Pressure-temperature evolution and thermal regimes in the Barrovian zones, Scotland

SARAH H. VORHIES¹* & JAY J. AGUE^{1,2}

¹Department of Geology and Geophysics, Yale University, PO Box 208109, New Haven, CT 06520-8109, USA ²Peabody Museum of Natural History, Yale University, New Haven, CT 06511, USA *Corresponding author (e-mail: sarah.vorhies@yale.edu)

Abstract: We constrain the P-T evolution of the Barrovian metamorphic zones from the southwestern to the northeastern coasts of Scotland using thermobarometry and pseudosection analysis based on mineral composition data, garnet zoning profiles and 2D garnet maps. Twenty-five samples were investigated from the garnet to the sillimanite zones. In the western half of the field area there was relatively high-P metamorphism (0.9–1.1 GPa) followed by near-isothermal decompression. In and around the Barrovian type area of Glen Clova maximum pressures were also high (c. 0.8-0.9 GPa); however, peak-T conditions were driven by a brief (of the order of 1 Ma or less) thermal pulse or pulses during exhumation at c. 0.6 GPa. Pressures at peak-T conditions along the eastern coast were the lowest observed, c. 0.4-0.5 GPa. These rocks were probably affected by the same thermal pulse activity evident around Glen Clova. All three regions initially developed during regional metamorphism associated with thermal relaxation of tectonically overthickened crust. The eastern part of the sequence, including Glen Clova, is fundamentally different from the western part because it required additional advective heat input to achieve peak thermal conditions. This heat was probably supplied by synorogenic magmas (e.g. Newer Gabbros) and the associated elevated crustal heat flow.

Supplementary material: Electron microprobe methods, mineral and rock analyses, mineral activity– composition relations, criteria for identifying prograde mineral compositions, pseudosection and diffusion modelling methods, and profiles of X_{Alm} and X_{Prp} from garnets in Figures 7–10 are available at http:// www.geolsoc.org.uk/SUP18491.

Barrovian-style metamorphism has been found in mountain belts across the world at least as far back in geological history as the Proterozoic. In his classic studies of the Scottish Highlands, Barrow (1893, 1912) concluded that pelitic rocks undergoing progressive regional metamorphism would exhibit systematically changing mineral assemblages as a function of metamorphic grade. The Barrovian type locality in the Scottish Highlands has been the focus of extensive investigation for over a century, yet questions remain regarding the peak pressures (P) and temperatures (T) of metamorphism, as well as regional P-T paths. It is clear from the mineralogy as well as available thermobarometric studies that different areas, from the northeastern coast near Aberdeen to the southwestern coast, were subject to different peak metamorphic P-T conditions (e.g. Tilley 1925; Chinner 1961, 1966; Harte & Johnson 1969; Atherton 1977). Moreover, strong evidence for multiple phases of metamorphism in some parts of the sequence has been discovered through study of mineral textural relationships, garnet zoning profiles, and timing and time-scale relationships (e.g. McLellan 1985; Ague & Baxter 2007).

Conventional models for Barrovian metamorphism involve conduction-dominated thermal relaxation of overthickened crust during exhumation (e.g. England & Richardson 1977; England & Thompson 1984; Thompson & England 1984). This type of model predicts that rocks will spend c. 10 Ma or more at or near peak thermal conditions, and that peak conditions will be reached at different times in different index mineral zones. Furthermore, the total time scales of orogeny needed to achieve high-grade conditions are predicted to be several tens of millions of years. Recent studies of Barrovian metamorphism in Scotland, however, are at variance with these predictions. For example, Oliver *et al.* (2000, 2008), Baxter *et al.* (2002) and Dewey (2005), among others, argued that the entire Grampian Orogeny took place over a time period as short as 10-15 Ma. Moreover, peak thermal conditions in the type locality were roughly synchronous across several index mineral zones, and almost certainly required a significant component of pulsed, advective magmatic heat transfer (Baxter *et al.* 2002; Ague & Baxter 2007). Heat input associated with magmatic activity has also been described in the Connemara region of Ireland to the SW (e.g. Yardley *et al.* 1987), in the Attic Cycladic Metamorphic Belt of Greece (Wijbrans & McDougall 1986, 1988) and in metamorphic core complexes around the world (Lister & Baldwin 1993, and references therein).

Quantitative thermobarometry provides a valuable, independent, test of the emerging picture of Barrovian metamorphism in the type locality. Classic studies of the region, however, have often not provided full mineral chemistry from analyses (see Baker 1985; Watkins 1985) so it is difficult to accurately recalculate P-T conditions using modern calibrations. In addition, the electron microprobe work in some earlier studies (e.g. Sivaprakash 1982) was carried out using energy-dispersive spectrometry (EDS), which is less accurate and precise than wavelength-dispersive spectrometry (WDS). Modern WDS analysis and the better spatial resolution for chemical maps that is now possible provide a new framework for understanding P-T evolution.

We present new mineral chemistry data, P-T estimates, and pseudosection results for a suite of 25 metapelite samples. The rocks range in grade from the garnet to the sillimanite zones.

Importantly, the area sampled extends from the northeastern to southwestern extremes of the Barrovian zones, making it possible to construct an internally consistent P-T framework for the entire region (Fig. 1). Our primary goals are to: (1) estimate peak P-T conditions and test for variations in conditions across the field area using both thermobarometry and pseudosection methods; (2) use garnet chemical profiles and maps to elucidate multiple growth stages; (3) use growth zoning preserved in garnet together with pseudosection analysis in an effort to reconstruct the P-T paths of metamorphism. In addition, we re-examine the garnet

diffusion profile modelling of Ague & Baxter (2007) to test those workers' conclusions regarding rapid thermal pulses of peak metamorphism.

Geological setting

The rocks sampled in this study are pelitic metasediments of the Dalradian Supergroup. They are from the Grampian Highlands Terrane, which lies between the Highland Boundary Fault and the Great Glen Fault (Fig. 1). The Dalradian metasediments also



Fig. 1. Map of the Scottish Highlands indicating metamorphic zones, sample locations, and locations of igneous rocks. The three major regions are: I, along the eastern coast; II, Glen Clova and surrounding glens; III, the western half of the Highlands. Au, Auchlee Granite; Ab, Aberdeen Granite; IG, Insch Gabbro; MC, Morven–Cabrach Gabbro; PSZ, Portsoy Shear Zone; St, Strichen Granite; Tf, Tillyfourie Granite. Modified from Atherton (1977), Baker (1985), Ague & Baxter (2007) and British Geological Survey (2007).

extend into Connemara, Ireland, where much of the metamorphic history is similar (e.g. Leake 1986; Chew *et al.* 2010). The original sediments were marine successions deposited on the margin of Laurentia. The margin started out as a rift associated with the break-up of Rodinia, and then was a passive margin on the Iapetus Ocean (MacDonald & Fettes 2007). Deposition continued until the initiation of the closure of Iapetus around 500 Ma. Around 480 Ma the loading of the Dalradian sediments began as Laurentia started to collide with the Midland Valley Arc, outboard microcontinents, and the Highland Border Ophiolite (Oliver *et al.* 2008; Chew *et al.* 2010).

Timing of metamorphism

Garnet-whole-rock Sm-Nd dating establishes that garnets grew over a *c*. 8 Ma interval from about 473 to 465 Ma (Oliver *et al.* 2000; Baxter *et al.* 2002). The time lapse between peak *T* attainment in the garnet and kyanite-sillimanite zones in Glen Clova was short or nonexistent, only 2.8 ± 3.7 Ma (Baxter *et al.* 2002).

Breeding *et al.* (2004) carried out sub-micrometre-scale, ionprobe depth-profiling of zircons from a garnet zone sample studied by Ague (1997) from the Stonehaven coast. The outermost (*c*. 1 μ m) edge of zircon from a vein margin had a concordant U–Pb age intercept of 462 ± 9 Ma. Breeding *et al.* (2004) concluded that this age reflects zircon growth or recrystallization during fluid infiltration and metamorphism; notably, it overlaps the *c.* 465–468 Ma garnet results of Oliver *et al.* (2000) and Baxter *et al.* (2002).

The pre-, syn-, and post-metamorphic igneous intrusions in the region also provide constraints on the tectonic activity during the orogeny (Fig. 1). The intrusions that are broadly synmetamorphic include the Auchlee Granite (475 Ma; Oliver *et al.* 2008), the Morven–Cabrach Gabbro (472 Ma; Rogers *et al.* 1994), the Tillyfourie Granite (471 Ma, Oliver *et al.* 2008), the Aberdeen Granite (470 Ma; Kneller & Aftalion 1987), the Insch Gabbro (468 Ma; Dempster *et al.* 2002), and the Strichen Granite (467 Ma; Oliver *et al.* 2000).

Four major deformational events affected the Dalradian (D_1 – D_4 ; e.g. Harte *et al.* 1984). Based primarily on textural evidence, McLellan (1989) came to the following general conclusions regarding the relative timing of metamorphic mineral growth and deformation in the Eastern Highlands: (1) garnet growth was largely syn- D_2 followed by another phase of growth syn- to post- D_3 ; (2) staurolite growth was syn- to post- D_2 ; (3) kyanite growth was pre- to syn- D_3 ; (4) sillimanite growth was syn- to post- D_3 . It is generally accepted that the peak thermal conditions were attained roughly syn- D_3 (Harte *et al.* 1984; McLellan 1985).

Previous work

Thermobarometry

Existing thermobarometry covers what we summarize here as three major regions, delineated primarily by regional isograd patterns (Fig. 1): the eastern coast (referred to herein as Region I), Glen Clova and nearby glens including Glen Esk and Glen Muick (Region II), and the western half of the Highlands (Region III). In Region III the isograds are widely spaced, progressing from the chlorite zone adjacent to the Highland Boundary Fault into the biotite and garnet zones farther north. In Regions I and II the zones are markedly thinner near the Highland Boundary Fault. Moreover, the higher-grade zones (staurolite, kyanite, and sillimanite) are nearly restricted to Regions I and II. The highest-grade area, at the heart of Region II, was metamorphosed at upper amphibolite- to granulite-facies conditions; metapelitic rocks are characterized by sillimanite + K-feldspar-bearing mineral assemblages (Baker & Droop 1983; Baker 1985).

In Region I, on the east coast between Stonehaven and Aberdeen, *T* increased from *c*. 375 °C in the chlorite zone, to *c*. 535 °C in the garnet zone and to *c*. 585–600 °C in the staurolite zone (Ague 1997; Masters *et al.* 2000). Ague (1997) estimated a *P* of 0.38 GPa in the garnet zone, consistent with regional phase relations (e.g. Carmichael 1978; Droop & Harte 1995). The results of Viete *et al.* (2011*a*) are similar to those of previous studies, but their *P* estimates are somewhat higher for the staurolite and sillimanite zones (0.5–0.6 GPa).

Published thermobarometry has focused largely on Region II, which includes the Barrovian type locality of Glen Clova (Barrow 1893). In and around Glen Clova, McLellan (1985) reported T ranging from as low as 465 °C in the staurolite zone to as high as 625 °C in the kyanite zone. Pressures were found to be between c. 0.45 and c. 0.8 GPa. For the kyanite zone, Baker (1985) calculated T between c. $610 \,^{\circ}$ C and c. $690 \,^{\circ}$ C at c. 0.6-0.7 GPa. Ague *et al.* (2001) estimated average peak-T conditions of c. 660 °C at c. 0.6 GPa for the sillimanitemuscovite zone in the northern part of Glen Clova, consistent with the earlier results of McLellan (1985) and those of Viete et al. (2011a) for nearby Glen Esk. Dempster (1985) concluded that peak T for the staurolite, kyanite, and sillimanite zones increased from c. 520 °C to c. 650 °C to the east of Glen Clova in Glens Lethnot and Esk. Pressures were estimated in the kyanite and sillimanite zones and were between about 0.55 and 0.75 GPa. Baker (1985) also investigated an area c. 30 km north of Glen Clova in the kvanite and sillimanite zones: T estimates range from 520 to 625 °C at c. 0.74 GPa. Finally, Baker (1985) reported conditions of c. 800 °C and 0.9-1.0 GPa for the highest-grade sillimanite-K-feldspar zone in Region II.

There have been somewhat fewer P-T studies done in Region III. For the southwesternmost Highlands, Skelton *et al.* (1995) examined pyrophyllite-kyanite equilibrium relations, reviewed previously published work (e.g. Graham *et al.* 1983; Dymoke 1988), and reported *T* increasing from *c.* 410 °C in the lower greenschist facies to 500–550 °C in the garnet zone. Pressure estimates for this area (Graham *et al.* 1983; Dymoke 1988; Skelton *et al.* 1995) are based on phengite geobarometry (e.g. Massonne & Schreyer 1987) and range from about 0.9 to 1.2 GPa. Similar high pressures have been estimated elsewhere in Region III by Sivaprakash (1982) and Watkins (1985).

Garnet profiles

Chemical zoning in Dalradian garnets has been investigated in relatively few studies, and we are unaware of any papers that compare regional zoning systematics from the SW to the NE. Additionally, the garnet profiles in many published studies lack the spatial resolution to constrain P-T histories or to perform diffusion modelling. Chemical profiles were presented and/or discussed by, for example, Atherton (1968), Baker (1985), Dempster (1985), McLellan (1985), Ayres & Vance (1997), Ague *et al.* (2001), Ague & Baxter (2007) and Viete *et al.* (2011*a*).

Methods

Twenty-five samples from the garnet, staurolite, kyanite, and sillimanite zones were investigated (Figs 1 and 2; Table 1). For brevity, the sample prefix JAB is omitted in the text. The low



Fig. 2. Detail maps of Regions I and II indicating metamorphic zones and sample locations (see Table 2). Samples 46B, 60A and 62A discussed in the text are all represented as part of the 'Ague *et al.* 2001' location. Index mineral zone shading is as in Figure 1.

sample density in Region III is due to the relative rarity of garnet (needed for thermobarometry) there. Compositions of plagioclase, biotite, muscovite, garnet and ilmenite were acquired, as were chemical profiles of garnets. Approximately five spots were analysed for each mineral; garnet profiles consisted of 25–85 spots depending on the garnet size. Profiles were collected across the largest garnets in thin section, in an attempt to sample through the geometric cores of the crystals.

P-T conditions for most samples were estimated using the three possible equilibria (any two of which are independent) between pyrope, almandine, grossular, muscovite, phlogopite, annite, anorthite and quartz (Ferry & Spear 1978; Ghent & Stout 1981). For samples containing aluminosilicate minerals we used the garnet–aluminosilicate–plagioclase (GASP) barometer as well (Ghent 1976). Rutile and ilmenite coexist in garnet rims in sample 257A, so the garnet–rutile–ilmenite–plagioclase–quartz barometer was applied (Bohlen & Liotta 1986). P-T estimates were made using version 2.3 of the winTWQ program (Berman 1988, 1991, 2007; database 2.32) and version 3.33 of Thermo-Calc (Powell & Holland 1988; Holland & Powell 1998; Powell *et al.* 1998; Holland & Powell 2003).

Pseudosections and isopleths were calculated using the Theriak-Domino program, version 01.08.09 (de Capitani & Petrakakis 2010). This program allows for the use of two databases, both of which were used for comparison. One (JUN92.bs) is based largely on the winTWQ database, and the other (tcdb55c2d.txt) is based on ThermoCalc. The standard heat of formation for Mgstaurolite was changed in JUN92.bs as described by Bucholz & Ague (2010).

P-T conditions for a Glen Muick metabasite (sample CL2H; Baker & Droop 1983) were recalculated using the Kohn & Spear (1990) hornblende–garnet–plagioclase barometer and the Ravna (2000) garnet–clinopyroxene thermometer. We also used the GASP barometer reaction to recalculate the pressure for two nearby sillimanite–K-feldspar samples (7 and 430) using the reported temperatures (Baker 1985).

Results and interpretations

Thermobarometry

P-T estimates calculated using winTWQ and ThermoCalc agree closely (Table 2). Average per cent differences between the estimates from the two databases are 5.5% for pressure (0.04 GPa) and 3.5% for temperature (20 °C); results from winTWQ are shown in the figures (Fig. 3). Table 3 presents *P* and *T* estimates for additional samples referenced in the text. Multiple equilibria for low-variance mineral assemblages from Regions I–III are plotted in Figure 4 to assess the degree of mineral equilibration. Clearly, intersections between reactions cluster tightly in *P*–*T* space, suggesting that the mineral compositions preserve a close approach to equilibrium (see Berman 1991). Standard deviations on the *P*–*T* intersections (Berman 1991) are <±0.025 GPa and <±18 °C in all cases.

Uncertainties on P-T estimates are difficult to quantify given the range of sources of error. Uncertainties on the chemical analyses, thermodynamic data, activity models and degree of equilibration all play a role. For graphical representation and petrological interpretation, we assign representative 50 °C and 0.2 GPa uncertainty ranges on all results. These ranges are comparable with the maximum differences between T and Pestimates calculated using the winTWQ and ThermoCalc databases (60 °C and 0.12 GPa). It is important to note that throughout this study we are primarily concerned with comparing pressures and temperatures between regions rather than making distinctions between similar P-T conditions. Because nearly all thermobarometric calculations were carried out using the same two programs and the same internally consistent datasets, the relative uncertainties on the P-T estimates will probably be considerably smaller than those we assign here (Berman 1991; Worley & Powell 2000).

In Region I, *T* estimates increase from *c*. 375 °C in the chlorite zone (Masters *et al.* 2000), to *c*. 535 °C in the garnet zone, to 575–600 °C in the staurolite zone, and finally to *c*. 620 °C in the sillimanite–muscovite zone (Fig. 3). Pressure estimates are remarkably consistent, ranging mostly between *c*. 0.4 and *c*. 0.55 GPa regardless of grade. These *P* and *T* estimates are plotted as functions of distance from the Highland Boundary Fault in Figure 5. Notably, there is an extremely steep metamorphic field temperature gradient (MFTG) in excess of 110 °C km⁻¹ across the first 2 km north of the fault. Consequently, the boundaries between metamorphic zones here are very closely spaced, reflecting a primary feature of the metamorphism (Dempster *et al.* 2000), later deformation (Harte & Hudson 1979; Harte & Dempster 1987), or some combination of these. In contrast,

-				
Sample name	Mineral assemblage used for thermobarometry*	Region	Zone	
JAB 15D	Bt-Grt-Ms-Pl	Ι	St	
JAB 18A	Bt-Grt-Ms-Pl	Ι	St	
JAB 21B	Bt-Grt-Ms-Pl-Qtz-Sil	Ι	Sil-Ms	
JAB 146A1	Bt-Grt-Ms-Pl	III	Grt	
JAB 152A3	Bt-Grt-Ms-Pl	III	Grt	
JAB 156A1	Bt-Grt-Ms-Pl	Ι	St	
JAB 159A	Bt-Grt-Ms-Pl	III	Grt	
JAB 160A	Bt-Grt-Ms-Pl	III	Grt	
JAB 161A	Bt-Grt-Ms-Pl	II	St	
JAB 162A	Bt-Grt-Ms-Pl	II	St	
JAB 164A	Bt-Grt-Ms-Pl	II	St	
JAB 235A1	Bt-Grt-Ms-Pl	II	Grt	
JAB 240D1	Bt-Grt-Ms-Pl	II	St	
JAB 242A	Bt-Grt-Ms-Pl	II	Ky	
JAB 245A	Bt-Grt-Ky-Ms-Pl-Qtz	II	Ky	
JAB 253A	Bt-Grt-Ms-Pl	II	Grt	
JAB 255A	Bt-Grt-Ms-Pl	III	Grt	
JAB 257A	Bt-Grt-Ilm-Ms-Pl-Qtz-Rt	III	Grt	
JAB 258D	Bt-Grt-Ms-Pl-Qtz-Sil	II	Sil-Ms	
JAB 261B1	Bt-Grt-Ms-Pl-Qtz-Sil	II	Sil-Ms	
JAB 262A1	Bt-Grt-Ky-Ms-Pl-Qtz-Sil	II	Sil-Ms	
JAB 264A2	Bt-Grt-Ms-Pl-Qtz-Sil	II	Sil-Ms	
JAB 268A	Bt-Grt-Ms-Pl	Ι	Sil-Ms	
JAB 269B	Bt-Grt-Ms-Pl	Ι	Sil-Ms	
JAB 277D1	Bt-Grt-Ms-Pl	Ι	St	
JAB 284A†	Bt-Grt-Kfs-Pl-Qtz-Sil	II	Sil-Kfs	

Table 1. Samples

* Mineral abbreviations after Kretz (1983).

† Thermobarometry not performed; see text and Table 3.

 Table 2. Pressure and temperature estimates

Sample	<i>P</i> (G	iPa)	Т		Region	Zone
	TWQ*	TC*	TWQ	TC		
JAB 15D	0.446	0.464	583	555	Ι	Staurolite
JAB 18A	0.489	0.525	604	599	Ι	Staurolite
JAB 21B	0.434	0.476	620	623	Ι	Sillimanite-muscovite
JAB 156A1	0.525	0.528	589	574	Ι	Staurolite
JAB 268A	0.462	0.511	607	597	Ι	Sillimanite-muscovite
JAB 269B	0.449	0.573	615	623	Ι	Sillimanite-muscovite
JAB 277D1	0.402	0.407	573	543	Ι	Staurolite
JAB 161A	0.658	0.655	613	609	II	Staurolite
JAB 162A	0.659	0.647	594	584	II	Staurolite
JAB 164A	0.829	0.853	644	662	II	Staurolite
JAB 235A1	0.647	0.626	556	527	II	Garnet
JAB 240D1	0.803	0.754	587	546	II	Staurolite
JAB 242A	0.572	0.525	539	492	II	Kyanite
JAB 245A	0.636	0.634	595	586	II	Kyanite
JAB 253A	0.507	0.461	503	441	II	Garnet
JAB 258D	0.602	0.624	613	626	II	Sillimanite-muscovite
JAB 261B1	0.647	0.651	630	640	II	Sillimanite-muscovite
JAB 262A1	0.634	0.633	610	613	II	Sillimanite-muscovite
JAB 264A2	0.600	0.603	611	608	II	Sillimanite-muscovite
JAB 159A	1.115	1.042	603	601	III	Garnet
JAB 160A	1.106	1.018	580	562	III	Garnet
JAB 255A	0.664	0.633	584	546	III	Garnet
JAB 257A	0.904	0.833	568	542	III	Garnet
JAB 146A1	1.139	1.104	633	651	III	Garnet
JAB 152A3	0.961	0.820	503	455	III	Garnet

* TWQ and TC denote estimates made using winTWQ and ThermoCalc, respectively.

beyond this region temperatures vary little and increase slightly from the staurolite to the sillimanite–muscovite zone.

T and P profiles for Region II through Glen Clova and on to Glen Muick (Fig. 6) are markedly different from the profiles for

Region I. Temperatures increase with distance from the Highland Boundary Fault, but relative to Region I the MFTGs are not as steep and the zone boundaries are farther apart. Temperature estimates increase from c. 500 °C in the lowermost garnet zone



Fig. 3. Pressure and temperature estimates for all samples considered in this study. The results shown were calculated using winTWQ with the exception of one of the Glen Muick samples (see Table 3). Dashed arrows represent inferred retrograde paths of indicated samples. Samples discussed specifically in the text are labelled with their sample number.

to c. 660 °C in the sillimanite–muscovite zone. Farther north, temperatures in the sillimanite–K-feldspar zone of Glen Muick are considerably higher, in the range of 750–800 °C (Baker 1985; this study). Calculated P values increase from c. 0.5 GPa in the garnet zone 4–5 km from the fault, to c. 0.8 GPa in the staurolite zone 8 km from the fault. This trend is disrupted by rocks in the kyanite and sillimanite–muscovite zones, which yield P estimates in the vicinity of 0.6 GPa. P estimates then return to higher values of c. 0.95 GPa in the sillimanite–K-feldspar zone of Glen Muick.

We infer that several of the amphibolite-facies rocks in Region II preserve retrograde temperatures. The most glaring examples are 242A from the kyanite zone (<550 °C; Figs 3 and 6), and several sillimanite–muscovite zone rocks that yield estimates below 650 °C. Considerable increases in Mn and decreases in Mg/Fe at the rims of these garnets indicate retrograde equilibration (see Kohn & Spear 2000; see below), consistent with observed garnet resorption and retrogressive chlorite growth at garnet rims.

Pressure estimates for Region III are high and range from c.

0.9 to c. 1.1 GPa. Temperature estimates increase from c. 500 °C at c. 0.9 GPa to c. 630 °C at c. 1.1 GPa (Fig. 3). Even though temperatures could reach over 600 °C, all samples from Region III are petrographically in the garnet zone. We conclude that staurolite, kyanite and sillimanite did not form at these high temperatures because the pressures were also high (see Powell *et al.* 1998; Caddick & Thompson 2008). Our results confirm the evidence for relatively high-*P* conditions presented in earlier studies (see above). However, unlike some previous estimates, which predicted blueschist-facies metamorphism, our *P*–*T* estimates fall within the greenschist or amphibolite facies and are consistent with observed mineral assemblages (see Diener *et al.* 2007).

Several samples fall outside the general region boundaries in Figure 3 (164A, 240D1, 255A); these are examined further below in the context of regional P-T paths.

Garnet profiles

Garnet zoning profiles are discussed by region in order of increasing complexity, from Region III to I to II.

Garnet profiles: Region III. The garnet profiles from Region III are the simplest of the three regions. The garnets are characterized by high X_{Grs} above 0.2 (Fig. 7; mineral abbreviations after Kretz 1983). The Ca-rich nature of the garnets reflects the high pressures of crystallization in this region, because although the bulk-rock composition is an important control on the absolute grossular content, high pressures generally favour elevated grossular mole fractions (Ghent 1976; Ghent & Stout 1981). The $X_{\rm Prp}/X_{\rm Alm}$ ratios generally increase toward the rim, consistent with the Fe-Mg partitioning expected for the garnet-biotite equilibrium during progressive heating (Ferry & Spear 1978). The Mn contents of three of the four examples decrease toward the rim, as expected for Rayleigh fractionation (Hollister 1966) and for changing equilibrium partitioning values during heating and compression (Caddick & Thompson 2008). There is an upturn in Mn content at the edge of the 160A profile, which may indicate retrograde resorption at the rim (see Tracy et al. 1976; Kohn & Spear 2000). The Mn profile for 152A3 remains relatively flat. Garnets are relatively rare in this sample (<1%mode), so it is likely that bulk-rock Mn was not strongly depleted by fractionation during garnet growth.

Garnet profiles: Region I. In Region I, the cores of garnets from both 101L (garnet zone) and 18A (staurolite zone) have high X_{Grs} values *c.* 0.2–0.25 (Fig. 8), similar to those in garnets from

Table 3. Pressure and temperature estimates for selected samples from other studies including those recalculated herein

Sample	P (GPa)	<i>T</i> (°C)	Region	Zone	Source	
CL2H*	0.97	758	II	Sillimanite-K-feldspar		
7†	0.89	807	II	Sillimanite-K-feldspar		
430†	0.92	798	II	Sillimanite-K-feldspar		
Average	0.57	657	II	Sillimanite-muscovite	Ague et al. (2001)	
JAB 101L	0.38	535	Ι	Garnet	Ague (1997)	
JAB 15B	_	590	Ι	Staurolite Masters <i>et al.</i> (2000)		
JAB 77A	_	375	Ι	Chlorite	Masters et al. (2000)	
_	_	584	Ι	Staurolite	Masters et al. (2000)‡	
-	_	604	Ι	Staurolite	Masters et al. (2000)‡	

* Pressure and temperature recalculated in this study using mineral chemistry data from Baker & Droop (1983) and the hornblende-garnet-plagioclase barometer of Kohn & Spear (1990) together with the garnet-clinopyroxene thermometer of Ravna (2000).

† Pressure recalculated in this study with winTWQ using temperature estimates and garnet and plagioclase mineral composition data from Baker (1985).

‡ Temperatures calculated using mineral composition data from Baltatzis (1979).

P-T EVOLUTION, BARROVIAN ZONES



Fig. 4. Graphic output from winTWQ program for low-variance mineral assemblages illustrating high degree of equilibrium attained between minerals. Mineral abbreviations after Kretz (1983).

Region III (Fig. 7). However, grossular contents drop markedly toward the rims. For 101L, X_{Grs} drops to *c*. 0.13 between *x c*. 500 and *c*. 300 µm, and then stays relatively flat to the rim (Fig. 8). For 18A, there is a sharp drop in X_{Grs} at *x c*. 700 µm, followed by a more gradual decrease toward the rim (Fig 8). Grossular profiles for the other garnets investigated from Region I are simpler; they lack the high-Ca cores, are relatively flat, and vary mostly between X_{Grs} *c*. 0.05 and *c*. 0.10 (Fig. 8). The profiles suggest that garnets in 101L and 18A record a multi-stage growth history, whereas the others do not.

The $X_{\rm Prp}/X_{\rm Alm}$ values either increase toward the rim or remain relatively flat (Fig. 8), with the exception of 268A in which $X_{\rm Prp}/X_{\rm Alm}$ decreases slightly over the course of the profile. In addition, in the amphibolite facies, $X_{\rm Prp}/X_{\rm Alm}$ can drop at the very outermost rim, consistent with partial re-equilibration during retrogression (e.g. 277D1, 268A, 269B; Fig. 8). For Mn, gradual decreases (e.g. 277D1, 269B) or more abrupt decreases (e.g. 18A) toward rims are observed, as are fairly uniform profiles (e.g. 101L). Small upturns in $X_{\rm Sps}$ at crystal margins, coincident with drops in $X_{\rm Prp}/X_{\rm Alm}$, are also consistent with retrogression (e.g. 277D1).

Garnet profiles: Region II. Garnets from Region II display the most diverse range of chemical behaviour. In the garnet and staurolite zones, two samples have X_{Grs} values that drop rel-

atively continuously from high values of 0.2–0.25 in their cores, to lower values <0.1 on their rims (235A, 162A; Fig. 9). For the other two examples, $X_{\rm Grs}$ is low (< *c*. 0.1) and the profiles are fairly flat (Fig. 9). $X_{\rm Prp}/X_{\rm Alm}$ ratios increase and $X_{\rm Sps}$ values decrease from core to rim, consistent with prograde growth. Retrograde drops in $X_{\rm Prp}/X_{\rm Alm}$ and increases in $X_{\rm Sps}$ may be present on rims.

Similar patterns are observed for some higher-grade garnets from Region II as well, but there are also major exceptions and we will focus on these here. Perhaps the most striking are the grossular profiles for kyanite zone sample 246A2 and sillimanite– muscovite zone samples 62A and 261B1 (Fig. 10). The garnets have core regions of low X_{Grs} around 0.1 or less. Moving outward from the core, there are sharp increases in X_{Grs} to values of *c*. 0.15–0.2. These are then followed by drops in X_{Grs} toward the rim; rim values are similar to those measured in the cores.

A very important feature of these 'three domain' garnets are the drops in X_{Prp}/X_{Alm} observed with increasing radius in the low X_{Grs} core regions (246A2, 62A, 261B1; Fig. 10). Normally, X_{Prp}/X_{Alm} would be expected to increase with prograde growth, as predicted by the garnet-biotite Fe-Mg partitioning reaction (Ferry & Spear 1978). At first glance, the extended drops in X_{Prp}/X_{Alm} would suggest significant growth during cooling, but this interpretation is inconsistent with the endothermic nature of nearly all garnet-producing reactions.



Fig. 5. Temperature (left *y*-axis) and pressure (right *y*-axis) estimates from Region I. Samples are projected onto a traverse perpendicular to the Highland Boundary Fault (HBF) and plotted with increasing distance northward. The trend lines shown were fitted by eye. The uncertainty bars are ± 0.1 GPa and ± 25 °C.

Another possibility is open-system reaction. The redox history of 62A was studied by Ague et al. (2001), who concluded that the rock was originally highly oxidized, but was reduced during synmetamorphic fluid infiltration. During the oxidized early history, the rock would have been rich in Fe³⁺-bearing oxides, and the Mg/Fe²⁺ ratio of the rock and the ferromagnesian silicates would thus have been high. However, as reduction proceeded, the bulk-rock Fe²⁺/Fe³⁺ ratio would have increased, leading to decreases in Mg/Fe²⁺. Garnets and biotites that grew during this reduction would have their Mg/Fe²⁺ ratios shifted to lower values as more and more Fe²⁺ became available. Consequently, our interpretation is that the rimward decreases in X_{Prp} X_{Alm} observed in 62A, 246A2 and 261B1 are powerful indicators of synmetamorphic reduction during prograde growth. Reduction is inferred to have been more or less completed at the point in the profiles where X_{Prp}/X_{Alm} begins to increase toward the rim.

Mn zoning profiles also provide evidence for open-system processes. For example, for the kyanite zone garnet in 245A, Mn content actually increased and then reached a plateau before decreasing near the rim (Fig. 10). This sample was taken adjacent to a large quartz-kyanite vein. We suggest that the garnet sequestered Mn from fluids passing through the vein and, thus, the typical Rayleigh fractionation profile is not observed.

In the sillimanite-K-feldspar zone temperatures were high enough, and time scales long enough, for diffusion to smooth out



Fig. 6. Temperature (left *y*-axis) and pressure (right *y*-axis) estimates from Region II, plotted against perpendicular distance northward, away from the Highland Boundary Fault as in Figure 5. The trend lines were fitted by eye. The uncertainty bars on most samples are ± 0.1 GPa and ± 25 °C. The data point from Ague *et al.* (2001) represents the average *P* and *T* of 10 closely spaced samples; the 2σ standard errors are ± 16 °C and ± 0.035 GPa.

much of the compositional growth zonation (284A; Figs 10 and 11). However, the X_{Prp}/X_{Alm} profile is irregular and shows clear evidence of retrogression; X_{Prp}/X_{Alm} drops as a result of retrograde Fe–Mg exchange with biotite at the garnet rim and around biotite inclusions and cracks within the garnet.

Garnet maps

We made 2D chemical maps of representative garnets from each region using the electron microprobe (Fig. 11). We focus on Ca as it displays marked variations related to the baric history of metamorphism. The garnet from sample 159A (garnet zone; Region III) has relatively high and largely uniform grossular content. This most probably represents little variation in Ca partitioning into garnet during growth. It is unlikely that the Ca content was homogenized by intracrystalline diffusion given the peak temperature of the sample (600 °C).

In contrast, the garnet from 18A (staurolite zone; Region I) contains marked variations. The core is characterized by high Ca (Fig. 11). It has a euhedral outline, consistent with growth near equilibrium. Just outside the core, Ca drops significantly and displays irregular oscillatory zonation. We interpret these features to be growth zonation that records the crystal shape during



Fig. 7. Chemical profiles of garnets from Region III. All samples are from the garnet zone. The 2σ uncertainties for each component or ratio are indicated in the legend.

crystallization; the irregularity of the crystal margins probably reflects rapid growth relatively far from chemical equilibrium (Wilbur & Ague 2006). Finally, the outermost rim returns to a more euhedral shape indicative of growth closer to equilibrium.

The 'three domain' garnet in sample 62A from the sillimanitemuscovite zone of Region II has the most complex zoning observed. The low-Ca core is ringed by a high-Ca annulus, which is in turn rimmed by a zone of lower Ca. The boundaries between the annulus and the surrounding areas are sharp but irregular. The annulus is unlikely to be the result of resorption, as there is no Mn increase associated with it (see profile in Fig. 10).

Less variation is evident in the map for 284A from the sillimanite—K-feldspar zone of Region II (Fig. 11). This rock has undergone much higher-T metamorphism than the others, and thus Mn and Ca growth zoning has been largely smoothed by diffusion. Remnants of a higher Ca region are present near the rim. It is possible that this is what remains of a high-Ca annulus such as the one preserved in the three-domain garnet in sample 62A (Figs 10 and 11).

Pressure-temperature histories

Pseudosections, garnet zoning and pressure

Pseudosections are equilibrium phase diagrams drawn for a specific bulk composition (e.g. Connolly 1990; Powell *et al.* 1998; Powell & Holland 2008; de Capitani & Petrakakis 2010). They are extremely useful for displaying phase relations as functions of P and T, including the compositions of coexisting minerals. Here we examine a P-T pseudosection drawn for the representative bulk composition of sillimanite–muscovite zone sample 46B (Region II) determined by Ague *et al.* (2001). The pseudosection has wide stability fields for garnet + plagioclase + bioitite + quartz + white mica \pm chlorite, the most common

mineral assemblages in the rocks that we used for thermobarometry (Fig. 12). Other bulk compositions would yield different stability fields, but the general chemical relations discussed below would be unchanged.

Isopleths of the grossular component of garnet and the anorthite component of plagioclase are overlain on the pseudosection in Figure 12a. These isopleths are depicted because equilibria between garnet and plagioclase are generally pressure sensitive (e.g. Ghent 1976; Ghent & Stout 1981). The results clearly show that grossular-rich garnet ($X_{Grs} > c. 0.15$) would be expected to coexist with albite-rich plagioclase having $X_{An} < c$. 0.16 at high pressures in excess of c. 0.9 GPa (Fig. 12a; light grev shading). Importantly, however, grossular-rich garnet can also be stable at significantly lower pressures and somewhat lower temperatures, if it coexists with more calcic plagioclase (Fig. 12a; dark grey shading). The isopleths of Mg-number $[X_{Mg}]$ $(X_{Mg} + X_{Fe})$] of garnet illustrate the very different effects of Pand T (Fig. 12b). This ratio increases as T increases but there is little effect of P, consistent with the small volume change of garnet-biotite Mg-Fe exchange (Ferry & Spear 1978).

These general predictions have important implications for the occurrences of grossular-rich garnets. In Region III, uniformly grossular-rich garnets coexist with sodic plagioclase. The thermobarometry results indicate high pressures of *c*. 0.9 GPa or more, consistent with the pseudosection (Fig. 12a). Grossular-rich growth zones are found in some garnets from Regions I (101L, 18A, Fig. 8) and II (62A, 246A2, 261B1; Fig. 10). However, these growth zones do not necessarily indicate crystallization at high pressures, as high-grossular garnets are stable at much lower pressures if they coexist with more calcic plagio-clase (Fig. 12a). Consequently, it is critical to assess the plagioclase compositions equilibrated with areas of garnet having high grossular mole fractions before conclusions about P-T paths for Regions I and II can be drawn.



Fig. 8. Chemical profiles of garnets from Region I. Includes one garnet zone sample, two staurolite zone samples, and two sillimanite-muscovite zone samples. The 2σ uncertainties for each component or ratio are indicated in the legend.

For $X_{An} < c$. 0.15, the peristerite miscibility gap may be an issue (Spear 1993), but existing activity models for plagioclase do not account for it. If accounted for, the paragonite-bearing field would likely shrink, and be replaced by a field(s) containing two feldspars. The essential point of Figure 12a is still valid, however, as grossular-rich garnet would coexist with sodic plagioclase compositions at high pressures above *c*. 0.9 GPa. This is consistent with observations, as several high-*P* rocks from Region III contain oligoclase that rims albite.

Pressure-temperature paths

Coexisting plagioclase and garnet compositions are a strong function of P-T conditions (Fig. 12a). Thus, if plagioclase inclusions are preserved in zoned garnets, parts of the P-T path can be traced. Plagioclase inclusions are not exceptionally common, but are present in several samples. 'Three domain' garnets in sillimanite–muscovite zone sample 62A from Region II are particularly rich in inclusions (Fig. 11). We made a pseudosection using the bulk composition of 62A with isopleths of Grs and An content overlain (JUN92.bs database). Then, using compositions of plagioclase inclusions and coexisting internal

garnet compositions we constructed a P-T path for this garnet (Fig. 13). Two paths are shown, one using the isopleths constructed from the Berman-based database (JUN92.bs) and the other using the isopleths constructed from the Holland & Powell database (tcdb55c2d). Although rock Mg/Fe²⁺ decreased early in the garnet growth history as a result of reduction, we use the measured oxidation ratio (OR = molecular 2Fe₂O₃ × 100/ (2Fe₂O₃ + FeO); Chinner 1960) of 17 (Ague *et al.* 2001) as a representative 'average' for the calculations (see below). Importantly, our conclusions based on Grs and An isopleths are robust for a range of reasonable variations in rock Mg/Fe²⁺.

The two databases yield similar results. The path starts out with three points that have Grs c. 10-13% and An c. 47.5-52.5%, corresponding to a *P* of c. 0.3-0.5 GPa and a *T* of c. 500-550 °C (1, 2a and 2b in Fig. 11). Next are points with Grs c. 12.5% and An c. 45%, corresponding to a *P* of c. 0.5-0.6 GPa and a *T* of c. 550-575 °C (3 in Fig. 11). Further from the core in the high-Ca annulus, the Grs content is c. 20% and plagioclase inclusions are absent (4 in Fig. 11). The growth of calcic garnet without plagioclase corresponds to *P* of at least c. 0.75 GPa at c. 570 °C (designated by ellipses in Fig. 11). Next there are points representing Grs c. 7.4% and An c. 34%, corresponding to c.



Fig. 9. Chemical profiles of garnets from Region II. Two samples are from the garnet zone and two are from the staurolite zone. The 2σ uncertainties for each component or ratio are indicated in the legend.

0.65–0.75 GPa and *T c*. 660–690 °C (5 in Fig. 11) The final points are the composition of the rim of the garnet (Grs = 7.4%) and plagioclase from the matrix (An = 34%), corresponding to a *P* of *c*. 0.65–0.75 GPa at *c*. 660–690 °C. This result compares well with the published *P* (0.62–0.65 GPa) and *T* (650 °C) for this sample, as well as the average including the surrounding area (Fig. 13). The peak-*T* mineral assemblage predicted by the pseudosection agrees with that found in the rock, although kinetically preserved kyanite with abundant rutile inclusions is the dominant Al₂SiO₅ polymorph (Ague *et al.* 2001).

Using the high-resolution field emission gun electron microprobe, we can confirm that kyanite and sillimanite inclusions may be present in the outer parts of garnets in 62A. The chemical mapping now allows us to locate them more precisely relative to 2D chemical variations in garnet than was possible in earlier studies. We find that the polymorphs are consistent with those predicted by the pseudosection. For example, the 62A garnet mapped in Figure 11 contains kyanite inclusions 125-200 µm from the outer edge of the crystal, corresponding to points on the P-T path in the kyanite field, just before the sillimanite field is reached (Fig. 13). Thus the Al₂SiO₅ inclusions, earlier P-T work (Ague et al. 2001; Baxter et al. 2002), and the pseudosection modelling carried out here all support the conclusion of Baxter et al. (2002); namely, that the growth of the outer parts of garnets in 62A spanned kyanite-sillimanite zone conditions (their fig. 7).

Intersections of grossular and anorthite isopleths with garnet Mg-number isopleths could also be used to construct the P-T path. Interpretation of Mg-number relations must account for the synmetamorphic reduction of sample 62A (Ague *et al.* 2001), which changed the bulk Mg/Fe²⁺ of the rock during garnet growth. Figure 14 shows the locations of the intersections of Grs, An and Mg-number isopleths with the bulk Mg/Fe²⁺ ratio changing across the diagram, calculated using the tcdb55c2d database. As discussed above, the sample was more oxidized in

the early stages of garnet growth; therefore for the innermost three points (1, 2a and 2b) a pseudosection and isopleths were calculated using a representative bulk-rock composition with an OR of 30 (see Ague *et al.* 2001). The isopleths intersect at *c.* $540-575 \,^{\circ}$ C and *c.* 0.4-0.5 GPa. The rest of the isopleths were calculated using an OR of zero and these three intersections are shown at *c.* $560 \,^{\circ}$ C and *c.* 0.5-0.55 GPa (point 3), *c.* $550 \,^{\circ}$ C and *c.* 0.8-1 GPa (point 4), and *c.* $640-670 \,^{\circ}$ C and *c.* 0.6 GPa (points 5 and 6). The rim point agrees well with the published average P-T value of sample 62A and nearby samples (Fig. 14; Ague *et al.* 2001).

The Mg-number isopleths calculated using the JUN92.bs database did not intersect as well as those shown. One potential reason for this discrepancy is that the biotites in this study are highly aluminous, yet JUN92.bs does not include the eastonite component of biotite. An additional degree of uncertainty that exists using either database is that we did not account for the effect that mineral zoning will have on the bulk composition (e.g. Evans 2005; Tinkham & Ghent 2005). However, given the modal abundance of garnet in sample 62A it is unlikely that this would have a major effect on the shape of the *P*-*T*-*t* path (Zuluaga *et al.* 2005). A further limitation is that our calculations do not include the effects of Fe³⁺ in silicates. None the less, the proposed *P*-*T* paths shown in Figures 13 and 14 are very similar.

We also consider the P-T results for sillimanite–muscovite zone samples that yield T of c. 610 °C, which we infer to reflect retrogression (258D, 262A1, 264A2; Table 2). Although T values are anomalously low, P is still in the range of 0.6–0.65 GPa, comparable with the P recorded by rocks that preserve 'peak' T of c. 660 °C (Ague *et al.* 2001). This suggests that retrograde cooling occurred without major decompression. Consequently, the path is not broadly curved, but instead appears to have a relatively sharp thermal 'excursion' to peak-T conditions (Figs 13–15). Cooling with little decompression is consistent with the



Fig. 10. Chemical profiles of garnets from Region II. Four samples are from the kyanite zone, three are from the sillimanite–muscovite zone, and one is from the sillimanite–K-feldspar zone. Grey rectangle on profile for sample 62A indicates the region modelled for diffusion herein and by Ague & Baxter (2007). The different scale on the y-axis of the graph for 284A should be noted. The 2σ uncertainties for each component or ratio are indicated in the legend.

observation of widespread retrograde kyanite and staurolite at Glen Clova (Chinner 1961).

Samples 164A and 240D1 are from the staurolite zone, Region II. Both yield P estimates of c. 0.8 GPa, well in excess of those for the kyanite and sillimanite-muscovite zones (Fig. 3). We infer that these samples record the earlier, higher-P stage of the P-T path (e.g. ellipses in Fig. 13) that has been largely obscured by peak thermal conditions in the higher-grade rocks.

Garnet cores from sample 101L (Region I) are calcic (Fig. 8) and contain calcic plagioclase inclusions (c. An₅₀). In a general sense, the pseudosections indicate that calcic garnet and plagio-

clase will coexist at relatively low pressures and temperatures (Fig. 12a). Our work indicates that garnets began growing at roughly 500–520 °C. We used the measured matrix muscovite, garnet core and plagioclase inclusion compositions, and adjusted the Fe–Mg ratio of the matrix biotite to yield temperatures in this range (the calculations are very insensitive to the muscovite composition used and muscovite compositions vary little throughout our dataset). The pressures corresponding to these temperatures are between 0.45 and 0.5 GPa. This result can be compared with the *P* of 0.38 GPa estimated for the peak *T* of 535 °C using the garnet rim (Ague 1997). The general result of



Fig. 11. Maps showing the relative concentrations of Ca in garnets from the garnet zone of Region III (159A), the staurolite zone of Region I (18A), the sillimanite-muscovite zone of Region II (62A) and the sillimanite-K-feldspar zone of Region II (284A). Light yellow indicates higher Ca concentrations and dark purple indicates lower Ca concentrations. It should be noted that the colours in different maps do not correspond to exactly the same Ca contents. For reference, sample 159A core $X_{\text{Grs}} \approx 0.25$; sample 18A core $X_{\text{Grs}} \approx 0.23$; sample 18A rim $X_{\text{Grs}} \approx 0.05$; sample 62A annulus $X_{\text{Grs}} \approx 0.2$; sample 62A core and rim $X_{\text{Grs}} \approx 0.1$; sample 284A $X_{\text{Grs}} \approx 0.05$. Analysis points shown on 62A map were used for pseudosection P-T path modelling (Figs 13 and 14).

increasing T during exhumation is similar to that recorded by the garnet in 62A. Unlike 62A, however, maximum pressures were only c. 0.5 GPa.

We used a similar approach to estimate the pressures recorded by the core of garnets in 18A from the staurolite zone of Region II (Figs 8 and 11). Like garnets in 101L, these garnets have Carich cores and low-Ca rims. Plagioclase inclusions are absent. However, the plagioclase in the surrounding matrix is zoned, and has calcic cores (c. An₄₁) and more sodic rims. Assuming that the calcic garnet and plagioclase cores grew at the same time, and employing the estimation approach used for 101L, we estimate core formation pressures of c. 0.56–0.58 GPa at T of 500–520 °C. The values at peak T obtained using the garnet and plagioclase rims were about 0.5 GPa and 600 °C (Table 2). Thus, T increased during exhumation, but the T increase was large compared with the drop in P.

Reconstructing P-T paths is difficult for Region III, as grossular contents are fairly uniform and plagioclase inclusions are rare. In Figure 3, we note that sample 255A is from Region III but yields a relatively low P estimate of c. 0.65 GPa. However, nearby sample 257A retains the expected higher Pvalues. The most likely explanation for this difference is that mineral compositions in 255A record part of the retrograde history (e.g. Hodges & Royden 1984). We infer that the results for 255A and 257A together record part of the P-T path, which in this case was near-isothermal decompression over c. 10 km or more. The path is different from those for Regions I and II, which indicate heating during exhumation. The initial growth conditions of the Region III garnets are difficult to constrain. It is possible that the garnet cores coexisted with calcic plagioclase at relatively low pressures (e.g. Fig. 12); however, there is no evidence of relic calcic cores in plagioclase.

Peak thermal time scales, Regions I and II

Metamorphic time-scale information can be obtained from the modification of mineral growth zoning by intracrystalline diffusion (e.g. Ganguly *et al.* 1996; Faryad & Chakraborty 2005; Carlson 2006; Ague & Baxter 2007). At elevated temperatures, original growth zoning will be smoothed to some degree by diffusion. The extent of smoothing is primarily a function of T and time; the longer a crystal is held at elevated T, the more diffusional smoothing there will be. Thus, if peak T is known from thermobarometry and the diffusion characteristics of an element or group of elements in the mineral of interest are known, then the extent of smoothing constrains the maximum time scale of peak heating. As shown in Figures 7–11, garnets can retain significant growth zoning at all metamorphic grades except the very highest-grade rocks of the sillimanite–K-feldspar zone.

Ague & Baxter (2007) modelled Sr diffusion in apatite (Region I) and multicomponent (Mg, Fe, Ca, Mn) diffusion in garnet (Region II). They found that the thermal peak of metamorphism was remarkably short, lasting c. 1 Ma or less. Those workers used the diffusion coefficient calibrations of Carlson (2006) for garnet, which yielded peak thermal time scales of several hundred thousand years. In this section, we reexamine this modelling using two different sets of diffusion



Fig. 12. Pseudosections with the bulk composition of sillimanite– muscovite zone sample 46B (Ague *et al.* 2001): Si (2.9468), Al (2.0333), Fe²⁺ (0.3422), Mg (0.1558), Na (0.1697), Ca (0.0729), Mn (0.0123), K (0.5582). The oxidation ratio for this sample is 41.9 (Ague *et al.* 2001). Mineral assemblages coexist with muscovite, quartz, and H₂O. (a) Isopleths of the grossular component of garnet and the anorthite component of plagioclase are overlain on the pseudosection. The lighter shaded field represents garnet with high X_{Grs} coexisting with plagioclase with low X_{An} . The darker shaded field represents garnet with high X_{Grs} coexisting with plagioclase with high X_{An} . (b) Isopleths of the Mgnumber of garnet are overlain on the pseudosection.

coefficients: (1) Faryad & Chakraborty (2005); (2) Faryad & Chakraborty (2005) with the diffusion coefficient for grossular replaced by the recent calibration of Vielzeuf *et al.* (2007). We model the same two garnet profiles studied by Ague & Baxter (2007) from sillimanite–muscovite zone rocks of the Glen Clova type locality, 62A (shown in Figures 10 and 11) and 60A (illustrated by Ague & Baxter 2007).

Inspection of the profile and Ca map for 62A shows that the

crystal preserves extremely steep compositional gradients, particularly on the margins of the grossular-rich annulus (Figs 10 and 11). Qualitatively, this means that the rock could not have been held at sillimanite–muscovite zone peak thermal conditions of c. 660 °C for long, otherwise considerable diffusional smoothing would have resulted. The Sm–Nd garnet–whole-rock dating of both 62A and 60A proves that they formed during Barrovian metamorphism (Baxter *et al.* 2002), and the P-T path for 62A demonstrates that the steep gradients around the annulus must have been established prior to the peak T of metamorphism (Fig. 13).

The diffusion calculations follow those of Ague & Baxter (2007). The mean best-fit results for each set of diffusion coefficients range from 5.0×10^5 to 5.6×10^5 years for 60A, and from 7.0×10^5 to 1.3×10^6 years for 62A. The model profile shapes are virtually identical to those shown in figures 6 and 7 of Ague & Baxter (2007). Carlson's independent set of coefficients (Carlson, 2006) yields time scales of the order of a few hundred thousand years (Ague & Baxter 2007). Thus, three different sets of diffusion coefficients all indicate that the sillimanite–muscovite zone rocks of Glen Clova type locality were held at peak thermal conditions of *c*. 660 °C for a total of *c*. 1 Ma or less. There may have been a single heating 'pulse' at this temperature, or a series of shorter pulses spread out over a



Fig. 13. Pseudosection with the composition of sample 62A (Ague et al. 2001): Si (2.8407) Al (1.905), K (0.3434), Fe²⁺ (0.3975), Mg (0.1435), Mn (0.0111), Na (0.1763), Ca (0.1082). Mineral assemblages coexist with muscovite, quartz, and H_2O . The P-T points on the pseudosection represent intersecting Grs and An compositions of garnet and feldspar at different points within the garnet grain shown in Figures 10 and 11. Closed symbols, results using JUN92.bs database (Berman 1988); open symbols, results using tcdb55c2d.txt database (Holland & Powell 1998). Star indicates P-T estimate for sample 62A (Ague et al. 2001); box shows the average ($\pm 2\sigma$ standard error) sillimanite-muscovite zone P and T from Ague et al. (2001), which includes sample 62A (see Fig. 6). Grey fields lack plagioclase feldspar. Plagioclase analysis points were chosen based on: (1) absence of cracks, sericitic alteration, albitic alteration, irregular grain boundaries, and/or dissolution-reprecipitation textures; (2) presence of sharp, crystallographically controlled internal contacts with garnet.

longer time that yielded the same integrated diffusion history (Ague & Baxter 2007; Lancaster *et al.* 2008).

Of course, there are uncertainties on the diffusion coefficient calibrations. Consequently, somewhat longer time scales of a few million years cannot be ruled out. However, the main point is that long peak thermal time scales of 10 Ma or more are extremely unlikely, thus precluding simple conductive relaxation of overthickened crust (Baxter *et al.* 2002; Ague & Baxter 2007).

Although agreeing that short time-scale thermal events occurred during Barrovian metamorphism, Viete et al. (2011a) also argued for long (c. 1000 µm or more) length scales of Mn diffusion in garnets from Regions I and II during metamorphism to sillimanite-muscovite zone conditions. This would necessitate longer integrated time scales of peak heating than we calculate above. Viete et al. (2011a) posited that heterogeneities in garnet Ca and Mn growth zoning should vary over similar length scales, but stated that they observed no such coincidences in high-grade rocks. Reasoning that diffusion of Ca will be slower than Mn, they concluded that Mn zoning had been smoothed, whereas Ca zoning was better retained. However, interpretation of Viete et al.'s chemical profiles (Viete et al. (2011a) is not straightforward. The Ca and Mn variations in at least four of their eight examples are probably the result of analytical artefacts (e.g. inclusions) in their laser ablation inductively coupled plasma mass spectrometry results, as they stated on p. 121 of their paper.

Our results, moreover, show that heterogeneities in Ca and Mn zoning are complex and need not be coupled spatially. For example, in samples 101L from the garnet zone and 18A from the staurolite zone (Fig. 8), marked changes in X_{Grs} at x c. 400– 600 μ m (101L) and x c. 600 μ m (18A) are not mirrored by any significant shifts in X_{Sps} . The garnet zone rocks of Figures 7–9 provide further examples. The Mn zoning in these garnets must be due mostly to growth, as typical garnet zone temperatures are insufficient to homogenize Mn at c. 1000 µm scales, as recognized by Viete et al. (2011a). For example, using any of the three diffusion coefficient calibrations discussed herein, it would take over 10^8 years to smooth a step in Mn concentration over c. 1000 µm scales at a typical garnet zone T of 550 °C. Considerable smoothing of Ca would be expected as well, but is not observed. Such impossibly long time scales show that the broad X_{Sps} profiles and oscillatory X_{Grs} profiles in the same garnet zone crystal must both be due to growth, illustrating that heterogeneities in Ca need not be coupled spatially to heterogeneities in Mn (e.g. sample 146A1, Fig. 7).

On the other hand, there are instances where Mn and Ca zoning heterogeneities do coincide. Examples can be found in Regions I and II in the staurolite zone (162A; Fig. 9), the kyanite zone (246A2; Fig. 10), and the sillimanite–muscovite zone (62A, 261B1; Fig. 10). Clearly, significant Mn zoning was preserved, even in the amphibolite facies. Moreover, the heterogeneities in X_{Sps} could be retained over length scales of as little as a few hundred microns.

The above evidence demonstrates that heterogeneities in Ca zoning cannot be used as proxies for heterogeneities in Mn zoning when determining diffusion length scales. Furthermore, we document preservation of Mn zoning features at length scales considerably shorter than c. 1000 µm in amphibolite-facies rocks.

Viete *et al.* (2011*a*) also hypothesized that certain asymmetries in Mn zonation around inclusions indicate significant diffusional smoothing. However, in at least one of the two examples cited, the inclusions form connected trails that lead out to the matrix (their fig. 5). Consequently, interpretations are complicated because of probably direct chemical communication between the interior of the garnet and the surrounding matrix, yielding results that differ from those expected for simple radial growth or diffusion.

Finally, Viete *et al.* (2011*a*) described thin (*c.* 100 um) zones of diffusive relaxation, which they referred to as 'fuzzing bands'. They argued that these developed between the lower-grade garnet cores and the highest-grade, sillimanite–muscovite zone rims as a consequence of brief, late thermal overprinting in the sillimanite zone. Viete *et al.* (2011*a*) equated these bands with the gradients in composition modelled herein and by Ague & Baxter (2007) for samples 60A and 62A.

We concur that short length-scale compositional heterogeneities in high-grade garnets indicate brief pulsed heating. However, the discontinuity in composition used for diffusion modelling in the 'three domain' garnet of 62A lies between the lower-grade, innermost core and the margin of the high-Ca, high-*P* annulus as indicated by the grey rectangle in Figure 10. The pseudosection analysis shows that these compositional gradients must have been established before sillimanite– muscovite zone conditions were reached (Figs 13 and 14). Viete *et al.* (2011*a*) predicted that Mn zoning resulting from these earlier stages of growth would be diffusively relaxed to *c.* 1000 µm length scales, yet shorter length-scale variations clearly remain inside this and other amphibolite-facies garnets of the kyanite zone (246A2) and sillimanite–muscovite zone (261B1).

Sr diffusion profiles in apatite indicate that the time scale for peak metamorphism in the garnet and staurolite zones of Region I was also brief (Ague & Baxter 2007). Viete *et al.* (2011*a*) contested this result on two main grounds. First, they speculated that pressure effects would have significantly slowed Sr diffusion, but no experimental or field evidence exists to support this claim for Sr in apatite. Second, they based their discussion on estimates of general closure temperatures (Dodson 1973), but these



Fig. 14. Intersection locations of isopleths of Grs and Mg-number in garnet and An component of plagioclase for points (numbered) within sample 62A (analysis numbers shown in Fig. 11). The star indicates the *P* and *T* of sample 62A (Ague *et al.* 2001) and the box represents the average ($\pm 2\sigma$ standard error) sillimanite–muscovite zone *P* and *T* from Ague *et al.* (2001), which includes sample 62A (see Fig. 6).

estimates are not directly comparable with the detailed modelling of actual step discontinuities in crystals presented by Ague & Baxter (2007).

Discussion and conclusions

Ague & Baxter (2007), building on the earlier work of Baxter *et al.* (2002), postulated that in Regions I and II a pulse (or pulses) of advective heating was superimposed on a much longer timescale (10-15 Ma) background regional metamorphic regime controlled by burial and thermal relaxation of overthickened crust during exhumation. Below, we examine this model in the context of the results presented herein.

The region was loaded, thickened and heated for a time span of the order of 10-15 Ma (Oliver *et al.* 2000, 2008), consistent with the *c*. 8 Ma range of garnet growth ages found by Baxter *et al.* (2002) and the 1-10 Ma duration of biotite zone metamorphism found by Viete *et al.* (2011*b*). The loading was probably largely in response to collisional thickening as described above (Oliver *et al.* 2008; Chew *et al.* 2010). The evidence for high pressures during this stage is well preserved in the 0.9–1.1 GPa rocks of Region III, as well as in the 'three domain' garnet growth zoning (Fig. 13) and the 0.9–1.0 GPa sillimanite–Kfeldspar zone rocks of Region II (Fig. 3). Some diffusional relaxation of garnet major element zoning would probably have occurred during this protracted stage of prograde metamorphism (Caddick *et al.* 2010), and may account for some of the putative smoothing of chemical profiles inferred by Viete *et al.* (2011*a*).

Starting c. 475 Ma, asthenospheric upwelling in response to slab breakoff (Oliver et al. 2008) and/or lithospheric extension (Viete et al. 2010) produced decompression melting, large volumes of mafic magma, and elevated crustal heat flow. This activity provided the heat needed for pulsed peak Barrovian metamorphism in Regions I and II in the NE, as well as for Buchan metamorphism (Baxter et al. 2002; Ague & Baxter 2007; Lyubetskaya & Ague 2010). The regional isograd map shows the striking spatial correlation between the high-grade amphibolite-facies portions of the Barrovian and Buchan zones and the region of synorogenic magmatism in the NE, including the massive Newer Gabbros (Insch and Morven-Cabrach Gabbros) as well as smaller granitic bodies (Fig. 1). The orogen also began to undergo exhumation, possibly as the result of extensional tectonism (Viete et al. 2010). Oliver et al. (2008) suggested that high rainfall and a buoyant crust contributed to rapid exhumation of the rocks by c. 440 Ma.

Two-dimensional models of heat and mass transfer show that mafic magma intrusion over a range of depths and times can easily produce the pulsed, short time-scale peak heating events, the steep regional metamorphic field temperature gradients, and the penecontemporaneous Barrovian, Buchan and granulite-facies metamorphism observed in the northeastern Scottish Dalradian (Lyubetskaya & Ague 2010). Conduction away from advectively emplaced magmas would have been the major mode of heating, although there may also have been contributions from fluid flow. Magma-driven thermal spikes are expected to decay rapidly (Fig. 16), consistent with near-isobaric cooling of sillimanite-muscovite zone rocks back through the kyanite and staurolite zones in Glen Clova (Fig. 15). Shear zones could have channelized magma intrusion, and contributed shear heating (Viete et al. 2011a); however, it is unclear how effective deformational heating would have been, as much of the energy could have been absorbed by endothermic devolatilization reactions (see Lyubetskaya & Ague 2009).

Magmas almost certainly intruded at different depths and

1.0 Staurolite zone Region I 0.9 0.8 Pressure (GPa) 0.7 0.6 Thermal pulse 0.5 or pulses 0.4 0.3 600 700 500 1.0 Region II Sillimanitemuscovite zone 0.9 0.8 Pressure (GPa) 0.7 Thermal 0.6 pulse or pulses 0.5 0.4 0.3 700 500 600 1.0 Region III Garnet zone 0.9 0.8 Pressure (GPa) 0.7 0.6 0.5 0.4 0.3 500 600 700 Temperature (°C)

Fig. 15. Representative pressure–temperature–time paths for each of the three regions. Open circles along the paths are P-T points from sample 18 (Region I), 62A (Region II; see Fig. 13), and 255A and 257A (Region III). Aluminosilicate polymorph equilibrium phase boundaries shown for reference.

times. For example, the c. 800 °C sillimanite–K-feldspar zone rocks of the Glen Muick area (in Region II) attained their peak temperatures at pressures of c. 0.9–1.0 GPa. Thus, in this area, magma intrusion occurred early while the rocks were still deeply buried. In the type area of Glen Clova (in Region II), the thermal pulse or pulses that drove the rocks to sillimanite–muscovite zone conditions took place at c. 0.6 GPa, after significant exhumation had already occurred (Figs 13–15). The P-T path work described herein (Fig. 15) and Sr-in-apatite diffusion modelling (Ague & Baxter 2007) also support the hypothesis of a thermal pulse or pulses in Region II. However, this region was not loaded as much as Regions II and III, and thus it probably represents an intrinsically shallower crustal section (maximum P c. 0.5–0.6 GPa or c. 19–22 km; Figs 3 and 15).

As there appears to be some confusion in the literature, we emphasize that by the 'time scale of peak metamorphism' we are referring to the time spent at maximum temperature conditions. The time needed to heat the rock to peak conditions, and the time needed for cooling are not included. Consequently, the 'time scale of peak Barrovian metamorphism' and the 'time scale of Barrovian metamorphism' mean two very different things. The latter was clearly 10 Ma or more, whereas brief thermal peaks superimposed on this history lasted for considerably less time. The brief, intrusiondriven peaks have thus far been found only in Regions I and II. In Region III, in the absence of magmatism, the duration of peak metamorphism was probably significantly longer, as expected for thermal relaxation of thickened orogens according to the classic models of, for example, England & Richardson (1977), England & Thompson (1984) and Thompson & England (1984). None the less, it is possible that some farfield, conductive heat transfer away from the area of intense magmatism in Regions I and II also influenced thermal development in the northeastern part of Region III. The absence of large T increases during decompression from c. 1.0 GPa in Region III (Fig. 15) is consistent with relatively rapid exhumation rates.

It remains unclear how much of the thermal pulse activity affected the lower-grade rocks in Regions I and II (chlorite, biotite and lower garnet zone). It is possible that they preserve a record of both the original loading and the post-loading thermal perturbations caused by magmatism during exhumation. This may account for the wide range of mica ⁴⁰Ar/³⁹Ar ages obtained by Viete et al. (2011b). Of course, the extent of magmatic overprinting must have been limited, as the rocks did not reach high-grade conditions. We hypothesize that prior to mafic magma intrusion the field area was mostly in the greenschist facies, with maximum grades corresponding to garnet zone conditions and perhaps lower amphibolite facies locally. The mafic magmas and associated high heat flow are inferred to have supplied the heat to produce the rocks of the regional staurolite, kyanite, sillimanite-muscovite and sillimanite-K-feldspar zones in Regions I and II, as well as the high-grade Buchan zones (see Hanson & Barton 1989; Annen & Sparks 2002; Annen et al. 2006; Lyubetskaya & Ague 2010). Some pre-existing garnet zone rocks of Regions I and II may have experienced additional garnet growth during pulsed heating, but remained in the garnet zone; sharp core-rim discontinuities in garnet composition may reflect such histories (Figs 8 and 9). Sm-Nd dating of garnet shows that the difference in time between attainment of peak garnet zone and kyanite-sillimanite zone conditions was only 2.8 ± 3.7 Ma, statistically indistinguishable from zero and indicative of regional advective heat input, not slow, conduction-dominated thermal relaxation of tectonically overthickened crust (Baxter et al. 2002).

The northeastern Dalradian was intruded by multiple magmas, so there were probably multiple brief pulses of heating across this part of the orogen, separated in space and time. As a result, peak conditions in one geographical area need not have been exactly synchronous with peak conditions in another. The timing and time scales of peak attainment would have been controlled by the tempo of magma emplacement and thermal conduction into surrounding wallrocks. Thus, three broad time scales, from longest to shortest, are critical (Fig. 16): (1) the time scale of the overall orogenic cycle of burial and exhumation (c. 10-15 Ma); (2) the total length of time over which magmas were intruded (<10 Ma); (3) the integrated time scale of brief thermal events recorded by peak metamorphic mineral assemblages (of the order of 1 Ma or less). Although uncertainties in diffusion coefficients permit time scales of perhaps a few million years for (3), available best-fit diffusion results range from a few hundred thousand to around a million years.

The effects of the shorter two time scales ((2) and (3), above) will be different depending on the distance between the mag-



Fig. 16. Schematic diagram for Region II of the P-T paths that would result in rocks proximal (a) and distal (b) to repetitive mafic sill injection. Three important time scales are shown: (1) the time scale of the overall burial and exhumation (c, 10– 15 Ma); (2) the total length of time over which magmas were intruded (<10 Ma); (3) the integrated time scale of brief thermal events recorded by peak metamorphic mineral assemblages (of the order of 1 Ma or less). The actual number of pulses is unknown and probably varied spatially; three are shown for illustration purposes. The effects of repetitive mafic sill injection on wallrocks will depend on the time needed for the pulsed heat to reach the rocks and then conduct away. The figure contains some elements modified from Lyubetskaya & Ague (2010).

matic intrusions and the affected rock. Proximal to the intrusions the added heat would have raised the temperature of the wall-rocks sharply and then would have quickly conducted away, resulting in a brief thermal pulse for each intrusion or closely spaced set of intrusions. Further from the intrusions the peak T of the wallrocks would be lower overall and the attainment of the temperature maximum would be delayed because of the time needed for longer length-scale heat conduction (Fig. 16). Further high-precision geochronology is clearly required to define the spatial and temporal tapestry of Grampian tectonometamorphic events.

Recently Viete et al. (2011a) proposed a model that relies on magmas and other heat sources active during extensional tectonism to explain Barrovian and Buchan metamorphism. In their model, the regional heating built up through multiple heating events operative over a range of time and length scales; the total timespan of activity is envisioned to have been a few million years (Viete et al. 2011a). This model has a number of features in common with that presented by Ague & Baxter (2007), Lyubetskaya & Ague (2010) and herein, including the requirement of short, pulsed heating and the involvement of magmas. However, metamorphic mineral growth during loading and thermal relaxation of overthickened crust (e.g. Thompson & England 1984) is not part of Viete et al.'s model. Consequently, it cannot address the evidence we present for the significant role played by crustal loading during the metamorphic evolution, or the fact that the deeply exhumed southwestern half of the Dalradian displays no indication of regional pulsed, advective magmatic heating (Region III; Fig. 1).

We conclude that heat transfer processes during Barrovian metamorphism in Scotland varied greatly across the terrane. P-T relations for Region III in the SW and for the background metamorphic regime in Regions I and II to the NE are consistent with the conventional model of burial followed by conductive thermal relaxation of overthickened crust during exhumation (England & Thompson 1984; Thompson & England 1984). Region I underwent the smallest amount of loading. In Regions I and II, heating to peak thermal conditions required additional heat input from synorogenic magmas, predominantly the Newer Gabbros. Conductive heat flow away from the magmas may have influenced thermal evolution in the northeasternmost part of Region III.

We gratefully acknowledge J. O. Eckert, Jr. for help with the microprobe; E. Baxter for discussions; M. Andrews, C. Bucholz, I. Derrey and J. Stevenson for assistance in the field; M. Caddick and E. Ghent for their thoughtful reviews; and the National Science Foundation Directorate for Geosciences (NSF EAR-0509934 and 0744154 to J.J.A.) and The Geological Society of America (Graduate Student Research Grant to S.H.V.) for support.

References

- AGUE, J.J. 1997. Crustal mass transfer and index mineral growth in Barrow's garnet zone, northeast Scotland. *Geology*, 25, 73–76.
- AGUE, J.J. & BAXTER, E.F. 2007. Brief thermal pulses during mountain building recorded by Sr diffusion in apatite and multicomponent diffusion in garnet. *Earth and Planetary Science Letters*, **261**, 500–516.
- AGUE, J.J., BAXTER, E.F. & ECKERT, J.O., JR 2001. High *f*₀₂ during sillimanite zone metamorphism of part of the Barrovian type locality, Glen Clova, Scotland. *Journal of Petrology*, **42**, 1301–1320.
- ANNEN, C. & SPARKS, R.S.J. 2002. Effects of repetitive emplacement of basaltic intrusions on thermal evolution and melt generation in the crust. *Earth and Planetary Science Letters*, 203, 937–955.
- ANNEN, C., SCAILLET, B. & SPARKS, R.S.J. 2006. Thermal constraints on the emplacement rate of a large intrusive complex: The Manaslu leucogranite,

Nepal Himalaya. Journal of Petrology, 47, 71-95.

- ATHERTON, M.P. 1968. The variation in garnet, biotite and chlorite composition in medium grade pelitic rocks from the Dalradian, Scotland, with particular reference to zonation in garnet. *Contributions to Mineralogy and Petrology*, 18, 347–371.
- ATHERTON, M.P. 1977. The metamorphism of the Dalradian rocks of Scotland. Scottish Journal of Geology, 13, 331–370.
- AYRES, M. & VANCE, D. 1997. A comparative study of diffusion profiles in Himalayan and Dalradian garnets: constraints on diffusion data and the relative duration of the metamorphic events. *Contributions to Mineralogy and Petrology*, **128**, 66–80.
- BAKER, A.J. 1985. Pressures and temperatures of metamorphism in the eastern Dalradian. Journal of the Geological Society, London, 142, 137–148.
- BAKER, A.J. & DROOP, G.T.R. 1983. Grampian metamorphic conditions deduced from mafic granulites and sillimanite-K-feldspar gneisses in the Dalradian of Glen Muick, Scotland. *Journal of the Geological Society, London*, 140, 489– 497.
- BALTATZIS, E. 1979. Staurolite-forming reactions in the eastern Dalradian rocks of Scotland. Contributions to Mineralogy and Petrology, 69, 193–200.
- BARROW, G. 1893. On an intrusion of muscovite-biotite gneiss in the south-eastern highlands of Scotland, and its accompanying metamorphism. *Quarterly Journal of the Geological Society of London*, **49**, 330–354.
- BARROW, G. 1912. On the geology of the lower Dee-side and the southern highland border. Proceedings of the Geologists' Association, 23, 149–156.
- BAXTER, E.F., AGUE, J.J. & DEPAOLO, D.J. 2002. Prograde temperature-time evolution in the Barrovian type-locality constrained by Sm/Nd garnet ages from Glen Clova, Scotland. *Journal of the Geological Society, London*, 159, 71–82.
- BERMAN, R.G. 1988. Internally-consistent thermodynamic data for minerals in the system Na₂O-K₂O-CaO-MgO-FeO-Fe₂O₃-Al₂O₃-SiO₂-TiO₂-H₂O-CO₂. Journal of Petrology, **29**, 445–522.
- BERMAN, R.G. 1991. Thermobarometry using multi-equilibrium calculations: a new technique with petrological applications. *Canadian Mineralogist*, 29, 833–855.
- BERMAN, R.G. 2007. winTWQ (version 2.3): a software package for performing internally-consistent thermobarometric calculations. Geological Survey of Canada, Open File, 5462, edn 2.34.
- BOHLEN, S.R. & LIOTTA, J.J. 1986. A barometer for garnet amphiboles and garnet granulites. *Journal of Petrology*, 27, 1025–1034.
- BREEDING, C.M., AGUE, J.J., GROVE, M. & RUPKE, A. 2004. Isotopic and chemical alteration of zircon by metamorphic fluids; U-Pb age depth-profiling of zircons from Barrow's garnet zone, northeast Scotland. *American Mineralo*gist, 89, 1067–1077.
- BRITISH GEOLOGICAL SURVEY 2007. Bedrock Geology UK North, 5th edn, 1:625 000. British Geological Survey, Keyworth, Nottingham.
- BUCHOLZ, C.E. & AGUE, J.J. 2010. Fluid flow and Al transport during quartzkyanite vein formation, Unst, Shetland Islands, Scotland. *Journal of Metamorphic Geology*, 28, 19–39.
- CADDICK, M.J. & THOMPSON, A.B. 2008. Quantifying the tectono-metamorphic evolution of pelitic rocks from a wide range of tectonic settings: Mineral compositions in equilibrium. *Contributions to Mineralogy and Petrology*, **156**, 177–195.
- CADDICK, M.J., KONOPASEK, J. & THOMPSON, A.B. 2010. Preservation of garnet growth zoning and the duration of prograde metamorphism. *Journal of Petrology*, 51, 2327–2347.
- CARLSON, W.D. 2006. Rates of Fe, Mg, Mn, and Ca diffusion in garnet. *American Mineralogist*, **91**, 1–11.
- CARMICHAEL, D.M. 1978. Metamorphic bathozones and bathograds: a measure of the depth of post-metamorphic uplift and erosion on the regional scale. *American Journal of Science*, 278, 269–297.
- CHEW, D.M., DALY, J.S., MAGNA, T., PAGE, L.M., KIRKLAND, C.L., WHITEHOUSE, M.J. & LAM, R. 2010. Timing of ophiolite obduction in the Grampian orogen. *Geological Society of America Bulletin*, **122**, 1787–1799.
- CHINNER, G.A. 1960. Pelitic gneisses with varying ferrous/ferric ratios from Glen Clova, Angus, Scotland. *Journal of Petrology*, 1, 178–217.
- CHINNER, G.A. 1961. The origin of sillimanite in Glen Clova, Angus. Journal of Petrology, 2, 312–323.
- CHINNER, G.A. 1966. The distribution of pressure and temperature during Dalradian metamorphism. *Quarterly Journal of the Geological Society of London*, **122**, 159–181.
- CONNOLLY, J.A.D. 1990. Multivariable phase-diagrams—an algorithm based on generalized thermodynamics. *American Journal of Science*, 290, 666–718.
- DEMPSTER, T.J. 1985. Garnet zoning and metamorphism of the Barrovian type area, Scotland. Contributions to Mineralogy and Petrology, 89, 30–38.
- DEMPSTER, T.J., FALLICK, A.E. & WHITTEMORE, C.J. 2000. Metamorphic reactions in the biotite zone, eastern Scotland: high thermal gradients, metasomatism and cleavage formation. *Contributions to Mineralogy and Petrology*, **138**, 348–363.
- DEMPSTER, T.J., ROGERS, G., ET AL. 2002. Timing of deposition, orogenesis and

glaciations within the Dalradian rocks of Scotland: constraints from U-Pb ages. Journal of the Geological Society, London, 159, 83-94.

- DE CAPITANI, C. & PETRAKAKIS, K. 2010. The computation of equilibrium assemblage diagrams with Theriak/Domino software. *American Mineralogist*, 95, 1006–1016.
- DEWEY, J.F. 2005. Orogeny can be very short. Proceedings of the National Academy of Sciences of the USA, 102, 15286–15293.
- DIENER, J.F.A., POWELL, R., WHITE, R.W. & HOLLAND, T.J.B. 2007. A new thermodynamic model for clino- and orthoamphiboles in the system Na₂O-CaO-FeO-MgO-Al₂O₃-SiO₂-H₂O-O. Journal of Metamorphic Geology, 25, 631-656.
- DODSON, M.H. 1973. Closure temperature in cooling geochronological and petrological systems. *Contributions to Mineralogy and Petrology*, 40, 259– 274.
- DROOP, G.T.R. & HARTE, B. 1995. The effect of Mn on the phase relations of medium-grade pelites: constraints from natural assemblages on petrogenic grid topology. *Journal of Petrology*, 36, 1549–1578.
- DYMOKE, P.L. 1988. Geochronological and petrological studies of the thermal evolution of the Dalradian, south west Scottish Highlands. PhD thesis, University of Edinburgh.
- ENGLAND, P.C. & RICHARDSON, S.W. 1977. The influence of erosion upon the mineral facies of rocks from different metamorphic environments. *Journal of* the Geological Society, London, 134, 201–213.
- ENGLAND, P.C. & THOMPSON, A.B. 1984. Pressure-temperature-time paths of regional metamorphism I. Heat transfer during the evolution of regions of thickened continental crust. *Journal of Petrology*, 25, 894–928.
- EVANS, T.P. 2005. A method for calculating effective bulk composition modification due to crystal fractionation in garnet-bearing schist: implications for isopleths thermobarometry. *Journal of Metamorphic Geology*, 22, 547–557.
- FARYAD, S.W. & CHAKRABORTY, S. 2005. Duration of Eo-Alpine metamorphic events obtained from multicomponent diffusion modeling of garnet: a case study from the Eastern Alps. *Contributions to Mineralogy and Petrology*, 150, 306–318.
- FERRY, J.M. & SPEAR, F.S. 1978. Experimental calibration of the partitioning of Fe and Mg between biotite and garnet. *Contributions to Mineralogy and Petrology*, 66, 113–117.
- GANGULY, J., CHAKRABORTY, S., SHARP, T.G. & RUMBLE, D., III 1996. Constraint on the time scale of biotite-grade metamorphism during Acadian orogeny from a natural garnet–garnet diffusion couple. *American Mineralogist*, 81, 1208–1216.
- GHENT, E.D. 1976. Plagioclase-garnet-Al₂SiO₅-quartz; a potential geobarometer-geothermometer. American Mineralogist, 61, 710-714.
- GHENT, E.D. & STOUT, M.Z. 1981. Geobarometry and geothermometry of plagioclase-biotite-garnet-muscovite assemblages. *Contributions to Miner*alogy and Petrology, 76, 92–97.
- GRAHAM, C.M., GREIG, K.M, SHEPPARD, M.F. & TURI, B. 1983. Genesis and mobility of the H₂O-CO₂ fluid phase during regional greenschist and epidote amphibolite facies metamorphism, a petrological and stable isotope study in the Scottish Dalradian. *Journal of the Geological Society, London*, 140, 577– 599.
- HANSON, R.B. & BARTON, M.D. 1989. Thermal development of low-pressure metamorphic belts: results from two-dimensional numerical models. *Journal* of Geophysical Research, 94, 10363–10377.
- HARTE, B. & DEMPSTER, T.J. 1987. Regional metamorphic zones: tectonic controls. Philosophical Transactions of the Royal Society of London, Series A, 321, 105–127.
- HARTE, B. & HUDSON, N. C. F. 1979. Pelite facies series and the temperatures and pressures of Dalradian metamorphism in E Scotland. In: HARRIS, A.L., HOLLAND, C.H. & LEAKE, B.E. (eds) The Caledonides of the British Isles— Reviewed. Geological Society, London, Special Publications, 8, 323–337.
- HARTE, B. & JOHNSON, M.R.W. 1969. Metamorphic history of Dalradian rocks in Glens Clova, Esk, and Lethnot, Angus, Scotland. *Scottish Journal of Geology*, 5, 54–80.
- HARTE, B., BOOTH, J.E., DEMPSTER, T.J., FETTES, D.J., MENDUM, J.R. & WATTS, D. 1984. Aspects of the post-depositional evolution of the Dalradian and Highland Boundary rocks in the southern Highlands of Scotland. *Transactions* of the Royal Society of Edinburgh, Earth Sciences, 75, 151–163.
- HODGES, K.V. & ROYDEN, L.H. 1984. Geothermometry and geobarometry of retrograded metamorphic rocks: An indication of the uplift trajectory of a portion of the northern Scandinavian Caledonides. *Journal of Geophysical Research.* 89, 7077–7090.
- HOLLAND, T.J.B. & POWELL, R. 1998. An internally-consistent thermodynamic dataset for phases of petrological interest. *Journal of Metamorphic Geology*, 16, 309–344.
- HOLLAND, T. & POWELL, R. 2003. Activity-composition relations for phases in petrological calculations: an asymmetric multicomponent formulation. *Contributions to Mineralogy and Petrology*, **145**, 492–501.

HOLLISTER, L.S. 1966. Garnet zoning; an interpretation based on the Rayleigh

fractionation model. Science, 154, 1647-1651.

- KNELLER, B.C. & AFTALION, M. 1987. The isotopic and structural age of the Aberdeen Granite. Journal of the Geological Society, London, 144, 717–721.
- KOHN, M.J. & SPEAR, F.S. 1990. Two new geobarometers for garnet amphibolites, with applications to southeastern Vermont. *American Mineralogist*, 75, 89–96.
- KOHN, M.J. & SPEAR, F.S. 2000. Retrograde net transfer reaction insurance for pressure-temperature estimates. *Geology*, 28, 1127–1130.
- KRETZ, R. 1983. Symbols for rock-forming minerals. American Mineralogist, 68, 277-279.
- LANCASTER, P.J., BAXTER, E.F., AGUE, J.J., BREEDING, C.M. & OWENS, T.L. 2008. Synchronous peak Barrovian metamorphism driven by syn-orogenic magmatism and fluid flow in southern Connecticut, USA. *Journal of Metamorphic Geology*, 26, 527–538.
- LEAKE, B.E. 1986. The geology of SW Connemara, Ireland: a fold and thrust Dalradian and metagabbroic-gneiss complex. *Journal of the Geological Society, London*, 143, 221–236.
- LISTER, G.S. & BALDWIN, S.L. 1993. Plutonism and the origin of metamorphic core complexes. *Geology*, **21**, 607–610.
- LYUBETSKAYA, T. & AGUE, J.J. 2009. Effects of metamorphic reactions on thermal evolutions in collisional orogens. *Journal of Metamorphic Geology*, 27, 579– 600.
- LYUBETSKAYA, T. & AGUE, J.J. 2010. Modeling metamorphism in collisional orogens intruded by magmas: II. Fluid flow and implications for Barrovian and Buchan Metamorphism, Scotland. *American Journal of Science*, **310**, 459–491.
- MACDONALD, R. & FETTES, D.J. 2007. The tectonomagmatic evolution of Scotland. Transactions of the Royal Society of Edinburgh: Earth Sciences, 97, 213–295.
- MASSONNE, H.J. & SCHREYER, W. 1987. Phengite geobarometry based on the limiting assemblage with K-feldspar, phlogopite and quartz. *Contributions to Mineralogy and Petrology*, 96, 212–224.
- MASTERS, R.L., AGUE, J.J. & RYE, D.M. 2000. An oxygen and carbon isotopic study of multiple episodes of fluid flow in the Dalradian and Highland Border Complex, Stonehaven, Scotland. *Journal of the Geological Society, London*, 157, 367–379.
- McLellan, E.L. 1985. Metamorphic reactions in the kyanite and sillimanite zones of the Barrovian type area. *Journal of Petrology*, **26**, 789–818.
- MCLELLAN, E.L. 1989. Sequential formation of subsolidus and anatectic migmatites in response to thermal evolution, Eastern Scotland. *Journal of Geology*, 97, 165–182.
- OLIVER, G.J.H., CHEN, F., BUCHWALDT, R. & HEGNER, E. 2000. Fast tectonometamorphism and exhumation in the type area of the Barrovian and Buchan zones. *Geology*, 28, 459–462.
- OLIVER, G.J.H., WILDE, S.A. & WAN, Y. 2008. Geochronology and geodynamics of Scottish granitoids from the late Neoproterozoic break-up of Rodinia to Palaeozoic collision. *Journal of the Geological Society, London*, 165, 661– 674.
- POWELL, R. & HOLLAND, T.J.B. 1988. An internally consistent thermodynamic dataset with uncertainties and correlations: 3. Application methods, worked examples and a computer program. *Journal of Metamorphic Geology*, 6, 173–204.
- POWELL, R. & HOLLAND, T.J.B. 2008. On thermobarometry. Journal of Metamorphic Geology, 26, 155–179.
- POWELL, R., HOLLAND, T. & WORLEY, B. 1998. Calculating phase diagrams with THERMOCALC: methods and examples. *Journal of Metamorphic Geology*, 16, 577–588.
- RAVNA, E.K. 2000. The garnet-clinopyroxene Fe²⁺-Mg geothermometer: an updated calibration. *Journal of Metamorphic Geology*, 18, 211–219.
- ROGERS, G., PATERSON, B.A., DEMPSTER, T.J. & REDWOOD, S.D. 1994. U-Pb geochronology of the 'Newer' Gabbros, NE Grampians (abstract). In: Caledonian Terrane Relationships in Britain. British Geological Survey Programme with Abstracts, 8.
- SIVAPRAKASH, C. 1982. Geothermometry and geobarometry of Dalradian metapelites and metabasites from the Central Scottish Highlands. Scottish Journal of Geology, 18, 109–124.
- SKELTON, A.D.L., GRAHAM, C.M. & BICKLE, M.J. 1995. Regional 3-D fluid flow patterns during greenschist facies metamorphism of the Dalradian of the SW Scottish Highlands. *Journal of Petrology*, 36, 563–586.
- SPEAR, F.S. 1993. Metamorphic Phase Equilibria and Pressure-Temperature-Time Paths. Mineralogical Society of America Monographs, 1.
- THOMPSON, A.B. & ENGLAND, P.C. 1984. Pressure-temperature-time paths of regional metamorphism II. Their inference and interpretation using mineral assemblages in metamorphic rocks. *Journal of Petrology*, 25, 929–955.
- TILLEY, C.E. 1925. A preliminary survey of metamorphic zones in the southern Highlands of Scotland. *Quarterly Journal of the Geological Society of London*, 81, 100–112.
- TINKHAM, D.K. & GHENT, E.D. 2005. Estimating P-T conditions of garnet growth with isochemical phase diagram sections and the problem of effective bulk

composition. Canadian Mineralogist, 43, 35-50.

- TRACY, R.J., ROBINSON, P. & THOMPSON, A.B. 1976. Garnet composition and zoning in the determination of temperature and pressure of metamorphism, central Massachusetts. *American Mineralogist*, 61, 762–775.
- VIELZEUF, D., BARONNET, A., PERCHUK, A.L., LAPORTE, D. & BAKER, M.B. 2007. Calcium diffusivity in alumino-silicate garnets: an experimental and ATEM study. *Contributions to Mineralogy and Petrology*, **154**, 153–170.
- VIETE, D.R., RICHARDS, S.W., LISTER, G.S., OLIVER, G.J.H. & BANKS, G.J. 2010. Lithospheric-scale extension during Grampian orogenesis in Scotland. *In:* LAW, R.D., BUTLER, R.W.H., HOLDSWORTH. R.E., KRABBENDAM, M. & STRACHAN, R.A. (eds) *Continental Tectonics and Mountain Building. The Legacy of Peach and Horne.* Geological Society, London, Special Publications, 335, 121–160.
- VIETE, D.R., HERMANN, J., LISTER, G. & STENHOUSE, I. 2011a. The nature and origin of the Barrovian metamorphism, Scotland: diffusion length scales in garnet and inferred thermal time scales. *Journal of the Geological Society*, *London*, 168, 115–132.
- VIETE, D.R., FORSTER, M.A. & LISTER, G.S. 2011b. The nature and origin of the Barrovian metamorphism, Scotland: ⁴⁰Ar/³⁹Ar age patterns and the duration of metamorphism in the biotite zone. *Journal of the Geological Society*, *London*, **168**, 133–146.

WATKINS, K.P. 1985. Geothermometry and geobarometry of inverted metamorphic

zones in the W. central Scottish Dalradian. Journal of the Geological Society, London, 142, 157-165.

- WIJBRANS, J. & MCDOUGALL, I. 1986. ⁴⁰Ar/³⁹Ar dating of white micas from an Alpine high-pressure metamorphic belt on Naxos (Greece): the resetting of the argon isotopic system. *Contributions to Mineralogy and Petrology*, 93, 187–194.
- WIJBRANS, J. & MCDOUGALL, I. 1988. Metamorphic evolution of the Attic Cycladic Metamorphic Belt on Naxos (Cyclades, Greece) utilizing ⁴⁰Ar/³⁹Ar age spectrum measurements. *Journal of Metamorphic Geology*, 6, 571–594.
- WILBUR, D.E. & AGUE, J.J. 2006. Chemical disequilibrium during garnet growth: Monte Carlo simulations of natural crystal morphologies. *Geology*, 34, 689– 692.
- WORLEY, B. & POWELL, R. 2000. High-precision relative thermobarometry: theory and a worked example. *Journal of Metamorphic Geology*, 18, 91–101.
- YARDLEY, B.W.D., BARBER, J.P., GRAY, J.R. & TAYLOR, W.E.G. 1987. The metamorphism of the Dalradian rocks of western Ireland and its relation to tectonic setting. *Philosophical Transactions of the Royal Society of London*, 321, 243–270.
- ZULUAGA, C.A., STOWELL, H.H. & TINKHAM, D.K. 2005. The effect of zoned garnet on metapelite pseudosection topology and calculated metamorphic P-T paths. American Mineralogist, 90, 1619–1628.

Received 11 May 2010; revised typescript accepted 9 May 2011. Scientific editing by Chris Clark.