The source of Dalradian detritus in the Buchan Block, NE Scotland: application of new tools to detrital datasets

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Short title: **Detrital zircon ages in the Buchan Block**

ABSTRACT

Detrital zircon from four samples of upper Dalradian metasedimentary rocks from the Buchan Block in the NE Grampian Highlands of Scotland were analysed by laser ablation inductively coupled mass spectrometry to establish their U–Pb age and trace element composition. The analysed grains (magmatic cores) mainly yield concordant ages ranging from Neoproterozoic to Eoarchaean. Kernel density plots of the data show pronounced peaks in the late Mesoproterozoic, Paleoproterozoic and Neoarchaean eras. The data are indistinguishable from detrital zircon age spectra from Dalradian rocks elsewhere, an interpretation supported by application of a non-parametric multidimensional scaling algorithm, and are consistent with a Laurentian source. Similar to existing studies from other Dalradian rocks, the age spectra from the Buchan Block reveals an increase in the relative proportion of older detritus with time, suggesting derivation from late Mesoproterozoic (Grenville) then Palaeoproterozoic orogens before widespread exposure and denudation of their Archaean basement rocks. Application of a novel approach to estimate the most likely time of radiogenic-Pb loss indicates some detrital zircon grains were affected by element mobility around 470–450 Ma as a result of Grampian orogenesis.

Supplementary materials: Laser ablation inductively coupled mass spectrometry U–Pb and trace element data, a matrix showing results of Kolmogorov–Smirnov (K–S) test, cathodoluminescence imaging of zircons and selected trace element plots are available at https://doi.org/???/???.

Key words: Buchan Block, Dalradian, U–Pb detrital zircon age, Laurentia, provenance.

INTRODUCTION

The Dalaradian Supergroup of Scotland and Ireland is a thick sequence of Neoproterozoic to lower Palaeozoic rocks that were deposited along the eastern margin of Laurentia, then deformed and metamorphosed during the complex Cambrian to Devonian Caledonian orogenic cycle, during the opening and subsequent closure of the Iapetus Ocean (McKerrow et al. 2000; Chew and Strachan 2014). The rocks have a long history of research dating back to Hutton's *Theory of the Earth* (1788), and have been key to the development of many fundamental geological concepts (see Stephenson et al. (2013a) and references therein).

The absolute age and age distribution of detrital minerals is a proven tool in constraining the source and depositional age of siliciclastic rocks, which may provide critical information on larger scale models of crustal evolution (Košler et al. 2002; Andersen 2005; Cawood et al. 2012b, 2013; Spencer and Kirkland 2015). Much of the Dalradian Supergroup records the legacy of sedimentary basins formed during the Neoproterozoic era, a dynamic period in Earth history where climactic extremes may have been the environmental forcing that spawned complex life (Hoffman and Schrag 2002; Prave et al. 2009). However, of the published detrital zircon age data from (meta)sedimentary rocks from the Dalradian Supergroup (Cawood et al. 2003; Banks et al. 2007; Chew et al. 2009, 2010; McAteer et al. 2010b; Strachan et al. 2013), there are none from the Buchan Block, a structurally-bound package of upper Dalradian Supergroup rocks in north-east Scotland that exhibits profound differences in its sedimentological, structural, magmatic and metamorphic history when compared to the rest of the Grampian Terrane (Figs 1 & 2). These differences have led some workers to regard the Buchan Block as an allochthonous crustal terrane comprising pre-Caledonian basement gneisses and cover rocks that were thrust into their current position during the Grampian phase of Caledonian orogenesis (Sturt et al. 1977; Ramsay and Sturt 1978).

Here we present laser ablation inductively coupled mass spectrometer (LA–ICP–MS) U–Pb age and rare earth element (REE) data from detrital zircons in four metasedimentary rocks from the Buchan Block. These data are compared with existing data from Dalradian Supergroup rocks with the aim of better understanding the age and source of detritus within the Buchan Block.

REGIONAL GEOLOGY

The Grampian Terrane, comprising the Dalradian Supergroup, its basement and intrusive rocks, is one of several major crustal blocks that amalgamated to form the northern part of the British Isles. It comprises a NE–SW-trending belt of rocks that extends from the Shetland Islands through the highlands of Scotland and into northern and northwestern Ireland, and is bound to the north by the Great Glen Fault and to the south by the Highland Boundary Fault–Fair Head–Clew Bay Line (Fig. 1). The rocks record a complex sequence of tectonomagmatic events, termed the Caledonian orogenic cycle (McKerrow et al. 2000; Chew and Strachan 2014), related to the opening and closure of the Iapetus Ocean during supercontinent breakup and reassembly in the lower Palaeozoic (Cambrian to Devonian) (Soper 1994; Dewey and Mange 1999; Cawood et al. 2003, 2007a; Chew et al. 2009; Kirkland et al. 2013; Chew and Strachan 2014). Recent reviews on the Caledonides of Scotland and Ireland are provided by Stephenson et al. (2013a), Chew and Strachan (2014), Tanner (2014) and Dewey et al. (2015), and of the geology of the north-east Grampian Highlands, including the Buchan Block, by Stephenson et al. (2013b).

The dominant component of the Grampian Terrane is the mid-Neoproterozoic to early Palaeozoic Dalradian Supergroup, a sequence of deformed and metamorphosed rocks dominated by marine siliclastic rocks with some carbonate and volcanic units that are intruded by pre- to post-orogenic igneous bodies ranging from peridotite to granite. From base to top, the Dalradian Supergroup comprises the Grampian, Appin, Argyll and Southern Highland Groups, which have a total aggregate thickness in the order of 20–25 km (Harris 1994; Stephenson et al. 2013a). Deposition of the Dalradian Supergroup probably commenced at around 730 Ma and continued until c.520–510 Ma (Tanner and Pringle 1999; Tanner and Sutherland 2007; Stephenson et al. 2013a), although these ages are debated and the base of the succession may be older than 800 Ma (Prave et al. 2009).

At the base of the Dalradian Supergroup in Scotland, the Grampian Group is dominated by psammite and metamorphosed semi-pelite deposited within a number of fault-bounded NE–SW-trending basins (Leslie et al. 2013). Analysis of detrital zircon, in which grains with Archaean ages are scarce, indicates derivation from Palaeo- and Mesoproterozoic (meta)granitic rocks (Cawood et al. 2003) that could have been sourced both from the west and/or east, as there is little difference in the protolith ages of the major crustal blocks that comprise east Laurentia and west Baltica (Banks et al. 2007; Kirkland et al. 2011). The Grampian Group is conformably overlain by the Appin Group, which consists of quartzite, psammite, metapelite and metacarbonate, the latter increasing towards the top. Parts of the Appin Group show remarkable stratigraphic continuity across the Grampian Terrane and may be traced laterally over several hundred kilometres. A Re–Os age of 659.6 ± 9.6 Ma from a pyritiferous graphitic slate from the Ballachulish Slate Formation (mid Appin Group) is interpreted as the age of deposition (Rooney et al. 2011). Detrital zircon spectra from a single sample of interlayered psammite–semipelite, also from the Ballachullish Subgroup, show peaks in the Neoarchaean era (2800–2650 Ma) and late Palaeoproterozoic era (1950–1775) Ma with only a single zircon grain of Mesoproterozoic age (Cawood et al. 2003).

At the base of the overlying Argyll Group, the Port Askaig Tillite is probably correlative with the global Middle Cryogenian (Sturtian) glaciation (Brasier and Shields 2000; McCay et al. 2006; Chew et al. 2009; Prave et al. 2009), and passes upwards into metamorphosed quartzite, pelite and limestone. At its top, the Argyll Group is characterised by extensive metamorphosed volcanic rocks and subvolcanic sills that are interbedded with carbonate. U–Pb zircon ages of 595 ± 4 Ma (Halliday et al. 1989) and 601 ± 4 Ma (Dempster et al. 2002) from volcanic rocks within the Tayvallich Volcanic Formation provide an age of deposition of the uppermost Argyll Group. Detrital zircon age data from Argyll Group rocks reveal a broad spread of dates from Archaean to Neoproterozoic in which pronounced age peaks are generally absent (Cawood et al. 2003). The Southern Highland Group is a thick turbidite sequence volumetrically dominated by (metamorphosed) greywacke with shale, limestone and volcanic rocks. The detritus is mostly of Neoarchaean or Mesoproterozoic age, of which the former become dominant towards stratigraphically higher levels (Cawood et al. 2003). In all Dalradian rocks there is a general scarcity of detrital ages in the range 2400–2000 Ma.

In general, sedimentation of the Dalradian Supergroup records a transition from relatively shallow continental shelf to deep water turbidite deposits, whose depositional environment is commonly ascribed to protracted episodic lithospheric stretching and rifting during breakout of Laurentia from Rodinia during birth of the Iapetus Ocean (Harris et al. 1978; Anderton 1982, 1985, 1988; Soper and Anderton 1984; Soper 1994; Glover et al. 1995). The lower parts of the Dalradian succession represents deposition on a stable slowly subsiding continental shelf, which later broke up into numerous fault-bounded sedimentary basins contemporaneous with basic volcanism; palaeocurrent studies indicate a sedimentary source to the northwest (Anderton 1985; Stephenson et al. 2013a). The uppermost Dalradian strata, which are characterised by a major influx of feldspar, are dominated by deep-water turbidites reflecting widening of the newly-formed Iapetus Ocean. Mineralogical characteristics of the uppermost Dalradian sedimentary rocks have been used to suggest the detritus was derived from a continental landmass to the southeast (Harris et al. 1978), while others propose the emergence of granitoid basement following the stripping of cover rocks from a source area to the northwest, consistent with sparse palaeocurrent data (Harris and Pitcher 1975; Harris et al. 1978; Plant et al. 1984; Anderton 1985).

The Buchan Block in northeast Scotland forms a broad horseshoe-shaped outcrop pattern of Dalradian rocks that are generally right way up (Fig. 1). It is bounded to the west and south by major shear zones and exhibits some profound differences compared with the rest of the Grampian Terrane (Stephenson *et al*., 2013b; Fig. 1a). These differences include the presence of large layered mafic–ultramafic intrusions (the North-east Grampian Basic Suite), numerous peraluminous granite bodies and metasedimentary migmatites from which the granites may have been derived (Johnson et al. 2003), and the widespread development of low-pressure (andalusite to sillimanite) Buchan-type regional metamorphism (Read 1952; Harte and Hudson 1978) rather than Barrovian (kyanite to sillimanite) metamorphism (Barrow 1893, 1912) that characterises Dalradian rocks outside of the Buchan Block. Although the Buchan Block has been regarded by some as an exotic terrane thrust into place during Grampian orogenesis (Sturt et al. 1977; Ramsay and Sturt 1978), it is now generally regarded as autochthonous (Johnson et al. 2001b, 2015; Stephenson et al. 2013b). At lower stratigraphic levels, rocks comprising semipelites, graphitic metapelites and psammites with minor metalimestones and metavolcanic rocks, are generally ascribed to the Argyll Group, whilst at higher stratigraphic levels within the core of the Buchan Block, a thick sequence of metaturbidites belongs to the Southern Highland Group (Fig. 2).

ANALYTICAL METHODS

Sample selection, preparation and characterisation

Data were collected from four metasedimentary rocks (from west to east, samples BB1, BB3, BB5 and BB6) collected from coastal exposures within the Buchan Block (Fig. 2). One sample (BB6) is from the Argyll Group, and assigned to the Crinan Subgroup (Goodman 1991; Stephenson et al. 2013b); the others are from the Southern Highland Group of which, based on a structural cross-section of the area (Stephenson and Gould 1995), the proximity of the samples to the Argyll Group–Southern Highland Group contact and the metamorphic grade of the rocks (which increases down stratigraphy), BB1 is stratigraphically lowest and BB3 stratigraphically highest. BB6 is a coarse-grained granulite facies metapelitic migmatite (Johnson et al. 2001a, b; Johnson et al. 2015); BB1 (amphibolite facies staurolite zone) and BB3 (greenschist facies biotite zone) are from massive psammite units interbedded with metapelite; BB5 (amphibolite facies andalusite zone) is a semipelite containing sparse Mn-rich garnet.

Detrital zircon grains were separated from approximately 1 kg of each sample using SelFrag high voltage pulse power fragmentation and heavy liquid separation at the Department of Applied Geology, Curtin University. Grains were hand picked and mounted in 25 mm diameter epoxy resin discs. The grain mounts were polished to approximately half grain thickness then cleaned and carbon coated for backscattered, secondary electron and cathodoluminescence (CL) imaging on a Tescan MIRA3 scanning electron microscope (SEM) at the Microscopy & Microanalysis Facility, John de Laeter Centre, Curtin University using a working distance of 15 mm and an accelerating voltage of 10 kV.

Laser ablation ICP–MS analysis: U–Pb dating and trace element determination

LA–ICP–MS data were collected at the GeoHistory Facility in the John de Laeter Centre, Curtin University. Zircons were analysed using a single spot placed in the core of grains, the precise location of which was chosen to avoid thin overgrowths and/or inclusions based on the CL images. Grains were ablated using a Resonetics RESOlution M–50A–LR, incorporating a

COMPex 102 excimer laser. Following a 15–20 second period of background analysis, samples were spot ablated for 30 s at a 7 Hz repetition rate using a 33 μm beam and laser energy of 1.7 J/cm^2 at the sample surface. The sample cell was flushed with ultrahigh purity He (flow rate of 0.68 L min^{-1}) and N_2 (2.8 mL min-1). Isotopic intensities were measured using an Agilent 7700s quadrupole ICP–MS with high purity Ar as the plasma gas (flow rate 0.98 L min^{-1}). Most elements were monitored for 0.01 seconds with the exception of ^{88}Sr (0.02 s), ^{139}La (0.04 s), ^{141}Pr (0.04 s), ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb (all 0.03 s), ^{232}Th (0.0125 s), and ^{238}U (0.0125 s). International glass standard NIST 610 was used as the primary standard to calculate elemental concentrations (using ^{29}Si as the internal standard element and assuming 14.76% Si in zircon) and to correct for instrument drift. For improved matrix matching, ^{178}Hf in zircon was determined using GJ-1 (Jackson et al. 2004) with ^{91}Zr as the internal standard element. Standard blocks were typically run after 20 unknown analyses. During the time-resolved analysis, contamination resulting from inclusions and compositional zoning were monitored and only the relevant part of the signal was integrated. The trace element results for NIST 612 (secondary standard) using NIST 610 as the reference material indicate that the accuracy was better than 2% for most elements. Only analyses with negligible common Pb were considered when placing age constraints.

The primary reference material used for U–Pb dating in this study was GJ-1 (601.7 ± 1.4 Ma (Jackson et al. 2004; Kylander-Clark et al. 2013) with 91500 (1062.4 ± 0.4 Ma; (Wiedenbeck et al. 1995) and Plesovice (337.13 ± 0.37 Ma; (Sláma et al. 2008) used as secondary age standards. ^{238}U/^{206}Pb ages calculated for all zircon age standards, treated as unknowns, were found to be within 3% of the accepted value. For example, the mean ^{238}U/^{206}Pb age determined for 91500 across all runs was 1062 ± 8 Ma (2σ, n = 24, MSWD = 1.8), consistent with the recommended values. The time-resolved mass spectra were reduced using the U_Pb_Geochronology3 and Trace Element data reduction schemes in Iolite (Paton et al. 2011) and references therein) and in-house excel macros. We consider those analyses within analytical uncertainty (2σ) of the concordia curve to be concordant. In cases where the true location of the mean data point can be assumed to fall on the concordia curve, it is possible to calculate a 'concordia age' (Ludwig, 1998), which makes best use of all $^{207}Pb^{*}/^{206}Pb^{*}$ and $^{238}U/^{206}Pb^{*}$ ratios. This approach typically yields a more precise mean age than by using either ratio alone, and also provides an objective and quantitative measure of concordance. The full data set is provided in Supplementary data Tables S1 (U–Pb) and S2 (trace elements).

RESULTS

Zircon morphology

Analysed zircon grains from samples BB1 and BB3 are mostly 100–200 μm in the longest dimension and have low aspect ratios (2:1 or less). Those from BB5 and BB6 are smaller (mostly 50–100 μm) and contain a higher proportion of prismatic grains with aspect ratios up to 5:1. In all samples, the majority of grains are rounded suggesting significant transport distances, although faceted grains are not uncommon.

The zircon grains exhibit diverse internal morphologies when imaged by CL. They range from simple broadly homogeneous grains to crystals with complex cores showing variable CL response that are commonly associated with one or more overgrowths (Fig. S1). Zircon cores commonly show fine oscillatory zoning typical of growth in a magmatic environment. In other cases cores exhibit sector or parallel zonation and/or irregular, diffuse patterns in CL response, the latter probably reflecting multiple phases of resorption and reprecipitation. Cores are commonly surrounded by overgrowths of broadly uniform and brighter CL response that are up to a few tens of microns in width, although overgrowths with CL responses darker than cores also occur. The overgrowths likely record zircon precipitation during some discrete (i.e. postmagmatic) metamorphic, metasomatic or hydrothermal event. In many cases the overgrowths are sharply truncated, suggesting they may have developed prior to deposition of their sedimentary host rocks. However, some examples, particularly in the highest-grade migmatitic sample (BB6), are continuous and may record growth of new zircon during high-grade (Grampian) metamorphism of the sedimentary host rocks (Johnson et al. 2015).

Detrital zircon age data

The age data are discussed below in order of the inferred decreasing age of deposition of the metasedimentary protoliths (i.e. first BB6 then BB1, BB5 and BB3). Tera–Waserburg concordia diagrams for the four samples are shown in Fig. 3. Figure 4 shows frequency distribution diagrams, in which the grey filled area is the kernel density estimate for concordant data only and the dashed grey line is the kernel density estimate incorporating all data; the thin black line is the probability estimate for the concordant data only (Vermeesch 2012). All dates reported in the text are concordia ages with uncertainties quoted at the two-sigma level.

In the oldest sample (BB6) from the Argyll Group, 64 (73%) of 88 grains analysed were concordant (i.e. overlap the concordia curve within the 2σ limit of uncertainty). In two of the three Southern Highland Group samples, the majority of analysed grains ages were concordant (in BB1 75% of 100 grains; in BB3 of 62% of 98 grains). However, for sample BB5, of 91 grains analysed only 32 (35%) were concordant (Fig. 3).

Of the concordant data from the Argyll Group sample (BB6), the vast majority lie within a more-or-less continuous spread of ages from the youngest grain at 585 ± 20 Ma to c. 2000 Ma (Fig. 3a). Four grains have Neoarchaean ages between c. 2500 and 2700 Ma, and a single grain has an age (3231 ± 36 Ma) close to the Neoarchaean–Mesoarchaean transition. Kernel density estimates for the data from sample BB6 indicate a prominent late Mesoproterozoic age peak at

1000–1100 Ma, with less well-defined peaks at around 1500 Ma and between 2500 and 3000 Ma (Fig. 4a).

Of the concordant data from sample BB1, most have ages between c. 900 and 2000 Ma, with the remaining data scattered to older ages, the oldest of which are around 3000 Ma (Fig. 3b). Compared to BB6, kernel density estimates again show a dominant late Mesoproterozoic peak but a more pronounced Palaeoproterozoic peak at 1700–1800 Ma. The oldest data yields a much smaller broad peak of Archaean ages between 2500 and 3000 Ma (Fig. 4a).

Of the relatively few concordant data from sample BB5, there is a clear cluster of ages between 1700 and 2000 Ma and a smear of Neoarchaean ages; a few zircon cores have ages that are both younger and older (Fig. 3c). The youngest concordant age is 948 ± 30 Ma, and the oldest is 3008 ± 16 Ma. Kernel density estimates for sample BB5 yield two clear age peaks at around 1850 Ma and 2700 Ma (Fig. 4c). Much of the discordant data appears to define two broad trends, one extending from the concordant Archaean data towards younger ages, and another from the Palaeoproterozoic data towards younger ages. These trends are consistent with partial resetting of detrital zircon during Caledonian (*sensu lato*) tectonothermal events.

Similar to sample BB5, the concordant data from the youngest sample (BB3) show a tight cluster of ages at 1800–2000 Ma and a smear of older ages from around 2400 Ma to 3000 Ma (Fig. 3d). A single grain with an Eoarchaean age of 3654 ± 18 Ma is the oldest from all samples analysed. Most notably, there are no concordant data younger than Mesoproterozoic in this sample, with the youngest grain having an age of 1786 ± 30 Ma. Kernel density estimates for sample BB3 again yield two clear age peaks, one at 1800–1900 Ma and a dominant Archaean peak at 2700–2800 Ma (Fig. 4d). In all samples there is a scarcity of concordant ages between c. 2000 and 2400 Ma (Fig. 3 & 4).

Trace element composition of zircon

Considering only those grains yielding concordant U–Pb ages, the analysed trace element compositions of the detrital zircons show significant scatter and few clear trends with age (Fig. S2). Although the maximum concentration of Th in Archaean grains is smaller than in Proterozoic grains, there is no obvious difference in concentrations of U or in the U/Th ratio with age. All grains have typical steep chondrite-normalised (McDonough and Sun 1995) REE patterns although the absolute abundance of REE in individual grains varies by almost two orders of magnitude (Fig. 5a). Most grains, particularly those with low overall REE abundances, exhibit a negative Eu anomaly (Fig. 5a). In a plot of age vs Eu/Eu^*, Mesoproterozoic grains (dominant ages of c. 1000 Ma) show a more restricted range of $(Eu/Eu^*)_N$ (<0.5) compared with Palaeoproterozoic grains (~1800 Ma), with Archaean examples showing the highest measured values that in some cases exceeds 0.9 (Fig. 5b). The samples show a significant range in the relative enrichment of heavy REE, although in most cases there is a significant slope in the middle to HREE in which $(Gd/Yb)_N$ is below 0.1. However, a significantly larger range [$(Gd/Yb)_N$ up to 0.57] is shown by Palaeoproterozoic grains compared to those with Mesoproterozoic and Archaean ages (Fig. 5c). The range in concentration of both Nb and Ta are significantly higher in Mesoproterozoic grains compared to older examples. There are little clear differences in concentrations of Sr or Sr/Y ratios with age. Considering the discordant data, a clear correlation between the degree of discordance, which is up to 77%, and the concentrations of many elements, in particular Sr, Fe, Th and LREE, suggests enhanced incorporation of non-formula elements in altered zircon or the presence of micro-inclusions of other phases (Nasdala et al. 2010).

DISCUSSION

Concordant age data

Detrital source areas

The concordant detrital age data for samples from the Buchan Block yield spectra similar to those reported from upper Dalradian Supergroup rocks from the Central Highlands of Scotland (Cawood et al. 2003) and Shetland (Strachan et al. 2013), and from the overlying Highland Border Complex (Cawood et al. 2012a). Kernel density estimates yield three clear age peaks in the Neoarchaean (c. 2800–2700 Ma), Palaeoproterozoic (c. 1900–1800 Ma) and late Mesoproterozoic (c. 1100–1000 Ma) eras that correspond to known tectonomagmatic events in both Laurentia and Baltica (Gower et al. 1990; Gower 1996; Rivers 1997; Bingen and Solli 2009). However, based on sparse faunal (Fletcher and Rushton 2007) and palaeocurrent evidence (Anderton 1985; Stephenson et al. 2013a), the Dalradian Supergroup is generally regarded as having been derived from, and deposited on the southeastern margin of, Laurentia (Cawood et al. 2003, 2007b; McAteer et al. 2010a,b; Strachan et al. 2013; Chew and Strachan 2014; Dewey et al. 2015). Sparse palaeocurrent data from the Buchan Block similarly indicates source areas to the north and west (Loudon 1963).

The data from the Argyll Group sample (BB6) are dominated by late Mesoproterozoic (Grenville) ages with a significant contribution from Palaeoproterozoic and early Mesoproterozoic ages, likely corresponding to detritus derived from the Ketilidian–Makkovik, Labradorian, Torngat, New Quebec, Nagssugtoqidian and Pinwarian orogenic belts (Hoffman 1988; Gower 1996; Kerr et al. 1997; Rivers 1997; Wasteneys et al. 1997) (for paleogeographic reconstructions see fig. 2 of Cawood et al. 2003b and fig. 6 of Strachan et al., 2013). Successively younger samples from the Southern Highland Group show a decrease in the proportion of late Mesoproterozoic material and an increase in both Palaeoproterozoic and Archaean aged detritus, consistent with the trend noted in other studies (Cawood et al. 2003, 2007b; Strachan et al. 2013). Combined, these data are consistent with erosion of the late

Mesoproterozoic then Palaeoproterozoic orogens to expose Archaean basement rocks of the Superior and/or North Atlantic cratons, which may have been uplifted in the footwalls of rift faults due to the continued breakup of Rodinia and opening of Iapetus (Cawood et al. 2007b).

To statistically assess the similarity of the source rocks, we compare the concordant data from the Buchan Block with existing detrital zircon data from Dalradian and equivalent strata elsewhere (Cawood et al. 2003; Breeding et al. 2004; Banks et al. 2007; Chew et al. 2008; McAteer et al. 2010a,b; Strachan et al. 2013) [see Table S1]. This is achieved by means of a Kolmogorov–Smirnov (K–S) test, which is widely used to test the null hypothesis that two distributions come from the same population. To further visualise the results of this statistical test we apply multi-dimensional scaling of the D value in the K–S test, as discussed in Vermeesch (2013) and Spencer and Kirkland (2016). This approach creates a two-dimensional map of points that summarises the differences in the age population structure (Fig. 6). In this procedure samples that are similar plot together, while those that are dissimilar are widely spaced, while the distance from the centre reflects the increasing incorporation of a detrital component that may characterize a specific population grouping. It is important to note that the orientation of the axes in Fig. 6 is arbitrary.

The results show that the detrital age spectra from the two oldest samples (BB6 and BB1) are statistically indistinguishable (at the 95% confidence level), as are those from the two youngest samples (BB5 and BB3) (Fig. 6). In addition, the age data from each of the Buchan Block samples is indistinguishable from several other Dalradian rocks, including some from the older Grampian Group near the base of the Dalradian Supergroup (Fig. 6). Considering all data, two broad trends are evident (grey arrows on Fig. 6) that are subparallel to the lines joining similar Buchan Block samples. Based on the age spectra for these samples, the vector joining BB6 and BB1 represents an increase in Palaeoproterozoic relative to late Mesoarchaean detritus, and the vector from BB5 to BB3 an increase in Archaean detritus. However, such simple relationships are not so clearly defined by data from Dalradian rocks elsewhere (Fig. 6).

Together, the concordant data suggest that Dalradian rocks in the Buchan Block were derived from similar source rocks to those exposed elsewhere in the Grampian Terrane, including rocks in Ireland and Shetland. These similarities strengthen the argument that the Buchan Block is autochthonous.

Age of the Buchan Block samples

The youngest concordant analysis is from the core of a grain within sample BB6, which yields a concordia age of 585 ± 20 Ma. Although this grain does not display oscillatory zoning typical of magmatic zircon, comprising a fractured CL-bright core surrounded by a darker CL-dark region and a thin (<10 μm) discontinuous CL-bright rim, it shows no depletion in HREE [$(Gd/Yb)_N$ = 0.11; Fig. 5a] and growth during high-grade metamorphism in the presence of garnet, which is characterised by flat middle to heavy REE patterns, is not supported (Rubatto and Hermann 2007; Taylor et al. 2015). Although growth in some non-magmatic environment is possible, the size (~80 μm) and textural features of this grain suggests it grew prior to incorporation into the sedimentary precursor of this rock (i.e. it is not a fragment of a metamorphic rim). If so, and given that no radiogenic-Pb loss can be detected in the U–Pb systematics of the analysis, then this age suggests that deposition of part of the Crinan Subgroup occurred no more than 8 Ma before deposition of the uppermost Argyll Group sediments at 601 ± 4 (Dempster et al. 2002).

Discordant age data

In order to better understand the most likely timing of radiogenic-Pb loss we model the discordant age data from sample BB5 using a variety of times of assumed Pb loss with the resultant population compared to concordant data using the K-S statistic following the approach discussed in Morris et al., (2015). The approach assumes that the discordant population is derived from a similar geological province with similar zircon age spectra to the concordant zircon population. For any specified time of Pb loss, the discordant data in concordia space (Fig. 3c) can be used to calculate an upper intercept that, for that specified time of Pb loss, defines a model age. The process is repeated for every possible time of radiogenic Pb loss to produce a range of upper-intercept (model) ages for the discordant population that can then be compared with the concordant population. In a simple situation in which only one episode of Pb loss occurred, the greatest similarity between the modelled discordant population and the concordant population will be represented by a single probability peak that reflects the most likely time of that Pb loss event. Where multiple episodes of Pb loss may have occurred, the resultant probability distribution of model and concordant ages may not yield a single probability peak. However, provided some grains were significantly influenced only by a single Pb loss event, the method can yield important information.

The results of the stastistical modelling for sample BB5 are shown in Fig. 7. That the probability curve does not rise to single well-defined peak is interpreted to reflect the effect of at least two radiogenic Pb loss events, including recent Pb mobility that affected at least some of the discordant population (Fig. 7). Nevertheless, a distinct peak in the probability curve at c. 470-450 Ma is consistent with at least some of the zircon having been significantly affected by Pb loss during this time period (Fig. 7). Ages of c. 470 Ma are consistent with regional metamorphism, ductile deformation and intrusion of voluminous gabbroic magmas in the Buchan Block (Dempster et al. 1995; Carty et al. 2012), and are broadly synchronous with Barrovian metamorphism elsewhere in the Grampian terrane (Oliver et al. 2000; Baxter et al. 2002; Viete et al. 2013). Ages of 450 Ma broadly correspond to the youngest reported mica $^{40}Ar/^{39}Ar$ and Rb–Sr ages that date cooling of the Dalradian following the Grampian event (Dempster 1985; Dempster et al. 1995).

Trace element compositions

There are few clear trends between the age of concordant detrital zircon grains and the concentrations or ratios of analysed trace elements. The overall increase in Eu/Eu^* with age (Fig. 5b) is difficult to interpret, but may reflect a systematic change in the abundance or composition of coexisting plagioclase and/or oxygen fugacity as magmatic zircon grew (Bédard 2006). The larger range of values of $(Gd/Yb)_N$ in Palaeoproterozoic grains compared to those with Mesoproterozoic and Archaean ages (Fig. 5c) might suggest more zircon equilibrated with garnet and a deeper origin for a greater proportion of the Palaeoproterozoic source rocks (Rubatto and Hermann 2007; Taylor et al. 2015). The lack of any clear trends in the bulk of the trace element data, and the large scatter in the data for which any trend that may exist, suggests the late Mesoproterozoic to Archaean source rocks were not significantly different.

CONCLUSIONS

- Concordant age spectra from Dalradian Supergroup sediments deposited in the fault-bounded Buchan Block were dominantly derived from late Mesoproterozoic and Palaeoproterozoic orogens and their Archaean basement rocks. The data are consistent with a Laurentian source;
- Archaean basement rocks (Superior and/or North Atlantic cratons) remained largely covered until deposition of the upper Dalradian rocks (Argyll and Southern Highland Groups)
- The source areas of sediments on the Buchan Block are not dissimilar to Dalradian rocks elsewhere – although the Buchan Block may conceivably have been translated significant distances into its current position during Grampian orogenesis, it is not exotic;

- Some detrital zircons were variably affected by Pb-loss at around 470–450 Ma, corresponding to Grampian orogenesis.
- Multidimensional scaling, REE content, and Pb-loss modelling are useful tools in maximizing the information extracted from detrital zircon datasets.

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Figure captions

Fig. 1. Regional map of the British Isles showing the location of the Grampian Terrane and major faults including the inferred position of the Iapetus suture. FHCBL = Fair Head–Clew Bay line. Modified after Neilson et al. (2009), Stephenson et al. (2013a) and Strachan et al. (2013).

Fig. 2. Simplified geological map of the Buchan Block and surrounding rocks in the northeast Grampian Highlands of Scotland, showing the distribution of Dalradian Supergroup, intrusive rocks and the overlying Old Red Sandstone (Devonian) based on bedrock data from DiGMapGB-625, with the permission of the British Geological Survey. The position of the regional (D2) shear zones is from Ashcroft et al. (1984). The location of the four studied samples are indicated. The inset shows the location of the study area within Scotland.

Fig. 3. Tera–Waserburg concordia diagrams for detrital zircons from the four analysed samples. Open circles are ages in Ma. The samples are arranged in inferred stratigraphic order. The oldest, sample, BB6, is from the Argyll Group (a); the others (b–d) are from the Southern Highland Group (SHG). Black symbols show concordant data that are within 2σ error of the concordia; grey symbols are discordant.

Fig. 4. Frequency–distribution diagrams of detrital zircon ages from the four analysed samples arranged in inferred stratigraphic order. The grey filled area is the kernel density estimate for concordant data (conc.) only; the dashed grey line is the kernel density estimate incorporating all data. The fine black line is the probability estimate for the concordant data only. The thin vertical lines demarcate boundaries between the Hadean (Had.), Archaean, Proterozoic and Phanerozoic (Phan.) eons; the Proterozoic is further subdivided into eras.

Fig. 5. Trace element data from zircon. (a) Chondrite-normalised REE plots of analysed zircon from the four samples (undifferentiated). The composition of the youngest grain (BB6–42) is indicated. Binary variation diagrams showing the chondrite-normalised (McDonough and Sun 1995) ratio of: (b) Eu/Eu*, and (c) Gd/Yb.

Fig. 6. Non parametric multidimensional scaling plot of the detrital zircon age spectra from Dalradian Supergroup and related samples. The orientation of the diagram is arbitrary. Less dissimilar samples plot closer together. The thin lines join samples whose detrital zircon age data are statistically indistinguishable at the 95% confidence level. Sources of the U–Pb data: Banks et al. (2007), Cawood et al. (2003), Chew et al. (2008), McAteer et al. (2010a,b) and Strachan et al. (2013).

Fig. 7. Probability (P) of dissimilarity between discordant and concordant detrital zircon populations vs. time of radiogenic Pb loss.

Supplementary information

Fig. S1. Cathodoluminescence images of zircon from the four analysed samples.

Fig. S2. Selected chondrite-normalised trace element plots.

Table S1. U–Pb age data (LA–ICPMS).

Table S2. Chondrite normalised trace element data (LA–ICPMS).

Table S3. Matrix showing results of Kolmogorov–Smirnov (K–S) test comparing the Buchan Block samples of the current study with other Dalradian and related samples. The hypothesis that two samples come from the same source is rejected when the probability (*p*) drops below 0.05, indicating that we have 95% confidence that the samples are different. Those samples whose detrital zircon age data are statistically indistinguishable at the 95% confidence level are highlighted in yellow.

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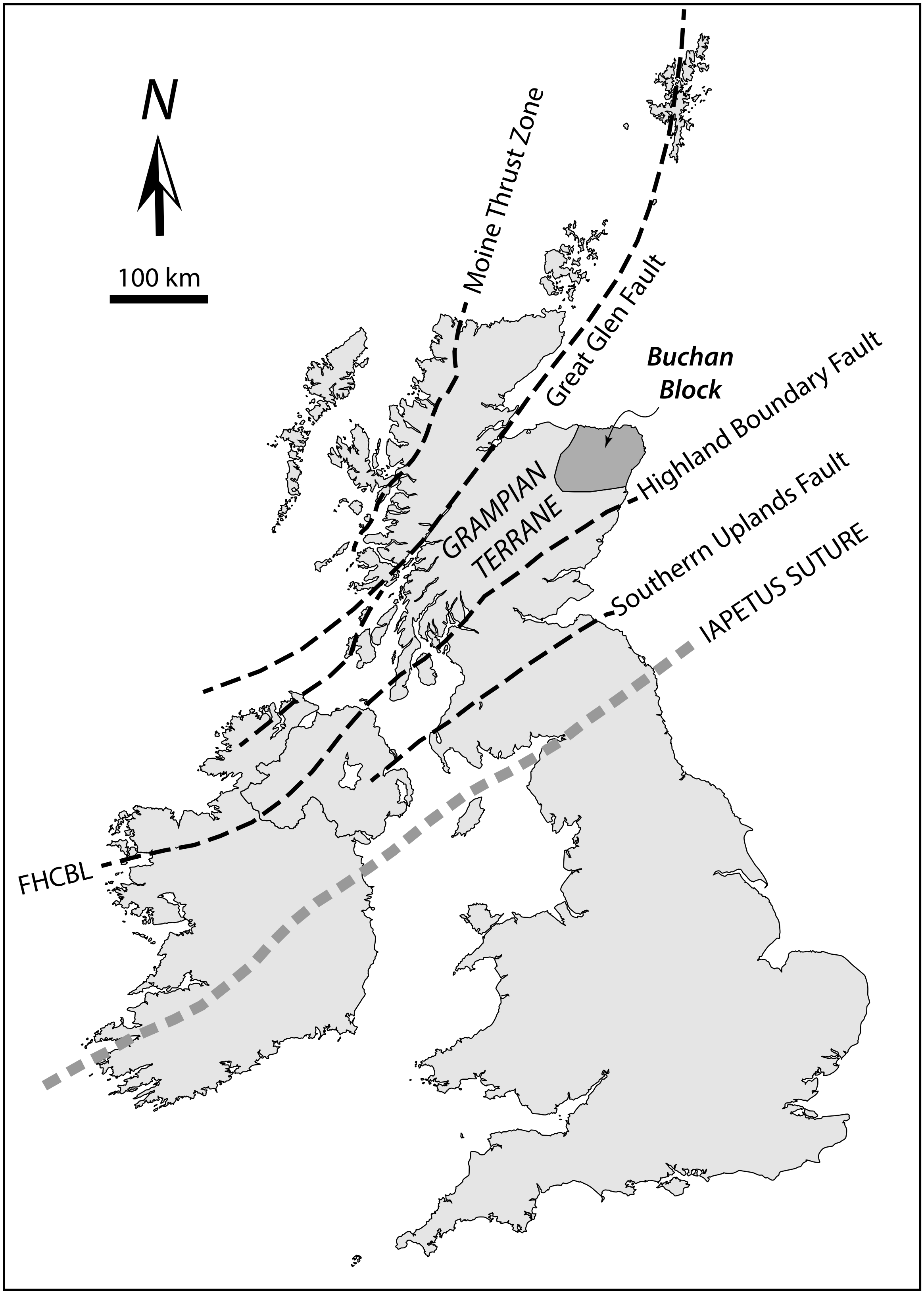
N
100 km
Moine Thrust Zone
Great Glen Fault
Buchan
Block
Highland Boundary Fault
GRAMPIAN
TERRANE
Southerrn Uplands Fault
IAPETUS SUTURE
FHCBL

Figure 1

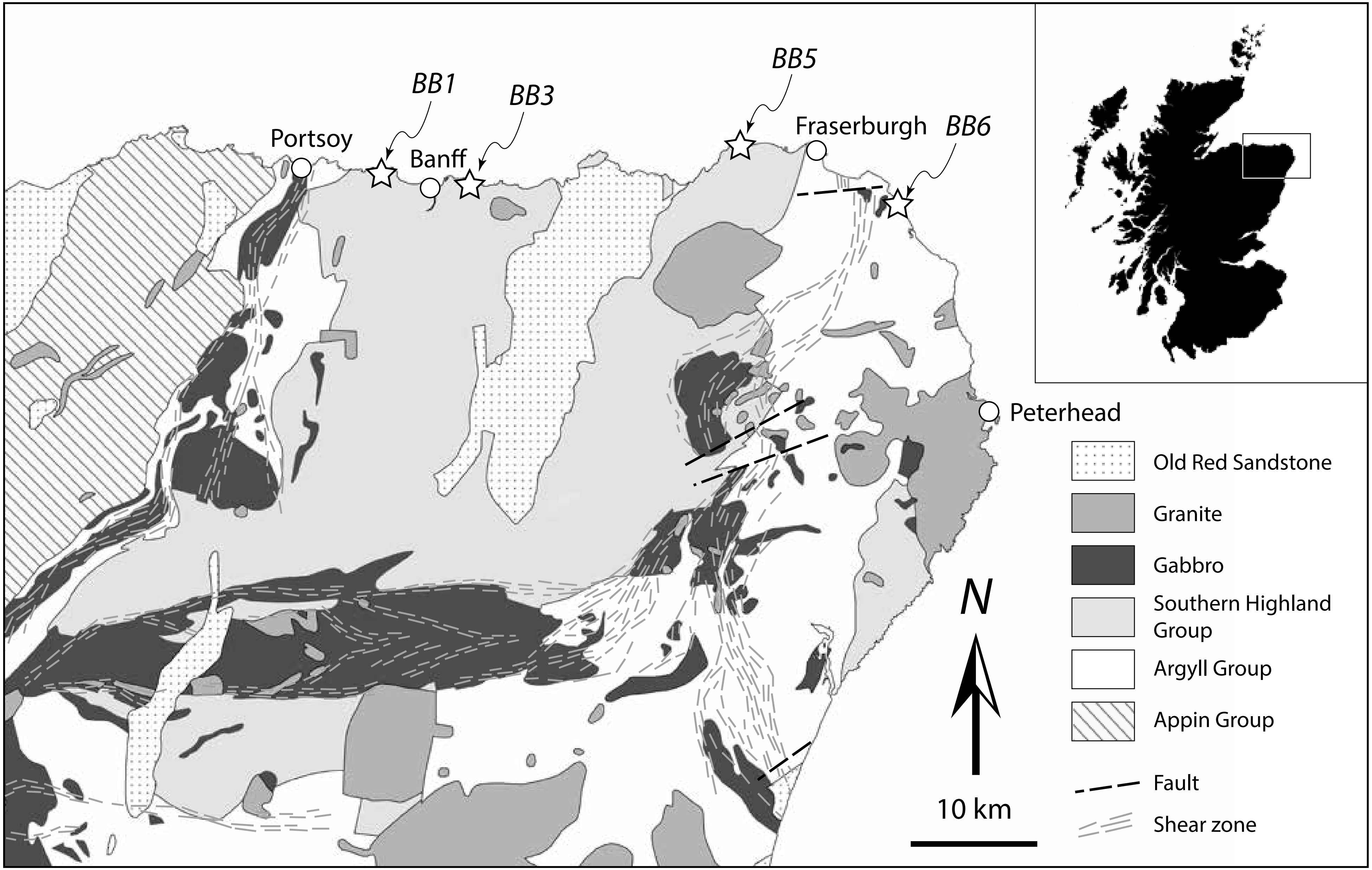
BB1
BB3
BB5
BB6
Portsoy
Banff
Fraserburgh
Peterhead
N
10 km
Old Red Sandstone
Granite
Gabbro
Southern Highland Group
Argyll Group
Appin Group
Fault
Shear zone

Figure 2

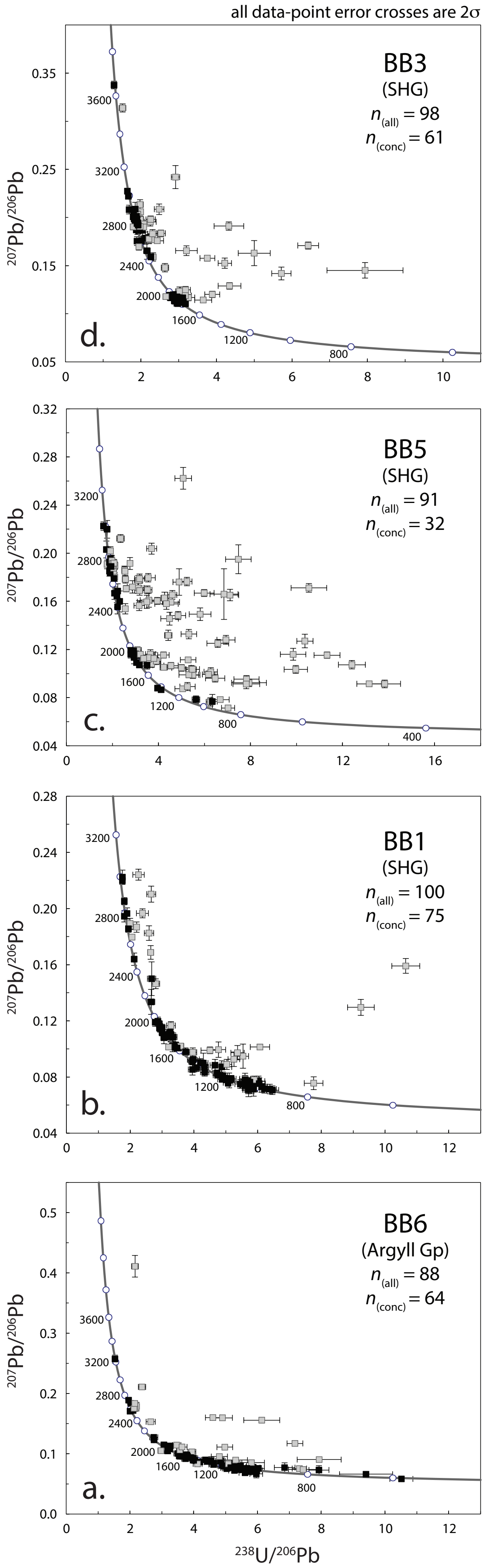
all data-point error crosses are 2σ
BB3
(SHG)
n(all) = 98
n(conc) = 61
d.
BB5
(SHG)
n(all) = 91
n(conc) = 32
c.
BB1
(SHG)
n(all) = 100
n(conc) = 75
b.
BB6
(Argyll Gp)
n(all) = 88
n(conc) = 64
a.
207Pb/206Pb
238U/206Pb

Figure 3

Figure 4

Click here to download Figure Fig4 PROB_DENSITY.pdf

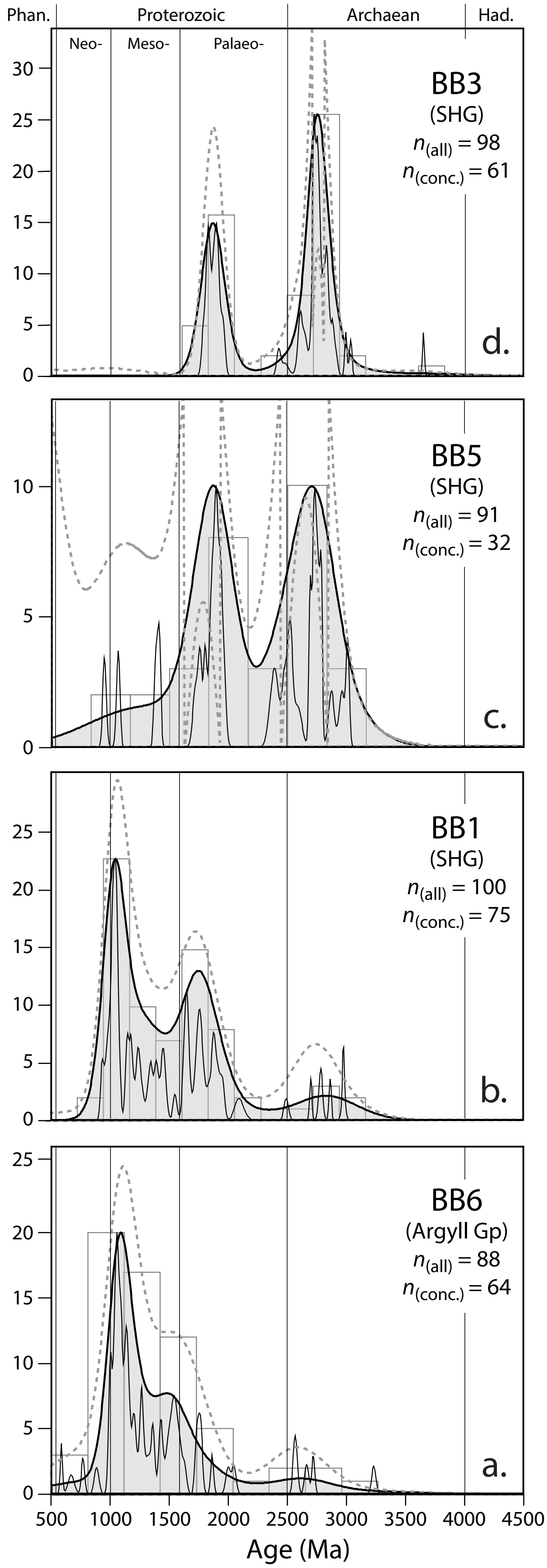

Figure 4

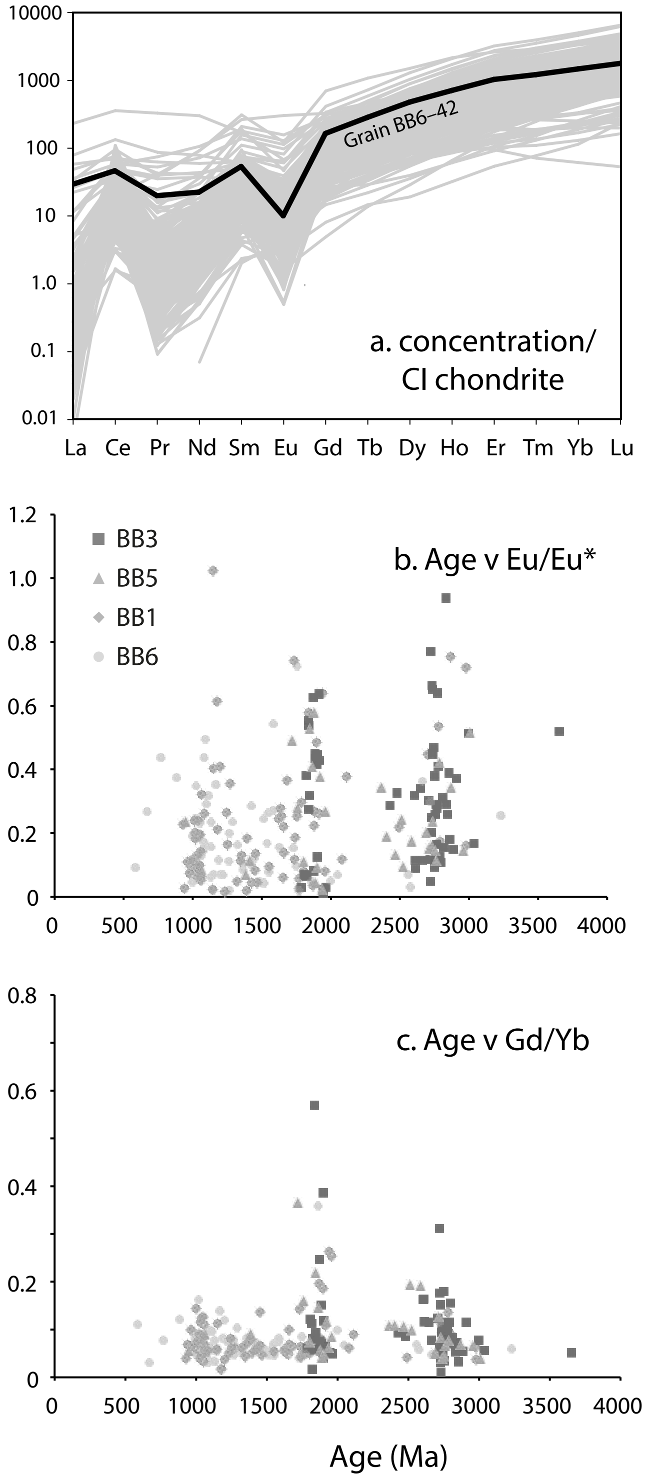
10000
1000
100
10
1.0
0.1
0.01
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Grain BB6–42
a. concentration/
CI chondrite
1.2
1.0
0.8
0.6
0.4
0.2
0
BB3
BB5
BB1
BB6
b. Age v Eu/Eu*
0 500 1000 1500 2000 2500 3000 3500 4000
0.8
0.6
0.4
0.2
0
c. Age v Gd/Yb
0 500 1000 1500 2000 2500 3000 3500 4000
Age (Ma)

Figure 5

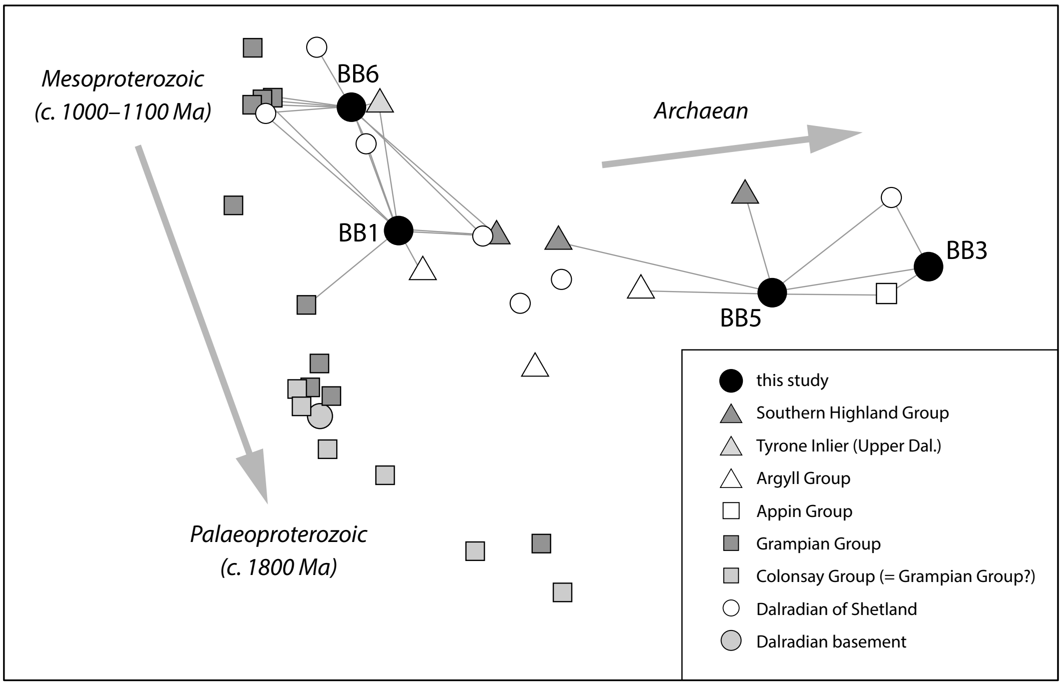
Mesoproterozoic
(c. 1000–1100 Ma)
BB6
Archaean
BB1
BB3
BB5
Palaeoproterozoic
(c. 1800 Ma)
this study
Southern Highland Group
Tyrone Inlier (Upper Dal.)
Argyll Group
Appin Group
Grampian Group
Colonsay Group (= Grampian Group?)
Dalradian of Shetland
Dalradian basement

Figure 6

Figure 7

Click here to download Figure Fig7 BB5 Pb loss.pdf

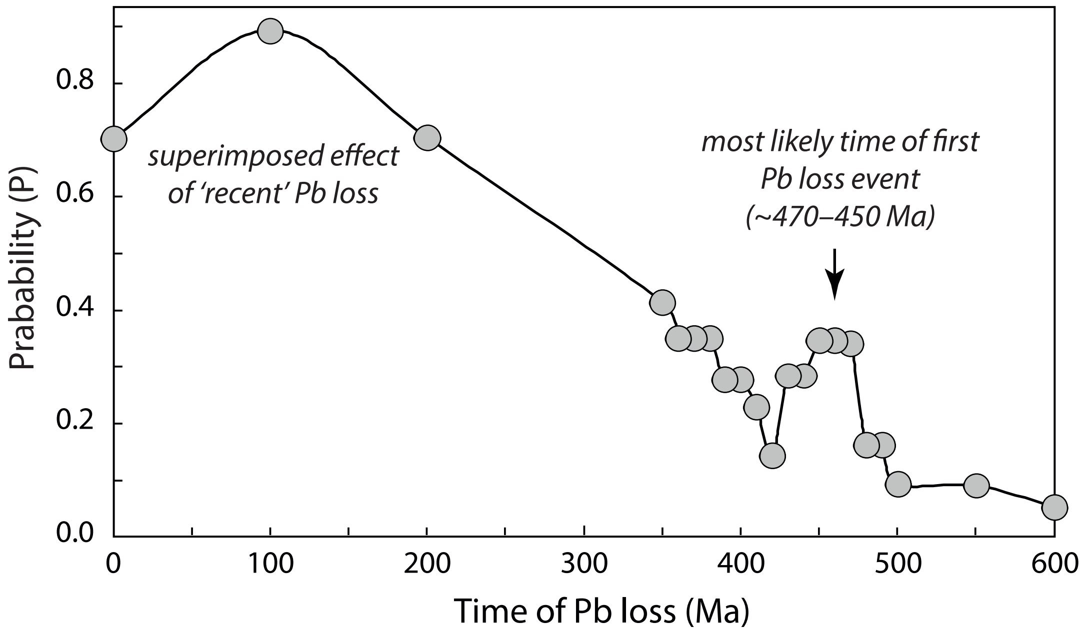

Figure 7

Dataset (U-Pb)

Click here to access/download
Dataset
Table S1.xls

Dataset (trace elements)

Click here to access/download
Dataset
Table S2.xls

Dataset (multi d scaling)

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Dataset
Table S3.xlsx

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Supplementary material (not datasets)
Fig S1 CL images.png

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Supplementary material (not datasets)
Fig S2 TRACES.pdf