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Prograde temperature–time evolution in the Barrovian type–locality constrained by Sm/Nd garnet ages from Glen Clova, Scotland

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Abstract: The timing of garnet growth during metamorphism associated with the Grampian Orogeny in the sillimanite zone of the Barrovian type-locality in Glen Clova, Scotland, was determined by Sm/Nd geochronology. Two high precision garnet-whole-rock ages were achieved by employing HF partial dissolution of garnet separates to optimize purity. Multiple garnet growth generations were identified on the basis of the geochronology and detailed textural and chemical data: an early stage, at 472.9 ± 2.9 Ma, during D_2 deformation under garnet zone conditions (*c.* 500–550 °C), and a later stage, at 464.8 ± 2.7 Ma, during or slightly after D_3 deformation mostly under sillimanite zone conditions (peak temperature of *c.* 660 °C), but possibly including some growth during kyanite zone conditions. When combined with recently published garnet ages from the kyanite and garnet zones the data suggest that peak metamorphic temperatures in at least these three of Barrow's zones were achieved roughly contemporaneously. The difference between garnet zone and sillimanite zone peak temperature attainment is 2.8 ± 3.7 Ma. The near contemporaneity of peak temperature attainment in different metamorphic zones requires an additional source of heat beyond thermal relaxation of a variably over-thickened crust. We suggest that local igneous intrusions, with synmetamorphic ages, provided that additional heat.

Keywords: Barrovian-type deposits, metamorphism, garnet, geochronology.

The exposed cliffs in Glen ∂Clova, Angus, Scotland (Fig. 1) are part of the type locality for Barrovian regional metamorphism, as defined by Barrow in his landmark paper (Barrow 1893), where he equated progressively increasing grades of metamorphism to index mineral zones passing through the now familiar chlorite, biotite, garnet, staurolite, kyanite and sillimanite zones. These rocks were metamorphosed during the Grampian Orogeny. Despite the renown and importance of the Glen Clova locality there exists no directly determined age of peak metamorphism for these amphibolite facies rocks. As this field site is part of Barrow's original zonal sequence, the study of which has recently experienced something of a renaissance (Ague 1997; Soper *et al.* 1999; Dempster *et al.* 2000; Oliver *et al.* 2000; Ague *et al.* 2001), a more thorough understanding of the process of the metamorphic cycle at this locality would be valuable in the context of studying Barrovian terranes throughout the world. Here, we present the first direct age measurements for the Grampian Orogeny at this locality by dating the growth of one of Barrow's key index minerals: garnet. The goal is to independently test other existing age constraints on Barrovian metamorphism during the Grampian and to elucidate further the metamorphic history of the Barrovian type-locality.

Geological setting

The metasedimentary rocks of Glen Clova, Scotland, are part of the Dalradian Supergroup, a sequence of late Proterozoic to early Palaeozoic metasediments deposited on the evolving continental shelf of Laurentia, during the break-up of the Proterozoic Supercontinent and the opening of the Iapetus Ocean (Harris *et al.* 1994). The Dalradian extends from northern Scotland into northern Ireland, bounded on the north by the Great Glen Fault and on the south by the Highland Boundary Fault and its extension into Northern Ireland (Fig. 1). These sediments were metamorphosed during the Grampian Orogeny, which was brought about by collision and accretion of an island arc and crustal fragments along the Laurentian continental margin as the Iapetus Ocean began to close (Lambert & McKerrow 1976; Dewey & Ryan 1990; Friedrich *et al.* 1999*a*; Oliver *et al.* 2000). The Dalradian Supergroup in Scotland underwent four distinct deformational events during this time (D_1–D_4) distinguished on the basis of structural analysis of fold sets, cleavages, and facing directions (Harte *et al.* 1984). Textural and mineralogical evidence (Harte *et al.* 1984; McLellan 1985) suggest that peak metamorphism was attained roughly syn-D_3. McLellan (1989) summarized microtextural evidence for the relative timing of prograde porphyroblast growth and deformation as follows: garnet growth was mostly syn-D_2 with a second generation syn- to post-D_3; staurolite growth was syn- to post-D_2; kyanite growth was pre- to syn-D_3; sillimanite growth was mostly syn- to post-D_3. The second generation of garnet growth described by McLellan (1985), is characteristic of 'type IIIb' pelites which have high modal muscovite to biotite ratios and are iron rich. Sillimanite is found as fibrolite inclusions in these second generation garnets (McLellan 1985). Peak conditions in the sillimanite zone were *c.* 650–700 °C and *c.* 6 kbar (Ague *et al.* 2001; McLellan, 1985).

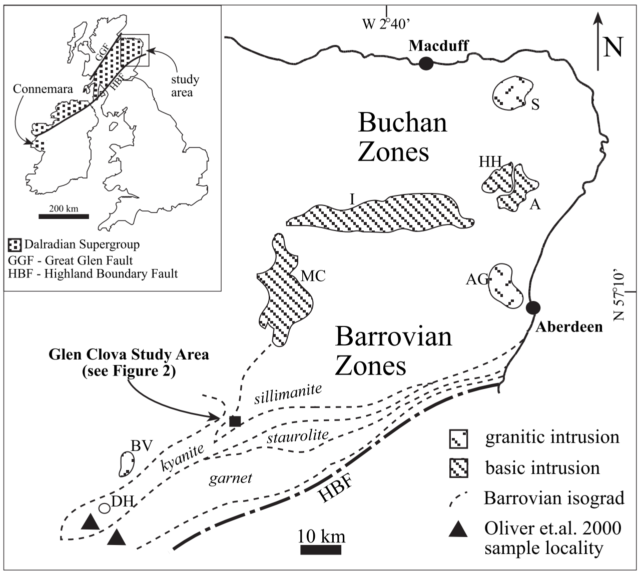

Fig. 1. Map of the Dalradian Sediments and the Grampian Orogeny in Northeastern Scotland showing the location of the field study at Glen Clova. Barrovian isograds have been extrapolated based on the maps of Barrow (1912), McLellan (1989), and Kennedy (1948). Mineral zones are indicated in italics. Lowest grade Barrovian zones are omitted for clarity. Note that the Glen Clova locality is within the sillimanite zone and the two garnet sample locations of Oliver *et al.* (2000) lie in the kyanite and garnet zones, respectively. Geological features mentioned in the text, including basic and granitic intrusions which have been dated in past studies, include: Arnage Mass (A), Aberdeen Granite (AG), Ben Vuirich Granite (BV), Dunfallandy Hill Granite (DH), Haddo House Gabbro (HH), Insch Gabbro (I), Morvern–Cabrach Gabbro (MC), and the Strichen Granite (S). Other geological features are omitted for clarity. Modified from map of Bell (1968).

Existing age constraints

Table 1 shows a summary of efforts to constrain the timing of peak Grampian metamorphism in Scotland and Ireland. Geochronology of the post-metamorphic 'Newer Granites' (for example, see Pankhurst 1970) is not discussed here. The earliest efforts are largely based on Rb/Sr whole-rock isochrons of gabbros and associated metamorphic aureoles that have been inferred, on the basis of field observations, to have been syn D_2–D_3 (Pankhurst 1970; Pankhurst & Pidgeon 1976). However, Rb/Sr whole-rock geochronology may be problematic due to the adverse affects of synmetamorphic isotopic exchange between layers resulting in ages anywhere between the original protolith age and the metamorphic age (e.g. DePaolo & Getty 1996). An early estimate for the age of peak Grampian metamorphism in Scotland, 520–490 Ma (Harte *et al.* 1984), was based on the assumption that metamorphism must have occurred at or before the emplacement age of these syn- to late-metamorphic gabbros and after the emplacement of the Ben Vuirich Granite, originally thought to be syn-D_2–D_3 (Harte *et al.* 1984). The age of the Ben Vuirich Granite, constrained by U/Pb dating of zircons, has since been updated from 515 ± 7 Ma (Pankhurst & Pidgeon 1976) to 590 Ma (Rogers *et al.* 1989) and closely re-examined structural observations suggest it is actually pre-metamorphic (see Soper *et al.* 1999). Recently, two of the synmetamorphic gabbros, the Insch and the Morven–Cabrach, have been re-dated at 468 Ma and 472 Ma, respectively (Rogers *et al.* 1994) but details of these data are not published. Soper *et al.* (1999) synthesized existing geochronology and highlighted a biostratigraphic constraint of 485 Ma (Molyneux 1998) on protolith deposition of some of the metamorphosed sediments. Oliver *et al.* (2000) correlated the timing of obduction of the Ballantrae Ophiolite complex during island arc/Laurentian collision with the beginning of Grampian metamorphism and D_1 deformation. The inferred date of the ophiolite obduction is 478 ± 8 Ma (Bluck *et al.* 1980). Finally, Oliver *et al.* (2000) have recently published two garnet Sm–Nd ages, directly dating metamorphism, one from the kyanite zone of the Barrovian Type locality in Scotland at 472 ± 2 Ma and the other from the garnet zone at 467.6 ± 2.5 Ma. Thus, considering all reliable data from Scotland, the best current estimate for the age of peak Grampian metamorphism is *c.* 470 Ma.

Recent work from correlative Dalradian metasediments in Connemara, Ireland (Friedrich *et al.* 1999*a*, *b*) employing U/Pb dating of zircons, monazites, and titanites in synmetamorphic gabbros and two metamorphic migmatites also yield ages clustering around 470 Ma. These data agree with the data from Scotland, and the metamorphic migmatite ages agree closely with the gabbro ages, confirming their contemporaneity.

The history of efforts to constrain the age of Grampian metamorphism in Scotland shows the uncertainties inherent in field interpretations of the relative timing of magmatism and metamorphism as well as the use of different dating techniques and minerals, some of which have since been shown to be inaccurate for this type of application. The most recent studies from Scotland, and corroborating data from Connemara, Ireland, show that the accepted age of Grampian metamorphism in Scotland is converging on about *c.* 470 Ma.

Sample characteristics

The field area for this study is located in Glen Clova, Angus, Scotland (Figs 1 & 2). The rocks under consideration are interlayered pelitic and psammitic metasediments outcropping along the steep valley walls. These rocks underwent peak metamorphism at *c.* 660 °C and *c.* 6 kbar (Ague *et al.* 2001) and lie just within the regional sillimanite zone. Metapelite mineral assemblages include quartz, plagioclase, biotite, muscovite, garnet, aluminosilicate, Fe–Ti oxide phases and accessory sulphides. Chinner (1960), McLellan (1985) and Ague *et al.* (2001) have described intercalated metapelite rocks of differing bulk rock FeO/Fe_2O_3 and redox states. Ague *et al.* (2001) define two end members: 'oxidized' and 'reduced'. The 'oxidized' variety, representative of 94% of the metapelitic rocks observed at Glen Clova, have calculated $\log f_{O_2}$'s of *c.* 2.0 log10 units above the quartz–magnetite–fayalite buffer (ΔQFM) and include rhombohedral oxides and magnetite. The rare "reduced" layers, representative of the other 6%, have $\log f_{O_2} \approx -0.5$ ΔQFM and contain ilmenite but lack magnetite. Ague *et al.* (2001) provide evidence that the most reduced of these rocks may have experienced an episode of interaction with an advecting, reducing fluid during metamorphism. The metamorphic mineral compositions, fluid compositions and oxygen fugacities of these rocks are discussed in detail by Ague *et al.* (2001).

Two samples were chosen for age analysis to represent the two end members of garnet-bearing metapelitic rocks in the area. The two samples were collected *in situ* from outcrops just 50 m apart (Fig. 2). The first sample, JAB60a, is representative of the common 'oxidized' metapelite. The aluminosilicate in JAB60a is sillimanite. Sample JAB60a also includes *c.* 5% garnet porphyroblasts as large as 4 mm in diameter. The second sample, JAB62a, is the most 'reduced' metapelite sample reported by Ague *et al.* (2001) in the area, having a calculated $\log f_{O_2}$ of −0.75 ΔQFM. The aluminosilicate in JAB62a is both sillimanite and kyanite. Sample JAB62a also includes abundant

Table 1. *Summary of existing geochronology for Grampian metamorphism*

AGE (Ma)	±	Location	Technique	Mineral	Rock type	Comments	Reference
Scotland ages							
472.9	2.9	Glen Clova	Sm–Nd	Garnet	Metapelite – oxidized	Sample JAB60A – oxidized	This study
464.8	2.7	Glen Clova	Sm–Nd	Garnet rim	Metapelite – reduced	Sample JAB62A – reduced	This study
467.6	2.5	Kinnard House	Sm–Nd	Garnet	Metapelite	Garnet zone	Oliver *et al.* 2000
472.0	2.0	Grandtully rapids	Sm–Nd	Garnet	Metapelite	Kyanite zone	Oliver *et al.* 2000
467.1	5.9	Strichen	U–Pb	Zircon	Granite	Synmetamorphic	Oliver *et al.* 2000
478.0	8.0	Ballantrae Ophiolite Complex	Structural–K/Ar	Hornblende	Ophiolite	Syn D_1	Oliver *et al.* 2000; and Bluck *et al.* 1980
485		Macduff	Biostratigraphic	Veryhachium cf. Lairdi	Slate	Protolith deposition of Metamorphosed sediments	Soper *et al.* 1999 and Molyneux 1998
468	?	Insch	U–Pb	Zircon	Gabbro	D_2–D_3	Rogers *et al.* 1994
472	?	Morven–Cabrach	U–Pb	Zircon	Gabbro	D_2–D_3	Rogers *et al.* 1994
590	2	Ben Vuirich	U–Pb	Zircon	Granite	See Soper *et al.* (1999): the Ben Vuirich is pre-metamoprhic, certainly pre-D_2.	Rogers *et al.* 1989
470	1	Aberdeen	U/Pb	Monazite	Granite	Synmetamorphic	Kneller & Aftalion 1987
520–490		Scotland	Deformational	NA	NA	Based on earlier Ben Vuirich age and whole rock ages of Pankhurst 1970	Harte *et al.* 1984
514	7	Ben Vuirich	U–Pb	Zircon	Granite	Later updated by Rogers *et al.* (1989)	Pankhurst & Pidgeon 1976
481	15	Dunfallandy Hill	Rb–Sr WR	WR	Granite	D_2–D_3: with decay const. Correction	Pankhurst & Pidgeon 1976
482	12	Arnage	Rb–Sr WR	WR	Granites/ gneisses	Post-metamorphic peak: with decay constant correction	Pankhurst 1970
487	23	Haddo House	Rb–Sr WR	WR	Metamorphic aureole	During or after metamorphic peak: with decay constant correction	Pankhurst 1970
492	26	Insch	Rb–Sr WR	WR	Gabbro	During or after metamorphic peak: with decay constant correction	Pankhurst 1970
Ireland ages: Connemara							
462.8	0.7	Southern Connemara	^{207}Pb–^{235}U	Titanite	Calsilicate	Migmatite zone	Friedrich *et al.* 1999*a*
468.4	1.5	Southern Connemara	^{207}Pb–^{235}U	Monazite	Metapelite	Anatectic metapelite associated with igneous intrusions	Friedrich *et al.* 1999*a*
470.1	1.4	Cashel–Lough Wheelaun	U–Pb	Zircon	Gabbro	Synorogenic	Friedrich *et al.* 1999*b*
474.5	1	Currywongaun	U–Pb	Zircon	gabbro	Synorogenic	Friedrich *et al.* 1999*b*

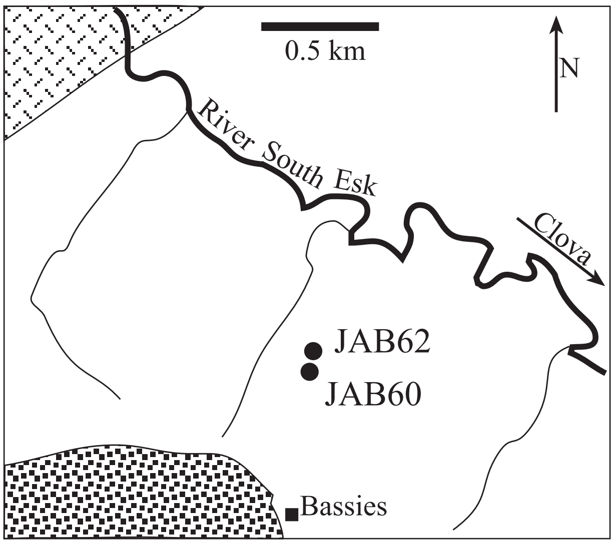

Fig. 2. Detail of the Glen Clova sample locality. Sample locations for JAB60a and JAB62a, just 50 meters apart are shown. The unpatterned area is sillimanite grade metasediments. The dark stippled area is para-amphibolite 'Green Beds'. The cross-hatched area is 'newer' post peak metamorphic intrusive rock.

(20–30%) garnet porphyroblasts as large as 5 mm in diameter. Sample JAB62a shows minor weathering due to oxidation of the pyrrhotite in its matrix. Sample JAB62a has a significantly greater modal proportion of muscovite to biotite (85:15) than JAB60a (50:50). Also, JAB62a has a lower bulk Mg/(Mg + Fe) ratio (0.231) than JAB60a (0.352). In this way, sample JAB62a is closely analogous to the 'type IIIb' pelites of McLellan (1985).

Garnet chemistry

Chemical profiles from electron microprobe traverses across representative garnets from each sample show important differences. Garnet profiles from JAB60a (Fig. 3a, b) have characteristics consistent with prograde zoning (decreasing spessartine content and increasing Mg/(Mg + Fe) from core to rim) with perhaps some evidence for high temperature and/or retrograde diffusional modification of the outer few hundred microns. These rocks are fairly manganese rich (e.g. Chinner 1960), and contain relatively little garnet, which could also explain why we do not see a more pronounced 'Rayleigh fractionation' depletion of spessartine from core-to-rim. Grossular content fluctuates slightly about a mean of 7 mol%. There are no inclusions of aluminosilicate anywhere within the garnets from JAB60a. Therefore, these garnets most likely reflect prograde growth during garnet zone conditions (>*c.* 500 °C, Spear & Cheney 1989) which was completed before the growth of kyanite or sillimanite (<*c.* 550 °C, minimum kyanite zone temperature from McLellan 1985). Garnet may have grown while aluminosilicate existed in the matrix without actually preserving inclusions of kyanite or sillimanite (e.g. Vance & Holland 1993), but because other garnet in the area does include aluminosilicate (see below) the simplest explanation is that growth of JAB60a garnet preceded aluminosilicate growth entirely.

Chemical profiles for garnet in JAB62a are remarkably different (Fig. 3c, d). Most significant is the sharp jump in grossular content, by a factor of 2, at a radius of about 1.4 mm. This jump from about 10 mol% to 20 mol% grossular coincides with a shift in Mg/(Mg + Fe) ratio from decreasing to increasing with radius. On the basis of these chemical features, we define two distinct domains in this garnet, the 'core' and the 'rim' (Fig. 3c, d). Spessartine content is low, and only slightly bell-shaped in the garnet interior, but at the point of grossular increase, spessartine shows a noticeable downturn. The outermost few tens of microns were probably affected by some retrograde diffusional re-equilibration. Finally, of particular note is the existence of sillimanite inclusions in the outer 'rim' portion of garnet JAB62a, but no aluminosilicate inclusions in the 'core' of the garnet.

The history of the JAB62a garnet is complex, but for the current purpose, the most important information is that this garnet clearly records multiple episodes of growth: the earliest characterized by the core, and the latter characterized by the highly calcic 'rim' portion with sillimanite inclusions. The garnet core most likely grew during an initial period of growth, similar to the growth of garnets in JAB60a, during garnet zone conditions and before aluminosilicate growth. The garnet 'rim' grew during a second generation of garnet growth during sillimanite (or kyanite, see below) zone conditions.

Conditions and relative timing of garnet growth

The existence of more than one generation of garnet growth in sample JAB62 is corroborated by the observations ofMcLellan (1985, 1989). Recall that sample JAB62a is analogous to the 'type IIIb pelites' of McLellan (1985) on the basis of bulk rock Fe/Mg ratio and modal muscovite/biotite ratio. A third similarity between JAB62a and McLellan's (1985) 'type IIIb pelites' is the existence of 'fibrolite inclusions in late (syn- or post D_3) garnets'. This later generation of garnet growth, restricted to the 'type IIIb pelites', was mostly the result of staurolite breakdown by the generalized reactions: staurolite + biotite + quartz = garnet + muscovite + H_2O and, either simultaneously or at somewhat higher temperatures, staurolite + quartz = garnet + Al_2SiO_5 + H_2O (reactions 4 and 2 of McLellan (1985), respectively). The former reaction accounts for the large muscovite:biotite ratio in 'type IIIb pelites' and in JAB62a, whereas the latter accounts for Al_2SiO_5 inclusions in garnet. Both reactions contributed to the growth of garnet beyond garnet and staurolite zone conditions.

In the more common 'oxidized' pelites, analogous to our sample JAB60a, there was no garnet forming reaction operating above staurolite zone conditions (McLellan 1985). Staurolite broke down according to: staurolite + muscovite + quartz = biotite + Al_2SiO_5 + H_2O (reaction 3, McLellan 1985). The relatively large amount of biotite and the lack of Al_2SiO_5 inclusions in garnet in JAB60a are consistent with this reaction. From this, we conclude that the garnet of JAB60a (and JAB62a garnet core) grew before staurolite breakdown and aluminosilicate growth, most likely during typical garnet zone conditions. The outer 'rim' portions of garnets in JAB62a grew later and incorporated inclusions of Al_2SiO_5 after the rocks had passed from staurolite zone conditions into higher grades.

In an effort to more directly assess the conditions of JAB62a garnet 'rim' growth, the GASP (grossular + aluminosilicate + quartz = anorthite) geobarometer was used, along with the TWEEQ thermodynamic program of Berman (1991), to estimate a range in P and T recorded by plagioclase inclusions and the surrounding garnet composition. Plagioclase inclusions are present in the grossular rich 'rim' (*c.* 1.5–1.7 mm; Fig. 3c) and are as calcic as An_{55}: unusually high for typical pelitic rocks.

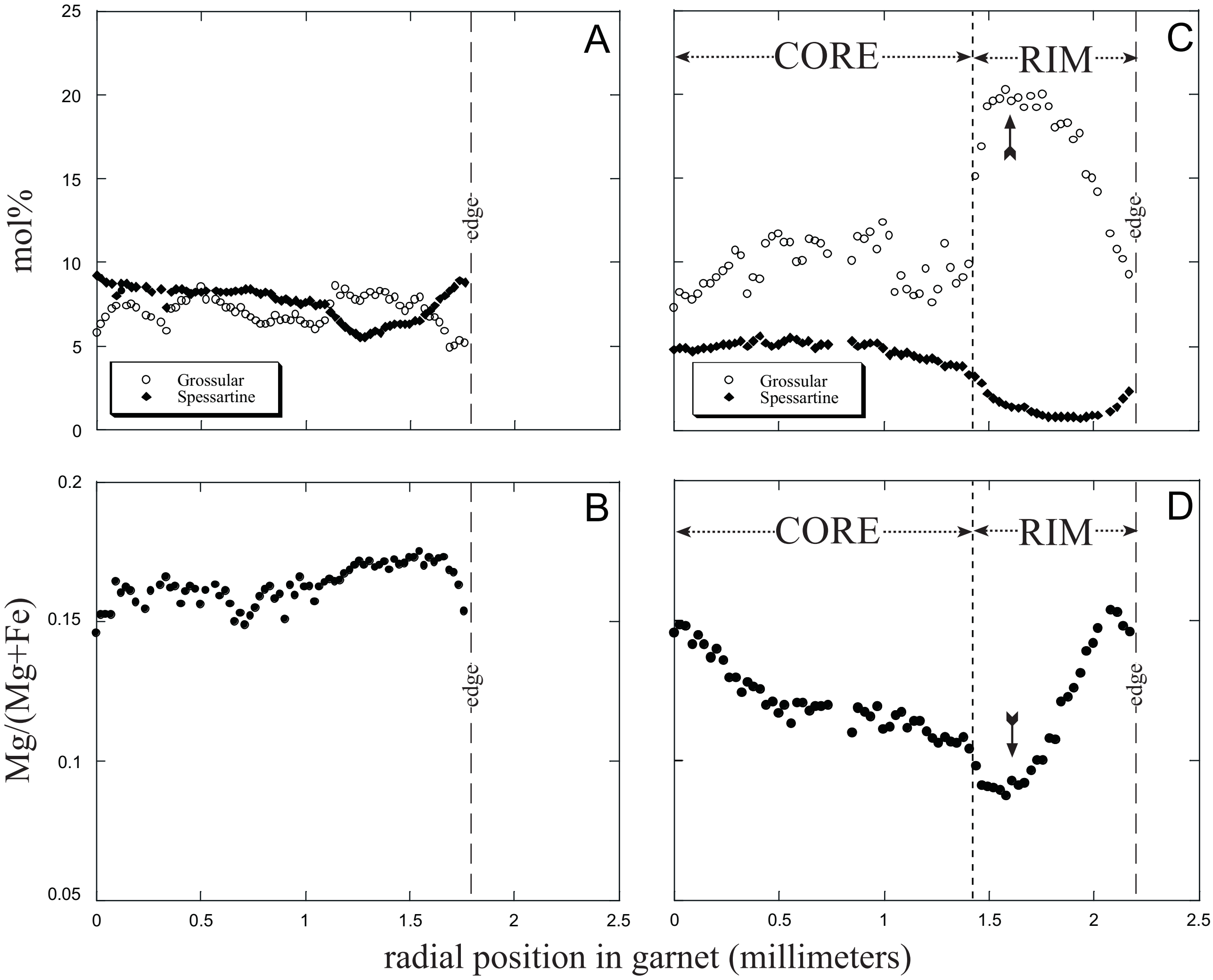

Fig. 3. Electron microprobe traverses of garnet from JAB60a (**a, b**) and JAB62a (**c, d**). Both traverses begin in the chemical center of the garnet and run to the edge. JAB60a profiles are generally consistent with prograde garnet growth. JAB62a shows a marked jump in grossular and Mg/(Mg + Fe) at about 1.4 mm which defines a transition between 'core' and 'rim' generations of growth. Sillimanite inclusions were found only in the 'rim' portion of JAB62a. No aluminosilicate inclusions were found in JAB60a garnet. The arrows in (3c,d) denote the radial position of the An_{55} plagioclase inclusion mentioned in the text and the garnet compositions used in *P–T* calculations for growth of the 'rim' portion. Analytical methods are described in Ague *et al.* (2001).

Using these included plagioclase compositions and the garnet compositions immediately surrounding them (arrows in Fig. 3c, d), for a temperature range of 550 °C to 650 °C, the calculated pressures are 7.2 kbar and 9.2 kbar respectively, indicating conditions well within the kyanite stability field, regardless of temperature. This result is problematic because sillimanite, not kyanite, is included in the 'rim' portion of this garnet from which the *P–T* estimate was made. There are two explanations for this apparent paradox: (1) the sillimanite originally grew and was included as kyanite and has since converted to sillimanite at higher temperatures or (2) the *P–T* calculated from the plagioclase–garnet compositions is in error due to disequilibrium between the garnet and plagioclase when the garnet grew and included it. Texturally, the sillimanite inclusions exist as fine mats of fibrolite with no textural indication of a pseudomorph after primary kyanite. Plagioclase–garnet disequilibrium with respect to calcium is possible if an advecting fluid imposed the high Ca content in the garnet but the pre-existing plagioclase failed to fully equilibrate with it. Disequilibrium of calcium in garnet with respect to other phases has been demonstrated in other studies (e.g. Baxter & DePaolo 2000; Chernoff & Carlson 1997). Because we cannot prove which of these two possibilities explains this apparent paradox, we can conclude only that the second generation of garnet growth recorded in the 'rim' portion of garnet JAB62a grew during either or both kyanite and sillimanite zone conditions. Recall also that the final 'peak' metamorphic conditions determined from matrix phase and garnet edge compositions from this and other samples gives 650–700 °C and *c.* 6 kbars, well within the sillimanite zone (Ague *et al.* 2001; McLellan 1985).

Geochronological technique

The Sm/Nd isochron method for dating the age of garnet porphyroblast growth was chosen for several reasons. First, the Sm/Nd system is not easily reset by post-garnet growth events nor is it subject to potential disequilibrium effects introduced by fluid rock interaction in heterogeneous systems, a problematic issue in the Rb/Sr system (Baxter & DePaolo 2000). Thus, the Sm/Nd system should preserve the true age of garnet growth. Second, garnet typically has a very high Sm/Nd ratio which, when compared to the matrix, can yield a large spread in Sm/Nd and, hence, the possibility for a very precise age. The benefit of this large spread in Sm/Nd is partially offset by low concentrations of Sm and Nd (*c.*1 ppm or less), which limit our ability to precisely measure individual isotope ratios on small volumes of garnet. The Glen Clova garnets also have inclusions of matrix minerals which make preparation of pure garnet separates difficult. If included minerals contaminate the garnet sample, they may be detrimental in two ways. First, since most inclusions have low Sm/Nd ratios and high Sm and Nd concentrations, their presence even in small quantities will result in a 'garnet' separate with lower Sm/Nd ratio and ultimately a less precise age. Second, if the inclusions record an older age of growth, they will skew the accuracy of the measured age of the garnet inappropriately. This second effect becomes insignificant for 'garnet' separates with high enough Sm/Nd ratios because inclusions are so similar to the matrix that any remaining inclusion contamination is essentially just pulling the true garnet composition down along the isochron.

Two-point garnet-whole-rock (WR) isochrons are used as they provide a measure of a specific metamorphic event, namely the growth of garnet, rather than an 'average' metamorphic age as would be determined from a multi-mineral isochron, which would include minerals that grew and closed isotopically at different times during metamorphism. Furthermore, dating garnet directly provides an unequivocal metamorphic age as opposed to other estimates of metamorphic timing based on dates of igneous intrusions inferred to have been synmetamorphic from field observations. Here, bulk garnet samples will be analysed which represent a specific time *interval:* that of garnet growth. Thus the measured age will correspond to an average time within that interval, dominated by the age of the outer portions given the roughly concentric growth geometry of a garnet.

Sample preparation

To ensure that a pure garnet sample was analysed, a careful series of sieving, magnetic separation, and partial dissolution steps were utilized to remove inclusions from the garnet before dissolution. The garnet inclusion population includes (in decreasing order of abundance), quartz, biotite, rhombohedral oxides, plagioclase and chlorite ± aluminosilicate. Whole-rock chunks weighing 50–150 g were trimmed of obviously weathered surfaces, ultrasonically cleaned in distilled water, and coarsely crushed with a tungsten carbide mortar and pestle. Two cuts were then separated: one for making a whole-rock powder and one for garnet mineral separate preparation. A portion of the whole-rock cut was powdered in an agate ball mill. The other cut was sieved through a 100 mesh screen and the fines were then separated with the Franz magnetic separator, yielding a magnetic cut consisting of *c.* 95% pure garnet plus inclusions. Obvious non-garnet contaminants were hand-picked and removed.

Next, the garnet separate was treated with a series of acids designed to preferentially dissolve away all non-garnet inclusions and preserve (most of) the pure garnet for isotopic analysis. Broadly similar partial dissolution techniques involving hydrofluoric acid (HF) have been successfully employed by Amato *et al.* (1999) for Sm/Nd dating of garnet. To accomplish this, a primary HF acid treatment was used to dissolve away inclusions. Roughly 1.5 ml of concentrated HF was added to the garnet separate and the mixture was heated for *c.*1 hour. This HF treatment dissolves silicate and oxide inclusions that are more susceptible to dissolution than the highly refractory garnet, as well as some of the garnet itself. After decanting the HF, and rinsing the residue several times in dilute HCl and water, a secondary acid treatment is needed to remove any secondary fluoride salts that precipitated from dissolved inclusions. Concentrated perchloric acid ($HClO_3$) was used for this purpose. We used perchloric acid because we found it much more effective at dissolving fluoride residues than either hydrochloric (HCl) or nitric (HNO_3) acid (see below). After the sample was heated and evaporated to dryness, 1.5N HCl was then added to bring any perchlorate residue into solution and was decanted.

After acid treatment, the remaining garnet was rinsed several times in distilled water in an ultrasonic bath and the result was a high purity garnet separate. Finally, whole-rock powders and pure garnet separates were dissolved with HF and perchloric acid, and the necessary elements were separated for conventional thermal ionization mass-spectrometric analysis using large volume ion exchange columns.

Tests of the partial dissolution acid treatment of garnet

To test, refine, and demonstrate the utility of the acid treatment technique described above, garnet samples from Townshend Dam, Vermont were treated and analysed (Baxter 2000). Figure 4 shows the results of these tests. Previous study shows that these garnets have an age of about 380Ma (see Kohn & Valley 1994 for a review). First, five garnet separates, each taken from the rim of the same garnet porphyroblast, were prepared and treated using the primary HF treatment and various secondary acid treatments. Three of the samples were treated with secondary HCl, nitric, and HCl + nitric acids respectively. However, these three garnet samples yielded very low Sm/Nd ratios, and anomalously old ages (see Fig. 4a) indicating that the analysed sample was still dominated by low Sm/Nd inclusions with older ages. The other two samples were treated with secondary perchloric acid and both yield high Sm/Nd ratios and statistically indistinguishable ages consistent with the expected age of these garnets. Finally, three additional garnet samples from other garnet porphyroblasts from Townshend Dam were measured with the final, primary HF + secondary perchloric acid treatment. The five total samples that were treated identically with primary HF acid and secondary perchloric acid all give ages which are statistically indistinguishable from each other and which define an average age of 381Ma (Fig. 4b). These test samples demonstrate the utility of the final acid treatment technique in achieving accurate and reproducible garnet Sm–Nd ages with lower individual uncertainties. The tests show that the use of perchloric acid is the most effective as a means of dissolving secondary fluoride precipitates.

Results

Figure 5 and Table 2 show the results of the Sm/Nd geochronology for the two samples from Glen Clova, JAB60a and JAB62a. The high Sm/Nd ratios confirm that the garnets have been well cleansed of low Sm/Nd inclusions. Despite the slightly higher than desired errors on the garnet data (due to small sample volumes and low concentrations) high precision ages were still achieved due to the large spread in Sm/Nd. The two ages, 472.9 ± 2.9 Ma and 466.8 ± 1.9 Ma respectively (2σ external age errors), indicate that two distinct generations of garnet growth are recorded in the rocks of Glen Clova. This is consistent with the microtextural observations summarized by McLellan (1985; 1989) who presented evidence for two distinct garnet growth episodes: the first during garnet grade conditions and D_2 deformation; the second during staurolite breakdown, Al_2SiO_5 growth, and syn- to post-D_3 deformation. This second, later, stage of garnet growth was observed by McLellan (1985, 1989) only in 'type IIIb' pelites, analogous to our sample JAB62a.

Discussion

The average age of 470 Ma from the two samples of this study is consistent with all current geochronological constraints discussed above (i.e. Rogers *et al.* 1994; Friedrich *et al.* 1999*a, b*; Soper *et al.* 1999; Oliver *et al.* 2000). This data strengthens the interpretation of Oliver *et al.* (2000) that exhumation was rapid to account for a detrital Barrovian age garnet found in

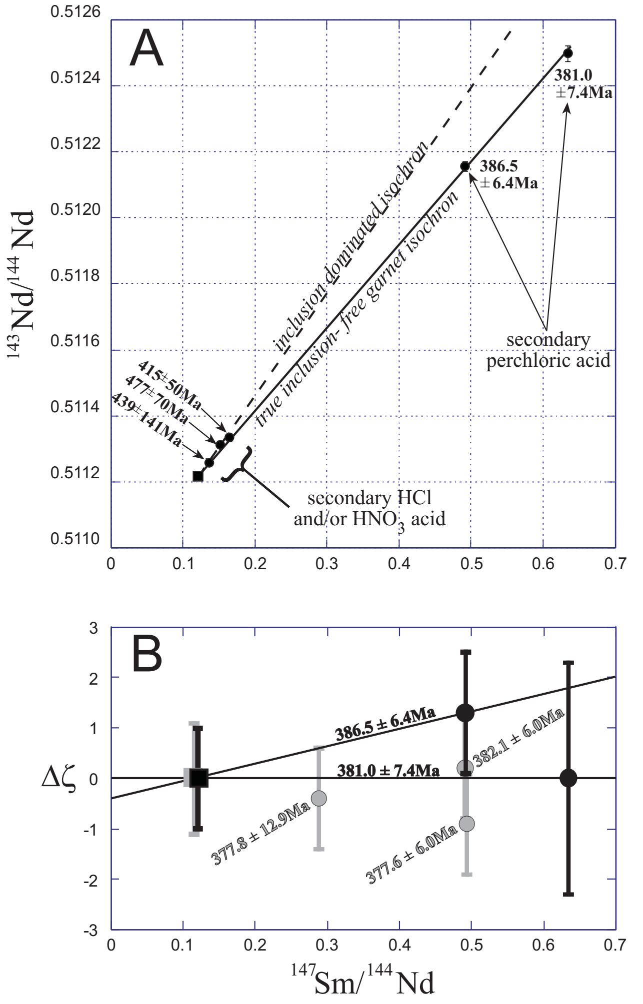

Fig. 4. Test results of the garnet acid treatment preparation technique. Test sample numbers are from Baxter (2000) collected at Townshend Dam, Vermont and have an expected age of about *c.*380 Ma (see Kohn & Valley 1994). (**a**) Isochron plot of data from five samples from the same garnet rim (sample 98BTD 1-E). All samples were treated identically with HF acid. The three samples treated with secondary HCl and/or HNO_3 yielded low Sm/Nd ratios, and older ages, which roughly define an older inclusion dominated isochron. The two samples treated with secondary perchloric acid yielded high Sm/Nd ratios and accurate and reproducible ages. (**b**) Deviation, in parts in 10^5 from the 381 Ma isochron for the data from the two test samples from (a) treated with secondary perchloric acid (black dots), and three additional garnet samples (98BTD 1-E3, 98BTD 1-O3, 98BTD 1-O5) (grey dots) also treated with secondary perchloric acid. These ages are statistically indistinguishable and define an average age of 381 Ma, equal to the expected age. The sample yielding the oldest age (386.5 ± 6.4 Ma) was crushed more coarsely than the others and perhaps retained more of its inclusions, which may explain why it appears to give a slightly older, yet still indistinguishable, age. All errors are 2σ age uncertainties. These tests demonstrate the accuracy, reproducibility and precision of individual ages for the refined acid treatment preparation technique.

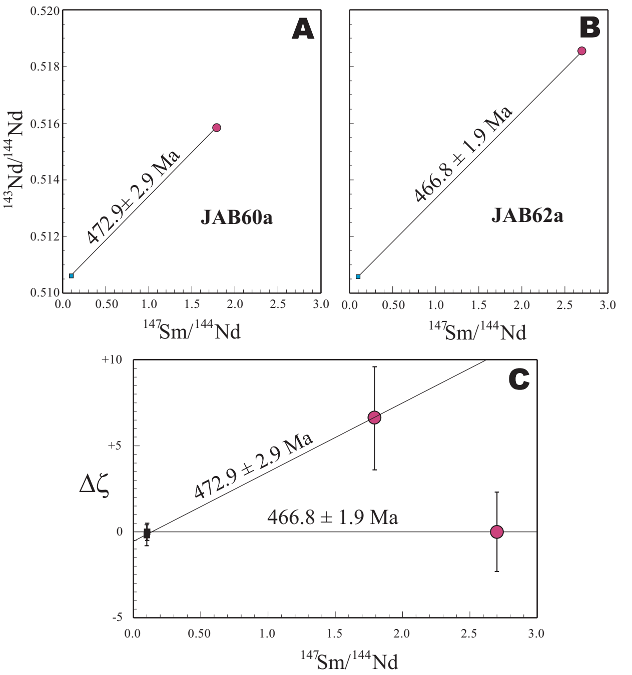

Fig. 5. Garnet–matrix isochron ages for samples JAB60a (**a**) and JAB62a (**b**). (**c**) The deviations in parts in 10^5 of the JAB60a data points from the isochron defined by the JAB62a data (Table 2). The data indicate that the garnet ages recorded in the two samples are significantly different from each other at the 2σ level shown. The Sm/Nd ratios attained in both garnet separates are high enough that any remaining inclusions will not significantly affect age accuracy. In comparison with Figure 4b, note the difference in scale.

Llanvirn conglomerates (depositional age 465 ± 2.5 Ma; time scale of Tucker & McKerrow 1995). However, the fact that the two garnets analysed in our study yielded significantly different ages merits further discussion. Let us begin with the simpler of the two samples: JAB60a. Recall that, based on the textural and chemical observations, these garnets formed during prograde metamorphism at garnet grade conditions, (>*c.* 500 °C, Spear & Cheney 1989), and before growth of kyanite or sillimanite (<*c.* 550 °C, McLellan 1985). Therefore, we conclude that the age of JAB60a garnet, 472.9 ± 2.9 Ma, is the age of garnet grade conditions (500–550 °C), provided that there was no loss of radiogenic Nd during peak conditions subsequent to garnet growth (see below).

The interpretation of the age of JAB62a garnet is somewhat more complicated. The sillimanite inclusions in the outer 'rim' portion of garnet JAB62a (absent from garnet JAB60a), indicate that that portion of the garnet formed during sillimanite (and/or kyanite) grade conditions up to peak temperatures, *c.* 660 °C, within the sillimanite stability field. The inner 'core' portion of this garnet most likely grew at the same time (472.9 ± 2.9 Ma) as JAB60a during garnet grade conditions (500–550 °C). So, the 466.8 ± 1.9 Ma age of garnet JAB62a is an average of two garnet age 'reservoirs'. 25%, by volume, is the garnet core to which we can assign an age of 472.9 ± 2.9 Ma. The other 75% is the outer rim portion. By assuming a constant Nd concentration throughout the garnet, and the volume proportions above determined by assuming roughly spherical garnet geometry, we calculate an age of 464.8 ± 2.7 Ma (2σ error) for growth of the outer rim portion of JAB62a garnet. The assumption of constant Nd concentration in the garnet is reasonable, in the absence of other information, because the measured Nd concentrations in both garnet samples is identical. Despite additional uncertainties associated with the assumptions in this calculation, we believe that 464.8 ± 2.7 Ma represents the most accurate assessment of the age of rim growth of garnet JAB62a.

Table 2. *Sm–Nd isotopic data for Barrovian samples*

Sample	Nd (ppm)	Sm (ppm)	^{143}Nd/^{144}Nd	±	^{147}Sm/^{144}Nd	±
JAB60a whole-rock	31.7	5.19	0.510592	0.000006	0.09890	0.00001
JAB60a garnet	0.23	0.67	0.515837	0.000030	1.79208	0.00078
JAB62a whole-rock	47.8	8.06	0.510603	0.000005	0.10196	0.00003
JAB62a garnet	0.23	1.04	0.518549	0.000023	2.7006	0.0068

All errors reported above are internal analytical 2σ uncertainties. Nd data was corrected for fractionation using ^{146}Nd/^{142}Nd=0.636151. Reproducibility of the standard was .511083 ± 10 for Nd (Ames Metal) over the duration of the analyses. Sm/Nd total external errors are ± 0.1% for all samples. The external precision (± 0.000010 for ^{143}Nd/^{144}Nd; ± 0.1% for ^{147}Sm/^{144}Nd) was used for error propagation in age calculations for all samples unless the internal analytical error (reported above) was higher, in which case it was used instead. Blanks are insignificant: <10 pg for Sm and Nd.

Nd diffusion modelling in garnet

Numerous studies have shown that the diffusional 'closure temperature' for garnets of >1 mm radius as in these rocks, is certainly no lower than *c.* 675 °C for a cooling rate of at least 10 °C Ma^{-1} (Coghlan 1990; Burton *et al.* 1995; Ganguly *et al.* 1998). However, the situation for JAB60a and JAB62a core garnet is not one of cooling, but of heating after growth and through peak conditions, so the closure temperature concept does not directly apply. To rigorously assess the important condition for accurate geochronology that no radiogenic Nd be lost from the garnet subsequent to its growth, a finite difference numerical model for Nd diffusion out of garnet was constructed. The model monitors the radial profile of radiogenic Nd content in a spherical garnet as it is produced *in situ* after growth and travels through a prescribed temperature-time path. Diffusional loss of Nd from the garnet as well as radiogenic growth of Nd in both garnet and matrix is included in the model. The model garnet resides in a matrix with an Sm/Nd ratio 200 times smaller than the garnet Sm/Nd ratio (e.g. 0.1 for matrix, 2.0 for garnet – representative of these rocks).

The partial differential equation solved in the numerical model is:

$$\frac{\partial C_{Nd*}}{\partial t}=D_s\left(\frac{\partial^2 C_{Nd*}}{\partial r^2}+\frac{2}{r}\frac{\partial C_{Nd*}}{\partial r}\right)+\lambda C_{147_{Sm}}$$

for each radial increment in the model garnet sphere (Crank 1975), where, $C_{\mathrm{Nd*}}$ is the radiogenic ^{143}Nd* produced since the start of the model, D_s is the solid-state diffusion of Nd in garnet at each time increment, r is the garnet radius, λ is the decay constant of ^{147}Sm (6.54 × 10^{-12} a^{-1}), and is the concentration of ^{147}Sm in the garnet. The initial condition is, $C_{Nd*} = C^{mtx}_{Nd*} = 0$, both in the garnet and in the surrounding matrix. The boundary condition is, $C^{mtx}_{Nd*} = \lambda \frac{C_{147_{Sm}}}{200} t$. The matrix, therefore, is treated as an infinitely capacitive reservoir for Nd* diffused out of the garnet: an appropriate approximation since the Nd concentration in the matrix (*c.*30–50 ppm) far exceeds the Nd concentration of the garnet (0.23 ppm).

For the modeling of JAB60a garnet, we take a garnet of radius 2 mm, which grew instantaneously at 473 Ma. We prescribe a crude temperature–time path appropriate for the Glen Clova rocks: beginning at 525 °C at 473 Ma, increasing linearly to 660 °C at 465Ma, and then decreasing linearly to 525 °C at 461 Ma. We use the recent diffusion parameters of Ganguly *et al.* (1998) to calculate the solid-state diffusivity of Nd in garnet from the temperature–time path.

The results of the modelling confirm that there is negligible loss of radiogenic Nd from the garnet subsequent to growth. Figure 6 shows the radial radiogenic Nd profile in the garnet after the 12 Ma duration of the model. Significant diffusional loss has only occurred in the outer 80 µm, which corresponds to a loss of just 1.5% of the total radiogenic Nd accumulated in the garnet. This would correspond to an age error of only 0.18 Ma, which is insignificant. For any reasonable temperature–time path for these rocks, the result is similar. For garnet JAB62a, the garnet core region is of smaller radius, but it will have been armoured from diffusive loss once the second generation begins to grow around it. Diffusional

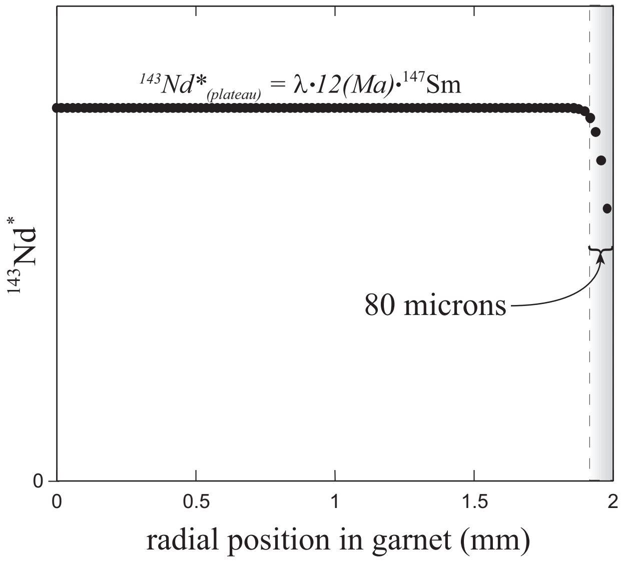

Fig. 6. Results of garnet Nd diffusion model. Shown is the amount of radiogenic ^{143}Nd* produced since garnet formation at 473 Ma and retained in the garnet, as a function of radius, after the specified 12 Ma temperature–time path (until 461 Ma) appropriate for these rocks as described in the text. If none of the ^{143}Nd* had been lost from the garnet, then it would entirely have a ^{143}Nd* value equal to the product of λ (in a^{-1}; the decay constant of ^{147}Sm), 12 000 000 (in years; the time after growth in the model) and ^{147}Sm (the ^{147}Sm concentration in the garnet). This value, (λ × 12 Ma × ^{147}Sm), is the undisturbed plateau for the bulk of the garnet as shown on the figure. Only the outer 80 µm have failed to retain this amount due to diffusive loss. Integrating over the spherical volume of the model garnet, we find that it has retained 98.5% of its radiogenic ^{143}Nd*. The loss of 1.5% corresponds to an age error of 0.18 Ma, which is insignificant. That age error does not change after 461 Ma because the garnet will quantitatively accumulate all of its ^{143}Nd* from then until the present.

modelling confirms that there will be no significant loss of Nd from any garnet subsequent to its growth, and thus, the ages as interpreted above are reliable.

Interpretation and temperature-time paths

The garnets analysed from Glen Clova produce two geologically meaningful age constraints on the prograde temperature–time evolution of these rocks. First, 472.9 ± 2.9 Ma is the age at which the system passed through garnet grade conditions, (*c.* 500–550 °C) before the growth of aluminosilicate. Second, 464.8 ± 2.7 Ma is the age of garnet growth at higher grades at Glen Clova during sillimanite (and/or kyanite) growth. The younger 464.8 ± 2.7 Ma age for the JAB62a garnet rim could be related to an advective pulse of reducing fluid, perhaps expedited by the D3-deformational event, that contributed to the reduction of this particular rock (Ague *et al.* 2001) and promoted the growth of the large, Ca-rich, garnet rims. It is also probable that the different whole-rock composition of JAB62a promoted secondary growth of garnet due to a staurolite breakdown reaction (i.e McLellan 1985, see above).

Figure 7 summarizes the existing temperature–time garnet data from Barrow's zones in Scotland. Garnet from the kyanite zone dated by Oliver *et al.* (2000) has no inclusions of aluminosilicate (G. J. H. Oliver pers. comm. 2000) so we assume that this garnet also grew during garnet grade conditions (500–550 °C) before kyanite growth. Garnet from the garnet zone dated by Oliver *et al.* (2000) by definition also grew during garnet zone conditions, which were also the peak conditions it reached.

The combined geochronological data, along with the corroborating textural observations of McLellan (1985, 1989), suggest the following interpretations. First, garnets from both the kyanite and sillimanite zones grew at *c.* 473–472 Ma, at temperatures of 500–550 °C, and during D_2 deformation. Second, garnet from the garnet zone, along with the second generation of garnet found in the sillimanite zone, grew at *c.* 467–464Ma, at their respective peak metamorphic temperatures, and during or slightly after D_3 deformation. The age of peak metamorphic temperatures in the kyanite zone is not directly constrained here, but it is reasonable to assume that it should conform to the evolution of the metamorphic zones surrounding it. Therefore, at least the garnet, kyanite, and sillimanite zones of the Barrovian terrane exposed today in Scotland experienced their respective peak metamorphic temperatures at the about the same time: *c.* 467–464 Ma. Statistically speaking, the difference in age between the attainment of peak temperatures in the garnet zone and the sillimanite zone is 2.8 ± 3.7 Ma, contemporaneous within 2σ uncertainty, and with a maximum difference of 6.5 Ma.

Model for regional metamorphism

The contemporaneity of peak temperature conditions in at least these three of Barrow's zones is contrary to traditional models of regional metamorphism, based on conductive thermal relaxation of over-thickened continental crust with an initial steady state geotherm, which predict that rocks from different metamorphic grade must reach their peak temperatures at different times (England & Richardson 1977; Thompson & England 1984; Philpotts 1990). The issue is that an observed 'field gradient' or '*P–T* array' across a metamorphic terrane reveals too shallow a slope in *P–T* space (too hot) to be interpreted as a steady state geotherm that, by the traditional model for regional metamorphism, must have produced it (see Philpotts 1990). But, if the *P–T* array does not represent a single 'time slice', then metamorphism may be explained simply by the conductive heating model with no additional heat source or gradient.

Thompson & England (1984) present two end member models for progressive metamorphism in over-thickened crust. The first (their fig. 8), involving a wedge-like overthrust sheet with an otherwise uniform heat flow distribution, produces the result that the difference in the time of peak temperature attainment between sillimanite and garnet zones would be about 10 Ma. The second (their fig. 9), incorporates an overthrust sheet of uniform thickness, but a laterally variable heat flow within the model terrane, and produces simultaneous peak temperature attainment in all zones. As Thompson & England (1984) suggest, the kind of geochronology collected and discussed in the current paper can be used to distinguish between these two models of progressive metamorphism.

Our data, with the data of Oliver *et al.* (2000), suggest that the difference (if any!) between peak temperature attainment in the garnet zone and peak temperature attainment in the sillimanite zone is very short: 2.8 ± 3.7 Ma. One way to explain the near contemporaneity of peak temperatures in the different zones, is an additional source of heat, beyond that provided by thermal relaxation of a wedge-shaped over thrust sheet with an initial steady state continental geotherm. A localized, additional heat source would provide a thermal regime analogous to the laterally variable heat flow model of Thompson & England (1984) (see above) for which peak temperature attainment was contemporaneous. Note in Figure 7 the ages of local syn-metamorphic igneous intrusions. The ages suggest that there was abundant heat available from these local igneous bodies (and likely others in the area that simply have not yet been dated) during prograde metamorphism up until the peak time. More precise ages on local igneous intrusions would be a useful additional test for this conclusion. Advecting aqueous fluids may have also transported heat (e.g., McLellan, 1989); it is possible that fluids exsolved from and/or thermally equilibrated with these synmetamorphic intrusions helped produce the required thermal perturbations. Furthermore, the highest grade rocks lie geographically closest to these intrusions (Fig. 1), suggesting that the intrusions may indeed have created the higher temperature gradient required. The high *T*–low *P* Buchan Zones to the north were also fuelled by synmetamorphic intrusions, and have recently been shown to be contemporaneous with Barrovian metamorphism as well (Oliver *et al.* 2000). Differential erosion rates could also change the time constant for thermal relaxation and the final pattern of exposed rocks and peak ages (Thompson & England, 1984; Fowler & Nisbet, 1982). However, in the absence of any supporting evidence for differential erosion within Barrow's Zones, and given the strong evidence for local heat sources, we favor the latter explanation.

It should also be noted that the models of Thompson & England (1984) are for erosion of the overburden over a period of about 100 million years. Data from the Barrovian Zones now suggests that the entire Grampian metamorphic event was very short: about 15 Ms from overthrusting to exhumation (see Oliver *et al.* 2000, and above). This order of magnitude difference in erosion rates would reduce the time constant for thermal relaxation for the entire Barrovian section, and would also serve to reduce (but not eliminate)

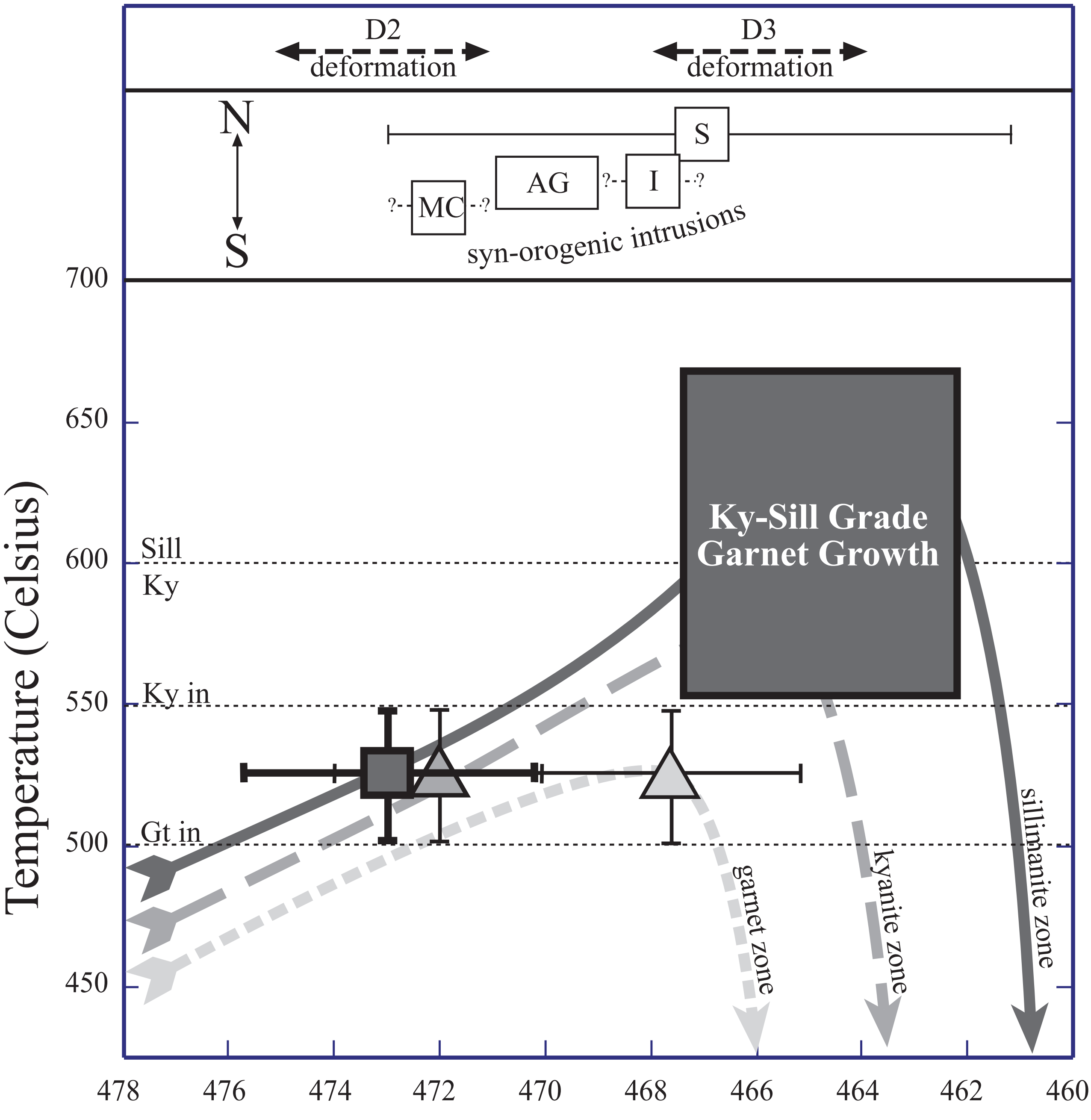

Fig. 7. Sketch of interpreted Barrovian temperature–time evolution for three of Barrow's zones based on the existing garnet geochronology from this study (dark boxes) and Oliver *et al.* (2000) (lighter triangles). Approximate temperatures for onset of key index mineral growth at peak pressures of *c.* 6 kbar are included for reference, but these temperatures could vary somewhat depending on rock composition and pressure. The garnet (Gt) isograd is based on Spear & Cheney (1989); kyanite (Ky) isograd is based on McLellan's (1985) estimate of peak kyanite zone conditions of *c.* 550–600 °C; sillimanite (Sill) isograd is based on Spear & Cheney (1989). The timing of kyanite–sillimanite grade garnet growth recorded in the 'rim' portion of garnet from JAB62a (large dark box) is calculated from the bulk JAB62a garnet age as described in the text. We depict this point as a filled box because we cannot constrain the exact path followed within it due to the uncertainty in the aluminosilicate paragenesis (see text). Statistically speaking, we cannot assume a Gaussian error distribution for this data point. We do know that the peak temperature reached was *c.* 660 °C. We leave it to future research to fill in the path within that box. Temperature ranges associated with peak metamorphism and garnet growth for each data point are discussed in the text. Also shown are the ages of syn-orogenic intrusives arranged in order of proximity to the field site from north to south. See Table 1 and Figure 1 for details. Relative timing of D_2 and D_3 deformation (McLellan 1989) is shown at the top of the figure.

the difference in age of peak temperature attainment between the various zones.

The idea that the progressive metamorphism in Barrow's Zones was driven, (at least in part), by heating from local intrusions was first proposed by Barrow himself (Barrow 1893), so it is not without learned precedent that we revisit this idea. In so far as the Barrovian Zones in Scotland are considered the type locality for regional 'Barrovian-style' metamorphism throughout the world, we suggest that these rocks may represent an intermediate style between end-member regional metamorphism, driven entirely by the relaxation of a perturbed regional thermal gradient in a variably over-thickened crust (i.e. Thompson & England 1984, fig. 8), and contact metamorphism, driven entirely by heat from local intrusions, and consequent lateral thermal gradients. The interpretation of the current study is that both processes contributed to the metamorphism of Barrow's Zones.

Conclusion

Direct determinations of the age of garnet growth in the sillimanite zone at Glen Clova, during the main Grampian Orogeny in Scotland, yield two distinct ages of 472.9 ± 2.9 Ma and 466.8 ± 1.9 Ma for samples of 'oxidized' and 'reduced' metapelitic schist, respectively. The older 472.9 ± 2.9 Ma age is interpreted as the date of garnet growth at 500–550 °C, contemporaneous with D_2 deformation. Garnet chemical zoning patterns show that the later age of 466.8 ± 1.9 Ma is actually an average of two ages: core growth at the same time (472.9 ± 2.9 Ma) and conditions as the earlier garnet, and outer rim growth at 464.8 ± 2.7 Ma during peak metamorphic conditions of sillimanite (and/or kyanite) growth up to *c.* 660 °C. This second generation of garnet growth has previously been documented on a textural basis by McLellan (1985, 1989) and occurs syn- to slightly post-D_3 deformation. Considering these data together with the garnet ages of Oliver *et al.* (2000) from the kyanite and garnet zones suggests an overall prograde metamorphic history for Barrovian metamorphism whereby progressive metamorphic zones reach garnet grade conditions as early as 472.9 ± 2.9 Ma and as late as 467.6 ± 2.5 Ma. Furthermore, the difference between the time of peak temperature attainment in the garnet zone and sillimanite zone is 2.8 ± 3.7 Ma suggesting that the entire package of Barrovian metamorphic rocks comprising garnet, kyanite and sillimanite zones reached their peak temperatures, the magnitude of which increases from zone to zone, nearly contemporaneously within *c.* 467.6–464.8 Ma. The near contemporaneity of peak temperatures in different zones requires an additional source of heat beyond relaxation of a variably over-thickened crust (Thompson & England 1984). We suggest local igneous intrusions, with synmetamorphic ages, provided that additional heat. We hope that the new geochronology presented here will provide a better framework by which geologists may understand the Barrovian type locality as a model for metamorphism, not only for petrology, but also for process.

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