles surrounding nearby plutons. Similar overlapping low pressure events have been described in detail for western Maine by Guidotti (1970, 2000). The results of the present study for the garnet rim/matrix thermobarometry are consistent with these assessments of the regional metamorphic conditions.

The higher pressure metamorphic conditions implied from thermobarometry on garnet cores is, however, not consistent with any known metamorphic conditions from the region and the reason for this high pressure "event" is not clear but two interpretations are possible. The first is that the garnet cores are exotic and may represent a detrital accumulation. This interpretation is consistent with the recorded

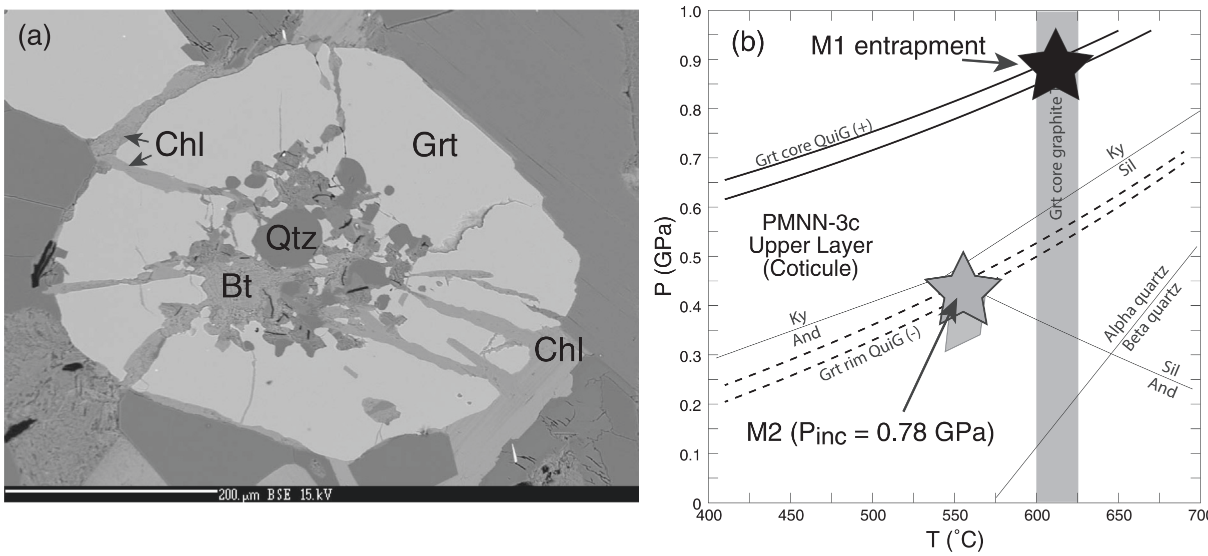

Fig. 8. (a) BSE image of garnet in the coticule immediately above the tourmaline layer (Fig. 6a). Note the large inclusions of quartz and biotite and the radial, chlorite-filled cracks. (b) P–T diagram showing the conditions of the early (M1) metamorphism at ca 625 °C, 0.9 GPa and the later (M2) metamorphism at ca 550 °C, 0.3 GPa. The inclusion pressure (P_{inc}) during M2 would have been 0.78 GPa which was sufficient for large quartz inclusions to produce cracks in host garnet.

P–T conditions in the garnet cores being so much higher pressure than the regional low-pressure mineral assemblages (e.g. andalusite-bearing). This interpretation is also consistent with the angular nature of many of the garnet cores in the coticule layer (Fig. 6b). The irregular shape of these garnet cores is in contrast to many reported coticules in which garnets are relatively idioblastic (e.g. Thomson, 2001).

There are two arguments against the interpretation that these are detrital garnets. Coticule from other localities are often associated with volcanic exhalents (e.g. Slack et al., 2000; Spry et al., 2000). The tourmaline layer in Fig. 6a is characteristic of these types of occurrences and there is no ready explanation why such a tourmaline layer should exist in a detrital deposit such as a beach sand. Secondly, garnet from both the coticule layer and the lower host layer have apparently experienced two metamorphic events at different pressures. Whereas the coticule could have formed from a heavy mineral detrital deposit, it is difficult to envision how the lower layer with sparsely distributed garnet could have formed in this way.

The second possibility is that these garnet cores record an earlier Acadian metamorphic event that was previously unrecognized and was nearly completely erased during the subsequent, low-pressure metamorphism. This possibility might be further examined by a more regional study of garnet parageneses in the Perry Mountain Formation. In addition, dating of the garnet cores might provide additional constraints on the significance of this possible polymetamorphism. Whichever explanation is correct (detrital or polymetamorphic), it is clear that QuiG barometry has the potential of preserving more than a single metamorphic event — in this case high P cores and low P rims — and that these distinct P–T conditions are not evident in the garnet zoning.

5. Discussion

The above examples demonstrate that in some cases QuiG barometry provides constraints on metamorphic P–T conditions that are consistent with previous estimates based on classical thermobarometry and thermodynamic calculations but in other cases there are major discrepancies. The question of whether QuiG, and other inclusion barometry, is providing an accurate assessment of the conditions of garnet nucleation and growth, is of considerable importance because many studies have utilized garnet zoning to infer P–T paths and may need to be reevaluated. Related to this question is the recognition that the shape of garnet zoning alone (e.g. bell-shaped Mn profiles) cannot be used to determine whether garnet has grown along a P–T path with growth driven by changing P–T conditions or whether garnet has grown under nearly isothermal, isobaric conditions driven by available affinity due to overstepping, as has been discussed by Spear (2017) and Spear and Wolfe (2018).

Furthermore, the results of this study suggest that QuiG, and presumably other types of inclusion barometry, may preserve different aspects of garnet growth in complex terranes. The advantages of QuiG and other inclusion-based methods are that they are fairly easy to apply, require far less data acquisition than traditional methods, and are subject to fewer assumptions than either thermobarometry or thermodynamic calculation methods. It remains to be seen what are the limits of inclusion barometry since there are few studies that have employed it. A recent regional study of the classic Barrovian terrane in the Connecticut Valley Trough of Vermont suggests that QuiG provides consistent results over a regional scale that are consistent with traditional thermobarometric methods and is also capable of providing information not accessible by those traditional methods (Wolfe and Spear, 2018). It is very promising, therefore, that inclusion barometry will be a very useful tool in the solution of tectonic problems.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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