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Initiation and duration of Grampian orogenesis constrained by refined Sm–Nd garnet geochronology of the Ballantrae ophiolite, Scotland

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Abstract: We report the results of Sm–Nd garnet geochronology on a mafic granulite from the metamorphic sole of the Ballantrae Ophiolite, Scotland. The resultant age of 477.6 ± 1.9 Ma (2σ) is interpreted to represent the obduction of the Ballantrae Ophiolite and the onset of the Grampian phase of the Caledonian Orogeny in Scotland. Thermodynamic modelling indicates peak conditions of c. 825°C and at least 10 kbar for the unit. In conjunction with a biostratigraphic constraint on metamorphic garnet deposition in sediments at 465 ± 2.5 Ma, this new age more precisely constrains the duration of Grampian metamorphism in Scotland to 12.6 ± 3.1 myr (2σ). In combination with this new age, previous geochronological work on sillimanite-zone garnet indicates a time-averaged initial heating rate of 106 ± 78°C myr⁻¹ (2σ), a rapid rate that may be inconsistent with orogenic self-heating via crustal overthickening alone. The calculated heating rate for the associated garnet zone is also rapid and more precisely constrained at 47 ± 14°C myr⁻¹ (2σ). These results together with the short overall duration of the event support the idea that the Grampian phase of the Caledonian Orogeny in Scotland included both rapid heating and correspondingly fast exhumation.

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The Grampian phase of the Caledonian Orogeny in Scotland is, perhaps, the longest-studied regional metamorphic event in history. From its initial characterization by Barrow in his seminal paper on regional metamorphism (Barrow 1893) to the more recent work on timescales of orogenesis (e.g. Oliver et al. 2000; Baxter et al. 2002; Ague & Baxter 2007; Chew et al. 2010; Vite et al. 2011, 2013; Vorhies & Ague 2011), this stretch of the Caledonides has been home to a large number of metamorphic studies. The Grampian episode is characterized by relatively short-lived medium-pressure metamorphism that followed closure of a marginal ocean basin (e.g. Dewey 1971; Van Staal et al. 1998; Stone 2014). The Ballantrae Ophiolite Complex represents a remnant of a marginal sea that was thrust onto continental crust; it is a common interpretation that the Ballantrae Ophiolite Complex represents oceanic lithosphere from a marginal basin that was thrust onto continental crust (Church & Gayer 1973; Spray & Williams 1980)(Fig. 1). The complex was first recognized as an ophiolite sequence (in the sense of Brongniart 1821) fairly early by Anderson (1936), who compared it with similar terranes in the Alps. With the subsequent development of plate tectonic theory, it was proposed that the Ballantrae Ophiolite Complex represents oceanic lithosphere from a marginal basin that was thrust onto continental crust (Church & Gayer 1973; Spry & Williams 1980). This fact, combined with poor exposure, makes it impossible to discern a true ophiolitic succession in the field; however, each of the expected lithologies (pelagic sediments, pillow lavas, sheeted diabase, gabbro, ultramafic cumulates and serpentinite mélange including blocks of blueschist) is present (Church & Gayer 1973).

The ophiolite proper is structurally underlain by a metamorphic aureole or ‘sole’ of variably metamorphosed basaltic rocks, which were studied in detail by Spry & Williams (1980). The metabasites are schistose and range in grade from greenschist to granulite facies. The entire sole is less than 50 m thick and exhibits an inverted metamorphic gradient; that is, higher grade rocks are structurally above those of lower grade (Spry & Williams 1980). The sequence is broadly divided into a plagioclase amphibolite and a lower-grade epidote schist. Spry & Williams (1980) further divided the amphibolite into four subunits: an upper and lower garnet-bearing amphibolite and an upper and lower garnet-free amphibolite. Thermobarometric estimates based on iron–magnesium exchange between garnet and clinopyroxene yielded peak temperatures of...
c. 850°C for the garnet amphibolite (Spray & Williams 1980). The tectonic significance of the ophiolitic sole is paramount, as it marks the deformation zone that separates oceanic lithosphere and continental crust. It is generally accepted that the metamorphic sole was formed via subduction beneath the Ballantrae Ophiolite (Bluck et al. 1980; Spray & Williams 1980; Oliver 2001). This subduction initiation is interpreted as the first step in the process of ophiolite obduction (e.g. Wakabayashi & Dilek 2003).

In the broader context of Caledonian orogenesis, it is often interpreted that the obduction of the Ballantrae Ophiolite marks the onset of the Grampian episode in Scotland (Oliver et al. 2000; Oliver 2001; Viete et al. 2013). The Ballantrae Ophiolite Complex initially formed in the back-arc of the Midland Valley Terrane (Spray & Williams 1980; Oliver 2001); when the Midland Valley Terrane docked on the Laurentian margin, the outboard Ballantrae Ophiolite was thrust over this terrane. Therefore the obduction of the Ballantrae Ophiolite was synchronous with the docking of the Midland Valley Terrane and the onset of orogenesis (Fig. 2; e.g. Oliver 2001; Stone 2014).

Prior to this study, the best constraint for the timing of obduction of the Ballantrae Ophiolite was a K–Ar hornblende age of 478 ± 8 Ma for the basal amphibolite unit (Bluck et al. 1980).

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Fig. 1. Maps of the Ballantrae Ophiolite. (a) Location of the Ballantrae Ophiolite in Scotland. (b) Geological map of the Ballantrae Ophiolite Complex modified after Spray & Williams (1980). The box indicates our sampling location. (c) Detailed geological map of the Ballantrae Ophiolite and its metamorphic sole near Knocklaugh, modified after Stephenson et al. (1999). The star marks the location of sample 11ESC-18A.

Fig. 2. Schematic representation of Grampian collision. Modified after Oliver (2001). Ages are approximate and intended only to show relative timing.
Obduction of the nearby Highland Border Ophiolite is measured at c. 490 Ma via 40Ar–39Ar hornblende and mica cooling ages (Chew et al. 2010), although its relationship to broader Caledonian orogenesis has been called into question (e.g. Tanner 2007; Tanner & Sutherland 2007; Henderson et al. 2009). Ballantrae obduction, on the other hand, is within error of estimates for obduction of the Bay of Islands Ophiolite in Newfoundland (475 ± 5 Ma 40Ar–39Ar age from Dollmeyer & Williams 1975), thus suggesting that Ballantrae Ophiolite obduction was associated with the large-scale closure of the Iapetus ocean basin (in addition to marginal basin closure) in the Ordovician period (Oliver 2001).

**Existing geochronology**

Although there is significant modern geochronology in the Scottish Highlands associated with the Grampian phase of the Caledonian Orogeny (e.g. Oliver et al. 2000; Oliver 2001; Baxter et al. 2002; Viete et al. 2011, 2013; Vorhies et al. 2013) there is a relative dearth of chronology in the Ballantrae Complex itself. Table 1 summarizes the existing geochronology. Ages range from 575 ± 32 Ma (Hamilton et al. 1984), evidently reflecting a pre-orogenic stage, to 470 ± 10 Ma (Sawaki et al. 2007; Henderson et al. 2009) during deformation. Most relevant to our study, the above-mentioned 505 ± 11 Ma for the aureole’s metapyroxenite (Hamilton et al. 1984) is probably unrelated to the Grampian event. Hamilton et al. (1984) suggested that the age records an earlier phase of shortening and thrusting prior to subduction initiation.

**Sample description**

Several metabasic rocks were collected from the metamorphic sole of the Ballantrae Ophiolite Complex near Knocklaugh. In the field, sample 11ESC-18A exhibited abundant garnet (abbreviated gb) and was therefore selected for geochronology. Preliminary analyses of garnet chemistry indicated unusually high (1 ppm) concentrations of Nd paired with high 147Sm/144Nd ratios; thus, the sample is ideal for high-precision chronology and is the focus of this study.

Sample 11ESC-18A was collected from an outcrop of dark, foliated metamorphic rock located near Knocklaugh (Fig. 1) that is cut by rare epidote + quartz veinlets (55°11.158 W, 004°52.765 N). Garnet porphyroblasts are highly poikiloblastic, range from c. 2 to c. 5 mm in diameter, and are rimmed by apparently secondary chlorite. In thin section the matrix minerals consist of c. 50% brown pleochroic amphibole, c. 33% heavily sericitized plagioclase, c. 5% clinopyroxene (abbreviated cpx) and accessory ilmenite with rare rutile cores. The matrix is texturally homogeneous; there is little variation in grain size, which averages about 1 – 2 mm. The garnet porphyroblasts include grains of clinopyroxene and plagioclase. The inclusions range in size from c. 0.1 to c. 0.5 mm and occupy up to c. 75% of the volume of each garnet porphyroblast. The sample belongs to the ‘garnet amphibolite’ unit of the Ballantrae Complex as defined and described in detail by Spray & Williams (1980). The rock is more appropriately classified as a mafic granulite, however, and we will use this term hereafter.

**Methods**

**Geochronology**

A c. 1000 cm³ sample free from veins or other visible evidence of later alteration was chosen for analysis. The weathering rim was removed with a rock saw and the remaining sample was crushed in a tungsten carbide mortar and pestle. A representative portion was separated for whole-rock chemical analysis and powdered in an agate ball mill. Garnet was separated from the remaining fraction via a combination of magnetic separation using a Frantz separator, further crushing, sieving and hand-picking. When a visually pure garnet separate was achieved it was crushed to a grain size of 74 – 149 µm. The fine material (<74 µm) was retained and labelled ‘garnet powder.’

The whole-rock fraction and garnet powder were fully dissolved in a multi-step dissolution procedure using concentrated HF, concentrated HNO3 and 1.5N HCl. The 74 – 149 µm garnet separate was treated in a partial dissolution cleansing procedure modified after Pollington & Baxter (2011). The aim of this procedure is to cleanse the separate of inclusions that cannot be removed mechanically, thus increasing the purity of the garnet separate. Several variations of this procedure were performed to determine the optimum duration of each step. Ultimately, the garnet was kept in a closed beaker of 1 ml concentrated HF and 1 ml 1.5N HCl at 120°C for 45 min. To remove secondary fluorides it was then treated with 2 ml of concentrated HClO4 at 150°C for 3 h and finally left in 2 ml of concentrated HNO3 at 120°C for another 3 h. At this stage the separate was considered as pure as possible and fully dissolved in the same manner as the whole-rock and powder.

Following full dissolution each sample was spiked with the 14Sm–150Nd mixed spike described by Harvey & Baxter (2009) and Sm and Nd from each sample were separated for analysis via multistep column chromatography. This procedure involved a clean-up cation exchange column to remove major elements (in particular Fe), a Tru-spec column to separate out the REE, and finally a 2-methyllic acid column to isolate Sm and Nd.

Three-column blanks from this procedure ranged from 4.6 to 24.6 pg Nd and <1 to 3 pg Sm. With a minimum sample size of 5.2 ng Nd, this yields a sample to blank ratio of at least 211:1. To quantify the effect of the blank on our calculations we perform a blank correction calculation on this smallest (and therefore most contamination-susceptible) sample, garnet 3. The 140Nd/144Nd of the blank was taken to be an average crustal value of 0.513 ± 0.001 (consistent with our direct poor-precision measurements of the blank 143Nd/144Nd and the 147Sm/144Nd of the blank was measured as 0.048 ± 0.035. Using a 10 000-iteration Monte Carlo simulation to propagate these uncertainties, blank-subtracted isotopic values for garnet 3 were calculated (Fig. 3). Although the isotopic values are statistically significantly different, the effect on any age calculation is negligible; the isotopic mixing between any garnet and blank reservoir occurs along a line that is subparallel to our calculated isochron, thus minimizing any effect on the accuracy of our ages. In this example, the age calculated using the measured values for garnet 3 is identical to the blank-subtracted age at 477.6 Ma. Thus, these procedural blanks do not affect the accuracy of calculated ages. Herein, we report isotopic values and ages that have not been blank-corrected.

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**Table 1. Existing chronology of the Ballantrae Ophiolite**

<table>
<thead>
<tr>
<th>Publication</th>
<th>Age ± 2SE (Ma)</th>
<th>Method</th>
<th>Tectonic context</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hamilton et al.</td>
<td>575 ± 32</td>
<td>Sm-Nd, whole-rock</td>
<td>Pre-orogenic, ‘eclogite’</td>
</tr>
<tr>
<td>Hamilton et al. (1984)</td>
<td>505 ± 11</td>
<td>Sm-Nd, whole-rock</td>
<td>Pre-obduction pyroxenite</td>
</tr>
<tr>
<td>Bluck et al. (1980)</td>
<td>484 ± 4</td>
<td>U–Pb zircon</td>
<td>Pre-obduction trondhjemite</td>
</tr>
<tr>
<td>Bluck et al. (2010)</td>
<td>478 ± 8</td>
<td>K–Ar hornblende</td>
<td>Synorogenic amphibolite</td>
</tr>
<tr>
<td>Sawaki et al. (2010)</td>
<td>470 ± 10</td>
<td>U–Pb zircon</td>
<td>Synorogenic tuff</td>
</tr>
</tbody>
</table>

Uncertainties are 2σ standard errors.
After separation, Sm and Nd were analysed by thermal ionization mass spectrometry (TIMS) on a Thermo-Finnigan TRITON system at the Boston University TIMS facility. Nd was loaded onto Re filaments with 2 µl of a Ta2O5 activator slurry described by Harvey & Baxter (2009). It was run as an oxide (NdO+) in static mode with amplifier rotation. A 4 ng UCB Ames NdO standard was run along with every barrel to quantify our external reproducibility. The average $^{143}$Nd/$^{144}$Nd for the time over which samples were run is 0.5121206 ± 0.0000089 (17.3 ppm, 2σ, n = 17). Sm was loaded onto zone-refined Re filaments and was run as a metal, also in static mode with amplifier rotation. $^{147}$Sm/$^{144}$Nd reproducibility is 0.023% based on repeat analysis of a gravimetrically calibrated mixed Sm–Nd solution.

### Results

#### Isotope data

Table 2 summarises the isotope data collected from whole-rock, garnets and garnet powders for sample 11ESC-18A. Nd concentrations in the garnet are fairly consistent, ranging from 0.854 to 1.196 ppm. The whole-rock has a much higher concentration of c. 9 ppm Nd, and the powders are intermediate, ranging from 0.925 to 2.279 ppm Nd. The $^{143}$Nd/$^{144}$Nd and $^{147}$Sm/$^{144}$Nd uncertainties reported here are the precisions (2σ SE) used for all subsequent calculations. In cases where the limit of our external reproducibility exceeds the internal precision, we report the external uncertainty (17.3 ppm or 0.023% respectively).

#### Garnet age

An eight-point Sm/Nd isochron age for all accepted data is initially calculated using the program Isoplot (Ludwig 2003), yielding an age of 477.6 ± 5.5 Ma. The uncertainty of this age can be attributed to scatter in the dataset; with an MSWD of 5.4, these data do not fall on a statistically robust line, and one of the powders (Pow 4) falls significantly off the line defined by the other points (Fig. 4). To account for this observation, a second Sm/Nd isochron age can be calculated for the remaining seven samples. This isochron gives a significantly improved MSWD of 2.0 and a more precise age of 477.6 ± 1.9 Ma (Fig. 4). For a seven-point isochron, an MSWD less than 2.26 is consistent with a true isochron; that is, data are not statistically discordant (Wendt & Carl 1991).

**Table 2. Isotopic data for all accepted samples from 11ESC-18A**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nd loaded (ng)</th>
<th>Nd (ppm)</th>
<th>Sm (ppm)</th>
<th>$^{147}$Sm/$^{144}$Nd</th>
<th>±2SE (abs)</th>
<th>143Nd/$^{144}$Nd</th>
<th>±2SE (abs)</th>
<th>±2SE (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WR1</td>
<td>28</td>
<td>9.774</td>
<td>3.385</td>
<td>0.20948</td>
<td>0.00005</td>
<td>0.513019</td>
<td>0.000009</td>
<td>17</td>
</tr>
<tr>
<td>WR2</td>
<td>21</td>
<td>8.940</td>
<td>3.064</td>
<td>0.20733</td>
<td>0.00005</td>
<td>0.512997</td>
<td>0.000016</td>
<td>31</td>
</tr>
<tr>
<td>Gr 3</td>
<td>5.2</td>
<td>1.009</td>
<td>1.937</td>
<td>1.16184</td>
<td>0.00089</td>
<td>0.515993</td>
<td>0.00025</td>
<td>48</td>
</tr>
<tr>
<td>Gr 5</td>
<td>6.1</td>
<td>0.854</td>
<td>1.649</td>
<td>1.16817</td>
<td>0.00043</td>
<td>0.516025</td>
<td>0.000013</td>
<td>26</td>
</tr>
<tr>
<td>Gr 7</td>
<td>12</td>
<td>1.196</td>
<td>2.326</td>
<td>1.17678</td>
<td>0.00029</td>
<td>0.516027</td>
<td>0.000015</td>
<td>29</td>
</tr>
<tr>
<td>Pow D</td>
<td>11</td>
<td>0.925</td>
<td>1.065</td>
<td>0.69621</td>
<td>0.00016</td>
<td>0.514532</td>
<td>0.000024</td>
<td>48</td>
</tr>
<tr>
<td>Pow C</td>
<td>49</td>
<td>2.279</td>
<td>2.137</td>
<td>0.56717</td>
<td>0.00013</td>
<td>0.514125</td>
<td>0.000016</td>
<td>31</td>
</tr>
<tr>
<td>Pow 4*</td>
<td>12</td>
<td>2.343</td>
<td>2.181</td>
<td>0.56323</td>
<td>0.00018</td>
<td>0.513984</td>
<td>0.000057</td>
<td>112</td>
</tr>
</tbody>
</table>

Uncertainties are 2σ standard errors. Where the internal precision of a given measurement exceeds our external reproducibility, the external limit is reported.

*This sample was excluded from the final isochron calculation (see text).
clumping of the whole-rock and garnet analyses means that our calculated isochron is better considered as a four-point isochron. In this case, Wendt & Carl (1991) suggested that an MSWD less than 3.0 is acceptable. Thus we have confidence in the reliability of this result, and suggest that omitting garnet powder 4 gives a better indication of the actual age of garnet crystallization.

It is not uncommon for uncleansed garnet powders to fall off an isochron; garnets may include inherited phases that did not isotopically equilibrate with the whole-rock (Dragovic et al. 2012; Baxter & Scherer 2013). Although it is true that powders C and D fit the isochron well, it is not implausible that powder 4 is compositionally different. Perhaps this particular scoop of uncleansed garnet powder (which can never be perfectly homogenized) contained an inherited (i.e. older) grain of monazite or another mineral with very low $^{147}$Sm/$^{144}$Nd. This so-called ‘nugget effect’ (Matheron 1963) could effectively contaminate powder 4 and pull it down slightly off the isochron (Baxter & Scherer 2013).

With all of this in mind, we assert that 477.6 ± 1.9 Ma is the most reliable age indicated by our isotopic measurements.

**Mineral chemistry**

Table 3 summarizes the results of quantitative electron microprobe spot analyses. Figure 5 shows chemical maps for Ca, Fe, Mg and Mn in a representative garnet. The Mn map is almost completely flat apart from higher concentrations at some apparently resorbed edges. The Ca map shows very broad zonation with slightly higher Ca garnet rims. The Fe and Mg maps both show haloes of probably retrograde diffusional exchange between the garnet and the clinopyroxene inclusions.

**Pseudosection results**

Figure 6 is the pseudosection resulting from thermodynamic modelling; the utilized whole-rock geochemistry, as calculated from mineral chemistry and model abundances, is provided in the figure caption. The two highlighted phase fields represent mineral assemblages consistent with what we observe in the rock today. The results of amphibole–plagioclase and garnet–clinopyroxene thermometry are also shown. The two highlighted phase fields describe the mineralogy observed in the sample with one difference: the lower...
pressure field contains both ilmenite and rutile whereas the higher-pressure field contains only rutile. We suggest that either field could represent peak pressure conditions; the ilmenite commonly occurs rimming the rutile, indicating that it may be retrograded from rutile and not a peak metamorphic phase. Thus we conclude that either of these phase fields may represent the peak conditions for 11ESC-18A. The dashed black line indicates the melt-in reaction for the modern bulk composition. The melt model used (White et al. 2007) Fig. 5. Chemical maps; 500 μm scale bar is shown. Maps obtained via wavelength-dispersive spectrometry with an accelerating voltage of 15 kV, beam current of 200 nA and a dwell time of 175 ms.

Fig. 6. Pseudosection for sample 11ESC-18A generated with the program Theriak-Domino. Ru, rutile; Gt, garnet; CPX, clinopyroxene; Amp, amphibole; Epi, epidote; Qz, quartz; Plag, plagioclase; OPX, orthopyroxene; Ol, olivine; Ilm, Ilmenite. Input in moles was Si 44.688, Ti 3.435, Al 20.909, Fe 11.629, Mg 10.427, Mn 0.166, Ca 12.161, Na 5.474, H 6.166 and O 168.107. The dashed lines represent the first appearance of melt in the up-temperature direction (solidus), but do not otherwise signify a change in the phase field. The black dashed line is the solidus predicted for the modern bulk composition and the grey dashed line corresponds to the same composition with reduced H₂O content. The shaded fields are consistent with the observed mineralogy. The 'cores' and 'rims' lines are the result of garnet–cpx thermometry (Ravna 2000). The ‘Amp–Pl’ line is the temperature estimate from the amphibole–plagioclase thermometer B of Holland & Blundy (1994).
is, however, not well suited for predicting melting greater than c. 5% in mafic compositions (De Paoli et al. 2012). Because the presence and composition of melt cannot be accurately predicted with the utilized model, we do not use this melting curve as a robust constraint. Furthermore, the position of the melting curve is heavily dependent on the water content of the rock. To quantify this effect, we calculate a melt-in curve for the same bulk composition but with the H2O content reduced from the measured value of 0.93 wt% to a lower 0.5 wt% (dashed grey line in Fig. 6). This change does not significantly affect the boundaries of the rutile–ilmenite phase fields relevant for barometry (apart from shifting them up-pressure by c. 0.1 kbar) but dramatically increases the predicted melting temperatures. This is consistent with very recent melt models applicable to mafic compositions, which show that partial melting in H2O-undersaturated mafic rocks can be delayed until temperatures in excess of 800°C are reached (e.g. Green et al. 2016, figs 3d and 4d). We suggest that water contents around 0.5 wt% at peak conditions are more appropriate than the modern value, as the sample has undergone some amount of retrograde hydration, as indicated by chlorite rims on garnet and the apparent lack of melt features at hand sample or outcrop scale. Regardless, we emphasize that the pseudosection is not used to precisely constrain the peak temperature but can provide a robust pressure constraint based on the rutile–ilmenite phase relations. These provide a minimum pressure estimate of c. 8–9 kbar.

**Thermometry**

The results of gt–cpx and amphibole–plagioclase thermometry are also shown in Figure 6. It should be noted that the gt–cpx thermometer of Ravna (2000) is based specifically on Fe2+/Mg ratios. A charge-balance recalculation of the ferric/ferrous iron ratio in clinopyroxene indicates that as much as 11% of the measured iron is ferric. This recalulation would effectively reduce the Fe2+/Mg ratio in the clinopyroxene and lower the calculated temperatures by c. 30°C. As this lies well within the ±100°C uncertainty reported for the Ravna (2000) thermometer, we choose to forgo this recalculating and its associated uncertainties and assume all Fe is FeO. For the garnet–clinopyroxene thermometer, we modelled a decrease in the mole fraction of grossular by 0.1, and increases in the mole fractions of pyrope, almandine and spessartine by 0.025, 0.025 and 0.05, respectively. We emphasize that the length and time scales of relaxation are nearly independent of the compositional values used. No-flux boundary conditions were imposed at the core and rim.

The results of radial diffusion modelling are presented in Figure 7 for Ca (gossular), the slowest diffusing component. Diffusion at 825°C for only 1.5 myr is sufficient to dramatically smooth the initial step function. This result is consistent with the very smooth, though not entirely obliterated zonation of Ca that we observe in chemical maps (Fig. 5), and suggests that peak conditions may have lasted only c. 1 myr.

**Discussion**

**Age significance: growth or closure?**

Given the garnet age and pressure–temperature history, what process is actually being dated? That is, should we consider 477.6 ± 1.9 Ma to be the age of garnet crystallization, cooling through a closure temperature, or something else? In general, diffusional resetting of Sm and Nd isotopes may begin above 700°C (Carlson 2012; Baxter & Scherer 2013; Smit et al. 2013). Given the thermobarometric results, we must consider the possibility that the garnet in our sample exchanged Sm and Nd with the whole-rock reservoir after growth. Were this to be the case, our reported age would be younger than the age of garnet crystallization.

The degree of resetting is heavily dependent upon the duration of high-temperature conditions, however, and we have reason to conclude that sample 11ESC-18A was not at its peak temperature for a very long time. First, garnet retains some Ca zonation. As high-temperature conditions, however, and we have reason to conclude that sample 11ESC-18A was not at its peak temperature for a very long time. Furthermore, in ophiolite soles around the world, the global pattern is one of high-7 metamorphism in excess of 800°C (e.g. Malpas 1979; Spray 1984; Jamieson 1986; Hacker & Mosenfelder 1996).

Our pressure estimate is somewhat higher than the 7 kbar value of Spray & Williams (1980). At lower pressures of c. 7 kbar, however, rutile would be unstable in the bulk composition studied herein. Moreover, Treloar et al. (1980) reported minimum pressures of 10 – 11 kbar for the adjacent garnet metapyroxenite and suggested that pressures may have been closer to 14 or 15 kbar. The garnet metapyroxenite is expected to have attained higher pressures than the amphibole-bearing granulate of this study (Spray & Williams 1980; Treloar et al. 1980); nonetheless, the metapyroxenite and granulate results, taken together, strongly suggest that the rock package was deeply buried.

To investigate the duration of peak conditions, we modelled radial diffusion of major elements in a spherical garnet using diffusion coefficients and methods from Chu & Ague (2015; e.g. fig. 11). We consider diffusion over 1.5 myr at 825°C in a garnet with a diameter of 2 mm. Although garnets in sample 11ESC-18A are slightly larger than this (c. 3 mm), they are so heavily included that a good estimate of the effective diffusive length scale is c. 1 mm (Fig. 5). A step function in composition at 0.50 mm along the radius was allowed to relax over this model time interval. The step comprised a decrease in the mole fraction of grossular by 0.1, and increases in the mole fractions of pyrope, almandine and spessartine by 0.025, 0.025 and 0.05, respectively. We emphasize that the length and time scales of relaxation are nearly independent of the compositional values used. No-flux boundary conditions were imposed at the core and rim.
the inverted temperature gradient that results from thrusting and ophiolite emplacement quickly re-equilibrates (by thermal conduction) and the thermal anomaly exists for only a very short period of time, typically <2 myr (e.g. Peacock 1988; Hacker 1990, 1991; Hacker et al. 1996; Wakabayashi & Dilek 2003; Agard et al. 2016). Consequently, the duration of peak conditions is remarkably brief. It should be noted that these models also predict peak temperatures in excess of 800°C, which is entirely consistent with the results of our work. Furthermore, cooling from high grade is also rapid; minerals commonly used for $^{40}$Ar-$^{39}$Ar move so quickly through their closure temperature that the age they give is within error of the start of metamorphism (e.g. Hacker et al. 1996; Wakabayashi & Dilek 2000; Agard et al. 2016); it is generally interpreted that the age of metamorphic minerals in an ophiolitic sole is approximately the age of subduction/obduction initiation (Spray 1984; Peacock 1988; Wakabayashi & Dilek 2003). Given the short durations associated with ophiolite emplacement and metamorphism, the internal uncertainty of our age measurement would completely encompass the start, peak and end of high-grade metamorphism in a typical sole. Thus although the calculated age of 477.6 ± 1.9 Ma may be a cooling age in the technical sense, it is almost certainly also representative of the timing of ophiolite obduction.

**Tectonic significance**

This new result is in good agreement with previous geochronological work on the metamorphic sole of the Ballantrae Ophiolite. In fact, our age is statistically indistinguishable from the K–Ar hornblende age reported by Bluck et al. (1980). Critically, however, with a four-fold improvement in age precision we can begin to draw conclusions about the style of orogenesis that were previously obscured by larger uncertainties.

First we can better examine the duration of the Grampian episode. As discussed above, the metamorphic age of the sole of the Ballantrae Ophiolite is linked to the timing of obduction and onset of orogenesis in Scotland. Our results indicate that the amphibole-bearing granulite unit at the base of the complex reached peak conditions at 477.6 ± 1.9 Ma. We and others (Bluck et al. 1980; Oliver et al. 2000; Oliver 2001) have concluded that this corresponds to the timing of onset of collision in the region. It is interesting to note that this result is statistically distinguishable from the reported age of onset of Grampian orogenesis in Ireland, which is slightly younger at 474.5 ± 1.0 Ma (Friedrich et al. 1999). At the other end of the Grampian episode, detrital high-temperature Barrovian-type metamorphic garnet in molassic conglomerates (Oliver et al. 2000) dated at 465 ± 2.5 Ma (biot stratigraphic age of Tucker & McKerrow 1995) signifies the start of erosion post-metamorphism. With our new date for the timing of Ballantrae obduction, we can refine our knowledge of the duration of the Grampian episode. Propagating the uncertainties of our measurement, we constrain the duration of the Grampian phase of the Caledonian Orogeny to 12.6 ± 3.1 myr (2σ). This represents a significant improvement on the previous constraint of 13.0 ± 8.4 myr (2σ; using the K–Ar age of Bluck et al. 1980).

In a region that has been the subject of multiple studies using ‘geospeedometry’ (e.g. Ague & Baxter 2000; Viete et al. 2011; Chu & Ague 2015), we can calculate a range of heating rates for Dalradian metasediments in the type locality for Barrovian-style metamorphism. It should be noted that these metasediments are not a part of the Ballantrae Ophiolite Complex. Instead, they represent continental sediments that were buried, metamorphosed and deformed as a result of early Caledonian orogenesis.

We first consider heating of the garnet-zone unit. Assuming sediments were at surface conditions (25°C) at the beginning of collision at 477.6 ± 1.9 Ma and reached at least 525°C (just above the ‘garnet-in’ minimum from Spear & Cheney 1989; see Ague 1997 and Vorhies & Ague 2011) by 467 ± 2.5 Ma (Oliver et al. 2000, consistent with Baxter et al. 2002), we can calculate a time-averaged initial heating rate. Increasing temperature by 500°C over the course of this 10.0 ± 3.14 Ma (2σ) interval yields a heating rate of 47 ± 14°C myr$^{-1}$ (2σ). For these moderate-temperature metamesis, the refined constraint on the onset of metamorphism allows us to calculate the heating rate with reasonable precision.

In the highest temperature unit (i.e. the sillimanite zone) we use the same set of assumptions and an initial garnet growth age of 472.9 ± 2.9 Ma (Baxter et al. 2002) to calculate a time-averaged initial heating rate of 106 ± 78°C myr$^{-1}$ (2σ). This significant uncertainty includes a wide range of possible heating rates. The upper bound on the heating rate in the sillimanite zone allows remarkably fast heating, inconsistent with heating owing solely to crustal overthickening and thermal relaxation (England & Thompson 1984; Thompson & England 1984). On the other hand, the slowest possible heating rate is 28°C myr$^{-1}$, comparable...
with the minimum heating rate of 33°C myr\(^{-1}\) calculated for the garnet zone. Both of these heating rate minima are probably achievable through orogenic self-heating. Lyubetskaya & Ague (2009) estimated initial heating rates well above 30°C myr\(^{-1}\) owing to conduction alone in the very earliest stages of metamorphism via crustal thickening (e.g. their fig. 10). The classical models of Thompson & England (1984) estimated initial heating rates in excess of 20°C myr\(^{-1}\) as well (their Fig. 5a). In addition, peak pressures of 10 kbar or more demonstrate that significant loading must also have occurred as part of the orogeny (Vorhies & Ague 2011). With only these constraints, it is plausible that early heating during the Grampian episode could have occurred via either classic crustal thickening or a much faster process.

Figure 9 represents this heating visually as a temperature–time path for Dalradian metasediments with garnet ages from Oliver (2001) and Baxter et al. (2002). The sillimanite-zone rocks exhibit the fastest heating whereas rocks in the kyanite and garnet zones indicate lower heating rates. Although the calculated rates do overlap within uncertainty, they are statistically distinguishable; because all rates are anchored to the same initial age, their absolute values are correlated. Thus the sillimanite-zone rocks must heat faster than those in the garnet zone under any scenario.

We also note that it may be inappropriate to consider gradual monotonic heating over this time period. It has been repeatedly suggested that Barrovian metasediments were subject to a rapid thermal pulse or pulses as the result of regional metamorphism associated with mafic intrusions and/or other short-lived heating processes (e.g. Ague & Baxter 2007; Lyubetskaya & Ague 2010; Viete et al. 2011, 2013; Vorhies & Ague 2011). If this is the case, a time-averaged heating rate does not truly apply. Rather, the time window of 4.7 ± 3.5 myr between collision and earliest garnet growth would simply represent a time interval containing some of these brief temperature spikes; we cannot rule out the possibility that one or more thermal spikes may have occurred along the prograde path. Nevertheless, our new constraint on the onset of orogenesis provides a starting point for the metamorphic history of these continental metasediments.

**Conclusions**

We report a Sm–Nd garnet age of 477.6 ± 1.9 Ma (2\(\sigma\)) for the amphibole-bearing granulite unit in the metamorphic sole of the Ballantrae Ophiolite. Given the evidence for rapid heating and cooling in the ophiolitic sole, we conclude that this age is representative of the timing of peak metamorphism. Most significantly, the new data reveal the timing of obduction of the Ballantrae Ophiolite Complex and the onset of the Caledonian Orogeny in Scotland. We use this constraint to calculate a total duration of 12.6 ± 3.1 Ma (2\(\sigma\)) for the entire Grampian episode. This is a maximum duration for the regional metamorphism given that the Dalradian metasediments inboard of the ophiolite itself may not have begun to metamorphose until somewhat later as the orogeny evolved. Calculated initial heating rates for these inboard sediments may be the result of rapid processes involving heat advection and/or production. Although we cannot rule out simple orogenic self-heating alone, the overall short duration of the Grampian episode suggests that other more rapid heating processes must be at play. In recent years the previously disparate conclusions of geochronology and diffusion modelling in the region have begun to converge on a single model for timescales of metamorphism. Our results are consistent with the interpretation that short-lived, transient thermal pulses were superimposed on the broader c. 13 myr timespan of the Grampian event.

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**References**


CaO

Al2O3

FeO

MgO

SiO2

MnO

Na2O

K2O

H2O

CO2

Cl


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