

Geochemical evolution of Dalradian metavolcanic rocks: implications for the break-up of the Rodinia supercontinent

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Abstract: Neoproterozoic basaltic magmatism in the Dalradian Supergroup of Scotland and Ireland was associated with the break-up of the Rodinia supercontinent. Magmas were erupted in rift-related basins along a strike length of at least 700 km and during a time period of c. 80 Ma. New major- and trace- element analyses of metabasalts from several formations are presented to trace the variations in magma compositions in time and space. The primary magmas resulted from variable degrees of mixing of melts derived from mantle sources similar to those of normal and enriched mid-ocean ridge basalts; some younger lavas also show evidence of contamination with continental crust. In contrast to speculations about magmatism elsewhere in Rodinia, the evidence here suggests that there was no involvement of a mantle plume in basalt generation. For example, the Scottish promontory of Laurentia drifted rapidly southwards through c. 25° over the duration of the magmatism, with no evidence of significant elevation above sea-level, as might be expected from involvement of a plume. Generation of the primary magmas might have taken place predominantly through decompression melting in depleted upper mantle containing enriched streaks and blobs. Both the Dalradian lithostratigraphy and the metabasaltic compositions are consistent with extreme lithospheric stretching and possibly rupture during the earliest phase of magmatism, whereas generation of later magmatism appears to have been associated with major fault systems, possibly on a foundering continental margin.

Supplementary material: Chemical analyses of Dalradian metavolcanic rocks (major elements recalculated to 100%, anhydrous) are available at www.geolsoc.org.uk/SUP18468.

Introduction

The break-up of the Rodinia supercontinent and formation of the Iapetus Ocean were accompanied by extensive basaltic magmatism in both the Laurentia and Baltica sectors (Fig. 1a). In Eastern Laurentia, the Iapetus margin was characterised by multiple stages of failed rifts, mafic dyke swarms, and various volcanic and intrusive sequences, as reviewed by Puffer (2002). Ernst & Buchan (1997) referred to that magmatism as the Central Iapetus magmatic province. In Baltica, the break-up of Rodinia resulted in successful and failed rift basins extending from Scandinavia to the Urals. The voluminous Volynian Flood Basalt Formation represents continental flood basalts preserved in basins in Ukraine, Poland, Belarus and Moldova and as such qualifies as a Large Igneous Province (Shumlyanskyy *et al.* 2007). Remnants of major dyke swarms and the early Iapetus ocean floor are preserved in allochthons in the Scandinavian Caledonides (Andréasson 1994; Bingen *et al.* 1998).

The emplacement of extensive sequences of eruptive and intrusive basaltic rocks in the late Neoproterozoic- to Cambrian- age Argyll and Southern Highland groups of the Dalradian Supergroup in Scotland and Ireland was broadly associated with the break-up of Rodinia (Soper 1994), the Dalradian rocks lying on the eastern margin of Laurentia (Greiling & Smith 2000) (Fig. 1b). Furthermore, the magmatism both predated and postdated continental rupture, thus presenting a good opportunity to study the rift-to-drift transition that is so difficult to study in young settings where the volcanic rocks are under water and buried beneath thick piles of continental-margin sediments.

In this paper, we present new geochemical data for several volcanic and subvolcanic sequences within the Dalradian Supergroup that were omitted from recent reviews of Rodinia magmatism (Puffer 2002; Shumlyanskyy *et al.* 2007). These data, together with published analyses, allow us to present a much fuller account of compositional variations with time along a strike length of at least 700 km. We then assess what these variations contribute to our understanding of the nature and timing of the mechanisms responsible for the break-up of Rodinia.

The age of initiation of the break-up is poorly constrained. In Scotland, Dalziel & Soper (2001) suggested that the bimodal magmatism recorded in the Moine Supergroup at c. 870 Ma represents the beginning of the break-up, as does bimodal magmatism of about the same age (850 Ma) in the Scandinavian Caledonides as suggested by Paulsson & Andréasson (2002). The first major break-up of the

supercontinent occurred along the western margin (present geography) of Laurentia, perhaps as early as 750 (Li *et al.* 2008). Rifting between the southeastern margin of Laurentia and the Amazonia craton led to break-up by c. 600 Ma (Li *et al.* 2008). The activity in this latter phase fell broadly into two age groups (Cawood *et al.* 2001; Puffer 2002); c. 615-564 Ma and c. 554-550 Ma. Svenningsen (2001) has suggested that the onset of seafloor spreading in the Iapetus Ocean along the margin between Laurentia and Baltica occurred at c. 608 Ma. In the Scottish Highlands the rifting is marked by bimodal magmatism, the beginning of which is poorly constrained (probably c. 650 Ma) and lasting until 590 Ma (Macdonald & Fettes, 2007). Overall it is probable that the phases of extensional tectonics were diachronous, from c. 700 Ma in east-central Laurentia to near the close of the Proterozoic (c. 545 Ma) in northeastern Laurentia (Li *et al.* 2008; Prave *et al.* 2009a).

Many studies of Rodinia basalts, in particular those of the Grampian Highlands of Scotland, have invoked the involvement of two mantle sources in magma genesis; one of them depleted, with some similarities to the source of normal mid-ocean ridge basalt (N-MORB), and the other one more enriched and comparable to the source(s) of enriched mid-ocean ridge basalt (E-MORB) and ocean island basalt (OIB) (Goodman & Winchester 1993; Zenk & Schulz 2004; Macdonald *et al.* 2005). It has been suggested that the more-enriched types might have had their source in a mantle plume or plumes (Puffer 2002). The recognition of plume involvement has usually been made on the basis of apparently diagnostic geochemical characteristics but as Fitton (2007) has stressed, geochemical criteria alone cannot uniquely characterise basalts formed from mantle plumes. Such geological features as magma volumes, the presence of regional uplift and the duration of magmatism must be used to provide important information on the mechanisms of magma genesis.

In both Baltica and Eastern Laurentia, there seems to have been a broad transition in magma affinity from tholeiitic in the older sequences to somewhat more alkaline in later rocks, although there is significant compositional variation around the overall trend. More specifically, Macdonald *et al.* (2005) suggested that, with time, magmas with the more-enriched component became dominant. However, their proposals were constrained by a lack of geochemical data for many of the Dalradian sequences, particularly those in the Grampian Highlands. Thus it has not been possible until now to present a full picture of how the compositions of the basaltic rocks vary

geographically and stratigraphically and thus to assess the relative contributions from the inferred mantle sources with time.

Geological setting

The Dalradian Supergroup is a sequence of shallow- and deep-water sedimentary and volcanic rocks ranging in age from late Neoproterozoic to, at least, Early Cambrian. The sequence was subjected to the Grampian Event of the Caledonian Orogeny (c. 475-465 Ma; Dewey & Shackleton 1984; Soper *et al.* 1999; Oliver *et al.* 2008), and the rocks subjected to metamorphism in the greenschist to upper amphibolite facies. The supergroup has conventionally been divided into, in ascending stratigraphic order, the Grampian, Appin, Argyll and Southern Highland groups (Fig. 2a) (Harris *et al.* 1994; Stephenson & Gould 1995). The lithostratigraphical groups reflect the evolving depositional environment at the Laurentian margin as Rodinia broke up. In particular, lithospheric stretching and basin instability during deposition of the Argyll Group was marked by increasing magmatic activity that continued into, at least, the lower part of the Southern Highland Group (Fig. 3).

Recently Tanner & Sutherland (2007) have argued that their Trossachs Group (comprising much of the Highland Border Complex) lies in stratigraphical continuity with the underlying Southern Highland Group and has been subjected to all the phases of the Grampian Event. They present palaeontological ages from the Trossach Group that extend the Dalradian succession to the early Arenig (c. 475Ma) and give a maximum age for the Grampian Event.

Volcanic rocks crop out throughout the strike length of the Argyll Group succession, from the west coast of Ireland (Winchester *et al.* 1987; Harris *et al.* 1994; Winchester & Max 1996) to Shetland (Flinn 2007; Flinn *et al.*, in press), a distance of at least 700 km and possibly up to 1000 km (on present configuration) (Fig. 2b). This study is concerned primarily with the central segment from NE Ireland to NE Scotland, a distance of c. 500 km. The geographical distribution of the main occurrences of Dalradian metabasaltic rocks within this segment is shown in Figure 2b and their lithostratigraphical relationships in Figure 3. The occurrences are detailed below. The current distribution of the metavolcanic rocks follows the regional SW-NE Caledonian trend. Since this was also the trend of the axes of the subsiding basins, it seems likely that the original distribution of the volcanic rocks relative to each other

was broadly similar to the present distribution. The volcanism may be considered to fall into three episodes (Fig. 3): (i) an early phase in the Islay Subgroup; (ii) a major phase predominantly in the Easdale Subgroup but extending into the lower part of the Crinan Subgroup; and (iii) a final phase in the Tayvallich Subgroup and the lower part of the Southern Highland Group. The Dalradian volcanism was thus extensive in both space and time. Indeed, the scale of the magmatism has perhaps been under-appreciated. For example, the lavas and sills of the Tayvallich Volcanic Formation alone have a minimum volume of 3000 km³, to which can probably be added comparable amounts of underplated material (Halliday *et al.* 1985; Macdonald & Fettes 2007). These volumes are substantial although significantly less than the plume-related large igneous provinces, where volumes are typically 10⁶-10⁷ km³; for example, the Oligocene Ethiopian Traps (1 x 10⁶ km³; Hofman *et al.* 1997).

Whereas the volcanism described above is associated with extension and the opening of Iapetus, pillow lavas in the upper part of the Trossachs Group are significantly younger (see below) and associated in time with subduction, arc-continent collision and the beginning of the Grampian event (Tanner & Sutherland 2007). As such they are not considered in the present study.

Main occurrences of volcanic rocks

The Argyll Group is characterised by the onset of instability, with rapidly deepening SW-NE basins. The group is divided into four subgroups, namely Islay, Easdale, Crinan and Tayvallich (Fig. 3; Stephenson & Gould 1995). Volcanic rocks occur in all the subgroups but are particularly abundant in the Easdale and Tayvallich.

ISLAY SUBGROUP

The Islay Subgroup records the onset of significant rifting on the Laurentian margin. During this time rapid deposition generally kept pace with marked subsidence (Stephenson *et al.* in press) and the subgroup is dominated by coarse metasandstones and quartzitic lithofacies. Volcanism was confined to two small occurrences in NE Scotland. The base of the subgroup is marked by a tillite horizon that can be traced across the Irish and Scottish Dalradian outcrops and provides an important age marker band (Stephenson & Gould 1995; see below).

Muckle Fergie metavolcanic rocks. At the base of the Muckle Fergie stream section in upper Banffshire (British Geological Survey 1996; Chew *et al.* 2009;

Mendum, in press) there is a metavolcanic unit within the *Auchnahyle Formation* of the Islay Subgroup (Fig.3). This stratigraphical age makes the unit the earliest indication of volcanic activity in the Dalradian. The unit consists of a coarse- to medium-grained amphibolitic layer with an internal structure resembling pillows. Although the pillows do not contain vesicles, they possess radial cracks, confirming their origin as lavas. Stratigraphically above this unit, in the Muckle Fergie section, there is a chlorite-rich amphibolite unit, interpreted as metavolcanic (J. Mendum, pers. comm., 2009), lying within the *Kymah Quartzite Formation* (British Geological Survey 1996, Fig. 3).

EASDALE SUBGROUP

The Easdale Subgroup represents a change to finer-grained sedimentation and more-varied lithofacies. The lower part of the succession comprises rapidly deposited deep-water sediments; the upper part is marked by basin filling and shallower water facies. This reflects increasing extension and subsidence, with the development of second-order, fault-controlled basins and the first appearance of major volcanism.

Delnadamph Volcanic Member The unit crops out over c. 12 km southeast from Tomintoul and lies within the Glenbuchat Graphitic Schist Formation of the Easdale Subgroup (British Geological Survey 1996). The unit comprises pillow lavas, fine-grained vesicular amphibolites and coarse-grained actinolitic amphibolites associated with metasandstone to metamudstone rocks (Stephenson & Gould 1995).

Glenga Amphibolite Member This unit lies in the Dart Formation and crops out intermittently in the Sperrin Mountains of Northern Ireland. The formation was originally placed at the base of the Southern Highland Group (Cooper & Johnston 2004) but is now considered to lie within the Crinan or Easdale subgroups (Geological Survey of Northern Ireland 2007, 2008). The unit consists of basaltic pillow lavas, breccias and volcanoclastic rocks ('green beds').

Laoigh Metabasites This informal unit lies close to the base of the Ben Lawers Schist Formation of the Easdale Subgroup. It crops out in Glen Fearnate and may be regarded as a local precursor to the extensive volcanic activity represented by the Farragon Volcanic Formation (Goodman & Winchester 1993; Smith *et al.* 2002). The succession comprises fine-grained hornblende schists with interbanded metasandstone and calc-silicate-rich metasedimentary rocks. The metavolcanic rocks consist predominantly of hornblende-plagioclase-quartz assemblages.

Farragon Volcanic Formation The formation lies at the top of the Easdale Subgroup and represents the earliest major volcanic episode within the Dalradian succession. The unit has a strike length of c. 60 km, centred around Ben Vrackie in central Perthshire, and a maximum thickness of 400 m (Goodman & Winchester 1993; Treagus 2000). The rocks are composed primarily of metabasalt and associated tuff, with subordinate metasandstone and metasilstone beds. Some sheets of coarser grained, basic meta-igneous rock, thought to be associated intrusions, are also present (Treagus 2000). The metabasalts consist predominantly of hornblende-plagioclase-quartz-chlorite-epidote \pm garnet assemblages (Goodman & Winchester 1993).

Ben Vrackie volcanic complex. This complex comprises a number of basic units centred on Ben Vrackie. The rocks have been interpreted as intrusive bodies, forming part of a volcanic complex from which the overlying Farragon Volcanic Formation was derived (Graham & Bradbury 1981; Crane *et al.* 2002). For the purposes of this study the Ben Vrackie basic rocks and the Farragon Volcanic Formation metabasalts are regarded as comagmatic.

Meall Dubh Metabasite Formation The formation lies at the top of the Easdale Subgroup; it crops out over a strike length of c. 4km to the southwest of Ballater and has a maximum thickness of c. 700m (Smith *et al.* 2002). The unit consists of medium-grained hornblendic rocks, with intercalated quartzose and epidotic layers. This association of amphibolites with interbedded metasandstones and metavolcaniclastic rocks is similar to those of the Farragon area and is indicative of an extrusive origin (Goodman & Winchester 1993; Smith *et al.* 2002). The predominant rock consists of hornblende and plagioclase with disseminated magnetite; detrital quartz grains are present in thin layers.

CRINAN and TAYVALLICH SUBGROUPS

The Crinan Subgroup is characterised by thick sedimentary units and deep water turbiditic facies, which may represent the onset of a rift-to-drift transition (Leslie *et al.* 2008). During this period volcanic activity was relatively low. The overlying Tayvallich Subgroup is characterised by metacarbonate rocks and the development of thick lava sequences.

Balnacraig Metabasite Member This unit lies within the Queen's Hill Gneiss Formation near the base of the Crinan Subgroup, and as such may be grouped with the underlying Easdale Subgroup occurrences (Goodman & Winchester 1993; Smith *et al.* 2002). It crops out over 2.5 km² at the north end of Glen Muick. The rocks are

fine-grained and finely foliated hornblende schists with intercalated bands of metasandstone and calc-silicate rock, similar to the underlying Meall Dubh Metabasite Formation (Goodman & Winchester 1993). The nature of the rocks contrasts with the coarser fabrics and mineralogy of the intrusive basic rocks and is consistent with formation of the unit from basic lavas, possibly erupted under water, with thin sedimentary layers between the flows (Goodman *et al.* 1990; Smith *et al.* 2002). The basic units consist of hornblende+plagioclase+quartz \pm garnet, consistent with upper amphibolite-facies conditions. The calc-silicate material may have resulted from metasomatic transfer from the metavolcanic to the metasedimentary layers (Smith *et al.* 2002).

Tayvallich Volcanic Formation This formation, centred on the Tayvallich area of Argyll, lies stratigraphically at the top of the Argyll Group (Stephenson & Gould 1995). These rocks represent by far the greatest expression of Dalradian volcanism, forming a lensoid outcrop, elongated along strike, of 10 x 60 km. The volcanic sequence comprises metamorphosed basaltic pillow lavas, hyaloclastites and tuffs that, together with subvolcanic sills, have a cumulative thickness of at least 3 km (Macdonald & Fettes 2007). The rocks have been metamorphosed predominantly in the greenschist facies.

Blackwater Formation The formation crops out in the Deveron valley, southwest of Huntly. It has a strike length of 10 km and a width of 2.5 km. It lies to the east of the Portsoy Lineament, a major shear zone. As such, its precise stratigraphical position is uncertain but it is thought to lie close to the top of the Argyll Group (Fettes *et al.* 1991) and thus may be regarded as broadly equivalent to the Tayvallich Volcanic Formation. The succession comprises metavolcanic units with intercalated metasedimentary beds. The rocks range from basic to ultrabasic and locally contain pillow structures and other features characteristic of subaqueous extrusion (Macdonald *et al.* 2005). The basic units consist of hornblende-plagioclase-quartz assemblages consistent with the amphibolite facies.

SOUTHERN HIGHLAND GROUP

The Southern Highland Group comprises thick, laterally impersistent, turbiditic units. Lavas and associated sills are confined to Argyll, although the extensive development of volcanoclastic beds ('green beds') throughout the Southern Highlands of Scotland and the north of Ireland indicates more widespread volcanic activity (Pickett *et al.* 2006).

Loch Avich Lavas Formation This unit crops out around Loch Avich in central Argyll. It is separated from the Tayvallich Volcanic Formation by the Loch Avich Grit Formation, a metasedimentary sequence rich in volcanoclastic detritus. The Loch Avich Lavas Formation forms a sequence of basaltic pillow lavas, c. 300m thick and with no significant metasedimentary interlayers (Borradaile 1976). The unit lies in the lower part of the Southern Highland Group and is the youngest expression of volcanism in the Dalradian. These lavas, and the underlying volcanoclastic beds, are regarded as a general equivalent of the 'green beds'.

Dunrossness Spilitic Formation This formation lies at the top of the Clift Hills Group of the East Mainland succession of Shetland and is considered broadly equivalent to the Loch Avich Lavas Formation (Flinn 2007; Flinn *et al.*, in press). This correlation has been challenged by Prave *et al.* (2009a), who argued that the Shetland volcanic rocks are younger than any sequence on the mainland (see below). The unit crops out over an area of c. 3 x 2 km on the east coast at Cunningsburgh. It consists primarily of a metavolcanic succession, with subsidiary volcanoclastic, quartzose and phyllitic layers. The metavolcanic rocks comprise a metabasaltic sequence and a serpentinised unit that has been proposed as originating from high-MgO lavas similar to komatiites (Flinn & Moffat 1985, 1986), although this was refuted by Nesbitt & Hartman (1986). The metabasaltic rocks contain pillow structures and are considered to be subaqueous extrusive rocks. They have been variably deformed and recrystallised under amphibolite-facies conditions and now consist of fine-grained hornblende and epidote after plagioclase (Flinn *et al.*, in press).

Age of volcanism

The Dalradian lithostratigraphy shows that volcanic activity occurred throughout the Argyll Group and the lower part of the Southern Highland Group but reached its greatest development in the Easdale and Tayvallich subgroups. The timing of volcanic episodes and their duration are poorly constrained. The only direct evidence comes from U-Pb zircon radiometric dates of 595 ± 4 Ma on a keratophyre intrusion (Halliday *et al.* 1989) and of 601 ± 4 Ma on a felsic tuff (Dempster *et al.* 2002), both from within the Tayvallich Volcanic Formation.

Recently, however, a coherent set of data has been developed based on glaciogenic metasedimentary rocks and the C-isotope signature of cap carbonates which has

linked Scottish and Irish glacial marker beds to global events (McCay *et al.* 2006; Prave *et al.* 2009b).

Three glacial episodes have been recorded in the Dalradian succession. These are, from youngest to oldest, as follows.

1) Leslie *et al.* (2008) and Prave *et al.* (2009b) correlated the Loch na Cille Boulder Bed (Elles 1934; Prave 1999), which marks the top of the Tayvallich Volcanic Formation in SW Scotland (Pickett, in press), with the Inishowen glacial beds in Donegal (Condon & Prave 2000) and the Macduff Boulder Bed in NE Scotland (Stoker *et al.* 1999). They suggested that these units represent the Gaskier global glacial event (c. 580 Ma). This is broadly consistent with the radiometric age for the Tayvallich metavolcanic rocks (see above).

2) The Stralinchy –Reelan formations in Donegal, Ireland lie at or close to the base of the Easdale Subgroup. The units have been considered to record the Marinoan global event at c. 635 Ma (McCay *et al.* 2006). As such they provide an approximate date for the beginning of the first major volcanic episode.

3) The Port Askaig Tillite Formation (Spencer 1971) and its equivalents can be traced along the whole strike length of the Dalradian succession. The formation marks the base of the Argyll Group and is stratigraphically very close to the earliest volcanic units (BGS 1996; Chew *et al.* 2009). It has been equated with the Sturtian global event (McCay *et al.* 2006; Prave *et al.* 2009b), although this view has been questioned by Leslie *et al.* (2008) and Stephenson *et al.* (in press) who suggest it is Marinoan (presumably an earlier phase than (2) above). The age and nature of the Sturtian event is still the subject of considerable ongoing research. The current literature suggests that it may have been episodic in the period c. 720-640 Ma (e.g., Fairchild & Kennedy 2007; Kendall *et al.* 2009; Macdonald *et al.* 2010). However Rooney *et al.* (in press) have published a Re-Os date of 659.6 ± 9.6 Ma from the Ballachulish Slate Formation (Appin Group), which they suggest makes the Port Askaig tillite a correlative of c. 650 Ma end-Sturtian events.

These correlations mark an important advance in determining the Dalradian time-scale. However, until the existing uncertainties, both in the correlations and the ages, are fully resolved, caution has to be exercised when using them to deduce the age of the volcanism. Accepting these reservations and given the above time-scales, our best estimates of the age of the volcanic episodes across the Dalradian belt may be summarised as follows.

- 1) The first, minor, volcanism occurred at the base of the Argyll Group (Islay Subgroup) in NE Scotland at c. 650-645 Ma
- 2) A major phase of activity occurred during deposition of the Easdale Subgroup at c. 630 to 620 Ma, associated with increased crustal extension.
- 3) The final phase took place during deposition of the Tayvallich Subgroup and the lower part of the Southern Highland Group between c. 610 and 590 Ma, with all activity finished by c. 570 Ma.

It is noteworthy, in this context, that an extensive suite of rift-related silicic intrusions, the Vuirich suite, is believed to have been emplaced at c. 600 Ma, suggesting a major episode of bimodal magmatism at that time (Tanner *et al.* 2006; Macdonald & Fettes 2007).

Conventional interpretations regard the Shetland successions as broadly conformable with the mainland Dalradian stratigraphy (Flinn *et al.* 1972; Harris *et al.* 1994; Stephenson *et al.*, in press). However, Prave *et al.* (2009a), using C-isotope chemostratigraphy, argued for a more radical interpretation, in particular that the major volcanism in Shetland is significantly later than 600 Ma and possibly even younger than 550 Ma. In this regard, we note that a short-lived episode of basic magmatism occurred at 560 - 570 Ma in the Seiland Igneous Province in the Norwegian Caledonides (Roberts *et al.* 2006).

As noted above, volcanism in the Trossachs Group postdates strata palaeontologically dated as early Arenig (c. 475 Ma) (Tanner & Sutherland 2007). It is therefore significantly younger than the volcanism described above and is temporally associated with regional collisional rather than extensional systems.

Sampling strategy and analytical methods

Samples were selected as follows. First, rocks were collected from successions for which there were no published geochemical data (Figs. 2b, 3). Second, in some cases existing data sets were expanded to include a wider range of trace elements, for example, the complete REE analyses of newly collected metavolcanic rocks from the central Highland sequences previously studied by Goodman & Winchester (1993) and the Dunrossness Spilitic Formation, and Nb data for lavas of the Tayvallich Formation, not reported in Graham (1976). Third, analyses were made of rocks from areas for which there were few published data, for example, the Loch Avich Lavas Formation. For reasons of analytical consistency, only the new data are used, with the

following exceptions; analyses from the Dalradian sequences of Northern Ireland are from Hyslop & Pickett (2001) and those from the Blackwater Formation are from Macdonald *et al.* (2005). The data set also includes the analyses of four rocks from the Loch Avich Lavas and Tayvallich formations published by Pickett *et al.* (2006) and previously unpublished BGS data for two Loch Avich and two Ben Vrackie samples. The total number of analyses presented in this study is 113.

Since an aim of the study was to use stratigraphically well-defined rocks, material was only collected if described as *extrusive* in the published literature or in unpublished British Geological Survey reports. Possible exceptions (intrusions) are noted below. There is no field or petrographical evidence that any sample represents a tuff or an intrusion into wet sediments. Since a further aim was to determine the mantle sources of the magmas, the focus was on rocks described as *basic*.

Fifteen rocks from the Auchnahyle Formation (sample CAB1), Kymah Quartzite Formation (CAB 4), Laoigh Metabasites (GF 1-5), Delnadamph Volcanic Formation (CAB2, 3), Balnacraig Metabasite Member (BAL1-2, 4-5), Meall Dubh Metabasite Formation (MD3), and Dunrossness Spilitic Formation (N12461) were selected for analysis. Rocks were broken using a hydraulic rock splitter, passed through a jaw crusher, and then c. 100 g ground to a fine powder in a tungsten carbide mill. Analyses were performed as follows: major elements by X-ray fluorescence spectrometry (XRF) in the British Geological Survey laboratories, Keyworth; Nb, Rb, Sr, Zr and Y by XRF at Edinburgh University; Th, Ta, Hf and the REE by ICP-MS at Royal Holloway, University of London.

REE analyses for Northern Ireland lavas were made by ICP-MS at Royal Holloway, University of London. Sixty-six rocks from the Ben Vrackie, Tayvallich and Loch Avich Lavas formations were analysed for major elements and for Ba, Cr, Cu, Nb, Ni, Rb, Sc, Sr, V, Y, Zn and Zr by XRF at Edinburgh University, using analytical conditions given in Fitton *et al.* (1998) and Fitton & Godard (2004), where details of analytical precision and analyses of international standards can be found. To take account of the variable hydration of the rocks, the major element data used in figures and subsequent discussion have been recalculated to 100% anhydrous. None of our samples was analysed in all laboratories to check for analytical consistency. However, the data sets show no systematic differences on any chemical plot and we have assumed that they are compatible.

The geochemical data are divided into six fairly coherent sets based on geochemistry but reflecting lithostratigraphical units, namely: (1) *Islay Subgroup* (comprises the Auchnahyle and Kymah Quartzite formations), (2) *Easdale Subgroup* (comprises the Delnadamp Volcanic Member, Laoigh Metabasites, Meall Dubh Metabasite Formation, Ben Vrackie volcanic complex, Farragon Volcanic Formation, Glenga Amphibolite Member and the Balnacraig Metabasite Member (although stratigraphically at the base of the Crinan Subgroup, this unit is geochemically consistent with units in the immediately underlying Easdale Subgroup)), (3) *Blackwater Formation*, (4) *Tayvallich (Awe)*, rocks from around Loch Awe and Knapdale (essentially the northeastern part of the crop of the Tayvallich Volcanic Formation; Fig. 2b), (5) *Tayvallich (Carsaig)*, rocks from the Tayvallich peninsula, including Carsaig and Crinan (essentially the southwestern part of the crop of the Tayvallich Volcanic formation; Fig. 2b), and (6) *Loch Avich Lavas Formation*. Sets (4) and (5) occupy the same stratigraphical position (Tayvallich Volcanic Formation) but are compositionally distinct.

Geochemistry

As is typical of metavolcanic rocks metamorphosed at greenschist to amphibolite facies, Ca, Na, K, Rb, Ba and Sr show wide scatter when plotted against differentiation indices, such as MgO, and have undoubtedly been mobile during metamorphism. We do not use those elements in further discussion. Magnesium may also be partly mobile under such conditions but we take a positive correlation between MgO and Ni (Fig.4) as evidence that Mg has been close to stable. In an attempt to minimise the effects of fractional crystallization on incompatible trace element (ITE) ratios (e.g. by Y entry into clinopyroxene), we restrict, with two exceptions, our discussion to rocks with MgO ≥ 6 wt% (on a recalculated basis). The exceptions have MgO contents (recalculated) of 4.57 and 5.17 wt% (GF2, CAB1). Although rocks with MgO >12 wt% are probably olivine+spinel-accumulitic (Macdonald *et al.* 2005), we include them here because the accumulation will not significantly have affected the (ITE) ratios which we use to identify magmatic affinities and to discriminate between eruptive sequences.

Metabasaltic rocks of the Tayvallich and Blackwater formations were recognised as high Fe-Ti tholeiitic basalt suites (Graham 1976; Goodman & Winchester 1993; Macdonald *et al.* 2005), which are typically developed at the tips of extensional plate

boundaries that are progressively breaking through rigid lithosphere (Harper 2003). Sinton *et al.* (1983) defined Fe-Ti basalts as having >12 wt% FeO* (total Fe as FeO) and >2 wt% TiO₂. On that basis, only some Dalradian metabasaltic rocks, notably the Blackwater and Tayvallich (Carsaig) formations, are Fe-Ti basalts. There is, in fact, a continuum, over the same MgO ranges, from rocks with 5 wt% FeO*, 1 wt% TiO₂ to rocks with 18 wt% FeO*, 6 wt% TiO₂, consistent with the suggestion that the Dalradian metavolcanic suites contain rocks showing a significant range of magmatic compositions (Goodman & Winchester 1993; Zenk & Schulz 2004; Macdonald *et al.* 2005). Comparable ranges in TiO₂ content have been recorded by Puffer (2002) from the late Neoproterozoic suites of Eastern Laurentia and by Shumlyanskyy *et al.* (2007) and Nosova *et al.* (2008) from the Volynian province. There is considerable variation in the Dalradian metabasaltic ITE ratios e.g. Ti/Zr 25 - 332 and Ce/Nb 0.7 - 6.1. Goodman & Winchester (1993) distinguished low-Nb and high-Nb trends in the metavolcanic rocks of Perthshire and Macdonald *et al.* (2005) noted that the Blackwater rocks followed two trends, at Zr/Nb 4.3 and 10, respectively. However, the Zr/Nb ratio of the whole data set ranges from 4 to 32, indicating a much larger range of compositions.

Chondrite-normalised REE patterns (Fig. 5) range from LREE-enriched to relatively LREE-depleted, close to N-MORB in composition. The rocks can be divided into two groupings, with $[La/Yb]_N$ (the subscript N denotes normalisation to chondrite values) less or greater than 6. The first group includes the rocks from the Islay Subgroup and, with one exception from the Laoigh Formation (GF2), the Easdale Subgroup, and the second group those from the Blackwater and Loch Avich Lavas formations and the exception from the Laoigh Formation. We have no data for high-MgO rocks from Tayvallich but analyses of two low-MgO rocks (3.47 and 1.93 wt%) in Pickett *et al.* (2006) strongly suggest that the Tayvallich (Carsaig) lavas are LREE-enriched. There is no correlation between $[La/Yb]_N$ and MgO content; indeed some of the most strongly LREE-enriched rocks are also the most magnesian (Blackwater). This suggests that the LREE-enrichment is a mantle feature modified by degree and depth of mantle melting, and not derived by a combined fractional crystallization-assimilation process.

Nature of the mantle source

We now consider possible mantle sources of the Dalradian magmatism using various trace-element features. First, we explain the use of the term E-MORB in this context. Iceland is composed of MORB, but Icelandic basalts are more enriched in highly incompatible elements than is N-MORB. Such basalts are termed enriched MORB (E-MORB) and Iceland is by far the most voluminous occurrence. On a Zr-Nb plot (Fig. 6), the Easdale Subgroup rocks occupy the fields of N-MORB and E-MORB (as represented by Icelandic lavas); all other rocks lie in the E-MORB or OIB fields. Within each field, increasing Zr and Nb abundances reflect low-pressure fractional crystallization of the magma and/or decreasing degrees of partial melting of the mantle sources. The range of Nb abundances at a given Zr level *within* each field, however, indicates that the mantle sources were heterogeneous. The effects of low-pressure fractional crystallization are eliminated by normalising the Nb and Zr abundances to a third incompatible element (Y) in Figure 7. On a logarithmic plot of Nb/Y against Zr/Y (Fig. 7), the ΔNb parameter (Fitton *et al.* 1997; Fitton, 2007) expresses the deviation, in log units, from a reference line ($\Delta\text{Nb} = 0$) separating the arrays of E-MORB (based on Icelandic basalts) and N-MORB. Virtually all N-MORB have $\Delta\text{Nb} \leq 0$, whereas E-MORB and OIB generally have $\Delta\text{Nb} \geq 0$. Most compositional parameters (e.g. K/Ti and La/Sm) that have been used to separate E-MORB from N-MORB suffer from their inability to distinguish the effects of source enrichment and the degree of source melting; the advantage of ΔNb is that it reflects source composition alone (Fitton *et al.* 1997; Fitton 2007). However, *within* both arrays the increases in Zr/Y and Nb/Y potentially reflect smaller degrees of partial melting of the mantle sources. Rocks of the Easdale Subgroup spread across the $\Delta\text{Nb} = 0$ dividing line (Fig. 7), especially those with lower Zr/Y and Nb/Y ratios. The Islay Subgroup and Tayvallich (Carsaig) rocks all plot within the E-MORB field, whereas the Loch Avich Lavas all have negative ΔNb (i.e. lie in the N-MORB field). The Blackwater and Tayvallich (Awe) lavas spread across the $\Delta\text{Nb} = 0$ line. The ΔNb values generally confirm the trace element evidence, outlined above (Figs. 5, 6), that at least two mantle sources, one more enriched and the other more depleted, were involved in magma genesis. We interpret the data as follows. The Islay Subgroup and Tayvallich (Carsaig) rocks were generated in E-MORB-type mantle and the Easdale in both N-MORB- and E-MORB-type sources. The Loch Avich Lavas and those from the Blackwater Formation and Tayvallich (Awe) with negative ΔNb values were

formed in E-MORB-type mantle but were subsequently contaminated within the continental crust (see below).

Mahoney *et al.* (2002) used $[\text{La}/\text{Sm}]_{\text{N}}$ to distinguish N-MORB from E-MORB, the latter having $[\text{La}/\text{Sm}]_{\text{N}} > 0.8$ (Fig. 8). $[\text{La}/\text{Sm}]_{\text{N}}$ ranges from 0.5 to 3.8 in the Dalradian metavolcanic rocks and is crudely positively correlated with ΔNb (Fig. 8), the majority of rocks falling into the N-MORB and E-MORB fields (cf. Figs. 6, 7). The Loch Avich Lavas and Blackwater rocks with negative ΔNb in Figure 8 are displaced towards the composition of average upper continental crust (Rudnick & Gao 2004), consistent with their position on Figure 8. Negative Nb and Ti anomalies on primitive mantle-normalised plots are commonly used as evidence of crustal contamination, the anomalies being expressed as $[\text{La}/\text{Nb}]_{\text{pm}} > 1$ and $[\text{Eu}/\text{Ti}]_{\text{pm}} > 1$. The Dalradian rocks have $[\text{La}/\text{Nb}]_{\text{pm}}$ ratios between 0.17 and 3.27 and $[\text{Eu}/\text{Ti}]_{\text{pm}}$ ratios between 0.67 and 3.92 and there are positive correlations between these ratios and ΔNb , consistent with the suggestion that some rocks have been contaminated within the crust. A rock from Glen Fearnate (GF2; Easdale Subgroup) has high $[\text{La}/\text{Sm}]_{\text{N}}$ (3.8) and $[\text{La}/\text{Yb}]_{\text{N}}$ (13), high Th (15.17 ppm) and positive ΔNb (0.31). It could represent an unusually small melt fraction from the mantle.

In summary, the trace-element data, such as ITE ratios, ΔNb , $[\text{La}/\text{Sm}]_{\text{N}}$ and $[\text{La}/\text{Yb}]_{\text{N}}$, indicate that the Dalradian metavolcanic rocks were derived by variable degrees of partial melting of mantle sources broadly varying in composition between N-MORB and E-MORB sources. There is no need to invoke a mantle plume source, as did Puffer (2002). With time, the nature of the dominant mantle source seems to have varied, from enriched during the Islay and some early Easdale subgroups, to depleted (later Easdale), with a switch back to enriched in younger sequences. Some rocks, notably those of the Loch Avich Lavas Formation and some Blackwater metabasalts, show indications of crustal contamination. The nature of the Dalradian basement is problematic. In part, at least, it is formed by the Mesoproterozoic Dava and Glen Banchor successions, which are now exposed south of the Great Glen Fault near Inverness, and upon which the Grampian Group rocks rest unconformably (Smith *et al.* 1999; Macdonald & Fettes 2007; Leslie *et al.* 2008). How far the Dava and Glen Banchor successions extend below the Dalradian succession is unknown and the younger Dalradian rocks may rest on older Proterozoic crust. However, whatever the age of the Dalradian basement, as a likely contaminant of the Dalradian basalts, it must have been at least locally LREE-enriched.

The lava from the Dunrossness Spilitic Formation, Shetland, has only 2.98 wt% MgO and has not, therefore, been included in the discussion here. However, various aspects of its composition, e.g. $[La/Yb]_N = 8.3$ and $[La/Sm]_N = 2.1$, make it highly likely that the parental magma had E-MORB affinity.

Discussion

Several recent studies of the magmatism associated with the break-up of Rodinia have ascribed the magmatism to a plume (Nosova *et al.* 2008) or superplume (Puffer 2002; Li *et al.* 2003, 2008). Li *et al.* (2003) suggested that the c. 870 Ma and c. 845 Ma igneous activity in the Scottish Highlands and Scandinavian Caledonides might have been the first indications of a superplume marking the initial breakup of Rodinia, although widespread plume activity did not happen until c. 825 Ma. Li *et al.* (2008) outlined the possible formation and morphology of the Rodinia superplume, suggesting that it may have appeared at the surface as the products of a cluster of secondary plumes (Courtillot *et al.* 2003; Schubert *et al.* 2004). Given, however, that the 850 Ma extension-related magmatism in the Scottish Highlands (Macdonald & Fettes 2007) was followed by a series of major compressional events (Cawood *et al.* 2010), some doubt must be cast on the presence of a developing plume.

There are several reasons for rejecting a plume, or plume-cluster, origin for the Dalradian basalts.

1. The existence of ubiquitous enriched domains in the convecting upper mantle is implied by the scale and distribution of modern E-MORB, which often occurs in close association with N-MORB on otherwise normal segments of mid-ocean ridge (e.g. Mahoney *et al.* 2002). The common assumption that the upper mantle is uniformly depleted in composition is false (Hofmann 2004). Conversely, plumes are not always composed entirely of enriched mantle. The earliest magmatism associated with the ancestral Iceland plume, for example, produced basalts in Baffin Island and West Greenland with compositions very similar to N- and E-MORB (Robillard *et al.* 1992; Starkey *et al.* 2009). Geochemical criteria alone cannot uniquely characterise basalts formed from mantle plumes, especially when they are applied to ancient and metamorphosed basalts. The composition of the Dalradian metavolcanic rocks, though consistent with a mantle-plume origin, does not require one. It can be

explained equally well by generation of the primary magmas in depleted upper mantle containing enriched streaks and blobs (e.g. Fitton 2007).

2. Magma *volume* is a much better indicator of mantle plume activity magma than is magma composition where plume activity is combined with lithospheric stretching and break-up. Although locally impressive, the total volume of Dalradian basaltic magma falls a long way short of what one might expect if the break-up of Rodinia was accompanied by mantle-plume activity. The Deccan and North Atlantic magmatic provinces, for example, formed along plume-affected volcanic rifted margins and have magmatic volumes in the order of 10^7 km^3 (Coffin & Eldholm 1994), at least three orders of magnitude larger than the likely total volume of Dalradian magma.
3. The magmatism was restricted to a relatively small area (c. 700 km along strike) for a period of c. 80 Ma, during which time the Scottish promontory of Laurentia drifted c. 25° southwards (Li *et al.* 2008; Pease *et al.* 2008). Magmatism of this duration on a rapidly moving plate is hard to reconcile with a mantle-plume origin. The longevity of the magmatism and the drift history of this part of Laurentia could be taken to imply that the source remained fixed to the lithosphere, but a lithospheric mantle source would be quickly exhausted and unable to sustain a supply of tholeiitic magma over c. 80 Ma. An upper mantle source tapped by prolonged lithospheric extension is a much more likely explanation.
4. The initiation of a mantle plume under Rodinia would be expected to cause rapid uplift over a wide area, but the Dalradian sedimentary record indicates that the region remained at or below sea-level throughout the 80 Ma period.

The most likely explanation for Dalradian magmatism is that passive extension of the continental lithosphere led to basin formation and to decompression melting of the upper mantle. Small amounts of extension might be expected to produce small melt fractions from only the more easily fusible (enriched) parts of the mantle and thereby generate OIB-like magmas. Further extension would cause more melting of these fusible parts and form less-enriched E-MORB. Still larger degrees of extension and ultimate continental rupture would cause more extensive decompression, larger degrees of melting involving both depleted and enriched parts of the mantle, and lead to the formation of both N- and E-MORB-type magmas. The initial magmatism in the

Islay Subgroup had E-MORB characteristics. However, during Easdale Subgroup times, the decompression melting of the mantle was sufficiently extensive to produce a majority of N-MORB magmas. The Dalradian thus represents an unusual case of passive extension leading to production of N-MORB-type magma (Fitton 2007). Later magmatism was again dominated by more-enriched E-MORB varieties, probably representing smaller degrees of partial melting involving larger proportions of the more-fusible enriched streaks and blobs that form part of the upper mantle. The significant ranges in ITE ratios, e.g. Zr/Nb, indicate the compositional heterogeneity of the melted mantle volumes.

The more-enriched rocks were emplaced in areas tectonically dominated by major crustal structures (Fig. 2b), the Cruachan Lineament for the Tayvallich Volcanic Formation (Graham 1986) and the Portsoy Lineament for the Blackwater Formation (Fettes *et al.* 1991). Some Blackwater, Tayvallich (Awe) and Loch Avich rocks were crustally contaminated, probably during residence in mid- to high-level magma chambers. The potential existed for partial melting of the host rocks and it is probably no coincidence that the largely anatectic, A-type granitic rocks of the Vuirich Suite (Tanner *et al.* 2006) were broadly coeval with these basalts. Tanner *et al.* (2006) noted that a link can be made between the Vuirich Suite and a swarm of diverse A-type intrusions and associated extrusive rocks which, in a Neoproterozoic (600 - 700 Ma) reconstruction, extends across the Appalachian fold belt.

The overall compositional trends in the Dalradian metabasaltic sequences create difficulties for any simple model of rift-to-drift transition. At some point in continental break-up and the formation of new ocean basins, OIB-like magmatism, if present, should give way to the eruption of N-MORB (Fitton 2007). For the evolution of the Dalradian basin, two features are important. Firstly, the earliest, although minor in volume, magmas (Islay Subgroup) have E-MORB characteristics. The first major phase (Easdale Subgroup) has a significant number of magmas with N-MORB composition, whereas the second major phase (the Blackwater and Tayvallich sets) showed enriched characteristics. Second, the first major phase of volcanism is geographically extensive along the Dalradian outcrop (both within the current study area and, with correlatives in the west of Ireland (Winchester & Max 1996), comprising an along-strike distance of c. 700 km), whereas the second major phase, although voluminous, is geographically constrained to SW and NE Scotland. The Dalradian lithostratigraphy, as discussed above, indicates increasing instability with

marked basin subsidence during Easdale Subgroup times. The significant development of N-MORB-type rocks in the Easdale Subgroup, especially at low Zr/Y values (Fig. 7), may reasonably be taken to indicate extreme lithospheric stretching and probable local rupture. This conclusion is supported by the extensive occurrence of ultramafic bodies, ultramafic detritus and stratabound mineral deposits along the whole Easdale outcrop from the west of Ireland to north-east Scotland (Chew 2001).

It is interesting to speculate that this rifting was aborted as full-scale rifting occurred outboard from the Dalradian basin, marking the start of the regional rift-to-drift phase. In this scenario, the predominance of turbiditic sediments in the Crinan Subgroup and Southern Highland Group successions may be taken to mark deposition on the foundering continental margin and the Trossachs Group succession to mark the passive-margin drift phase through to arc-continent collision. As noted above, the Tayvallich volcanic succession is associated with a trans-Caledonian lineament that might mark a localised pull-apart basin (Graham 1986) on the rifted margin, and the Blackwater lavas may relate to extension on the Portsoy Lineament (Macdonald et al. 2005).

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Fettes et al - Figure captions

Figure 1. (a) Global reconstructions showing the relative positions of Laurentia, Baltica and Amazonia (other continental masses omitted) as the supercontinent of Rodinia broke up. A, Amazonia; B, Baltica; L, Laurentia; Sc, Scotland. Based on Li *et al.*, 2008.

(b) Edge of Laurentia, in relation to Baltica and Amazonia showing the possible position of the Dalradian Supergroup as Iapetus began to open, ca 620-600 Ma. Simplified from Leslie *et al.*, 2008.

Figure 2. (a) Map of the Dalradian groups within the study area. Based on Macdonald & Fettes (2007) and Harris *et al.* (1994).

(b) Distribution of Dalradian metavolcanic units. 1, Glenga Amphibolite Member, 2, Tayvallich Volcanic Formation, 3, Loch Avich Lavas Formation, 4, Farragon Volcanic Formation, 5, Ben Vrackie volcanic complex, 6, Laoigh Metabasites, 7, Meall Dubh Metabasite Formation and Balnacraig Metabasite Member, 8, Delnadamph Volcanic Member, 9, Muckle Fergie rocks, 10, Blackwater Formation. Inset: Pull-apart basin model for the Tayvallich Volcanic Formation, after Graham (1986).

Figure 3. Stratigraphical relationships of Dalradian metavolcanic rocks. Updated from Macdonald *et al.* (2005). Fm, Formation; Mb, Member.

Figure 4. MgO-Ni plot for the Dalradian metavolcanic rocks. The overall positive correlation suggests that Mg has been relatively unaffected by regional metamorphism. Data from Supplementary Table.

Figure 5. Chondrite-normalised rare-earth element (REE) patterns for four of the stratigraphical groups. The highlighted pattern on the Easdale plot is from the anomalous sample GF2 (see text for discussion.) Normalising factors from McDonough & Sun (1995). Data from Supplementary Table.

Figure 6. Zr-Nb plot showing the relationship of the Dalradian metabasalts to the fields of OIB, N-MORB and Icelandic basalts (taken to represent E-MORB). Fields from Fitton & Godard (2004). Dalradian data from Supplementary Table. Open symbols represent samples from the older units and filled symbols (grey and black) represent samples from the younger units.

Figure 7. On a logarithmic plot of Nb/Y versus Zr/Y (Fitton et al., 1997), the solid lines enclose the field of Icelandic basalts, with relatively depleted rocks at the low Zr/Y end and enriched basalts at high Zr/Y. The array has been modelled (Fitton *et al.* 1997) by variable degrees of partial melting of a heterogeneous mantle source. N-MORB plot on a parallel array at lower Nb/Y, i.e. with $\Delta\text{Nb} < 0$. Dalradian metavolcanic rocks plot within both the E-MORB (Icelandic) and N-MORB arrays. The compositions of primitive mantle (+; from McDonough & Sun, 1995) and average upper continental crust (UC; from Rudnick & Gao, 2004) are also shown. The Dalradian metavolcanic rocks are thought to have formed by variable degrees of partial melting of heterogeneous mantle sources comparable to the N-MORB and E-MORB sources, followed in some cases by mixing of melts from different sources and/or crustal contamination. Data from Supplementary Table. Open symbols represent samples from the older units and filled symbols (grey and black) represent samples from the younger units.

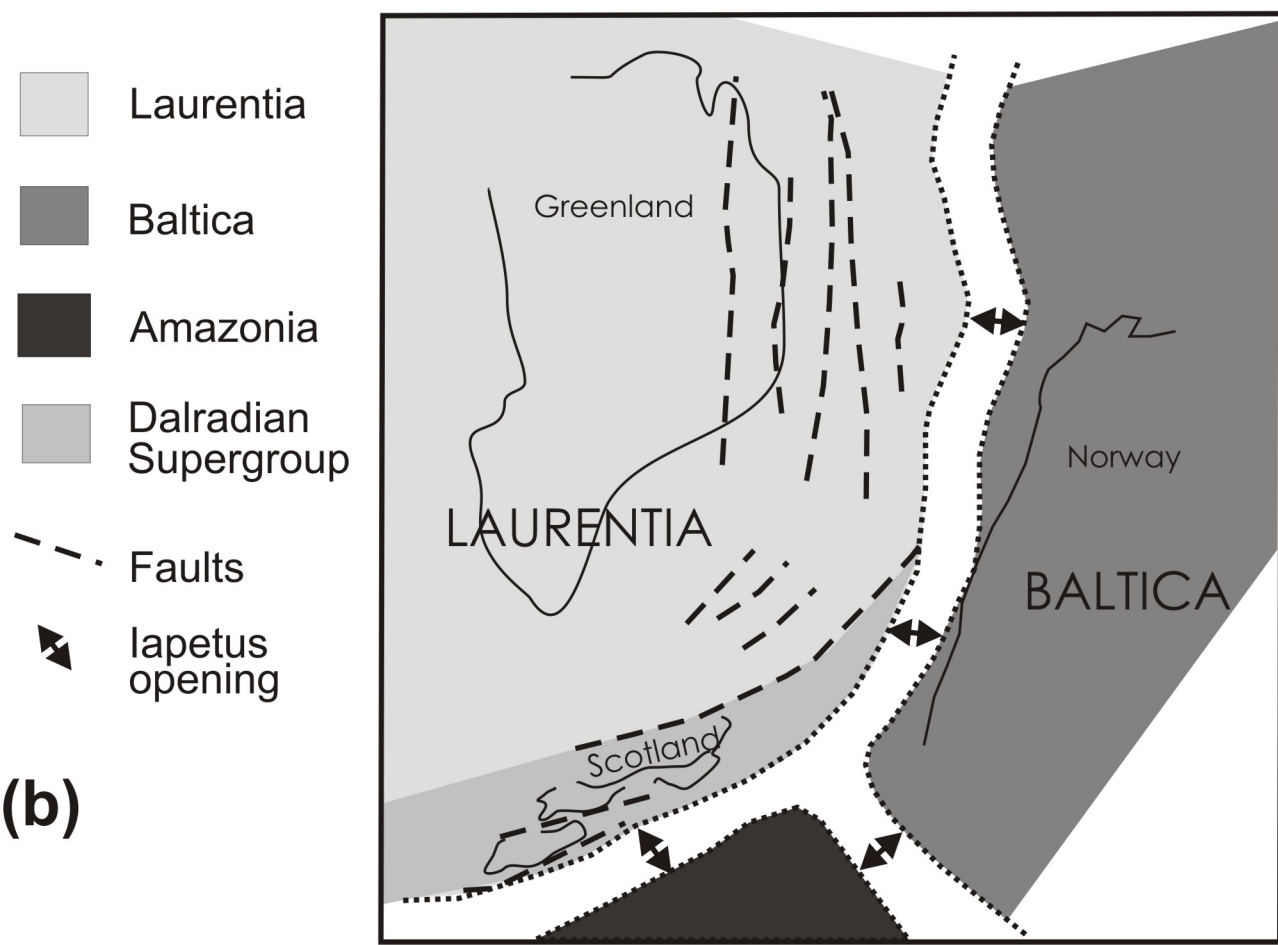
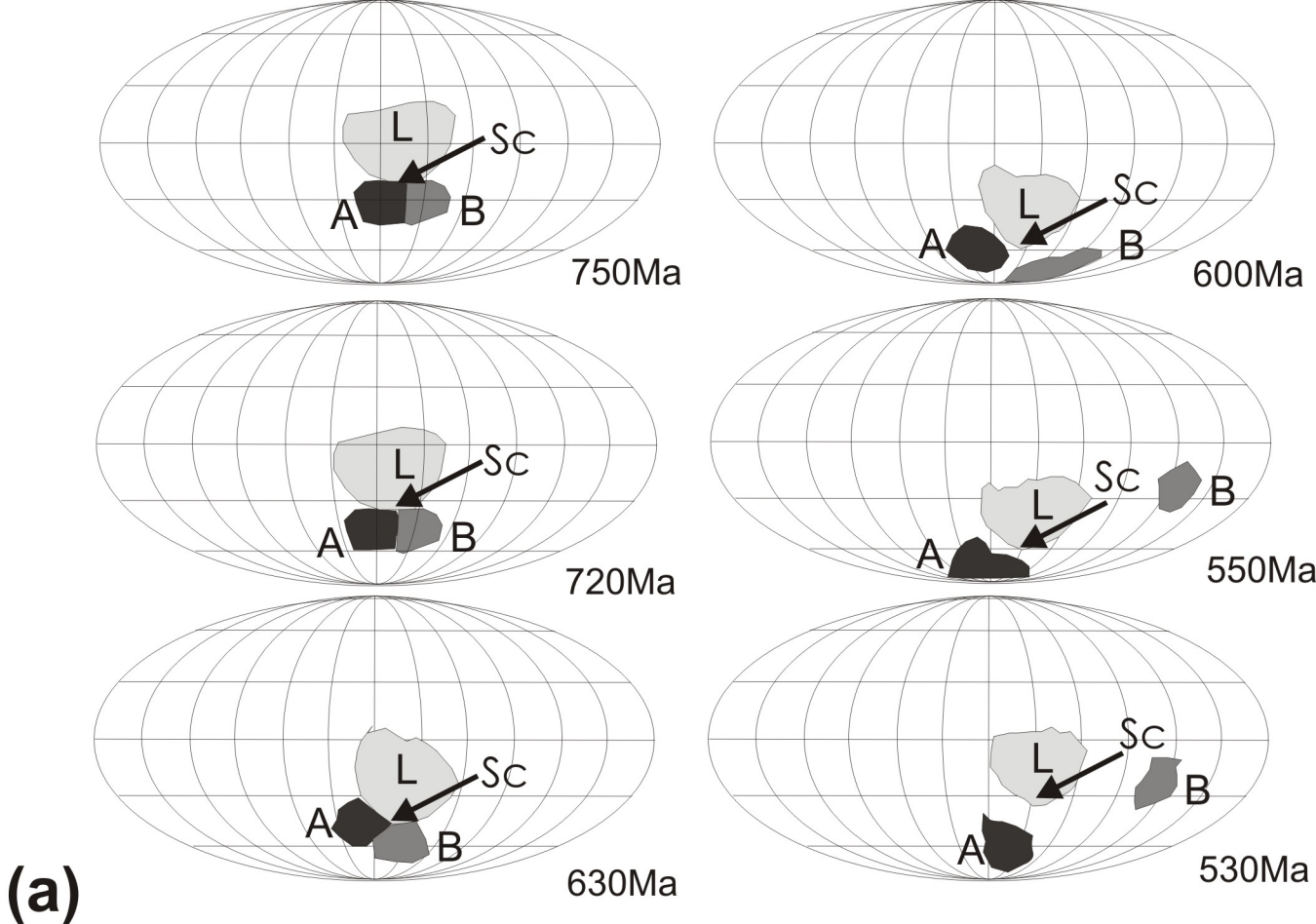
Figure 8. ΔNb (see Fig 8) plotted against $[\text{La}/\text{Sm}]_{\text{N}}$ for Dalradian basic metavolcanic rocks. The spread over the N-MORB and E-MORB fields, is consistent with generation in a N-MORB type source with enriched streaks and patches. Rocks from the Loch Avich Lavas Formation and some from the Blackwater Formation lie along a vector towards the composition of average upper continental crust (UC; from Rudnick & Gao, 2004). Data from Supplementary Table. Open symbols represent samples from the older units and filled symbols (grey and black) represent samples from the younger units.

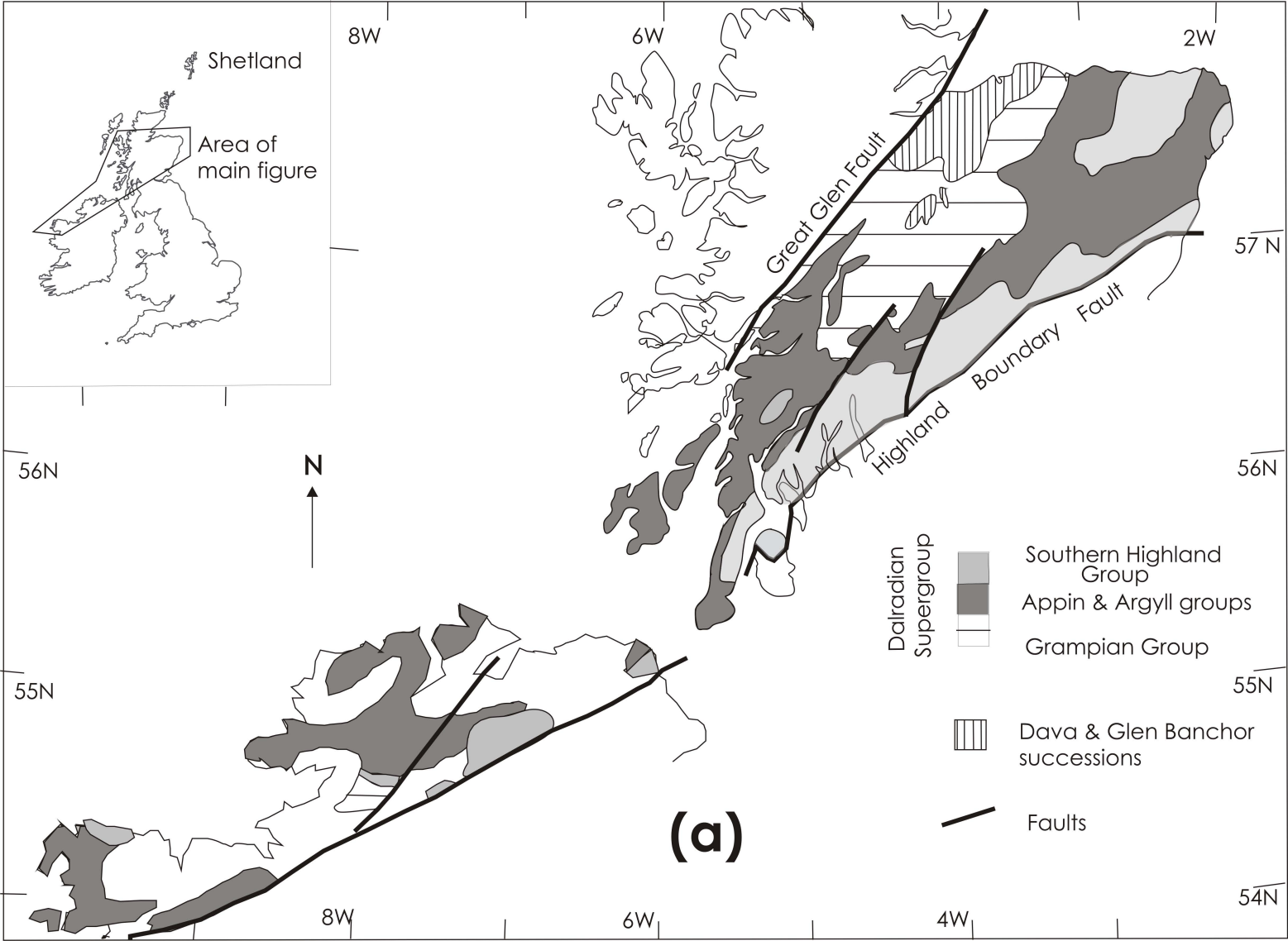
Index to Tables

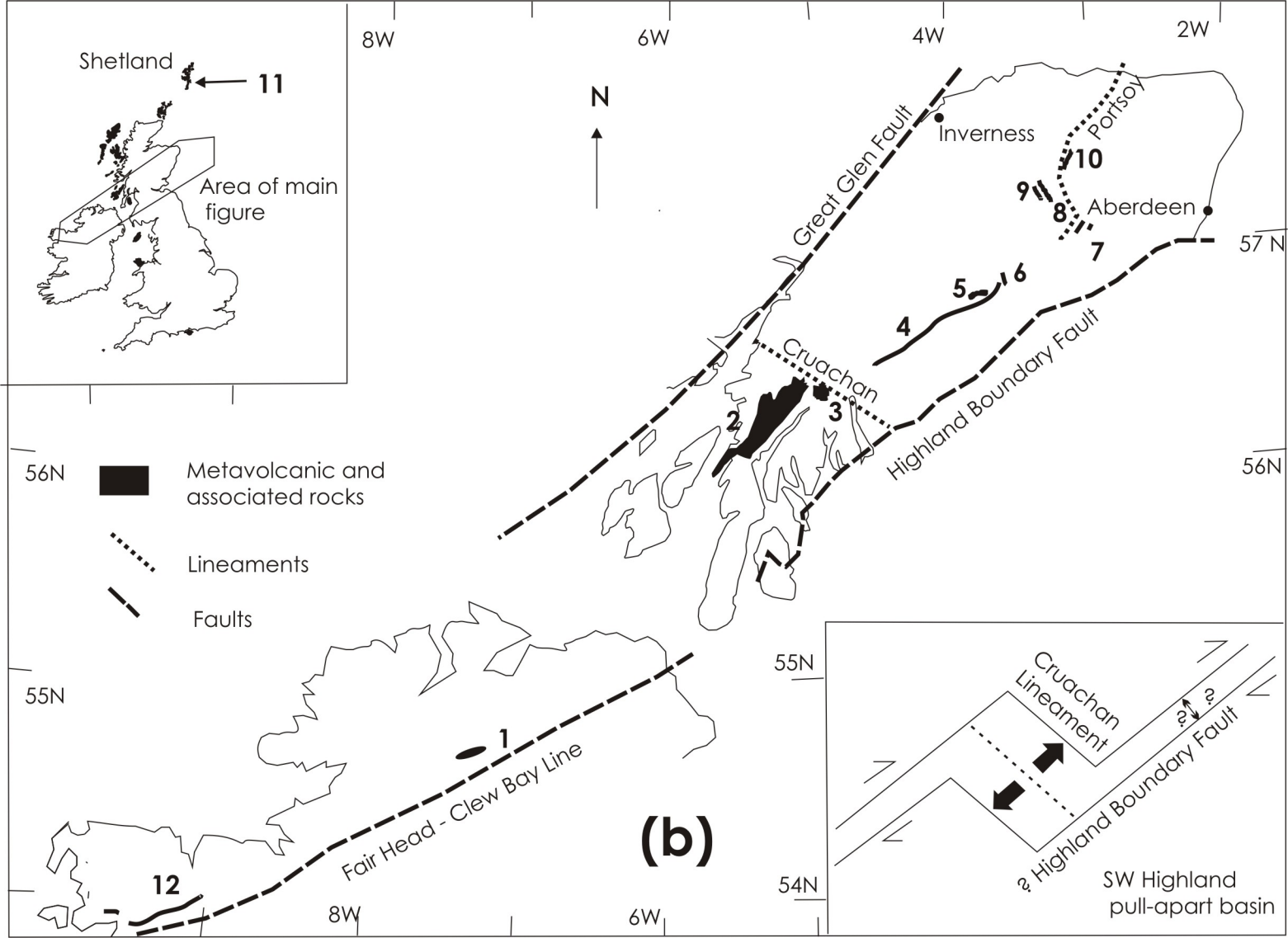
Table 1 New chemical analyses of Dalradian metavolcanic rocks (major elements recalculated to 100%, anhydrous).

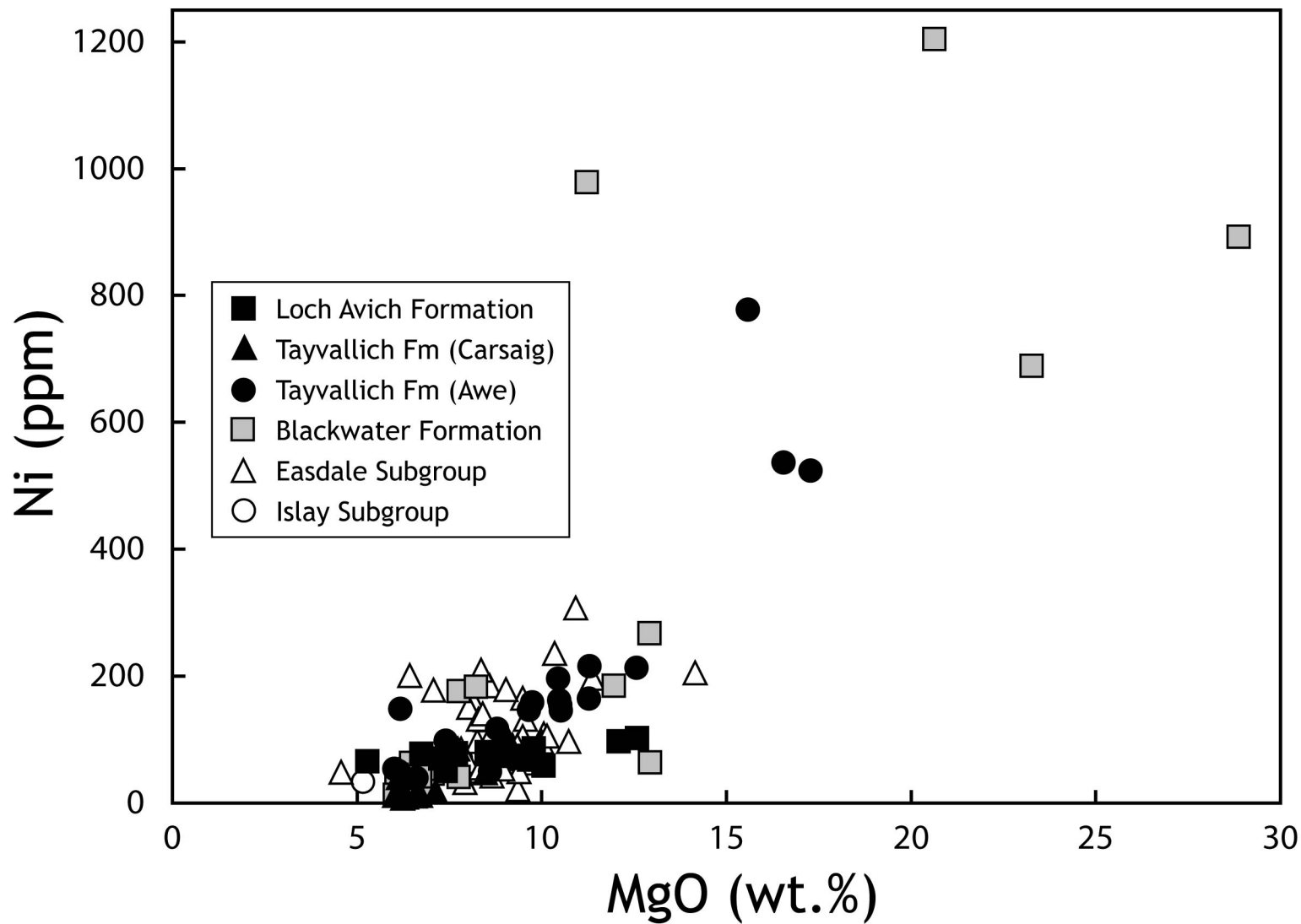
Table 2 Additional data for Northern Ireland rocks.

Supplementary Table Chemical analyses of Dalradian metavolcanic rocks (major elements recalculated to 100%, anhydrous).









REE/CI chondrite

