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The nature and origin of the Barrovian metamorphism, Scotland: $^{40}Ar/^{39}Ar$ apparent age patterns and the duration of metamorphism in the biotite zone

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Abstract: A geochronological traverse across the Barrovian metamorphic series, Scotland, shows $^{40}Ar/^{39}Ar$ apparent age spectra that reflect the influence of progressive metamorphism during the Grampian orogenic episode. The lowest-grade units of the Barrovian metamorphic series retain pre-Grampian detrital ages as components of their white mica $^{40}Ar/^{39}Ar$ apparent age spectra. These relict ages are progressively obliterated in the direction of increasing metamorphic grade, with a Grampian-age $^{40}Ar/^{39}Ar$ step-heating plateau first occurring in the biotite zone. The microstructure at this point shows only limited recrystallization, suggesting loss of argon mainly by diffusion. Forward modelling of argon diffusion from white mica grains was therefore carried out, for various thermal histories and grain sizes, to match $^{40}Ar/^{39}Ar$ step-heating apparent age spectra patterns preserved within the biotite zone of the Barrovian metamorphic series. The results imply a thermal duration of between 1 and 10 Ma for Barrovian metamorphism in the biotite zone. Such short time scales for metamorphism place a limit on length scales for the heat sources responsible. Mid-crustal extensional ductile shear zones that crop out in the NE of the Grampian Terrane once focused narrow, Grampian-age heat sources (e.g. magmas, hot fluids, shear heating) that drove a brief thermal episode, resulting in the Barrovian metamorphism.

Supplementary material: $^{40}Ar/^{39}Ar$ data tables and plots, including (1) data from analyses on flux monitors and plots used for *J*-factor determination, and (2) data from analyses on unknowns and $^{40}Ar/^{39}Ar$ step-heating spectra and inverse isochron plots for each unknown, are available at http://www.geolsoc.org.uk/SUP18442.

George Barrow's study of the Barrovian metamorphic series of Scotland (Barrow 1893, 1912) was the first to map progressive metamorphism through the use of mineral isograds. The mineral zones he mapped include, from lowest to highest grade, the clastic mica and (chlorite), biotite, garnet, staurolite, kyanite and sillimanite zones. Barrovian facies series have been recognized at numerous localities across the globe and throughout geological time (from the Archaean to the present) and indicate regional metamorphism at medium temperature/pressure (T/P) values corresponding to an apparent crustal geotherm of between 20 and 40 °C km^{-1}. Being the earliest-studied and best-described metamorphic sequence of its type, the Barrovian metamorphic series represents the classic locality for medium T/P regional metamorphism developed in pelitic lithologies. The Barrovian metamorphic series developed at *c*. 470 Ma (Oliver *et al.* 2000; Baxter *et al.* 2002), during the Grampian Orogeny (*sensu* Lambert & McKerrow 1976).

Worldwide, Barrovian-type metamorphic deposits occur in association with evidence of collisional orogenesis (e.g. Jamieson *et al.* 1998, and references therein). In consequence, models for regional metamorphism in orogenic settings have linked metamorphic heating to lithospheric thickening. England & Thompson (1984), succeeding the earlier work of Oxburgh & Turcotte (1974) and Bickle *et al.* (1975) in the Alps and Richardson & Powell (1976) in Scotland, produced the 'thermal relaxation model' for crustal heating and metamorphism in orogenic settings. The thermal relaxation model explained the origin of Barrovian-type metamorphism in collisional settings as the result of internal radioactive heat production and conductive heating from the base of the crust during thermal relaxation of an overthickened (and cool) lithospheric section and concomitant exhumation of the middle crust by erosional denudation. However, thermal relaxation models require conductive heat exchange on the scale of the lithosphere and predict production of typical Barrovian-type assemblages over durations of 50 Ma or more (Thompson & England 1984) for realistic rates of erosion and radiogenic heat production. In Scotland and Ireland, the Grampian orogenic episode, during which the classical Barrovian metamorphic series developed, has been restricted in its total duration to 12–18 Ma (Dewey & Mange 1999; Friedrich *et al.* 1999; Oliver *et al.* 2000; Dewey 2005). These data therefore challenge these now classical models for the source of heat during metamorphism.

The work presented in this paper has been carried out because precise constraints on the duration of the Barrovian metamorphism narrow the available options for the responsible heat sources, in particular because time scales for conductive dissipation are dependent on length scales for heating. In this study, $^{40}Ar/^{39}Ar$ apparent age spectra from the lowest- to the highest-grade units of the Barrovian metamorphic series, Scotland, have therefore been determined. Forward modelling of argon diffusion in white mica was undertaken to produce hypothetical $^{40}Ar/^{39}Ar$ step-heating spectra that match the variation across metamorphic grade in the pattern of observed $^{40}Ar/^{39}Ar$ apparent age spectra. Limits on the maximum duration for the Barrovian thermal event are thus obtained. Finally, we discuss the implications of the calculated limits on the thermal durations of the heat sources that produced the Barrovian metamorphic series.

Geological background

The Barrovian metamorphic series of Scotland developed in response to heating of the middle crust at *c*. 470 Ma (Oliver *et al.* 2000; Baxter *et al.* 2002), during the Grampian orogenic episode in Scotland and Ireland. The Grampian orogenic episode comprised three broad phases of tectonism, manifest as early-orogenic large-scale folds, middle-orogenic large-scale top-to-the-SE shear-related deformation and late-orogenic large-scale folds (see Harris *et al.* 1976; Krabbendam *et al.* 1997). The Barrovian metamorphism developed during the middle-orogenic top-to-the-SE shearing tectonic phase, but in the higher-grade zones also overlapped with the earliest stages of late folding (see Harte & Johnson 1969; Robertson 1994). Large-scale mafic magmatism was coeval with regional metamorphism, during the middle-orogenic top-to-the-SE deformation phase (Viete *et al.* 2010).

$^{40}Ar/^{39}Ar$ geochronology

Sample transects

The Barrovian metamorphic series of Scotland occurs in the SE of the Grampian Terrane (Fig. 1a). It trends approximately parallel to and is situated immediately adjacent to the terrane bounding, NE–SW-trending Highland Boundary Fault. Units of Barrovian metamorphic series increase in metamorphic grade to the NW, away from the Highland Boundary Fault. Thus, the manner with which $^{40}Ar/^{39}Ar$ apparent age spectra vary with increasing metamorphic grade across the Barrovian metamorphic series might be best studied using $^{40}Ar/^{39}Ar$ geochronological transects with a NW directional component. The $^{40}Ar/^{39}Ar$ ages presented in this paper were obtained from samples collected across two such transects. The first transect follows the River North Esk, in the region of Glen Esk (Fig. 1b), whereas the second was chosen to exploit the units that crop out on Scottish east coast, north of the town of Stonehaven (Fig. 1c).

$^{40}Ar/^{39}Ar$ geochronology was carried out on 18 samples collected from different metamorphic positions across the two transects through the Barrovian metamorphic series: eight from the Glen Esk transect (Fig. 1b) and 10 from the Stonehaven transect (Fig. 1c). Along each transect, sample locations were chosen to achieve the best possible spread through the metamorphic sequence, although higher sampling concentrations were employed for the low-grade parts of the series (chlorite and biotite zones), which retain pre-Grampian K/Ar and $^{40}Ar/^{39}Ar$ ages (Dempster 1985; Tanner & Pringle 1999). Sampling was biased toward pelitic lithologies that contained significant concentrations of mica. White mica was used for the $^{40}Ar/^{39}Ar$ work in all cases except one (DV06-48), for which biotite was used.

Method

For each sample, *c.* 500 g of material was crushed to gravel size, washed and then milled in tungsten carbide. Grains less than about 40 μm in size were separated using flotation techniques and discarded. The remaining material was sieved and separated to appropriate size fractions. The largest size fraction that included non-composite mica grains was chosen and run through conventional heavy liquid and magnetic separation techniques to improve concentration of the mineral being considered. Following this, hand picking of impurities from the separate allowed concentration of the target mineral to levels in excess of 99%.

Between 5 and 10 mg of concentrated mica separate was packed in aluminium foil for each sample and positioned between aluminium foil packages containing 77–600 hornblende [K/Ar age of 418.3 ± 1.3 Ma (Spell & McDougall 2003)] fluence monitors, within a cadmium-lined aluminium can (#ANU143). The can was irradiated in the HIFAR nuclear reactor at The Australian Nuclear Science and Technology Organisation (ANSTO) for 20 days (480 h) during November and December 2006, to achieve a desired $^{40}Ar/^{39}Ar$ ratio of about 28. The can was inverted three times, at 5 day intervals, to minimize variation in the neutron flux encountered by samples across the can.

Having allowed the samples to decay to safe levels of radioactivity, fluence monitor separates were repacked into *c.* 1 mg aliquots. For each unknown, 2–3 mg of mica separate was repacked into tin foil. Fluence monitors were analysed in the VG1200 gas source mass spectrometer at the Research School of Earth Sciences (RSES), The Australian National University (ANU), following bulk fusion of the sample at 1250 °C for 12 min. Prior to fusion, purification of the sample was achieved by heating at 600 °C for 2 h. This procedure was carried out 3–5 times for each fluence monitor and results were used to determine the irradiation parameter (*J* factor) for seven positions along the can. The *J* factors used for age determination of the unknowns were calculated from a linear fit to the data, and their respective uncertainties were estimated by linear interpolation between the uncertainties calculated for neighbouring fluence monitor positions. Unknowns were analysed in the VG1200 gas source mass spectrometer at the RSES, ANU, following gas liberation by temperature-controlled furnace step heating, which used a 12 min heating duration at each step. Data reduction was performed using the KArDate 2.0 program. Correction factors appropriate to the HIFAR nuclear reactor at ANSTO ($(36/37)_{Ca} = 3.06 \times 10^{-4} \pm 0.05 \times 10^{-4}$; $(39/37)_{Ca} = 7.27 \times 10^{-4} \pm 0.08 \times 10^{-4}$, and $(40/39)_{Ca} = 3.008 \times 10^{-1} \pm 0.138 \times 10^{-1}$; Tetley *et al.* 1980) were used in calculation of all $^{40}Ar/^{39}Ar$ ages presented in this paper. The ^{40}K decay constants proposed by Steiger & Jäger (1977) were used in calculation of the $^{40}Ar/^{39}Ar$ ages. Plateaux defined by $^{40}Ar/^{39}Ar$ step-heating spectra (plateau v. mixed spectra) were recognized using the default plateau identification criteria of the Excel-based Isoplot software, created for analysis of geochronological datasets.

Results

$^{40}Ar/^{39}Ar$ step-heating spectra from the Barrovian metamorphic series display systematic variation in their nature across grade. For both the Stonehaven and Glen Esk transects, $^{40}Ar/^{39}Ar$ step-heating spectra for the majority of the sequence display plateau ages (Fig. 2), whereas $^{40}Ar/^{39}Ar$ step-heating spectra for samples collected from regions immediately adjacent to the Highland Boundary Fault (from the chlorite zone to the higher-grade parts of the biotite zone) exhibit heterogeneous patterns (Fig. 3). For simplicity, ages associated with the two types of $^{40}Ar/^{39}Ar$ step-heating spectra are discussed separately and the two spectra types are henceforth referred to as Mode 1 and Mode 2 spectra, respectively.

Mode 1 spectra. Samples from the Stonehaven transect displaying Mode 1 spectra yielded $^{40}Ar/^{39}Ar$ plateau ages that range from 462.5 ± 1.2 to 457.3 ± 1.1 Ma, in addition to one sample that gave a 430.0 ± 0.9 Ma plateau age (Table 1; Fig. 2). A general decrease in age can be observed with increasing metamorphic grade, from the biotite to the sillimanite zone (Table 1). Figure 2 includes a frequency plot expressing the relative occurrence of step-heating ages in all Mode 1 samples from Stonehaven. The distribution is bimodal, with independent peaks at *c.* 461 Ma and *c.* 430 Ma. The *c.* 461 Ma peak reflects a grouping of step-heating ages from six of the seven Mode 1 samples, whereas the *c.* 430 Ma peak reflects a step-heating age contribution from the seventh sample (DV05-105).

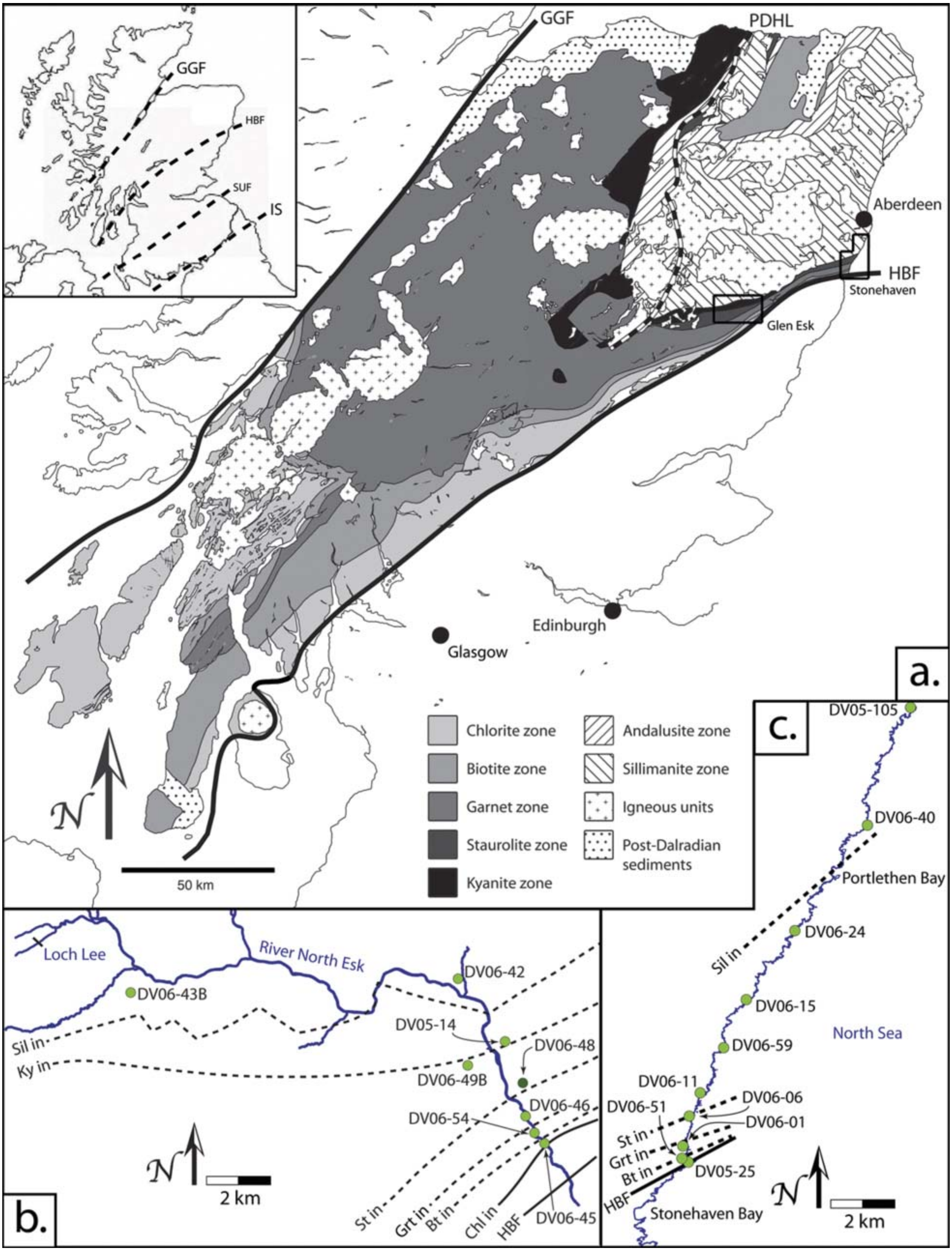

Fig. 1. Map of the Grampian Terrane, Scotland, showing (**a**) the distribution of metamorphic mineral isograds, magmatic bodies and post-Grampian sediments, (**b**) sample localities for $^{40}Ar/^{39}Ar$ samples from the Glen Esk transect (enlargement of rectangle of (**a**)) and (**c**) sample localities for $^{40}Ar/^{39}Ar$ samples from the Stonehaven transect (enlargement of polygon of (**a**)). Inset at top left of figure a provides a broader location map. GGF, Great Glen Fault; HBF, Highland Boundary Fault; IS, Iapetus Suture; PDHL, Portsoy–Duchray Hill Lineament; SUF, Southern Uplands Fault. Compiled after Barrow (1912), Elles & Tilley (1930), Hudson (1980), Fettes *et al.* (1986) and Harte (1987). Mineral abbreviations follow the recommendations of Kretz (1983).

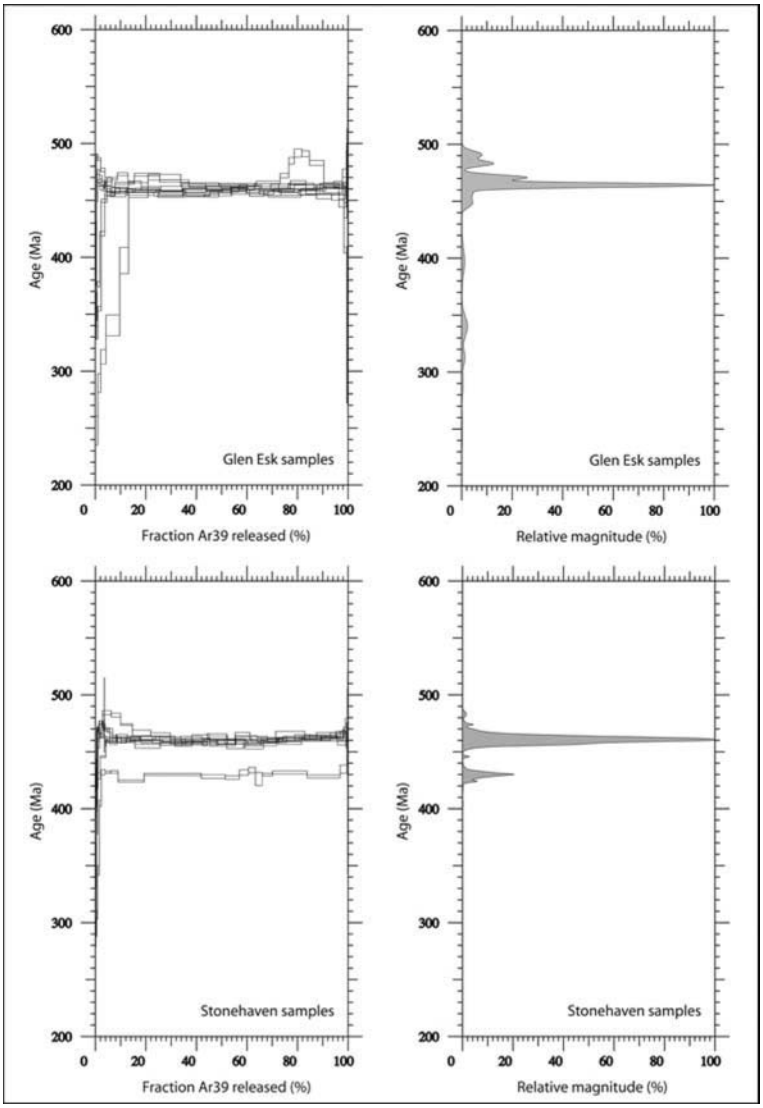

Fig. 2. $^{40}Ar/^{39}Ar$ apparent age spectra for samples from the Stonehaven and Glen Esk transects that display Mode 1 $^{40}Ar/^{39}Ar$ step-heating patterns. Frequency plots on the right of the respective $^{40}Ar/^{39}Ar$ spectra plots show the relative frequency of occurrence of step-heating ages.

Samples from the Glen Esk transect that exhibit Mode 1 spectra yielded $^{40}Ar/^{39}Ar$ plateau ages displaying a more considerable range, from 465.0 ± 1.5 to 455.6 ± 0.9 Ma (Table 1; Fig. 2). Like the Stonehaven samples, the Glen Esk samples display a general decrease in age with increasing grade (Table 1). The frequency plot for the Glen Esk transect exhibits a pronounced peak at *c*. 459 Ma (Fig. 2).

Mode 2 spectra. Of 18 samples analysed using the $^{40}Ar/^{39}Ar$ step-heating technique, only four samples produced Mode 2 patterns: three from the Stonehaven transect, and one from the Glen Esk transect. Samples that yielded Mode 2 spectra were collected from localities adjacent to the Highland Boundary Fault, in each case within 500 m of the terrane-bounding fault. Heterogeneous $^{40}Ar/^{39}Ar$ step-heating spectra can be difficult to interpret and, to achieve objectivity in analysis, the method of 'asymptotes and limits' (Forster & Lister 2004) was employed to extract information from Mode 2 $^{40}Ar/^{39}Ar$ spectra.

Implementation of the method of 'asymptotes and limits' used the beta release of the $^{40}Ar/^{39}Ar$ data interpretation program eAr for the Mac OS X platform. From the four Mode 2 samples, ages assigned significance by the method of 'asymptotes and limits' appear to define specific age ranges, including groupings at 1080–930 Ma, 780–700 Ma and 560–510 Ma (Fig. 3). In addition to the age clusters identified by the 'asymptotes and limits' method, a prominent spike occurs in the frequency plot at *c*. 485 Ma, defined by a grouping of 'significant' step-heating apparent ages from two of the Mode 2 samples collected on the Stonehaven transect (Fig. 3).

Significance of $^{40}Ar/^{39}Ar$ ages from the Barrovian metamorphic series

Samples that displayed Mode 2 $^{40}Ar/^{39}Ar$ spectra were each collected in the vicinity of the Highland Boundary Fault, within the upper reaches of the Dalradian stratigraphy. The upper parts of the Dalradian have been shown to be in stratigraphic contact with the Keltie Water Grit Formation (Tanner 1995; Tanner & Pringle 1999), which includes the late Early Cambrian Leny Limestone (Rushton *et al.* 2000). As the units that yielded Mode 2 $^{40}Ar/^{39}Ar$ spectra are Cambrian or younger in age, we interpret the age groupings (between 1080 and 510 Ma) to be detrital in origin, with the exception of the prominent spike at *c*. 485 Ma (Fig. 3). The preservation of these detrital ages indicates that

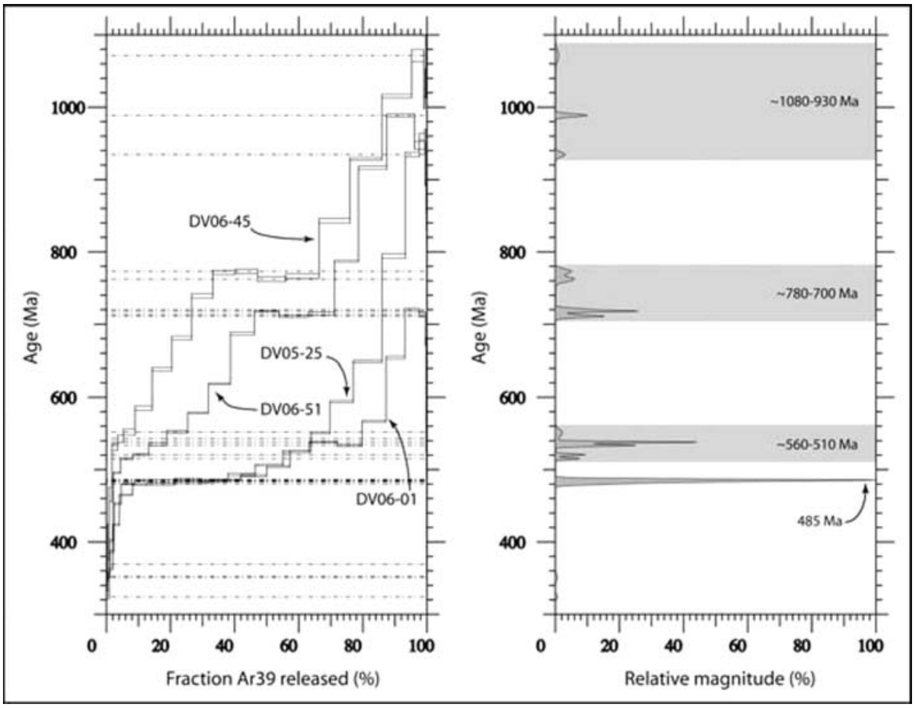

Fig. 3. $^{40}Ar/^{39}Ar$ apparent age spectra for samples from the Stonehaven and Glen Esk transects that display Mode 2 $^{40}Ar/^{39}Ar$ step-heating patterns. The frequency plot on the right shows the relative frequency of the step-heating ages identified as significant by the asymptotes and limits method of Forster & Lister (2004). Ages or age ranges defined by a cluster of peaks are highlighted and labelled on the frequency diagram.

Table 1. *$^{40}Ar/^{39}Ar$ plateau ages calculated for units of the Barrovian metamorphic serie*s

Transect, sample	Mineral zone	GPS	Mineral dated	Grain size (μm)	Spectrum type	*J* factor	*J* error (%)	Fusion age* (Ma)	Plateau age* (Ma)	MSWD, probability of fit
Glen Esk										
DV06-45	Chl zone	[NO58627331]	White mica	120–180	Mode 2	9.9992E − 3	0.9616	787.30 ± 7.42	n.a.	n.a.
DV06-54	Bt zone	[NO58307364]	White mica	120–180	Mode 1	1.0009E − 2	0.8260	461.42 ± 3.52	462.21 ± 1.16	1.7, 0.097
DV06-46	Grt zone	[NO58037416]	White mica	120–180	Mode 1	9.9743E − 3	0.9282	457.21 ± 3.88	460.59 ± 1.32	0.50, 0.81
DV06-48	St zone	[NO57947521]	Biotite	250–420	Mode 1	1.0049E − 2	0.7051	451.79 ± 7.02	465.02 ± 1.46	1.8, 0.13
DV06-49B	St zone	[NO56207575]	White mica	250–420	Mode 1	1.0039E − 2	0.6721	460.35 ± 2.76	459.41 ± 0.88	0.99, 0.44
DV05-14	Ky zone	[NO57387650]	White mica	250–420	Mode 1	9.8810E − 3	1.1447	456.83 ± 3.08	455.60 ± 0.88	2.1, 0.065
DV06-42	Sil zone	[NO55907847]	White mica	250–420	Mode 1	1.0095E − 2	0.7885	458.20 ± 2.98	459.05 ± 1.06	1.6, 0.12
DV06-43B	Sil zone	[NO45647802]	White mica	250–420	Mode 1	9.9397E − 3	0.9703	458.18 ± 5.72	457.57 ± 1.10	1.3, 0.18
Stonehaven										
DV05-25	Chl zone	[NO89248767]	White mica	90–120	Mode 2	9.8859E − 3	1.1966	568.92 ± 3.82	n.a.	n.a.
DV06-51	Bt zone	[NO89068778]	White mica	120–180	Mode 2	9.9644E − 3	0.8776	709.26 ± 3.60	n.a.	n.a.
DV06-01	Bt zone	[NO89088814]	White mica	120–180	Mode 2	1.0105E − 2	0.7955	528.38 ± 3.26	n.a.	n.a.
DV06-06	St zone	[NO89278901]	White mica	120–180	Mode 1	9.9152E − 3	1.2090	460.12 ± 3.28	462.47 ± 1.16	0.53, 0.83
DV06-11	St zone	[NO89598968]	White mica	120–180	Mode 1	9.9842E − 3	0.9788	463.85 ± 3.98	461.93 ± 1.12	1.7, 0.067
DV06-59	St zone	[NO90279098]	White mica	250–420	Mode 1	1.0059E − 2	0.7380	460.28 ± 3.74	459.95 ± 0.96	1.4, 0.16
DV06-15	St zone	[NO90939237]	White mica	250–420	Mode 1	1.0080E − 2	0.7780	458.67 ± 3.20	457.31 ± 1.08	1.6, 0.13
DV06-24	St zone	[NO92349436]	White mica	250–420	Mode 1	1.0019E − 2	0.6904	461.24 ± 4.08	460.63 ± 0.96	1.7, 0.058
DV06-40	Sil zone	[NO94439741]	White mica	250–420	Mode 1	9.9299E − 3	1.0658	459.48 ± 3.40	459.58 ± 1.00	1.2, 0.28
DV05-105	Sil zone	[NJ95690081]	White mica	250–420	Mode 1	9.8713E − 3	1.0410	427.63 ± 3.52	429.96 ± 0.92	1.5, 0.14

*Calculated using the decay constants of Steiger & Jäger (1977).
Uncertainties on *J*-factor values quoted to 1σ. Uncertainties on all ages are quoted to 2σ. Mineral abbreviations follow the recommendations of Kretz (1983).

metamorphism in the lowest-grade parts of the Barrovian metamorphic series was not sufficiently prolonged to induce complete Ar loss in detrital white mica grains.

The ages of Mode 1 samples from the Glen Esk and Stonehaven transects cluster at *c.* 459 Ma and *c.* 461 Ma, respectively (Fig. 2). $^{40}Ar/^{39}Ar$ age patterns show a trend in $^{40}Ar/^{39}Ar$ apparent age with metamorphic grade (Table 1) that suggests that $^{40}Ar/^{39}Ar$ systematics were set 4–5 Ma later in the higher grades relative to the lower grades. An additional 430.0 ± 0.9 Ma age occurs (DV05-105: Table 1), which is considered to represent localized resetting of Ar systematics in the vicinity of a post-Grampian (*c.* 430 Ma) granite intrusion, whose type and age are common in the study area (Oliver 2001).

The *c.* 485 Ma age defined by some Mode 2 samples is significantly older than the *c.* 460 Ma ages found for the Barrovian event (from the hotter parts of the biotite zone to the sillimanite zone). Samples that display *c.* 485 Ma plateau-like features (DV05-25 and DV06-01; Fig. 3) contain microscopic-scale recrystallized white mica within the fabric that is axial planar to folds of the early Grampian (pre-Barrovian) tectonic phase. The *c*. 485 Ma age is interpreted to date the timing of white mica partial recrystallization associated with earliest folding during the Grampian orogenic episode.

Detrital ages. Three detrital-age groupings have been recognized from the Mode 2 $^{40}Ar/^{39}Ar$ spectra: the 1080–930 Ma, 780–700 Ma and 560–510 Ma populations of Figure 3. Detrital zircon U/Pb ages that correspond to the 1080–930 Ma grouping occur in the Southern Highland Group, with frequency distribution diagrams for the Southern Highland Group displaying pronounced peaks at *c*. 1075 Ma and *c*. 1040 Ma (Cawood *et al.* 2003). Detrital zircon work on the Dalradian Supergroup has failed to reveal ages in the 780–700 Ma range. However, the $^{40}Ar/^{39}Ar$ ages overlap with the 737 ± 5 Ma (U/Pb titanite; Tanner & Evans 2003) and 740 ± 40 Ma (Rb/Sr mineral–whole-rock; Piasecki & van Breemen 1983) ages interpreted to date the controversial Knoydartian tectonothermal event in Scotland.

Diffusion v. recrystallization ages

In the higher-grade (staurolite, kyanite and sillimanite zone) units of the Barrovian metamorphic series, peak temperatures during the Barrovian metamorphism reached values in excess of 550 °C (Harte & Hudson 1979; Baker 1985). At such temperatures, diffusion of Ar from white mica is effective over small time scales, of the order of thousands of years (Harrison *et al.* 2009). We thus take the $^{40}Ar/^{39}Ar$ plateau ages obtained for micas of the staurolite, kyanite and sillimanite zones of the Barrovian metamorphic series to date cooling following the Barrovian metamorphism, rather than crystallization or recrystallization.

The lowest-grade example of a Mode 1 $^{40}Ar/^{39}Ar$ step-heating spectrum is that of sample DV06-54, from the higher-grade parts of the biotite zone on the Glen Esk transect (Fig. 1b). DV06-01 has a Mode 2 $^{40}Ar/^{39}Ar$ step-heating spectrum and was collected at an equivalent position to DV06-54, within the biotite zone on the Stonehaven transect (Fig. 1c). In both these samples, white mica occurs as thin 'shreds' (oriented in the axial plane of folds belonging to first-phase Grampian folding) and many grains have a detrital appearance (Fig. 4). However, some recrystallization of white mica in the early Grampian fold fabric (as discussed in the interpretation of the *c*. 485 Ma ages) is evident in thin section (Fig. 4).

An abrupt change in white mica compositional patterns across the Barrovian metamorphic series occurs in the garnet zone. White mica displays a systematic trend in maximum Ti content with increasing peak metamorphic temperature for samples that achieved peak metamorphic temperatures greater than *c*. 520 °C (the middle garnet zone) (Fig. 5). However, this trend is not apparent for samples that achieved peak metamorphic temperatures less than *c*. 520 °C (Fig. 5). Thus, white mica geochemistry of the Barrovian metamorphic series suggests that the lowest-grade examples of complete Barrovian-age recrystallization of white mica occur in the middle garnet zone. Moreover, in the direction of increasing metamorphic grade across the Barrovian metamorphic

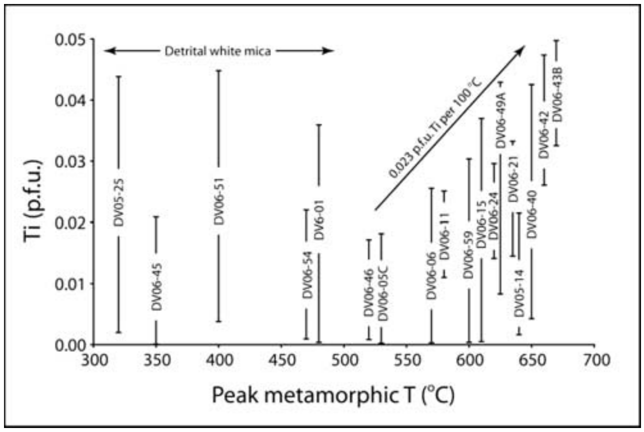

Fig. 5. Range of Ti in white mica values v. peak metamorphic temperature for each sample analysed for white mica geochemistry (from Viete 2009, p. 52, fig. 2.14). An 'average pelite' MnNCKFMASH pseudosection contoured for Si content in white mica was used to determine peak metamorphic temperature estimates on the basis of metamorphic mineral assemblage and white mica Si content for the samples (see Viete 2009). Peak metamorphic temperature estimates carry an uncertainty on the order of ±20 °C.

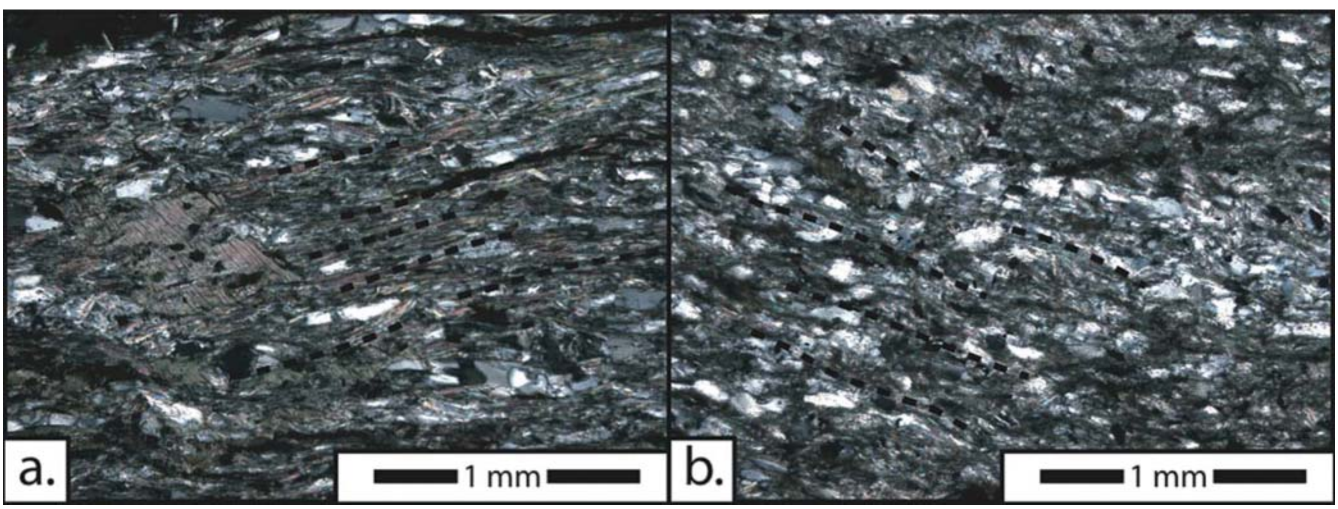

Fig. 4. Photomicrographs showing detrital white mica oriented in the axial plane of early Grampian folds: (**a**) from sample DV06-01 [GPS: NO89088814]; (**b**) from sample DV06-54 [GPS: NO58307364].

series, overprinting of the early orogenic fold fabrics by the Barrovian-age top-to-the-SE shear fabrics is not significant for units of lower metamorphic grade than those of the garnet zone (see Krabbendam *et al.* 1997). The structure of the Barrovian metamorphic series and the nature of variation in white mica compositions across it are consistent with the preservation of detrital white mica populations in the chlorite and biotite zones.

The presence of detrital white mica in a sample that has yielded a Grampian-age white mica $^{40}Ar/^{39}Ar$ plateau (DV06-54) suggests that the lowest-grade samples that display Barrovian plateau ages experienced Barrovian-age resetting of Ar systematics as the result of diffusive Ar loss, and not wholesale recrystallization of white mica.

Argon diffusion modelling

The temperatures of the transition between pre-Grampian mixed $^{40}Ar/^{39}Ar$ step-heating spectra (Mode 2 spectra) and $^{40}Ar/^{39}Ar$ step-heating spectra that yielded Grampian plateau ages (Mode 1 spectra) can provide additional information concerning the duration of the Barrovian thermal event. Forward modelling of Ar diffusion in white mica can be used to estimate the minimum duration thermal event required to reset K/Ar systematics in the lowest-grade units that display Mode 1 $^{40}Ar/^{39}Ar$ spectra. Conversely, it is also possible to use forward modelling of Ar diffusion in white mica to determine the maximum heating durations that the highest-grade units that display Mode 2 $^{40}Ar/^{39}Ar$ spectra could have undergone and still retain pre-Grampian ages. In this way, Ar diffusion modelling can be used to limit the maximum possible duration for metamorphism in the biotite zone.

The transition between units that display Mode 1 and Mode 2 $^{40}Ar/^{39}Ar$ spectra in the Barrovian metamorphic series occurs in the region between the middle of the biotite zone and the garnet-in isograd, which experienced peak metamorphic temperatures of between 450 and 500 °C (Viete 2009). The lowest-grade examples of Grampian-age plateaux in white mica $^{40}Ar/^{39}Ar$ step-heating spectra (DV06-54: Fig. 1b; Table 1) occur in white mica populations with a detrital component, and these ages reflect resetting of Ar systematics by diffusion of Ar from detrital white mica grains, in the absence of significant Barrovian-age metamorphic recrystallization. $^{40}Ar/^{39}Ar$ step-heating analyses for samples collected from the biotite and garnet zones (DV06-01, DV06-54, DV06-46) were carried out on white mica populations with grain size between 120 and 180 μm (Table 1).

Modelling approach

The diffusion modelling carried out for this study utilized a purpose-built modification of the MacArgon program of Lister & Baldwin (1996), updated for the Mac OS X platform. A homogeneous $^{40}Ar^*$ distribution that yields a 1000 Ma age was used as a starting condition and spherical diffusion geometry (see Harrison *et al.* 2009) was adopted for all models.

Arrhenius parameters for Ar diffusion in white mica. Kirschner *et al.* (1996) showed empirically that the Arrhenius parameters that govern Ar diffusion in white mica are very similar to those that govern Ar diffusion in phlogopite (see Giletti 1974). In the same year, Lister & Baldwin (1996) similarly constrained the Arrhenius parameters that govern Ar diffusion in muscovite to a range with an upper limit equivalent to the retentivity of phlogopite. Recently, Harrison *et al.* (2009) published the results of experiments designed to investigate the diffusion behaviour of Ar in white mica. Their results confirmed that the retentivity of muscovite had been significantly underestimated by the experiments of Robbins (1972) (see McDougall & Harrison 1999) and that Ar diffusion in white mica occurs at temperature-dependent rates similar to Ar diffusion in phlogopite. Therefore the Ar diffusion modelling reported on in this study was carried out using the most recent Arrhenius parameter set of Harrison *et al.* (2009), which was calculated for a spherical diffusion geometry from data collected from experiments carried out at 10 kbar pressure ($D_0 = 2.3 \times 10^{-4}$ m^2 s^{-1}, $E = 263.8$ kJ mol^{-1}). The Ar diffusion modelling was repeated using the Arrhenius parameter set of Harrison *et al.* (2009), adjusted to zero pressure, using a value of $\Delta V = 14 \times 10^{-6}$ m^3 mol^{-1} (Harrison *et al.* 2009) for diffusion volume. The disagreement between the 0 and 10 kbar modelling results gives an indication of the influence of metamorphic pressure on diffusivity. However, these results also give extreme values for thermal durations in the biotite zone of the Barrovian metamorphic series and the thermal duration estimates we promote in the discussion are valid for Arrhenius parameters corresponding to pressures intermediate between the 0 and 10 kbar models.

Decomposition of white mica during step-heating analyses. Decomposition of white mica by dehydroxylation and/or delamination during step heating may influence $^{40}Ar/^{39}Ar$ step-heating spectra (Sletten & Onstott 1998). However, the extent to which decomposition of different white mica populations (as opposed to volume diffusion) influences mixed $^{40}Ar/^{39}Ar$ step-heating spectra is equivocal (Forster & Lister 2004, and references therein). Forster & Lister (2004) have addressed the origin of mixed $^{40}Ar/^{39}Ar$ step-heating spectra (e.g. volume diffusion v. mica decomposition), and we refer the interested reader to their paper for detailed discussion on the topic.

White mica decomposition could undermine the validity of conclusions made on the basis of diffusion modelling used to replicate mixed (Mode 2) $^{40}Ar/^{39}Ar$ spectra obtained from step-heating analyses. However, it should be emphasized that the goal of the diffusion modelling effort reported here has been to identify the duration of the Barrovian metamorphic heating required to entirely reset biotite-zone white mica $^{40}Ar/^{39}Ar$ ages to Grampian values, and not to perfectly replicate the Mode 2 $^{40}Ar/^{39}Ar$ spectra obtained from step-heating analyses. In this aspect it is important only that pre-Grampian $^{40}Ar^*$ remains in the sample following metamorphic heating. The details of the mechanism of argon release from the bulk sample during step heating *in vacuo* in the mass spectrometer are not at all relevant. Decomposition may occur during step heating but this does not invalidate the basic conclusions made from the diffusion modelling, as these apply to the behaviour of argon in nature, not in the mass spectrometer.

Modelling using square-wave thermal histories

Initially, square-wave temperature–time (T–t) histories were used to investigate heating durations required to produce the $^{40}Ar/^{39}Ar$ age relations observed across the biotite zone of the Barrovian metamorphic series. The square-wave T–t paths used for the diffusion modelling exhibit an instantaneous temperature increase, at 470 Ma, from 0 °C to peak metamorphic temperatures and, at the cessation of heating, an instantaneous return to 0 °C. Peak metamorphic durations of 10, 20, 30, 50, 100, 200, 250, 300, 500 and 750 ka, and 1, 2, 3, 5 and 10 Ma were used for the square-wave modelling.

Square-wave duration estimates. Ar diffusion models were run using an average white mica grain size of 150 μm, at peak metamorphic temperatures of 450, 475 and 500 °C, which bracket the transition from Mode 2 $^{40}Ar/^{39}Ar$ step-heating spectra to Mode 1 $^{40}Ar/^{39}Ar$ step-heating spectra across the biotite zone of the Barrovian metamorphic series. Durations can be constrained to a range that will allow preservation of Mode 2 $^{40}Ar/^{39}Ar$ step-heating spectra in units that experienced peak metamorphic temperatures of 450 °C (units from the middle of the biotite zone; Fig. 6a and d) and those that allow Grampian-age resetting of $^{40}Ar/^{39}Ar$ systematics in units that experienced peak metamorphic temperatures of 500 °C (units from the garnet-in isograd; Fig. 6c and f). The model Ar spectra of Figure 6 suggest that acceptable square-wave durations for the Barrovian metamorphism lie between about 20 ka and 200 ka for metamorphism at 0 kbar and 250 ka and 2 Ma for metamorphism at 10 kbar.

The highest-grade sample that yielded a Mode 2 $^{40}Ar/^{39}Ar$ step-heating spectrum (DV06-01) and the lowest-grade sample that yielded a Mode 1 $^{40}Ar/^{39}Ar$ step-heating spectrum (DV06-54) were collected from between the middle of the biotite zone and the garnet-in isograd on the Stonehaven and Glen Esk transects, respectively. Both samples experienced similar peak metamorphic temperatures of around 475 °C, yet they display different $^{40}Ar/^{39}Ar$ step-heating spectra. Detrital white mica grains from sample DV06-54 are significantly smaller in grain size than those from sample DV06-01 (Fig. 4), and we attribute differences in their $^{40}Ar/^{39}Ar$ step-heating spectra to differences in grain size. Ar diffusion modelling was carried out for a peak metamorphic temperature of 475 °C and grain sizes of 120, 240 and 360 µm. The grain-size range for modelling was chosen to represent the smallest grains that will occur in the 120–180 µm white mica separates analysed for samples DV06-01 and DV06-54 (*c*. 120 µm), in addition to a conservative estimate of the largest detrital white mica grains that occur in sample DV06-01 (*c*. 360 µm). A lower estimate for the duration of the Barrovian metamorphism in the biotite zone is provided by the duration of the shortest thermal event that will reset $^{40}Ar/^{39}Ar$ ages to Grampian values in the 120 µm model (Fig. 7a and d). Conversely, a robust upper estimate for the duration of the

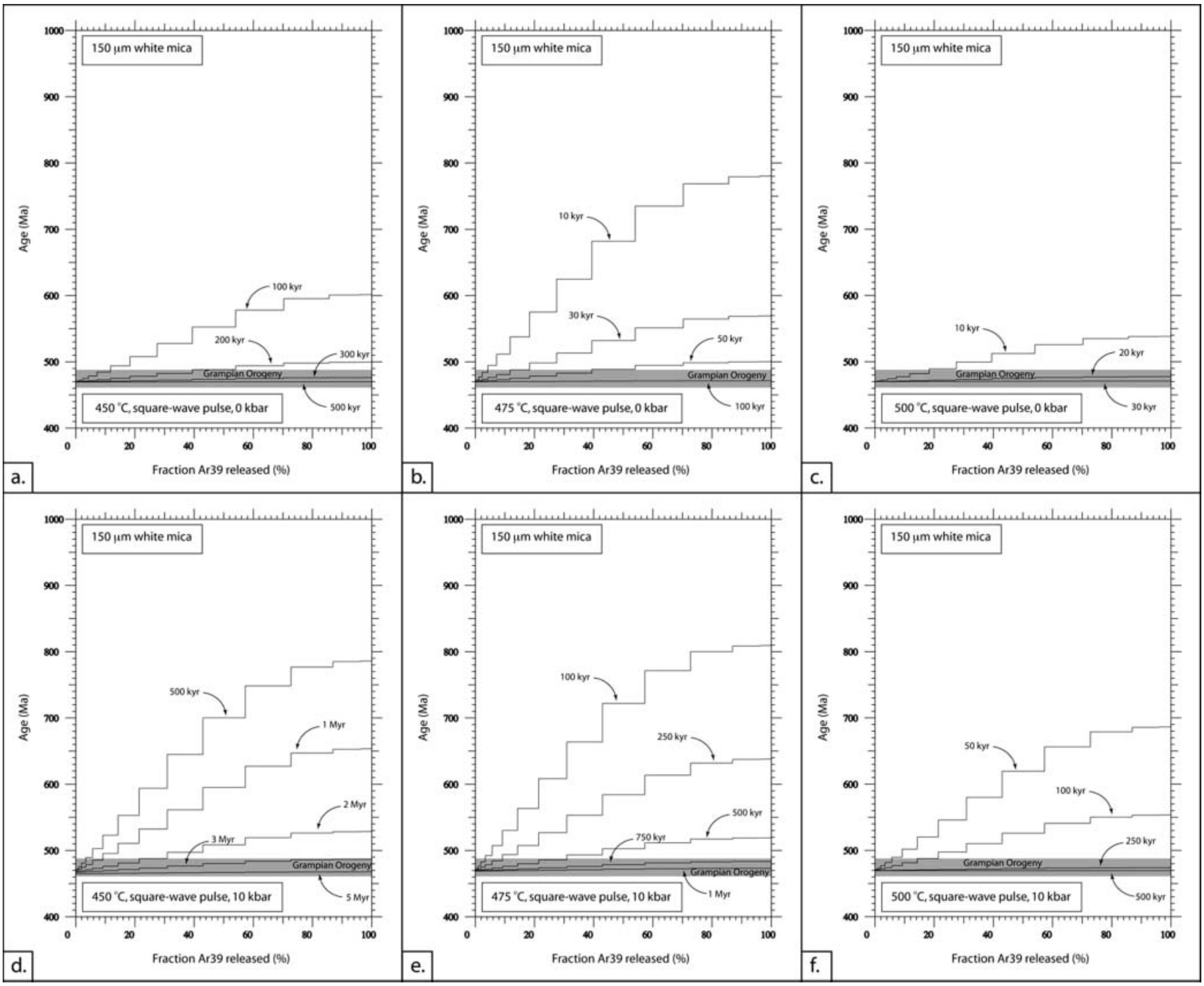

Fig. 6. Model $^{40}Ar/^{39}Ar$ step-heating spectra produced by Ar diffusion modelling using the MacArgon program, 150 µm diameter, spherical white mica grains and square-wave temperature–time curves of duration indicated. Plots show samples that experienced peak metamorphism at (**a**) 450 °C and 0 kbar, (**b**) 475 °C and 0 kbar, (**c**) 500 °C and 0 kbar, (**d**) 450 °C and 10 kbar, (**e**) 475 °C and 10 kbar, and (**f**) 500 °C and 10 kbar.

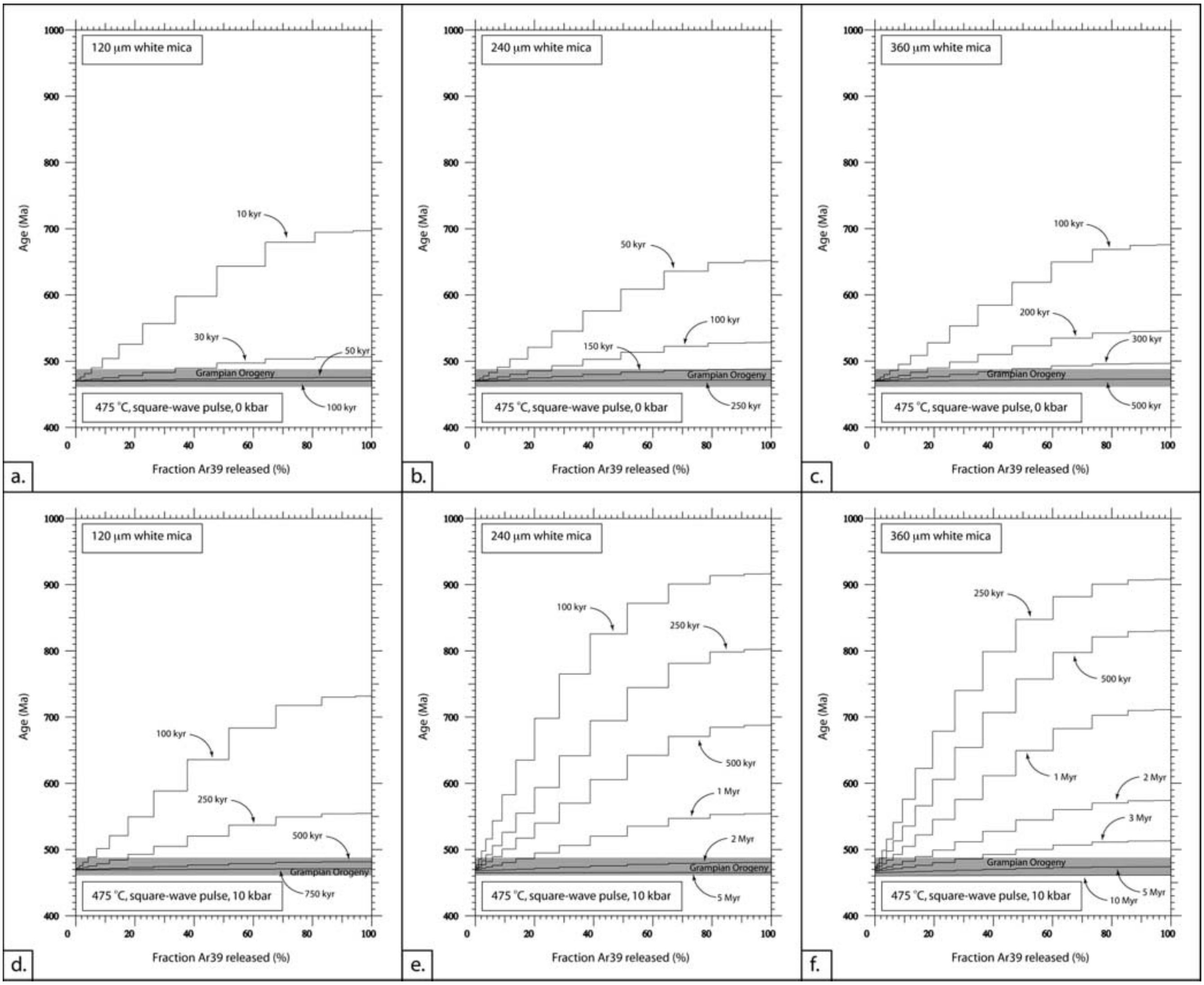

Fig. 7. Model $^{40}Ar/^{39}Ar$ step-heating spectra produced by Ar diffusion modelling using the MacArgon program and 475 °C (peak temperature) square-wave temperature–time curves of duration indicated. Plots show (**a**) 120 μm diameter white mica at 0 kbar, (**b**) 240 μm diameter white mica at 0 kbar, (**c**) 360 μm diameter white mica at 0 kbar, (**d**) 120 μm diameter white mica at 10 kbar, (**e**) 240 μm diameter white mica at 10 kbar, and (**f**) 360 μm diameter white mica at 10 kbar. A homogeneous $^{40}Ar/^{39}Ar$ distribution that yields a 1000 Ma age was used as a starting condition.

Barrovian metamorphism in the biotite zone is obtained from the duration of the longest duration thermal event that will not reset $^{40}Ar/^{39}Ar$ ages to Grampian values in the 360 μm model (Fig. 7c and f). Thus, from the square-wave modelling, metamorphism appears to have persisted for between about 50 ka and 300 ka for metamorphism at 0 kbar and 500 ka and 3 Ma for metamorphism at 10 kbar. (Fig. 7). A range of 200 ka to 2 Ma, corresponding to an intermediate pressure between 0 and 10 kbar, might represent a sensible recommendation for the square-wave duration of Barrovian thermal activity in the biotite zone.

Initial condition considerations. To investigate the effect of initial conditions on the results of the diffusion modelling, equivalent square-wave modelling was carried out for the 10 kbar model using a Knoydartian (740 Ma) starting condition (as an alternative to the 1000 Ma starting condition). The results of this additional modelling effort are summarized in Figure 8. On the same logic as used to interpret the results of the 1000 Ma initial condition, 10 kbar square-wave modelling, the 740 Ma initial condition, 10 kbar square-wave modelling suggests that Barrovian metamorphism of the biotite zone lasted for between 500 ka and 3 Ma. Thus, varying the initial conditions adopted for the diffusion modelling appears to have negligible effect on the conclusions made on the results of the modelling.

Cooling of the Barrovian metamorphic series occurred by conductive dissipation, which, like all diffusion processes, produces asymptotic decay behaviour. For a sizeable sequence, such as the *c*. 5000 m thick (Krabbendam *et al.* 1997) Barrovian metamorphic series, cooling from peak metamorphic temperatures is not instantaneous and square-wave heat pulses will misrepresent metamorphic durations. Below, we employ conductive heating-cooling curves superimposed on an ambient thermal regime to model the diffusion of Ar from white mica. The results provide more accurate Barrovian metamorphic duration estimates owing to the use of T–t paths that better represent natural heating-cooling behaviour.

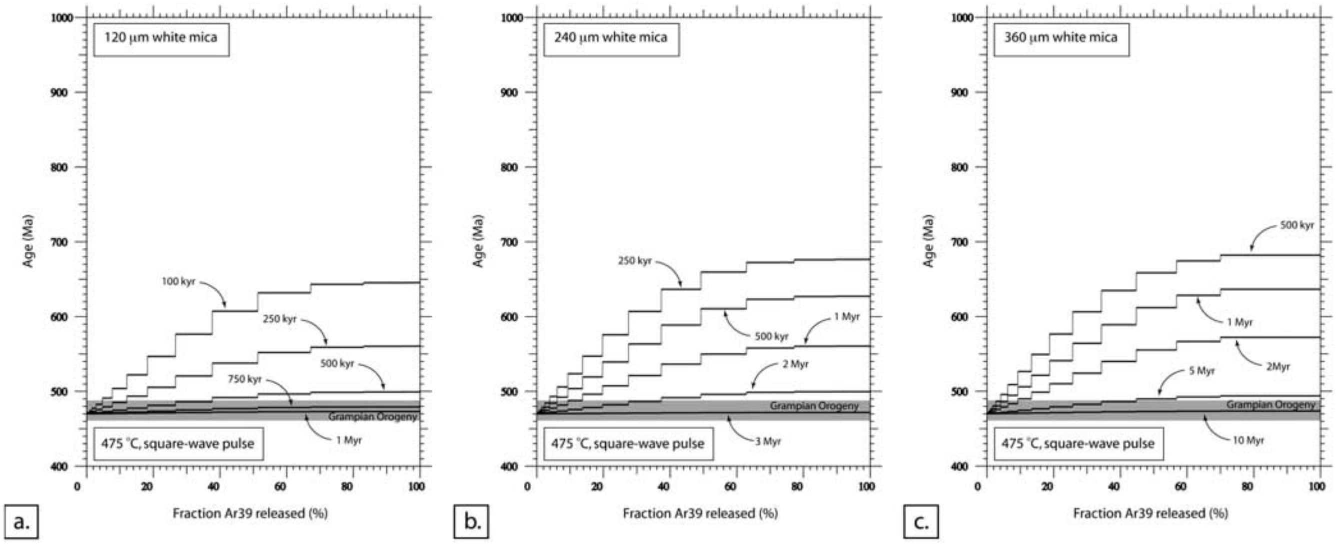

Fig. 8. Model $^{40}Ar/^{39}Ar$ step-heating spectra produced by Ar diffusion modelling using the MacArgon program and 475 °C (peak temperature) square-wave temperature–time curves of duration indicated. Plots show (**a**) 120 μm diameter white mica at 10 kbar, (**b**) 240 μm diameter white mica at 10 kbar, and (**c**) 360 μm diameter white mica at 10 kbar. A homogeneous $^{40}Ar/^{39}Ar$ distribution that yields a 740 Ma age was used as a starting condition.

Modelling using conductive heating-cooling histories

Conductive heating then cooling of a rock mass following emplacement of a hot body is a well-characterized problem in the Earth Sciences, and one that can be solved analytically for various initial and boundary conditions (see Carslaw & Jaeger 1959). An area of physics where application of analytical expressions for heat conduction is commonplace is in the fitting of *T–t* curves to experimental data in the 'Flash method' for thermal diffusivity measurement (see Parker *et al.* 1961). Cape & Lehman (1963) gave an infinite-series solution that can be approximated numerically to model the thermal evolution at the rear of an experimental plate heated on its front surface. The solution offers a simple approach to modelling conductive heating-cooling of regions affected by crustal heating.

An infinite-series solution for conductive heating-cooling histories. Cape & Lehman (1963) gave an infinite-series solution for the temperature evolution at the rear surface of a cylindrical plate of thickness l, radius r and thermal diffusivity a, heated uniformly over its entire front surface. Boundary conditions for the solution are such that the experimental plate experiences conductive heat loss at its front, rear and radial surfaces. The solution offered by Cape & Lehman (1963) can be expressed as follows:

$$T(Y_x, Y_r, \tau) = T_0 D_0(r, Y_r) \times \left[C_0 X_0 \exp\left(-\frac{2Y\tau}{\pi^2}\right) + \exp\left(\frac{2Y_r l^2 \tau}{\pi^2 r^2}\right) \times \sum_{m=1}^{\infty} C_m X_m \exp\left(-tm^2 - \frac{4Y\tau}{\pi^2}\right)\right] + T_{\mathrm{amb}} \quad (1)$$

where

$$z_0 \approx \sqrt{2Y_r}\left(1 - \frac{Y_r}{8}\right);$$

$$D_0(r, Y_r) = \frac{2Y_r}{{Y_r}^2 + {z_0}^2};$$

$$X_0 \approx \sqrt{2Y_r}\left(1 - \frac{Y_x}{12} + \frac{7{Y_x}^2}{288}\right);$$

$$X_m \approx m\pi + 2\frac{Y_x}{m\pi} - 4\frac{{Y_x}^2}{(m\pi)^2} - 2\frac{{Y_x}^3}{(m\pi)^3} - 16\frac{{Y_x}^4}{(m\pi)^4} \text{ for } m \geqslant 1$$

$$C_m = \frac{2a(-1)^m X_m}{l({X_m}^2 + 2Y_x + {Y_x}^2)}$$

$$Y = Y_x + \frac{Y_r l^2}{r^2}$$

T_0 is the total input energy over the total heat capacity (or maximum temperature increase); T_{amb} is the ambient crustal temperature prior to heating. Dimensionless time (τ) can be expressed in terms of time (t), plate thickness (l) and thermal diffusivity (a):

$$\tau = \frac{a\pi^2 t}{l^2}. \quad (2)$$

Y_x and Y_r are the basal and the lateral Biot numbers for the system in question, respectively.

For the purpose of simplicity, temperature dependence on thermal diffusivity within the crust is ignored and common values for thermal diffusivity are adopted for the Barrovian metamorphic series and lateral and overlying crustal regions. This has resulted in the use of basal and lateral Biot numbers of unity ($Y_x = Y_r = 1$) in equation (1). Using a radial Biot number (Y_r) of unity eliminates dependence of equation (1) on the magnitude of the radial dimension (r).

Metamorphic durations for the conductive heating-cooling paths are defined here as the duration over which temperatures remain above ambient values by one-tenth of the total temperature excursion (Fig. 9). For basal and lateral Biot numbers of unity, the conductive heating-cooling paths take durations of *c.* 14.27 in terms of dimensionless time (τ) (Fig. 9). With knowledge of the thickness of the heated system and the thermal diffusivity of the material that forms it, absolute thermal durations can be extracted from equation (2), using $\tau = 14.27$.

Conductive heating-cooling duration estimates. To model Ar diffusion from white mica of the biotite zone of the Barrovian metamorphic series, conductive heating-cooling curves that approximate *T–t* histories for the metamorphic units were produced using the Cape & Lehman (1963) approach and conductive length scales of 500, 1000, 2000, 2500, 3000, 5000, 7500, 10 000, 15 000, 20 000, 25 000 and 30 000 m. Pre-Barrovian temperatures of 300 °C (starting at 1000 Ma) and peak Barrovian temperatures of 475 °C for units between the middle biotite zone and the garnet-in isograd of the Barrovian metamorphic series were adopted, resulting in conductive heating-cooling curves being superimposed on ambient temperatures of 300 °C, such that peak metamorphic temperatures of 475 °C were achieved at 470 Ma. Temperatures following the Grampian orogenic episode (taken to have ended at 461 Ma) were held at 0 °C.

For the modelling scenario outlined above, hypothetical $^{40}Ar/^{39}Ar$ step-heating spectra produced using the modified MacArgon program demonstrate that conductive heating-cooling of 3000 m thick (0 kbar model: Fig. 10a) and 10 000 m thick (10 kbar model: Fig. 10d) sequences are required to reset $^{40}Ar/^{39}Ar$ ages to Grampian values for 120 μm white micas. Conductive heating and cooling of 7500 m thick (0 kbar model: Fig. 10c) and 25 000 m thick (10 kbar model: Fig. 10f) sequences will not quite reset $^{40}Ar/^{39}Ar$ ages to Grampian values for 360 μm white micas. Conductive heating-cooling length scales for Barrovian thermal activity in the biotite zone are likely to have been of the order of 5000–15 000 m, for metamorphic pressures intermediate between 0 and 10 kbar.

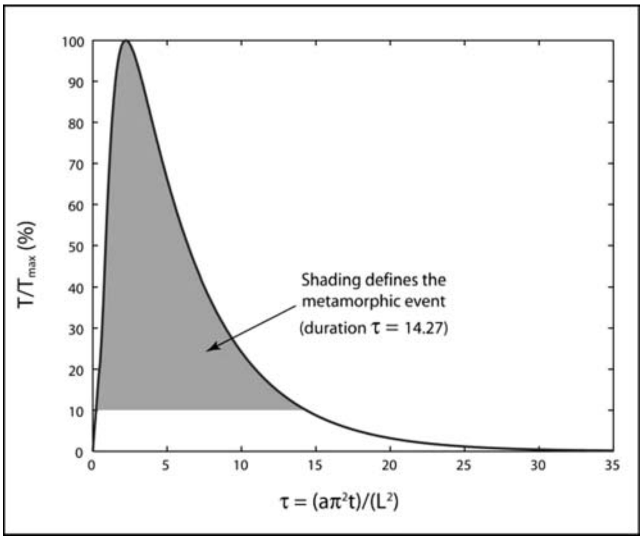

Fig. 9. Conductive heating-cooling curve constructed from equation (1). The curve demonstrates proportional temperature increase against dimensionless time. The curve can be expressed in terms of absolute temperature and time by substituting in values for the maximum temperature excursion (T_{max}), thermal diffusivity (a) and width of the system (L).

Assuming a thermal diffusivity of $a = 10^{-6}\ m^2\ s^{-1}$ for the Barrovian metamorphic units, conductive heating-cooling paths calculated for length scales of 5000, 10 000 and 15 000 m display thermal time scales of 1, 4.5 and 10 Ma, respectively. The results of the Ar diffusion modelling suggest that the Barrovian metamorphism of the biotite zone occurred over a duration of between about 1 and 10 Ma.

Comparison with the dimensions of the Barrovian metamorphic series. The Barrovian metamorphic series has a current-day thickness of *c.* 5000 m (Krabbendam *et al.* 1997). A lack of significant heat sources between the chlorite and sillimanite zones suggests that metamorphism of the lowest grade units was the result of conductive dissipation of heat over distances of 5000 m or more. Thus, duration estimates of less than 1 Ma (the time scale for conductive heating-cooling of a 5000 m sequence) can be disqualified on the structural dimensions of the Barrovian sequence.

The Barrovian metamorphic series experienced significant syn- to post-metamorphic attenuation (Krabbendam *et al.* 1997) and may have been considerably thicker than 5000 m when it developed. The results of Ar diffusion modelling using conductive heating-cooling histories suggest that the sequence was between 5000 and 15 000 m thick during metamorphism of the biotite zone. These values are consistent with the physical dimensions of the Barrovian metamorphic series and the evidence it records for syn- to post-metamorphic attenuation.

Discussion

$^{40}Ar/^{39}Ar$ step-heating spectra from the low-grade zones of the Barrovian metamorphic series preserve a detrital white mica component. $^{40}Ar/^{39}Ar$ step-heating spectra from units of higher metamorphic grade than the middle biotite zone display Grampian-age plateau and no such detrital age signature. Thus, the Barrovian metamorphic series records a distinct transition in the middle biotite zone (at peak metamorphic temperatures of about 475 °C) that separates mixed-age $^{40}Ar/^{39}Ar$ step-heating spectra in lower-grade units from Grampian-age $^{40}Ar/^{39}Ar$ step-heating plateaux in higher-grade units. The results of forward modelling of Ar diffusion from white micas of the biotite zone to reproduce the $^{40}Ar/^{39}Ar$ step-heating pattern preserved across the Barrovian metamorphic series provide evidence to suggest that metamorphism in the biotite zone spanned a duration of between 1 and 10 Ma.

Dewey & Mange (1999), using palaeostratigraphical time markers, studied the chronology of the Grampian orogenic episode in Ireland in detailed stratigraphy preserved within the Grampian-age South Mayo Trough of western Ireland. The chronological sequence they proposed from their study included a 2–10 Ma duration for the Grampian orogenic (Barrovian-type) metamorphism that represents the Irish equivalent of Scotland's Barrovian metamorphic series. Reverdatto & Polyansky (2004) modelled crustal heating (and regional metamorphism) associated with the intrusion of Grampian-age gabbros in Connemara, western Ireland, and arrived at an estimate of 5–6 Ma for the duration of the Irish Barrovian-type metamorphism during the Grampian orogenic episode. These estimates are both consistent with Barrovian metamorphic duration estimates from this study of 1–10 Ma for the biotite zone.

Recently, Ague & Baxter (2007), using the results of forward

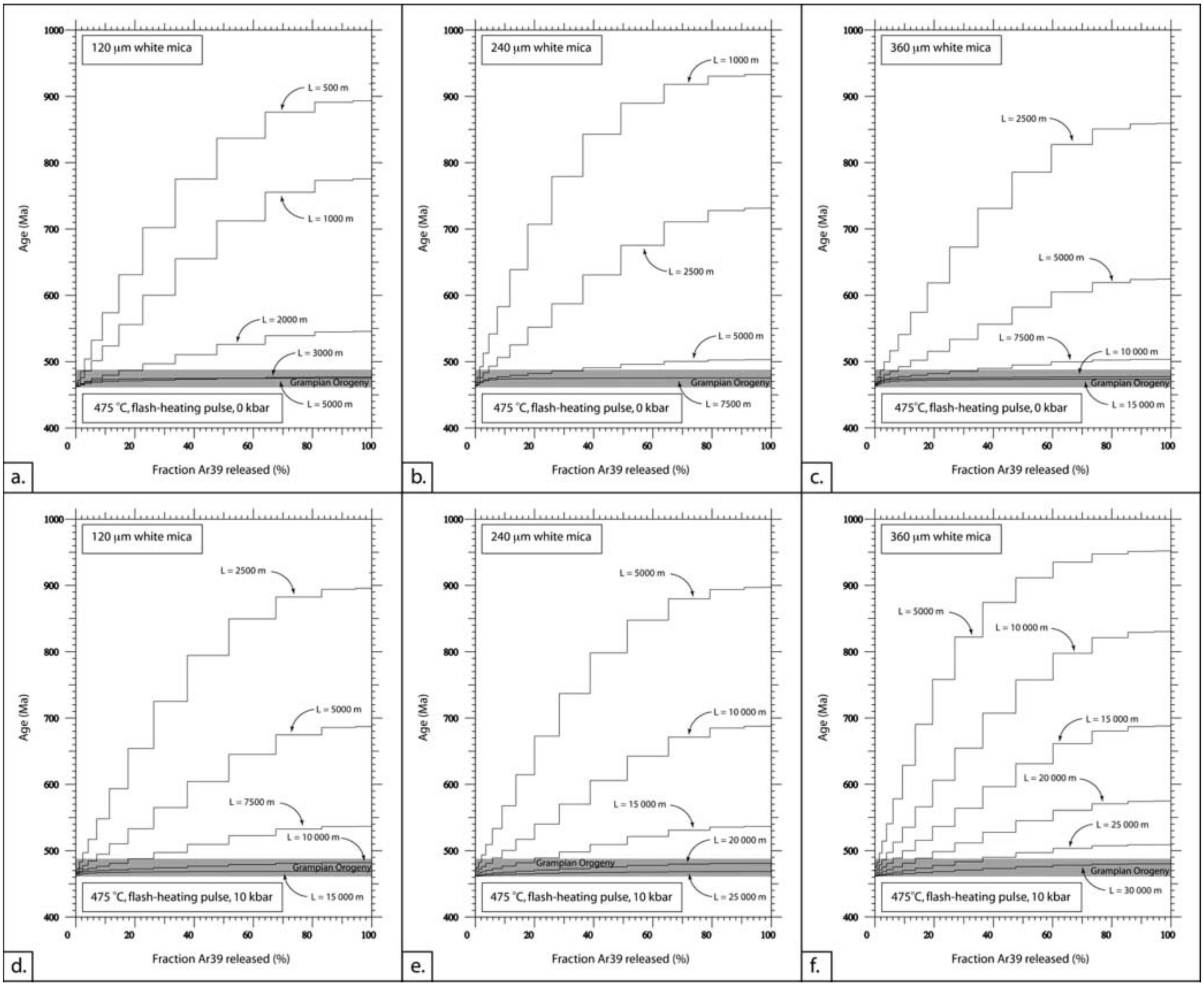

Fig. 10. Model $^{40}Ar/^{39}Ar$ step-heating spectra produced by Ar diffusion modelling using the MacArgon program and 475 °C (peak temperature) conductive heating-cooling paths of length scale indicated. Plots show (**a**) 120 μm diameter white mica at 0 kbar, (**b**) 240 μm diameter white mica at 0 kbar, (**c**) 360 μm diameter white mica at 0 kbar, (**d**) 120 μm diameter white mica at 10 kbar, (**e**) 240 μm diameter white mica at 10 kbar, and (**f**) 360 μm diameter white mica at 10 kbar. A homogeneous $^{40}Ar/^{39}Ar$ distribution that yields a 1000 Ma age was used as a starting condition.

modelling to match stranded Sr diffusion profiles in apatite and major element diffusion profiles in garnet, estimated the total duration of peak Barrovian metamorphism in Scotland at 270 ka (arithmetic mean of 10 values between 68 ka and 650 ka). Conductive dissipation of heat accumulated within a *c*. 5000 m thick metasedimentary sequence, such as the Barrovian metamorphic series, requires time scales in excess of 1 Ma. Accelerated cooling of the Barrovian metamorphic series by rapid exhumation of the sequence to the Earth's surface while 'hot' (as proposed by Ague & Baxter 2007) would have caused overgrowth of Barrovian sillimanite by andalusite. The Barrovian metamorphic series does not display such andalusite. Arguments made purely on the thickness of the Barrovian sequence (and time scales for dissipation of metamorphic heat from the sequence) preclude Barrovian metamorphism over time scales as short as those that Ague & Baxter (2007) estimated.

Discrepancies between the metamorphic duration we obtained from this study and the metamorphic durations Ague & Baxter (2007) calculated for the Barrovian metamorphism can easily be accounted for by uncertainties in the Arrhenius parameters adopted for each study (i.e. Sr in apatite: Cherniak & Ryerson 1993; Ar in white mica: Harrison *et al.* 2009).

The origin of the Barrovian metamorphic heat

The Barrovian metamorphism represents the dominant thermal event during the Grampian orogenic episode. On the basis of the Ar diffusion work discussed above, the total duration of thermal activity associated with Barrovian metamorphism of the biotite zone can be restricted to between 1 and 10 Ma. Models that invoke lithospheric-scale sources for metamorphic heat (e.g. post-thickening thermal relaxation, inherited lithospheric heat, radioactive heat production) require time scales for dissipation of metamorphic heat of the order of tens of millions of years and cannot account for such brevity. Metamorphic durations of the order of several million years are consistent with models for which metamorphic heating results from localized thermal permutations.

Localized heat sources that contributed to the Barrovian metamorphism may have had their origin in heat production or in advection of heat from hotter regions of the crust or mantle. A list of realistic options may include one, or any combination of: (1) heat advected from the lower crust or mantle in the form of magmas; (2) heat advected from the lower crust or mantle in the form of hot fluids; (3) production of heat by mechanical work within a thin zone of active deformation.

Camacho *et al.* (2005, 2009) and Mark *et al.* (2007, 2008) have associated brief metamorphic heating with the operation of large-scale crustal shear zones. Mid-crustal shear zones that concentrate advective heat sources (magmas and fluids) and produce heat through mechanical work provide an ideal candidate for the focused heating responsible for a brief Barrovian metamorphism. Ashcroft *et al.* (1984) described a series of shear zones decorated by large-scale magmatic bodies that occur in the NE of the Grampian Terrane, Scotland, and that are spatially associated with Grampian-age, high-grade metamorphic rocks (Kneller & Leslie 1984). Viete *et al.* (2010) showed that the shear zones of Ashcroft *et al.* (1984) accommodated large-scale extensional movements during development of the regional metamorphic pattern of the Grampian Terrane, Scotland, and acted as a locus for mid-crustal emplacement of mafic magmas, originating from decompression melting of the asthenospheric mantle, during regional metamorphism. The Barrovian metamorphic series of Scotland may have developed by dissipation of heat that accumulated within underlying, mid-crustal shear zones, during an extensional phase of the Grampian orogenic episode.

Conclusions

Forward modelling of Ar diffusion from white mica can be used to produce model $^{40}Ar/^{39}Ar$ step-heating spectra to match the variation across metamorphic grade in the pattern of calculated $^{40}Ar/^{39}Ar$ step-heating apparent age spectra. These data can therefore be used to constrain durations for the classic Barrovian metamorphism in Scotland. The results of Ar diffusion modelling provide evidence to suggest that the Barrovian thermal event lasted for between 1 and 10 Ma, in the biotite zone.

A thermal episode with a duration of several million years is not consistent with the models that suggest that the Barrovian metamorphism resulted from lithospheric-scale heat sources (e.g. post-thickening thermal relaxation, inherited lithospheric heat or radioactive heat production). The data are consistent with heating in the biotite zone as the result of heat sources in mid-crustal ductile shear zones, as occur in the NE of the Grampian Terrane, Scotland. These shear zones accommodated large-scale extension and acted as a locus for the emplacement of mafic magmas during Grampian-age regional metamorphism (Viete *et al.* 2010). They thus represent narrow regions of the crust that concentrated advective heat sources. Such a narrow region of heating can account for the brief regional thermal episode that produced the Barrovian metamorphic series in Scotland.

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