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# Do Neoproterozoic (Moine) calc-silicate rocks represent metamorphosed tuffs? A geochemical re-appraisal

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ABSTRACT: Following the identification of grey quartz–albite–chlorite–calcite–muscovite rocks in Meso- to Neo-proterozoic sequences in Scotland as metamorphosed tuffs of intermediate composition, it has been shown that this lithology will generate calc-silicate rocks at higher metamorphic grades. Both rock types occur as thin beds with sharp contacts with their host, occur as multiple beds in isolated suites, and share chemical compositions suggestive of volcanic sources with tholeiitic andesite affinities. The failure to recognise calc-silicate rocks as tuffs might explain the apparent scarcity of volcanogenic material through *c*.220 million years of early Earth history in Scotland.

KEY WORDS: Proterozoic volcanic ashes

Calc-silicate rocks, which are metamorphic rocks composed mostly of plagioclase feldspar, amphibole, garnet, quartz and occasionally epidote, are sporadically distributed throughout the Neoproterozoic Moine Supergroup of Scotland. The Moine Supergroup comprises a thick sequence of sedimentary rocks, deposited in fluviatile (Bonsor & Prave 2008) and shallow marine environments between *c*.950 Ma and 870 Ma (Mendum *et al*. 2009), intruded by some minor igneous intrusions, all of which were subjected to regional metamorphism and deformation events (Strachan *et al*. 2010). The sediments were derived from the denudation of the *c*.1000 Ma Grenville Orogen and deposited off the eastern margin of Laurentia into a foreland basin. The value of calc-silicate rocks as indicators of metamorphic grades was first established in Scotland by Kennedy (1949). Generally, they occur as thin bands or lenses, commonly less than 15 cm thick, and have sharp upper and lower contacts with their host metasediment. They are defined as containing less than 5 % free carbonate minerals (Rosen *et al*. 2004). Calc-silicates from the Moine rocks of NW Scotland occur within psammites and semi-pelites, and contain combinations of plagioclase feldspar, hornblende ± biotite, garnet, quartz, zoisite, and minor calcite (Winchester 1972). The amount of zoisite is inversely proportional to the amount of calcite, suggesting that the latter is consumed to create zoisite. Calcite is often preserved as inclusions in garnet, implying it was present in the rock before garnet formed. Grain sizes generally vary from 0.1 mm to 1 mm.

A study of Moine calc-silicate rocks from the Morar area charted the mineralogical changes which took place with increasing metamorphic grade (Tanner 1976). The lower grades are typified by quartz, albitic plagioclase feldspar, garnet, biotite ± hornblende and zoisite; whereas at higher grades, zoisite disappears and the plagioclase composition reaches bytownite and hornblende replaces biotite. The garnet Alm70-60–Gro30-40 is ubiquitous in the sequence. Further work on these rocks showed that Na and K are lost from the calc-silicate during prograde metamorphism (Tanner & Miller 1980).

Epidote-bearing calc-silicates within the Moine Supergroup of Scotland were described by Winchester (1975). These occurrences form bands and lenticles less than 10 cm thick and occur within the Morar and Loch Eil groups. While the bulk chemical composition is similar to that of the common zoisite-garnet type, it differs in that garnet is absent and epidote takes the place of zoisite. Concentrations of zirconium up to 766 ppm are reported, a value which is high for clastic sediments but normal for igneous rocks with alkaline/intermediate compositions. Winchester's (1975) conclusion was that epidote was a detrital mineral and the rock may have been related to an epidotic grit lithology, similar to that in the Sleat Group (Torridonian) described by Stewart (2002). Some epidotic calc-silicates were considered to have possibly originated from volcanic ash deposits (J. A. Winchester, pers. comm. 2009).

Historically, references to putative tuffs in the Proterozoic of Scotland are scarce, but four examples (one of Lewisian age and three of Moine age) are quoted here and are presented to show that volcanogenic rocks can masquerade as something different. One calc-silicate rock from the Scourian complex of NW Scotland has been described as a plagioclase–clinopyroxene–scapolite rock. However, when the chemical composition was re-calculated on a volatile-free basis, the rock became essentially a clinopyroxene–plagioclase rock (i.e., a gabbro) (Rollinson 1980). A study of hornblendic rocks from the Moine successions west of the Great Glen (Rock 1984) identified two samples whose chemical composition suggested they were formed from contemporary volcaniclastic deposits. Two epidote hornblende schists from the Moine Supergroup of Sutherland were considered to represent penecontemporaneous volcanic ash deposits (Moorhouse & Moorhouse 1979). Garnetiferous hornblende schists near to the contact of the Glenfinnan and Loch Eil groups. Moine Supergroup, were thought to represent volcanic horizons (Peacock 1977).

This work was triggered by the identification of grey quartz–albite–chlorite–muscovite–calcite rocks (cognate to altered variants named 'brown beds') in prehnite–pumpellyite to low greenschist facies environments in the Dalradian Supergroup (Batchelor 2004a, b) and in the Torridonian Supergroup (Batchelor *et al*. 2008; Batchelor 2011) which were all interpreted as tuffs. Circumstantial evidence from geochemical, mineralogical and field relationships led to the hypothesis that these grey tuffs could convert to calc-silicate rocks under amphibolite facies metamorphism. Three grey tuffs have CaO values of 9.8 %, 10.5 % and 16.1 %. Values of CaO in 75 published analyses of calc-silicates yielded a range of 3.0–21.6 % CaO (Winchester 1972, 1975; Tanner 1976) (Table 1).

This study is based on experimental petrology and geochemical analysis of suites of Moine calc-silicate rocks collected from

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**Table 1** Average values of major element oxide ratios for calc-silicate rocks, tuffs and metasediments.

| | Average 1 | Average 2 | Average 3 | Average 4 | Average 5 | Average 6 |
|---|---|---|---|---|---|---|
| $CaO/Al_2O_3$ | 0.65 | 0.71 | 0.60 | 0.55 | 0.40 | 0.85 |
| $CaO/MgO$ | 8.62 | 10.46 | 5.06 | 8.51 | 5.50 | 13.40 |
| $CaO/TiO_2$ | 13.86 | 18.47 | 12.05 | 12.96 | 8.66 | 20.42 |
| $CaO/Fe_2O_3$ | 2.21 | 2.87 | 1.70 | 2.25 | 1.35 | 3.11 |
| $Fe_2O_3/MgO$ | 3.90 | 3.64 | 2.98 | 3.79 | 4.06 | 4.31 |
| $TiO_2/MgO$ | 0.62 | 0.57 | 0.42 | 0.66 | 0.64 | 0.66 |

| | Average 7 | Average 8 | Average 9 | Average 10 | Average 11 |
|---|---|---|---|---|---|
| $CaO/Al_2O_3$ | 0.65 | 0.37 | 0.56 | 0.51 | 0.61 |
| $CaO/MgO$ | 14.84 | 5.37 | 8.40 | 9.30 | 25.30 |
| $CaO/TiO_2$ | 18.78 | 17.06 | 14.50 | 12.40 | 24.70 |
| $CaO/Fe_2O_3$ | 3.80 | 3.35 | 2.20 | 2.10 | 4.40 |
| $Fe_2O_3/MgO$ | 3.90 | 1.60 | 3.70 | 4.60 | 4.50 |
| $TiO_2/MgO$ | 0.79 | 0.31 | 0.60 | 0.75 | 0.75 |

| | GH/RB/112GY | SK/RB/05GY | TN/RB/026GY | Moine metasediments (3) |
|---|---|---|---|---|
| $CaO/Al_2O_3$ | 0.89 | 0.97 | 1.92 | 0.23 |
| $CaO/MgO$ | 12.20 | 10.17 | 24.75 | 1.72 |
| $CaO/TiO_2$ | 14.75 | 20.94 | 22.35 | 4.14 |
| $CaO/Fe_2O_3$ | 3.27 | 4.09 | 6.70 | 0.61 |
| $Fe_2O_3/MgO$ | 3.73 | 2.49 | 3.69 | 2.81 |
| $TiO_2/MgO$ | 0.83 | 0.49 | 1.11 | 0.42 |

Average 1: Epidotic calc-silicates (Winchester 1975)
Average 2: Garnet-zoisite calc-silicates (Winchester 1972)
Average 3: Calc-silicates from Fannich (Winchester 1972)
Average 4: Calc-silicates (Tanner 1976)
Average 5: Calc-silicates (this work), Mallaig (6)
Average 6: Calc-silicates (this work), Morar (10)
Average 7: Calc-silicates (this work), Arisaig (11)
Average 8: Calc-silicates (this work), Lochailort (12)
Average 9: Calc-silicates (this work), Ardalanish Bay, Mull (7)
Average 10: Calc-silicates (this work), Uisken Bay, Mull (5)
Average 11: Calc-silicates (this work), Cannich (6)

the Northern Highlands of Scotland. Their geographical distribution is shown in Figure 1 and their stratigraphical affiliations are shown below. The terminology for the Moine Supergroup stratigraphy is based on Mendum *et al.* (2009).

| GROUP | FORMATION | LOCALITY (Sample Numbers) |
|---|---|---|
| Loch Eil (*c.*860 Ma) | | Cannich (CS/RB/050–056) |
| Glenfinnan | Glenfinnan Schists | Ardalanish, Mull (CS/RB/34–40) |
| | Lochailort Pelite | Uisken, Mull (CS/RB/44–49) |
| Morar (*c.*950 Ma) | Upper Morar Psammite | Lochailort (CS/RB/18–24, TN/RB/69–73) |
| | Morar Pelite | Mallaig (CS/RB/1–6) |
| | Lower Morar Psammite | Morar (TN/RB/77–86),<br>Arisaig (CS/RB/7–17) |

## 1. Sample descriptions

### 1.1. Mallaig

A suite of six calc-silicate beds, not all contiguous in exposure, were sampled from roadside exposures at Mallaigmhor [NM 680 974]. Samples CS/RB/001–004 are situated on the west side of the road from Mallaig. CS/RB/005, 006 were collected *c.*60 m downhill from the former samples, on the east side of the road [NM 680 973]. Sample thicknesses vary from 10 mm to 30 mm. The host rocks are near-vertical semi-pelites of the Morar Pelite Formation, Morar Group. The general mineral assemblage is lamellar-twinned plagioclase feldspar, biotite (up to 2 mm long) with abundant pleochroic haloes (indicative of zircon), quartz (interlocking grains), poikilitic garnet, actinolite and rare zoisite, epidote and titanite. Only one sample (CS/RB/006) contains free calcite.

### 1.2. Morar

A stratigraphically-coherent suite of calc-silicate beds (TN/RB/077–TN/RB/086) occurs at a roadside cutting over a length of 53 m on the east side of the A830 at [NM 674 914], 2 km SSW of Morar village. Samples vary in thickness from 20 mm to 140 mm. The host rocks belong to the Morar Pelite Formation, Morar Group. One typical sample (TN/RB/083) displayed the following mineral assemblage: lamellar-twinned plagioclase feldspar; biotite (up to 2mm long) containing pleochroic haloes; quartz; zoisite; poikilitic garnet; calcite; and hornblende. Grain size varies from 0.1 mm to 0.2 mm. This suite belongs to the Zone 1–Zone 2 transition of Kennedy (1949). Four samples (TN/RB/078, 080, 081, 082) contain a narrow zone, varying from 5 mm to 50 mm, of a brown crumbly material within the boundaries of the calc-silicate rock, reminiscent of the Dalradian and Torridonian "brown beds" (Batchelor *et al.* 2008) (Fig. 2). It would be consistent with the effect of sub-aerial weathering of a residual calcite matrix, implying that all calcite was not consumed during the metamorphic transformation of the original lithology.

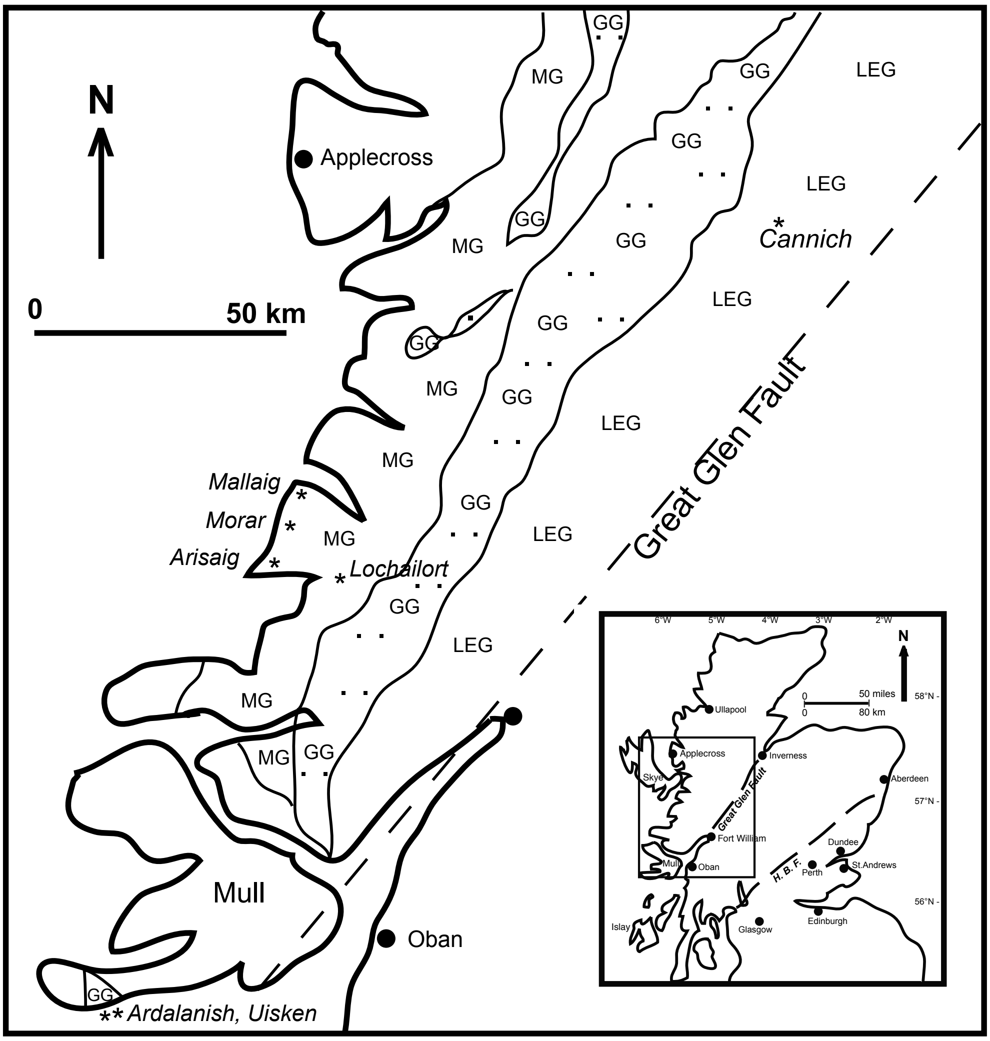

**Figure 1** Map of calc-silicate rock suites, with localities marked *. Moine groups adopted from Strachan *et al.* (2002). Abbreviations: GG = Grampian Group (with stippled ornament); HBF (inset) = Highland Boundary Fault; LEG = Loch Eil Group; MG = Morar Group.

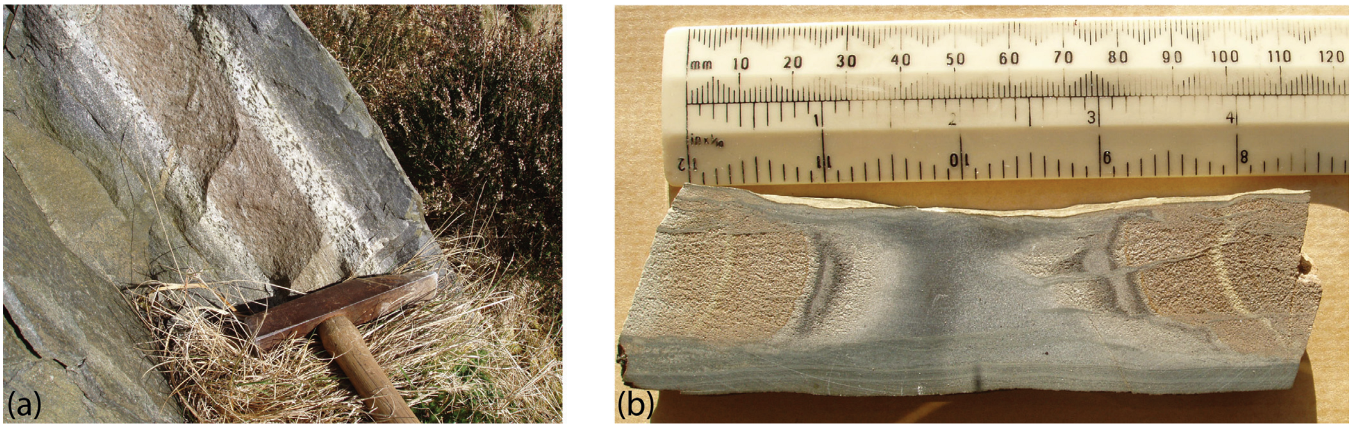

**Figure 2** Calc-silicate bed with crumbly brown interior band, Morar Group, Morar. Hammer head scale = 15 cm. (b) "Brown Bed" alteration product at the periphery of the central grey bed (tuff), Sleat Group, Torridonian Supergroup, Isle of Skye.

## 1.3. Arisaig

A relatively recent road exposure on the A830, 1.5 km E of Arisaig [NM 674 860], provided the opportunity to sample a continuous sequence of calc-silicate rocks CS/RB/007–017. Samples vary in thickness from 20 mm to 90 mm. The mineral assemblages comprise lamellar-twinned plagioclase feldspar, actinolite, biotite, quartz, calcite, poikilitic garnet, titanite and zoisite. Garnet often encloses calcite.

## 1.4. Lochailort

A near-vertical suite of psammites and semi-pelites are well-exposed in a roadside cutting on the north side of the A830, opposite its junction with the A861 [NM 767 823]. These rocks form part of the Upper Morar Psammite Formation, Morar Group (Johnstone & Mykura 1989; Mendum *et al.* 2009). Sample thicknesses vary from 12 mm to 50 mm. The mineralogy of this suite comprises lamellar-twinned plagioclase feldspar showing variable degrees of sericitisation, biotite which has partly altered to chlorite, quartz and garnet associated with calcite. These rocks differ from the previous three suites in lacking amphibole, zoisite and epidote.

### 1.5. Mull – Ardalanish Bay

Calc-silicate rocks occur within semi-pelites of the Assapol Group, tentatively assigned to the Glenfinnan Group (mid-Moine Supergroup) by Holdsworth *et al.* (1987), at Ardalanish Bay, 3.5 km south of Bunessan, Isle of Mull [NM 381 186]. Samples vary in thickness from 15 mm to 70 mm.

Samples were collected from west to east in the order CS/RB/034–040, and the succession here dips 50° NW. Sample CS/RB/040 from the east end of Ardalanish Bay yielded the following mineral assemblage: plagioclase feldspar (An40–80); poikilitic garnet; quartz; interstitial zoisite; actinolite, titanite; calcite (residual inside garnet); and subhedral zircon.

### 1.6. Mull – Uisken Bay

A sequence of psammites, which belong to the Assapol Group, tentatively assigned to the Glenfinnan Group by Holdsworth *et al.* (1987), is exposed around HWM [NM 392 188] in the middle of Uisken Bay. The general dip direction is 25° SE. Six calc-silicate rocks (CS/RB/044 to CS/RB/049) were collected; thicknesses varied from 20 mm to 70 mm over a horizontal distance of 13 m. The general mineral assemblage comprises clinozoisite, poikilitic garnet (enclosing calcite), zoisite, chlorite, quartz, titanite and calcite. One sample (045) contains no feldspar, while another (048) contains plagioclase feldspar and biotite, but no amphibole.

### 1.7. Cannich

A suite of seven calc-silicate rocks (CS/RB/050–056) were collected from a road cutting on the east side of the A831, 1 km east of Cannich [NH 349 315]. These beds occur in psammites and semi-pelites, assigned to the Upper Glenfinnan Group–Lower Loch Eil Group by Mendum *et al.* (2009), and dip 45° SE. Thicknesses vary from 40 mm to 150 mm. Sample 053 contains abundant zoisite, quartz, biotite (with pleochroic haloes after zircon), garnet and titanite. No feldspar was identified, implying it has been consumed in the formation of zoisite.

## 2. Experimental work

Two grey tuffs which occur in the Torridonian Supergroup (Batchelor 2005, 2011) comprise albite, chlorite, quartz, calcite and muscovite in prehnite–pumpellyite facies to low greenschist facies metamorphic environments. In order to test whether or not the grey tuffs could generate mineral assemblages similar to calc-silicates under high P/T conditions, their bulk chemical compositions were plotted on Eskola's ACF diagram, following Miyashiro (1994). The three variables were calculated on an atom basis thus: A = $Al_2O_3 + Fe_2O_3 - Na_2O - K_2O$; C = $CaO - (3.3xP_2O_5)$; F = $FeO + MgO + MnO$. The grey tuffs generated a mineral composition centred around vesuvianite (idocrase), with sample TN/RB/026GY trending towards the wollastonite pole. On this basis, experimental runs were carried out at the Grant Institute, University of Edinburgh. The two tuff samples (TN/RB/026GY from the Diabaig Formation and SK/RB/05GY from the Sleat Group) were run at 6kB/600°C (amphibolite facies) for 400 hours. Approximately 20 mg of powder from each sample were sealed dry into welded Pt capsules (length 1 cm, diameter 3 mm, wall thickness 0.1 mm). Samples were placed in an internally-heated gas vessel, brought to run pressure, and then heated to final run temperature over 15 minutes. Argon was used as the pressure medium, and $pO_2$ was close to the Ni–NiO buffer at the relevant temperatures. Samples were fast-quenched by cutting power to the vessels and subsequent cooling was exponential, with an 80 % temperature drop in five minutes.

**Table 2** Mineralogical composition of high P/T products. Sample locations: TN/RB026GY: Lower Diabaig, Highland Region, [NG 7925 6025], Diabaig Formation, Torridon Group. SK/RB/05GY: 1 km east of Kyle of Lochalsh, Highland Region, [NG 7725 2725], Loch na Dal Formation, Sleat Group, Torridonian.

| % | TN/RB/026GY Grey Tuff | TN/RB/026GY Amphibolite facies |
|---|---|---|
| Quartz | 32.6 | 28.7 |
| Muscovite | – | 0.7 |
| Calcite | 27.2 | 28.6 |
| Albite | 24.7 | 26.0 |
| Anorthite | 5.1 | 8.3 |
| K-feldspars | 2.5 | 4.0 |
| Chlorite | 5.3 | 1.0 |
| Zoisite | 0.8 | 0.4 |
| Epidote | 1.5 | 1.6 |
| Almandine | 0.4 | 0.3 |
| Grossular | – | 0.8 |
| TOTAL | 100.1 | 100.4 |

| % | SK/RB/05GY Grey Tuff | SK/RB/05GY Amphibolite facies |
|---|---|---|
| Quartz | 41.9 | 41.9 |
| Muscovite | – | 8.5 |
| Calcite | 18.9 | 16.4 |
| Albite | 15.5 | 13.5 |
| Anorthite | 4.8 | 5.2 |
| K-feldspars | 6.2 | 9.0 |
| Chlorite | 9.4 | 1.3 |
| Zoisite | 0.7 | – |
| Epidote | 1.6 | 0.8 |
| Almandine | 1.0 | – |
| Grossular | – | 1.8 |
| TOTAL | 100.0 | 98.4 |

The products were examined by X-ray Diffraction (XRD) to ascertain their mineralogical composition and the data were compared with the composition of the original material. The data are presented in Table 2. The output from XRD was re-calculated using Rietveld software. This software does not select minerals arbitrarily, so an estimate of likely phases has to be input manually. The main points to note are that Ca–plagioclase increases, chlorite decreases, zoisite falls and grossular garnet appears, the latter mineral being a key component of calc-silicate rocks. While not shown, amphibole grows at the expense of chlorite.

## 3. Geochemistry

Geochemical data for calc-silicates are presented in Table 3. The range for $SiO_2$ is 47.4–76.8 %, with an average value of 63.9 % (mean of 58). The first point to note is these new data (Averages 5–11) compare favourably with published data (Averages 1–4) and the grey tuffs, as displayed in Figure 3. Also worthy of note is how the data for the host metasediments differ from the calc-silicate chemistry, with the exception of $Fe_2O_3/MgO$. Values for Zr in the dataset reach 800 ppm (Table 3). Some epidotic calc-silicates from the Moine

**Table 3a** Geochemical data for a suite of calc-silicate rocks from Morar.

| % | TNRB077 | TNRB078 | TNRB079 | TNRB080 | TNRB081 | TNRB082 |
|---|---|---|---|---|---|---|
| $SiO_2$ | 56.78 | 47.42 | 61.38 | 48.51 | 51.93 | 53.66 |
| $TiO_2$ | 0.62 | 0.72 | 0.65 | 0.63 | 0.68 | 0.63 |
| $Al_2O_3$ | 18.88 | 13.54 | 18.67 | 13.03 | 13.30 | 15.57 |
| $Fe_2O_3$ | 5.16 | 4.21 | 4.69 | 4.37 | 4.23 | 4.31 |
| MnO | 0.34 | 0.36 | 0.40 | 0.40 | 0.45 | 0.40 |
| MgO | 1.17 | 1.09 | 0.92 | 1.15 | 0.87 | 0.98 |
| CaO | 9.24 | 20.24 | 6.45 | 20.37 | 17.33 | 14.26 |
| $Na_2O$ | 3.56 | 1.25 | 4.37 | 1.05 | 1.49 | 2.42 |
| $K_2O$ | 1.05 | 0.15 | 0.85 | 0.17 | 0.41 | 0.65 |
| $P_2O_5$ | 0.45 | 0.35 | 0.58 | 0.24 | 0.45 | 0.46 |
| LOI | 1.8 | 10.3 | 0.4 | 10.6 | 8.5 | 5.9 |
| TOTAL | 99.05 | 99.59 | 99.36 | 100.56 | 99.61 | 99.21 |
| **ppm** | | | | | | |
| V | 64 | 66 | 69 | 55 | 63 | 62 |
| Cr | 49 | 53 | 42 | 49 | 44 | 43 |
| Ni | 15 | 19 | 16 | 22 | 16 | 16 |
| Rb | 39 | 2 | 34 | 3 | 12 | 19 |
| Sr | 356 | 450 | 334 | 438 | 432 | 380 |
| Y | 35 | 35 | 42 | 31 | 49 | 36 |
| Zr | 133 | 504 | 162 | 238 | 448 | 203 |
| Nb | 14 | 18 | 21 | 12 | 16 | 18 |
| Ba | 182 | 43 | 158 | 47 | 124 | 102 |
| La | 42 | 71 | 38 | 49 | 70 | 44 |
| Ce | 90 | 148 | 78 | 105 | 143 | 92 |
| Nd | 40 | 71 | 38 | 48 | 66 | 40 |
| Th | 5 | 10 | 6 | 7 | 11 | 6 |

| % | TNRB083 | TNRB084 | TNRB085 | TNRB086 | TNRB083A Metasediment | TNRB086A Metasediment |
|---|---|---|---|---|---|---|
| $SiO_2$ | 60.99 | 58.50 | 53.66 | 61.96 | 61.30 | 59.76 |
| $TiO_2$ | 0.66 | 0.76 | 0.63 | 0.57 | 0.87 | 1.14 |
| $Al_2O_3$ | 15.33 | 17.03 | 16.91 | 14.60 | 16.11 | 16.93 |
| $Fe_2O_3$ | 3.58 | 4.68 | 3.88 | 3.59 | 6.12 | 7.38 |
| MnO | 0.30 | 0.35 | 0.43 | 0.36 | 0.07 | 0.04 |
| MgO | 0.98 | 0.93 | 0.82 | 0.96 | 2.13 | 2.68 |
| CaO | 10.46 | 10.69 | 13.32 | 10.37 | 2.97 | 4.62 |
| $Na_2O$ | 2.20 | 2.42 | 2.87 | 2.48 | 2.54 | 3.56 |
| $K_2O$ | 0.58 | 0.71 | 0.78 | 0.71 | 3.37 | 2.26 |
| $P_2O_5$ | 1.14 | 0.57 | 0.51 | 1.80 | 1.27 | 0.16 |
| LOI | 2.0 | 2.7 | 5.8 | 2.1 | 1.7 | 1.2 |
| TOTAL | 98.22 | 99.37 | 99.62 | 99.53 | 98.40 | 99.73 |
| **ppm** | | | | | | |
| V | 79 | 74 | 66 | 81 | 121 | |
| Cr | 40 | 51 | 43 | 41 | 74 | |
| Ni | 17 | 18 | 17 | 16 | 30 | |
| Rb | 20 | 28 | 32 | 31 | 117 | |
| Sr | 341 | 387 | 366 | 324 | 291 | |
| Y | 52 | 46 | 41 | 62 | 50 | |
| Zr | 144 | 233 | 153 | 158 | 206 | |
| Nb | 21 | 32 | 22 | 22 | 16 | |
| Ba | 87 | 121 | 146 | 139 | 935 | |
| La | 49 | 50 | 34 | 51 | 66 | |
| Ce | 96 | 98 | 70 | 99 | 126 | |
| Nd | 46 | 47 | 31 | 52 | 61 | |
| Th | 8 | 8 | 4 | 8 | 10 | |

Supergroup (Winchester 1975) also have values of Zr considered high for sedimentary rocks (400–700 ppm). These high levels of Zr were attributed by Winchester (1975) to the presence of heavy mineral bands.

Trace element data for each sampled area were averaged to generate a mean value for each group, in order to simplify the diagram (the number of samples are shown in parentheses). These mean data, together with three Proterozoic tuffs (Batchelor 2005, 2011; Batchelor *et al.* 2008), were normalised to a host Moine metasediment (TN/RB/083A from Morar) (Fig. 4). The diagram suggests the calc-silicate rock suites differ sufficiently from the metasediment to justify further investigation into their origin.

In order to discriminate between an igneous or a clastic origin, recourse was made to the use of geochemical discrimination diagrams for amphibolites. Winchester (1984) was able to distinguish between orthoamphibolites (igneous) and para-amphibolites (sedimentary) using $TiO_2$ *vs* Ni (Fig. 5a) and Ni

**Table 3b** Geochemical data for a suite of calc-silicate rocks from Mallaig.

| % | CSRB006 | CSRB005 | CSRB001 | CSRB002 | CSRB003 | CSRB004 |
|---|---|---|---|---|---|---|
| $SiO_2$ | 65.00 | 60.33 | 60.16 | 63.98 | 58.14 | 62.03 |
| $TiO_2$ | 0.63 | 0.81 | 0.85 | 0.70 | 0.82 | 1.12 |
| $Al_2O_3$ | 15.00 | 18.53 | 18.59 | 17.61 | 18.80 | 16.83 |
| $Fe_2O_3$ | 2.80 | 5.51 | 5.69 | 5.39 | 6.36 | 5.71 |
| MnO | 0.24 | 0.34 | 0.33 | 0.32 | 0.34 | 0.31 |
| MgO | 0.80 | 1.40 | 1.32 | 1.24 | 1.58 | 1.38 |
| CaO | 8.73 | 7.13 | 6.91 | 4.50 | 8.38 | 7.11 |
| $Na_2O$ | 2.39 | 3.45 | 3.60 | 4.48 | 2.94 | 2.66 |
| $K_2O$ | 0.90 | 1.07 | 1.08 | 0.99 | 0.90 | 1.05 |
| $P_2O_5$ | 0.18 | 0.65 | 0.60 | 0.26 | 0.59 | 0.57 |
| LOI | 3.2 | 0.7 | 0.7 | 0.4 | 1.0 | 1.1 |
| TOTAL | 99.87 | 99.92 | 99.83 | 99.87 | 99.85 | 99.87 |
| **ppm** | | | | | | |
| V | 51 | 70 | 68 | 56 | 95 | 77 |
| Cr | 34 | 47 | 47 | 40 | 54 | 54 |
| Ni | 10 | 19 | 21 | 19 | 24 | 19 |
| Rb | 39 | 47 | 47 | 46 | 33 | 54 |
| Sr | 379 | 425 | 407 | 440 | 389 | 372 |
| Y | 35 | 52 | 57 | 47 | 49 | 64 |
| Zr | 288 | 266 | 287 | 229 | 289 | 613 |
| Nb | 12 | 12 | 12 | 6 | 10 | 17 |
| Ba | 175 | 205 | 282 | 222 | 101 | 237 |
| La | 46 | 58 | 59 | 47 | 70 | 91 |
| Ce | 84 | 102 | 109 | 93 | 121 | 160 |
| Nd | 35 | 58 | 54 | 46 | 63 | 85 |
| Th | 9 | 9 | 11 | 10 | 10 | 20 |

**Table 3c** Geochemical data for a suite of calc-silicate rocks from Arisaig.

| % | CSRB007 | CSRB008 | CSRB009 | CSRB010 | CSRB011 | CSRB012 |
|---|---|---|---|---|---|---|
| $SiO_2$ | 70.99 | 66.30 | 73.81 | 68.27 | 58.41 | 67.67 |
| $TiO_2$ | 0.33 | 0.46 | 0.24 | 0.19 | 0.86 | 0.26 |
| $Al_2O_3$ | 13.47 | 14.23 | 9.62 | 8.66 | 18.93 | 7.89 |
| $Fe_2O_3$ | 1.80 | 1.99 | 1.28 | 1.29 | 3.50 | 1.49 |
| MnO | 0.27 | 0.28 | 0.18 | 0.24 | 0.44 | 0.28 |
| MgO | 0.36 | 0.41 | 0.41 | 0.37 | 0.76 | 0.39 |
| CaO | 5.45 | 7.51 | 7.22 | 11.09 | 8.58 | 12.04 |
| $Na_2O$ | 3.87 | 4.18 | 2.50 | 1.89 | 4.65 | 1.67 |
| $K_2O$ | 0.79 | 0.64 | 0.43 | 0.34 | 0.89 | 0.31 |
| $P_2O_5$ | 0.27 | 0.54 | 0.15 | 0.14 | 0.75 | 0.18 |
| LOI | 2.3 | 3.3 | 4.0 | 7.4 | 2.1 | 7.7 |
| TOTAL | 99.90 | 99.84 | 99.84 | 99.88 | 99.87 | 99.88 |
| **ppm** | | | | | | |
| V | 9 | 21 | 27 | 17 | 45 | 23 |
| Cr | 9 | 15 | 15 | 10 | 34 | 16 |
| Ni | 2 | 4 | 3 | 2 | 9 | 2 |
| Rb | 34 | 20 | 17 | 13 | 35 | 11 |
| Sr | 362 | 353 | 228 | 264 | 384 | 270 |
| Y | 25 | 20 | 22 | 15 | 40 | 22 |
| Zr | 156 | 221 | 114 | 104 | 306 | 154 |
| Nb | 8 | 14 | 6 | 5 | 23 | 5 |
| Ba | 262 | 158 | 138 | 71 | 231 | 71 |
| La | 15 | 22 | 18 | 18 | 35 | 32 |
| Ce | 36 | 47 | 36 | 38 | 70 | 60 |
| Nd | 5 | 14 | 17 | 11 | 30 | 28 |
| Th | 3 | 6 | 5 | 4 | 7 | 7 |

| % | CSRB013 | CSRB014 | CSRB015 | CSRB016 | CSRB017 |
|---|---|---|---|---|---|
| $SiO_2$ | 67.70 | 59.91 | 60.53 | 58.60 | 62.56 |
| $TiO_2$ | 0.25 | 0.44 | 0.45 | 1.39 | 0.50 |
| $Al_2O_3$ | 15.25 | 12.66 | 18.01 | 17.74 | 18.07 |
| $Fe_2O_3$ | 2.08 | 3.27 | 2.48 | 4.28 | 3.20 |
| MnO | 0.31 | 0.38 | 0.30 | 0.35 | 0.30 |
| MgO | 0.63 | 1.05 | 0.59 | 1.02 | 0.81 |
| CaO | 7.29 | 12.39 | 11.39 | 10.17 | 7.97 |

**Table 3c** Continued

| % | CSRB013 | CSRB014 | CSRB015 | CSRB016 | CSRB017 |
|---|---|---|---|---|---|
| $Na_2O$ | 3.60 | 1.57 | 2.51 | 2.87 | 3.77 |
| $K_2O$ | 0.56 | 0.97 | 0.54 | 0.96 | 0.85 |
| $P_2O_5$ | 0.24 | 0.18 | 0.39 | 0.59 | 0.43 |
| LOI | 1.9 | 7.0 | 2.7 | 1.8 | 1.4 |
| TOTAL | 99.81 | 99.82 | 99.89 | 99.77 | 99.86 |
| **ppm** | | | | | |
| V | 26 | 46 | 44 | 78 | 42 |
| Cr | 13 | 24 | 27 | 48 | 28 |
| Ni | 3 | 11 | 5 | 13 | 10 |
| Rb | 23 | 36 | 16 | 36 | 31 |
| Sr | 235 | 249 | 367 | 398 | 383 |
| Y | 22 | 28 | 22 | 42 | 30 |
| Zr | 52 | 181 | 157 | 800 | 174 |
| Nb | 7 | 11 | 10 | 24 | 11 |
| Ba | 126 | 188 | 82 | 200 | 208 |
| La | 12 | 28 | 29 | 56 | 24 |
| Ce | 28 | 59 | 55 | 105 | 54 |
| Nd | 14 | 20 | 13 | 41 | 31 |
| Th | 3 | 7 | 5 | 15 | 6 |

**Table 3d** Geochemical data for a suite of calc-silicate rocks from Lochailort.

| % | CSRB019 | CSRB020 | TNRB073 | TNRB072 | CSRB018 | CSRB023 |
|---|---|---|---|---|---|---|
| $SiO_2$ | 70.85 | 73.15 | 61.33 | 67.94 | 59.08 | 75.24 |
| $TiO_2$ | 0.15 | 0.20 | 0.74 | 0.24 | 0.46 | 0.15 |
| $Al_2O_3$ | 15.89 | 14.70 | 18.93 | 16.68 | 21.36 | 13.70 |
| $Fe_2O_3$ | 1.32 | 1.22 | 3.03 | 1.72 | 2.66 | 0.99 |
| MnO | 0.03 | 0.03 | 0.24 | 0.17 | 0.30 | 0.16 |
| MgO | 0.50 | 0.38 | 0.93 | 0.46 | 0.68 | 0.21 |
| CaO | 3.18 | 3.78 | 8.80 | 7.03 | 7.48 | 4.50 |
| $Na_2O$ | 4.16 | 4.41 | 3.05 | 3.28 | 4.79 | 3.35 |
| $K_2O$ | 2.63 | 0.74 | 0.85 | 0.84 | 1.23 | 0.49 |
| $P_2O_5$ | 0.15 | 0.21 | 0.25 | 0.31 | 0.77 | 0.38 |
| LOI | 0.9 | 1.0 | 1.7 | 1.2 | 1.0 | 0.6 |
| TOTAL | 99.76 | 99.82 | 99.85 | 99.87 | 99.81 | 99.77 |
| **ppm** | | | | | | |
| V | 17 | 18 | 47 | 21 | 42 | 8 |
| Cr | 18 | 11 | 32 | 8 | 23 | 5 |
| Ni | <1 | <1 | 8 | <1 | 4 | <1 |
| Rb | 38 | 20 | 25 | 26 | 42 | 18 |
| Sr | 466 | 511 | 551 | 494 | 544 | 268 |
| Y | 9 | 8 | 16 | 9 | 24 | 15 |
| Zr | 53 | 80 | 271 | 59 | 134 | 50 |
| Nb | 2 | 3 | 11 | 3 | 13 | 7 |
| Ba | 1021 | 203 | 121 | 146 | 187 | 116 |
| La | 12 | 20 | 26 | 21 | 20 | 16 |
| Ce | 32 | 46 | 47 | 44 | 38 | 32 |
| Nd | 24 | 20 | 23 | 4 | 18 | 4 |
| Th | 1 | 2 | 5 | 2 | 3 | 2 |

| % | TNRB071 | TNRB070 | TNRB069 | CSRB021 | CSRB022 | CSRB024 |
|---|---|---|---|---|---|---|
| $SiO_2$ | 69.41 | 71.36 | 71.41 | 73.52 | 68.62 | 75.20 |
| $TiO_2$ | 0.38 | 0.24 | 0.57 | 0.14 | 0.40 | 0.40 |
| $Al_2O_3$ | 15.80 | 14.71 | 14.48 | 13.00 | 16.05 | 12.36 |
| $Fe_2O_3$ | 1.79 | 1.57 | 1.85 | 1.21 | 1.63 | 1.71 |
| MnO | 0.14 | 0.16 | 0.15 | 0.15 | 0.14 | 0.14 |
| MgO | 0.47 | 0.38 | 0.49 | 0.25 | 0.42 | 0.42 |
| CaO | 5.69 | 5.82 | 5.94 | 5.53 | 6.07 | 6.06 |
| $Na_2O$ | 3.34 | 2.46 | 2.43 | 2.41 | 3.07 | 1.73 |
| $K_2O$ | 0.81 | 1.14 | 0.90 | 1.54 | 1.74 | 0.65 |
| $P_2O_5$ | 0.40 | 0.46 | 0.25 | 0.44 | 0.26 | 0.17 |
| LOI | 1.6 | 1.6 | 1.4 | 1.6 | 1.4 | 1.0 |
| TOTAL | 99.83 | 99.9 | 99.87 | 99.79 | 99.8 | 99.84 |

**Table 3d** Continued

| ppm | | | | | | |
|---|---|---|---|---|---|---|
| V | 24 | 19 | 34 | 9 | 31 | 26 |
| Cr | 23 | 9 | 28 | 6 | 21 | 20 |
| Ni | 2 | <1 | <1 | <1 | <1 | <1 |
| Rb | 33 | 63 | 45 | 75 | 73 | 27 |
| Sr | 361 | 318 | 371 | 321 | 386 | 265 |
| Y | 20 | 17 | 20 | 14 | 20 | 16 |
| Zr | 147 | 71 | 308 | 53 | 161 | 176 |
| Nb | 9 | 10 | 14 | 5 | 15 | 11 |
| Ba | 119 | 124 | 286 | 168 | 278 | 122 |
| La | 31 | 21 | 45 | 16 | 31 | 46 |
| Ce | 57 | 44 | 85 | 33 | 61 | 84 |
| Nd | 23 | 20 | 31 | 4 | 23 | 28 |
| Th | 6 | 3 | 10 | 2 | 6 | 8 |

**Table 3e** Geochemical data for a suite of calc-silicate rocks from Ardalanish Bay, Mull.

| % | CS/RB/034 | CS/RB/035 | CS/RB/036 | CS/RB/037 | CS/RB/037A | CS/RB/038 Metasediment |
|---|---|---|---|---|---|---|
| $SiO_2$ | 63.51 | 64.99 | 64.73 | 62.93 | 65.12 | 65.44 |
| $TiO_2$ | 0.61 | 0.64 | 0.58 | 0.65 | 0.74 | 0.64 |
| $Al_2O_3$ | 16.89 | 15.91 | 16.11 | 17.12 | 16.34 | 15.64 |
| $Fe_2O_3$ | 3.77 | 4.17 | 2.69 | 4.28 | 5.12 | 4.53 |
| MnO | 0.12 | 0.08 | 0.09 | 0.14 | 0.04 | 0.11 |
| MgO | 0.80 | 1.14 | 1.03 | 1.13 | 1.85 | 1.36 |
| CaO | 9.07 | 6.85 | 9.74 | 8.33 | 3.79 | 6.10 |
| $Na_2O$ | 1.02 | 1.69 | 0.80 | 0.92 | 3.74 | 1.74 |
| $K_2O$ | 1.51 | 1.97 | 0.94 | 1.68 | 1.81 | 1.52 |
| $P_2O_5$ | 0.47 | 0.31 | 0.31 | 0.33 | 0.19 | 0.29 |
| LOI | 1.51 | 1.68 | 1.43 | 1.29 | 0.83 | 1.41 |
| TOTAL | 99.28 | 99.43 | 98.45 | 98.80 | 99.57 | 98.78 |
| **ppm** | | | | | | |
| V | 90 | 91 | 102 | 88 | 80 | 86 |
| Cr | 30 | 34 | 30 | 34 | 44 | 37 |
| Ni | 8 | 16 | 11 | 13 | 21 | 14 |
| Rb | 74 | 90 | 45 | 86 | 90 | 73 |
| Sr | 344 | 336 | 358 | 335 | 372 | 275 |
| Y | 34 | 35 | 32 | 40 | 28 | 36 |
| Zr | 182 | 193 | 166 | 198 | 189 | 183 |
| Nb | 16 | 16 | 13 | 16 | 14 | 14 |
| Ba | 151 | 239 | 102 | 179 | 307 | 127 |
| La | 35 | 37 | 35 | 37 | 44 | 40 |
| Ce | 80 | 84 | 76 | 83 | 95 | 84 |
| Nd | 25 | 30 | 29 | 36 | 37 | 28 |
| Th | 8 | 9 | 7 | 8 | 8 | 10 |

| % | CS/RB/039 | CS/RB/040 |
|---|---|---|
| $SiO_2$ | 63.45 | 61.22 |
| $TiO_2$ | 0.64 | 0.58 |
| $Al_2O_3$ | 16.36 | 14.63 |
| $Fe_2O_3$ | 3.89 | 3.95 |
| MnO | 0.13 | 0.12 |
| MgO | 1.13 | 1.09 |
| CaO | 10.96 | 11.65 |
| $Na_2O$ | 0.43 | 0.82 |
| $K_2O$ | 0.77 | 0.98 |
| $P_2O_5$ | 0.27 | 1.59 |
| LOI | 1.35 | 2.05 |
| TOTAL | 99.38 | 98.68 |

**Table 3e** Continued

| ppm | | |
|---|---|---|
| V | 84 | 85 |
| Cr | 37 | 28 |
| Ni | 12 | 10 |
| Rb | 42 | 51 |
| Sr | 383 | 383 |
| Y | 34 | 38 |
| Zr | 244 | 236 |
| Nb | 15 | 16 |
| Ba | 67 | 108 |
| La | 41 | 40 |
| Ce | 88 | 86 |
| Nd | 34 | 27 |
| Th | 9 | 9 |

**Table 3f** Geochemical data for a suite of calc-silicate rocks from Uisken Bay, Mull.

| % | CS/RB/044 | CS/RB/046 | CS/RB/047 | CS/RB/048 | CS/RB/049 |
|---|---|---|---|---|---|
| $SiO_2$ | 67.23 | 76.67 | 63.11 | 70.49 | 76.80 |
| $TiO_2$ | 0.64 | 0.50 | 0.68 | 0.46 | 0.39 |
| $Al_2O_3$ | 13.39 | 10.73 | 16.52 | 13.68 | 10.57 |
| $Fe_2O_3$ | 3.26 | 2.93 | 4.85 | 3.24 | 2.40 |
| MnO | 0.13 | 0.05 | 0.15 | 0.08 | 0.06 |
| MgO | 0.69 | 0.55 | 0.98 | 0.79 | 0.63 |
| CaO | 10.66 | 4.27 | 7.94 | 5.44 | 5.22 |
| $Na_2O$ | 0.20 | 1.64 | 1.25 | 1.49 | 0.36 |
| $K_2O$ | 0.31 | 0.34 | 1.07 | 1.05 | 0.67 |
| $P_2O_5$ | 0.27 | 0.12 | 0.24 | 0.18 | 0.16 |
| LOI | 2.55 | 1.15 | 2.17 | 2.08 | 1.98 |
| TOTAL | 99.33 | 98.95 | 98.96 | 98.98 | 99.24 |
| **ppm** | | | | | |
| V | 70 | 54 | 87 | 67 | 50 |
| Cr | 30 | 24 | 38 | 22 | 23 |
| Ni | 7 | 6 | 20 | 7 | 3 |
| Rb | 16 | 18 | 55 | 45 | 28 |
| Sr | 306 | 285 | 313 | 230 | 159 |
| Y | 44 | 20 | 42 | 32 | 23 |
| Zr | 330 | 247 | 181 | 162 | 149 |
| Nb | 12 | 11 | 13 | 11 | 9 |
| Ba | 45 | 148 | 117 | 136 | 74 |
| La | 51 | 34 | 38 | 30 | 25 |
| Ce | 104 | 75 | 87 | 68 | 55 |
| Nd | 35 | 25 | 32 | 23 | 19 |
| Th | 10 | 8 | 10 | 7 | 6 |

**Table 3g** Geochemical data for a suite of calc-silicate rocks from Cannich.

| % | CS/RB/050 | CS/RB/051 | CS/RB/052 | CS/RB/053 | CS/RB/054 | CS/RB/055 |
|---|---|---|---|---|---|---|
| $SiO_2$ | 60.82 | 71.89 | 70.31 | 73.73 | 74.96 | 70.65 |
| $TiO_2$ | 0.14 | 0.32 | 0.42 | 0.27 | 0.27 | 0.60 |
| $Al_2O_3$ | 9.28 | 11.54 | 12.05 | 12.86 | 12.23 | 13.23 |
| $Fe_2O_3$ | 1.35 | 2.30 | 1.87 | 2.37 | 2.27 | 1.98 |
| MnO | 0.14 | 0.10 | 0.10 | 0.06 | 0.07 | 0.10 |
| MgO | 0.19 | 0.17 | 0.47 | 0.66 | 0.56 | 0.55 |
| CaO | 18.13 | 10.38 | 8.48 | 4.99 | 4.15 | 8.33 |
| $Na_2O$ | <0.05 | 0.14 | 1.38 | 2.16 | 2.77 | 1.30 |
| $K_2O$ | 0.06 | 0.17 | 0.69 | 0.97 | 0.97 | 0.25 |
| $P_2O_5$ | 0.04 | 0.11 | 0.11 | 0.12 | 0.14 | 0.13 |
| LOI | 9.49 | 2.07 | 3.12 | 0.96 | 0.90 | 1.68 |
| TOTAL | 99.69 | 99.19 | 99.00 | 99.15 | 99.29 | 98.80 |

**Table 3g** Continued

| **ppm** | | | | | | |
|---|---|---|---|---|---|---|
| V | 16 | 34 | 29 | 17 | 29 | 42 |
| Cr | 8 | 13 | 16 | 12 | 12 | 20 |
| Ni | 2 | 2 | 2 | 3 | 3 | 3 |
| Rb | 9 | 14 | 62 | 59 | 57 | 15 |
| Sr | 223 | 193 | 195 | 124 | 164 | 147 |
| Y | 25 | 40 | 40 | 33 | 43 | 56 |
| Zr | 69 | 172 | 248 | 135 | 122 | 426 |
| Nb | 5 | 8 | 11 | 10 | 10 | 19 |
| Ba | 9 | 25 | 94 | 172 | 154 | 52 |
| La | 21 | 36 | 29 | 18 | 29 | 44 |
| Ce | 55 | 88 | 78 | 46 | 62 | 107 |
| Nd | 12 | 21 | 28 | 15 | 25 | 36 |
| Th | 3 | 6 | 7 | 3 | 4 | 9 |
| % | **CS/RB/056** | | | | | |
| $SiO_2$ | 70.97 | | | | | |
| $TiO_2$ | 0.18 | | | | | |
| $Al_2O_3$ | 12.04 | | | | | |
| $Fe_2O_3$ | 0.94 | | | | | |
| MnO | 0.08 | | | | | |
| MgO | 0.20 | | | | | |
| CaO | 8.58 | | | | | |
| $Na_2O$ | 2.11 | | | | | |
| $K_2O$ | 0.59 | | | | | |
| $P_2O_5$ | 0.07 | | | | | |
| LOI | 3.54 | | | | | |
| TOTAL | 99.30 | | | | | |
| **ppm** | | | | | | |
| V | 13 | | | | | |
| Cr | 10 | | | | | |
| Ni | 3 | | | | | |
| Rb | 38 | | | | | |
| Sr | 206 | | | | | |
| Y | 28 | | | | | |
| Zr | 63 | | | | | |
| Nb | 7 | | | | | |
| Ba | 96 | | | | | |
| La | 21 | | | | | |
| Ce | 62 | | | | | |
| Nd | 12 | | | | | |
| Th | 3 | | | | | |

vs Zr/$TiO_2$ (Fig. 5b). The three grey tuffs and most of the Moine calc-silicates plot in the igneous field.

In order to assess how coherent or otherwise are the compositions of the separate calc-silicate rock assemblages, a Zr/Nb–Ti/Th plot was used (Fig. 6), where Zr/Nb reflects alkalinity and Ti/Th reflects magmatic fractionation. These elements were selected by the author as an alternative to the Zr/$TiO_2$–Nb/Y discrimination diagram of Winchester & Floyd (1977), when it was reported that Y can become mobile in altered rocks (Hill *et al.* 2000). Calc-silicate rocks compositions stretch across the dacite–andesite–alklaine potassic fields. This is in keeping with the major element compositions which range from 47 % $SiO_2$ to 77 % $SiO_2$. This diagram helps to discriminate between the Mallaig, Morar and Ardalanish (Mull) groups which form distinct domains. The Lochailort suite shows a bimodal distribution, with the five samples with higher Ti/Th (less evolved) representing the youngest five samples in the sequence. Two of the five Uisken (Mull) samples (047, 048) overlap with Ardalanish (Mull) sample 040, the oldest of that group, whilst Uisken 044 has an affinity with the Mallaig/Morar samples. The Arisaig group shows a wide scatter. The Morar set have a distinct alkaline affinity, with three exceptions (078, 081, 080), which plot with the Mallaig set, a group which has a more calc-alkaline nature. The Ardalanish samples display a more transitional character. The dotted line, which defines the oval ring in this diagram, represents the compositional field of Dalradian tuffs (Batchelor 2004a, b) and Torridonian tuffs (Batchelor 2005, 2011).

A subset of samples from each group was analysed by ICP–MS for the rare earth element (REE) content and these data are presented in Table 4. A chondrite-normalised REE spider diagram (Fig. 7) for all samples shows light REE (LREE) enrichment for most samples and modest negative Eu anomalies. The exceptions are the two Lochailort samples (CS/RB/019, 020) – the two lowermost dotted lines – which uniquely display a positive Eu anomaly and a strong heavy REE (HREE) depletion relative to the rest of the samples. This latter feature could reflect an augmented concentration of plagioclase, perhaps from a feldsparphyric source.

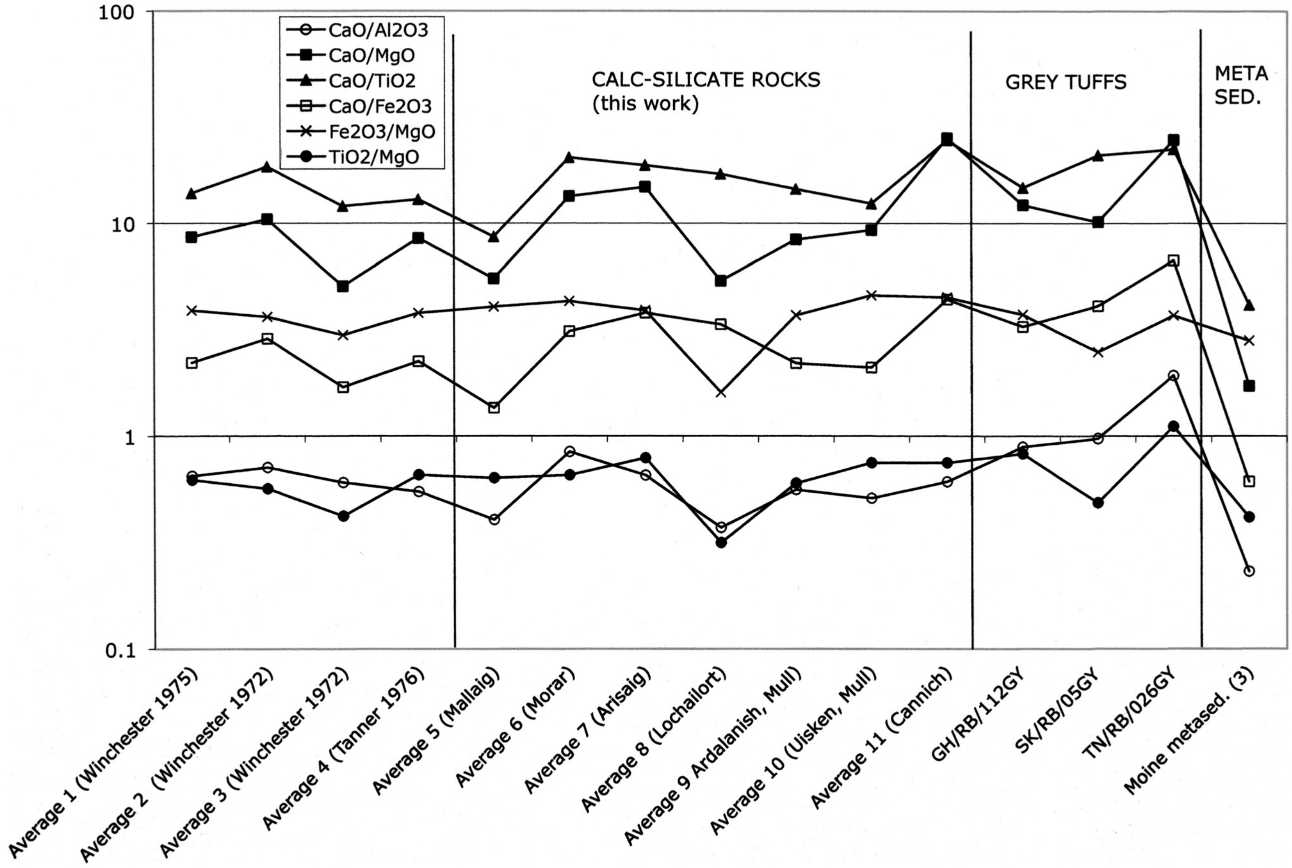

**Figure 3** Oxide ratios of data from published calc-silicate rocks and data from this work, Proterozoic tuffs and Moine metasediments.

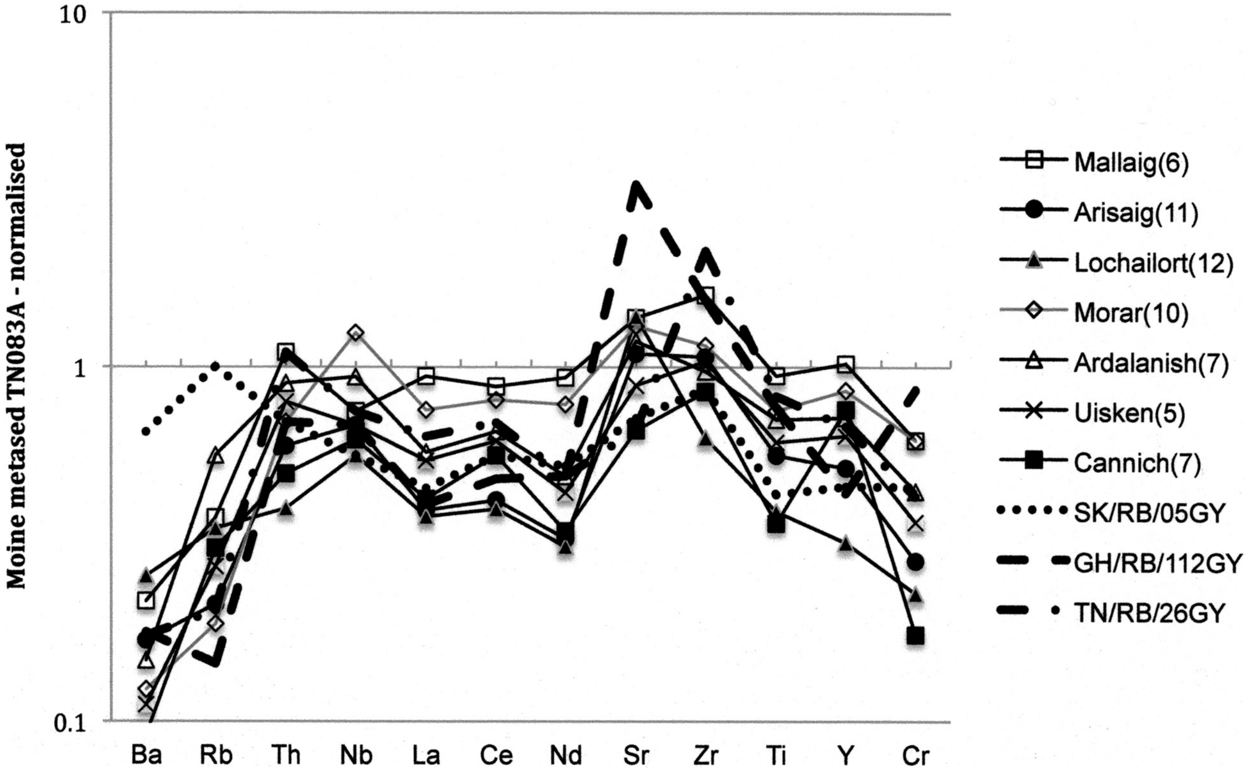

**Figure 4** Calc-silicate rock groups (mean of n samples) and Proterozoic tuffs, normalised to a host Moine metasediment (semi-pelite).

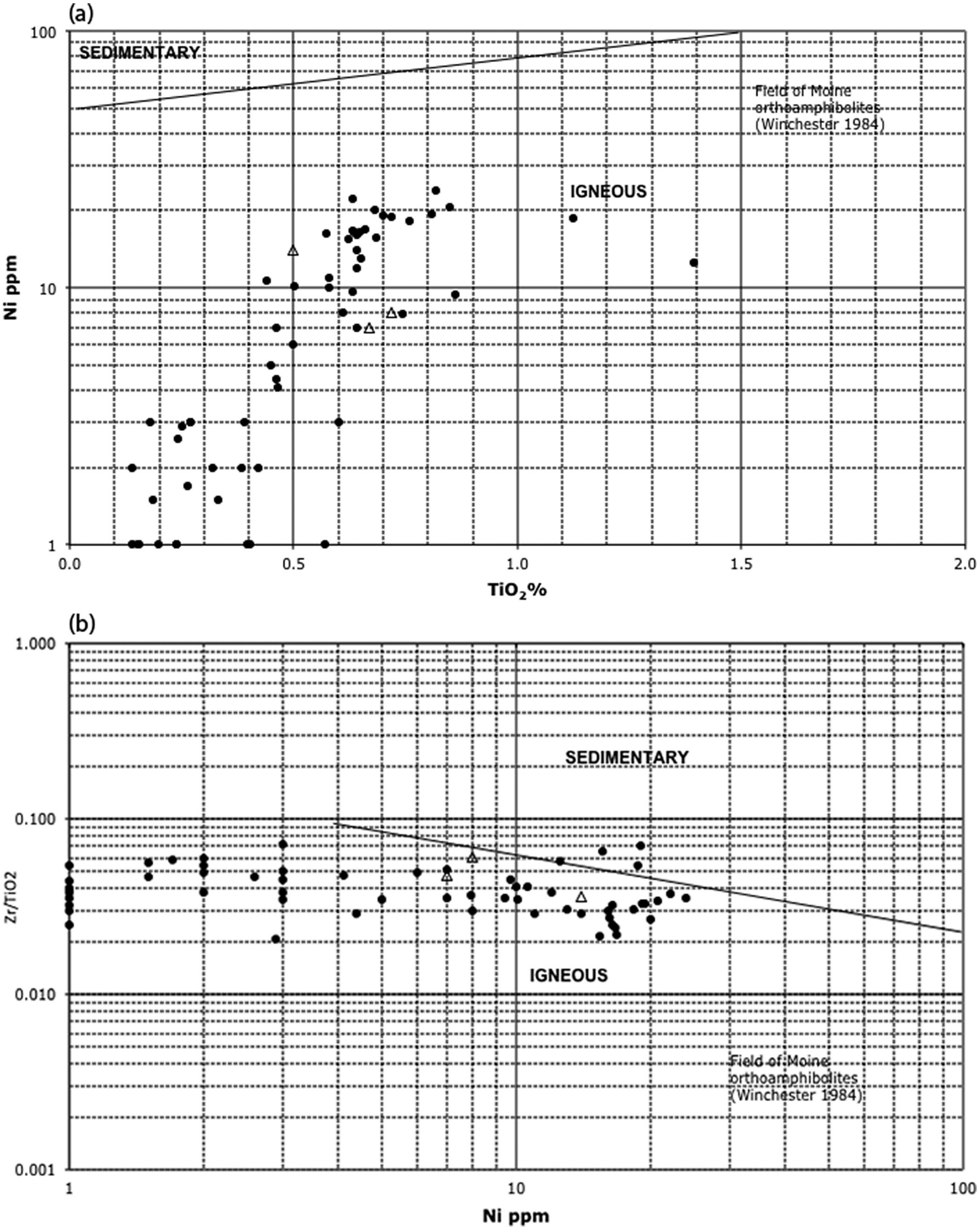

**Figure 5** (a) Bivariate plot of $TiO_2$ *vs*. Ni for all calc-silicate rocks. Open triangles represent grey tuffs. Sedimentary-igneous boundary after Winchester (1984). (b) Bivariate plot of Ni *vs.* $Zr/TiO_2$ for all calc-silicate rocks. Open triangles represent grey tuffs. Sedimentary–igneous boundary after Winchester (1984).

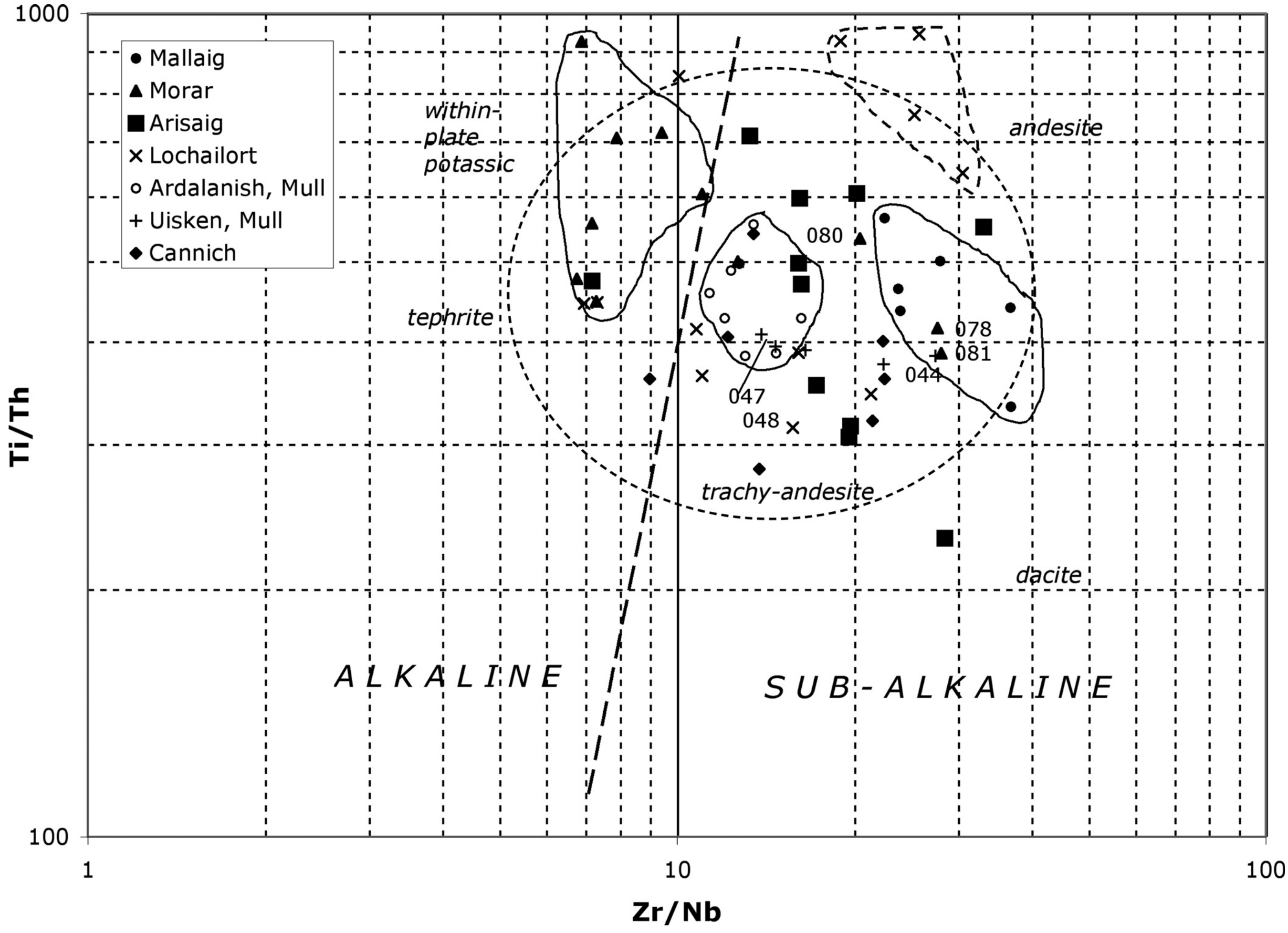

**Figure 6** Bivariate plot of Zr/Nb *vs.* Ti/Th. Volcanic rock fields data from Wilson (1989). Superimposed (dotted oval) represents the field of Dalradian tuffs (Batchelor 2004a, b) and Torridonian tuffs (Batchelor 2005, 2011).

## 4. Discussion

The recent identification in Scottish Meso- to Neo-proterozoic rocks of a grey lithology comprising albite, quartz, chlorite and calcite (with minor muscovite) as metamorphosed tuffs of an intermediate composition (Batchelor *et al.* 2008; Batchelor 2011) led to the speculation that they could be the precusors of calc-silicate rocks after higher grade metamorphism. Intriguingly, Kennedy (1949) predicted this possibility when he surmised that quartz–albite–chlorite–calcite rocks in the Sleat Group of the Torridonian Supergroup on the Isle of Skye could be precursors of Moine calc-silicate rocks, a statement which simultaneously explained the origin of calc-silicate rocks but also implied an age equivalence between Torridonian and Moine successions; an idea first controversially proposed by Ben Peach in Peach *et al.* (1907), but recently resurrected by Krabbendam *et al.* (2008).

Calc-silicate rock comprises plag + actin + gross gt + qtz ± cc (± epid ± zo). Epidote and zoisite are intermediate phases. Metamorphic mineral pathways from low-grade (prehnite–pumpellyite) metamorphism of three protolith assemblages to (indicated ≫) amphibolite facies assemblages are listed here:

ANDESITE: alb + cc + musc + chl + qtz ≫ plag (olig) + actin + gt + qtz + musc

GREY TUFF: alb + qtz + chl + cc + musc ≫ plag + actin + qtz + gross gt + musc

PELITE: chl + musc + qtz ± alb ± cc ≫ andal ± cord + bi + qtz + alm gt + plag

Clearly, andesite will generate a metamorphic assemblage similar to a grey tuff and calc-silicate rock, whereas a pelite will not. A lime-rich pelite (or marl) could generate a similar assemblage to andesite, depending on the relative amount of calcium and magnesium.

The similarities in bulk geochemical composition and field relationships between calc-silicates and the "grey beds" (tuffs) are suggestive of air-fall tuffs. The relatively high levels of plagioclase feldspar (20–30 %) also support an igneous protolith. This pre-supposes that the metamorphic reaction would be essentially a closed system, although Na and K can be lost (Tanner & Miller 1980). The tholeiitic character of the calc-silicate samples described here is clear as in all cases $Fe_2O_3$/MgO ≫1 (Fig. 2). The LREE enrichment (Fig. 7) is also characteristic of continental tholeiitic sequences (Wilson 1989). This is consistent with magmatism within an extensional tectonic environment, an environment known to have existed off the eastern margin of Laurentia during late-Mesoproterozoic and early-Neoproterozoic times (Cawood *et al.* 2004). Though 100 Myr older, the Keenawanan province is an example of a large flood tholeiitic basalt event *c.*1.1 Ga (van Schmus *et al.* 1990). The lithologies range from tholeiitic basalt to weakly alkaline basalt through to Fe-andesites and rhyolites. This range of lithologies encompass the $SiO_2$ ranges mentioned earlier (average value 63.9 %), which implies an intermediate igneous composition. The proposal that calc-silicate rocks originally formed as tuffs would imply an explosive regime fed by tholeiitic andesitic to dacitic magmas.

**Table 4** REE for selected calc-silicate rocks.

| | Mallaig CS/RB/004 | Mallaig CS/RB/006 | Arisaig CS/RB/007 | Arisaig CS/RB/008 | Arisaig CS/RB/009 | Arisaig CS/RB/010 |
|---|---|---|---|---|---|---|
| La | 80.4 | 41.4 | 17.6 | 21.6 | 24.0 | 17.4 |
| Ce | 133 | 77 | 35 | 42 | 47 | 34 |
| Pr | 19.9 | 9.7 | 3.8 | 5.0 | 5.3 | 3.6 |
| Nd | 76 | 36 | 15 | 18 | 19 | 14 |
| Sm | 13.3 | 6.4 | 2.7 | 3.2 | 3.1 | 2.4 |
| Eu | 2.90 | 1.70 | 1.01 | 1.13 | 0.79 | 0.67 |
| Gd | 11.4 | 5.6 | 2.5 | 2.9 | 2.7 | 1.9 |
| Tb | 1.67 | 0.87 | 0.40 | 0.47 | 0.43 | 0.33 |
| Dy | 10.00 | 5.42 | 3.11 | 3.11 | 3.02 | 2.12 |
| Ho | 2.06 | 1.10 | 0.76 | 0.59 | 0.68 | 0.46 |
| Er | 5.95 | 3.47 | 2.70 | 1.93 | 2.33 | 1.56 |
| Tm | 0.87 | 0.51 | 0.46 | 0.30 | 0.39 | 0.26 |
| Yb | 5.83 | 3.50 | 3.65 | 1.93 | 3.04 | 1.89 |
| Lu | 0.87 | 0.52 | 0.56 | 0.33 | 0.48 | 0.27 |
| ∑REE | 357 | 193 | 89 | 102 | 112 | 81 |

| | Arisaig CS/RB/011 | Arisaig CS/RB/012 | Arisaig CS/RB/013 | Arisaig CS/RB/014 | Arisaig CS/RB/015 | Arisaig CS/RB/016 |
|---|---|---|---|---|---|---|
| La | 31.7 | 26.7 | 11.8 | 25.3 | 24.1 | 46.5 |
| Ce | 62 | 53 | 23 | 50 | 44 | 93 |
| Pr | 7.7 | 5.6 | 2.9 | 6.0 | 5.6 | 11.4 |
| Nd | 30 | 20 | 10 | 23 | 22 | 42 |
| Sm | 5.7 | 3.7 | 2.2 | 4.5 | 4.0 | 7.9 |
| Eu | 1.74 | 0.82 | 0.71 | 0.96 | 1.42 | 2.15 |
| Gd | 4.8 | 3.0 | 2.1 | 3.6 | 3.5 | 6.8 |
| Tb | 0.83 | 0.50 | 0.40 | 0.57 | 0.51 | 1.04 |
| Dy | 5.64 | 3.01 | 2.69 | 3.76 | 3.33 | 6.49 |
| Ho | 1.23 | 0.64 | 0.64 | 0.86 | 0.68 | 1.36 |
| Er | 4.26 | 2.11 | 2.16 | 2.73 | 2.07 | 4.12 |
| Tm | 0.71 | 0.31 | 0.34 | 0.44 | 0.31 | 0.58 |
| Yb | 5.19 | 2.26 | 2.30 | 3.19 | 2.04 | 3.86 |
| Lu | 0.77 | 0.34 | 0.33 | 0.47 | 0.30 | 0.61 |
| ∑REE | 162 | 122 | 62 | 125 | 114 | 228 |

| | Arisaig CS/RB/017 | Lochailort CS/RB/019 | Lochailort CS/RB/020 | Ardalanish CS/RB/034 |
|---|---|---|---|---|
| La | 23.5 | 17.9 | 19.2 | 37.2 |
| Ce | 46 | 33 | 39 | 68 |
| Pr | 5.9 | 3.7 | 3.7 | 8.9 |
| Nd | 22 | 13 | 14 | 34 |
| Sm | 4.2 | 2.5 | 2.5 | 6.5 |
| Eu | 1.47 | 1.55 | 1.23 | 2.14 |
| Gd | 4.0 | 2.0 | 1.7 | 5.7 |
| Tb | 0.65 | 0.28 | 0.26 | 0.92 |
| Dy | 4.34 | 1.46 | 1.38 | 5.62 |
| Ho | 0.92 | 0.30 | 0.27 | 1.13 |
| Er | 2.86 | 0.77 | 0.82 | 3.23 |
| Tm | 0.42 | 0.10 | 0.12 | 0.46 |
| Yb | 2.96 | 0.71 | 0.88 | 3.14 |
| Lu | 0.45 | 0.11 | 0.12 | 0.47 |
| ∑REE | 120 | 77 | 85 | 177 |

| | Ardalanish Mull CS/RB/040 | Uisken, Mull CS/RB/044 | Uisken, Mull CS/RB/049 | Cannich CS/RB/051 | Cannich CS/RB/055 |
|---|---|---|---|---|---|
| La | 37.4 | 47.1 | 24.1 | 33.4 | 43.9 |
| Ce | 70 | 86 | 46 | 73 | 97 |
| Pr | 9.1 | 10.7 | 6.0 | 7.9 | 11.5 |
| Nd | 35 | 40 | 22 | 29 | 44 |
| Sm | 6.4 | 7.7 | 4.5 | 5.9 | 9.3 |
| Eu | 1.58 | 2.25 | 1.23 | 1.54 | 1.86 |
| Gd | 5.8 | 7.0 | 3.8 | 6.0 | 9.0 |
| Tb | 0.91 | 1.10 | 0.62 | 0.96 | 1.47 |
| Dy | 5.66 | 7.02 | 4.01 | 6.23 | 9.23 |
| Ho | 1.20 | 1.47 | 0.78 | 1.30 | 1.86 |
| Er | 3.57 | 4.52 | 2.29 | 3.59 | 5.35 |
| Tm | 0.50 | 0.68 | 0.34 | 0.52 | 0.82 |
| Yb | 3.41 | 4.47 | 2.29 | 3.48 | 5.36 |
| Lu | 0.52 | 0.67 | 0.33 | 0.46 | 0.78 |
| ∑REE | 181 | 221 | 118 | 173 | 241 |

**Table 4** Continued

| | Morar TN/RB/078 | Morar TN/RB/081 | Morar TN/RB/083 |
|---|---|---|---|
| La | 44.3 | 45.3 | 47.2 |
| Ce | 93 | 93 | 96 |
| Pr | 11.3 | 11.1 | 11.7 |
| Nd | 44 | 45 | 50 |
| Sm | 7.9 | 8.1 | 9.5 |
| Eu | 1.75 | 2.26 | 1.99 |
| Gd | 6.5 | 7.4 | 9.7 |
| Tb | 0.95 | 1.08 | 1.41 |
| Dy | 5.73 | 6.79 | 8.73 |
| Ho | 1.12 | 1.40 | 1.78 |
| Er | 3.29 | 4.17 | 5.13 |
| Tm | 0.48 | 0.60 | 0.74 |
| Yb | 3.25 | 4.27 | 5.31 |
| Lu | 0.52 | 0.67 | 0.84 |
| ∑REE | 225 | 231 | 250 |

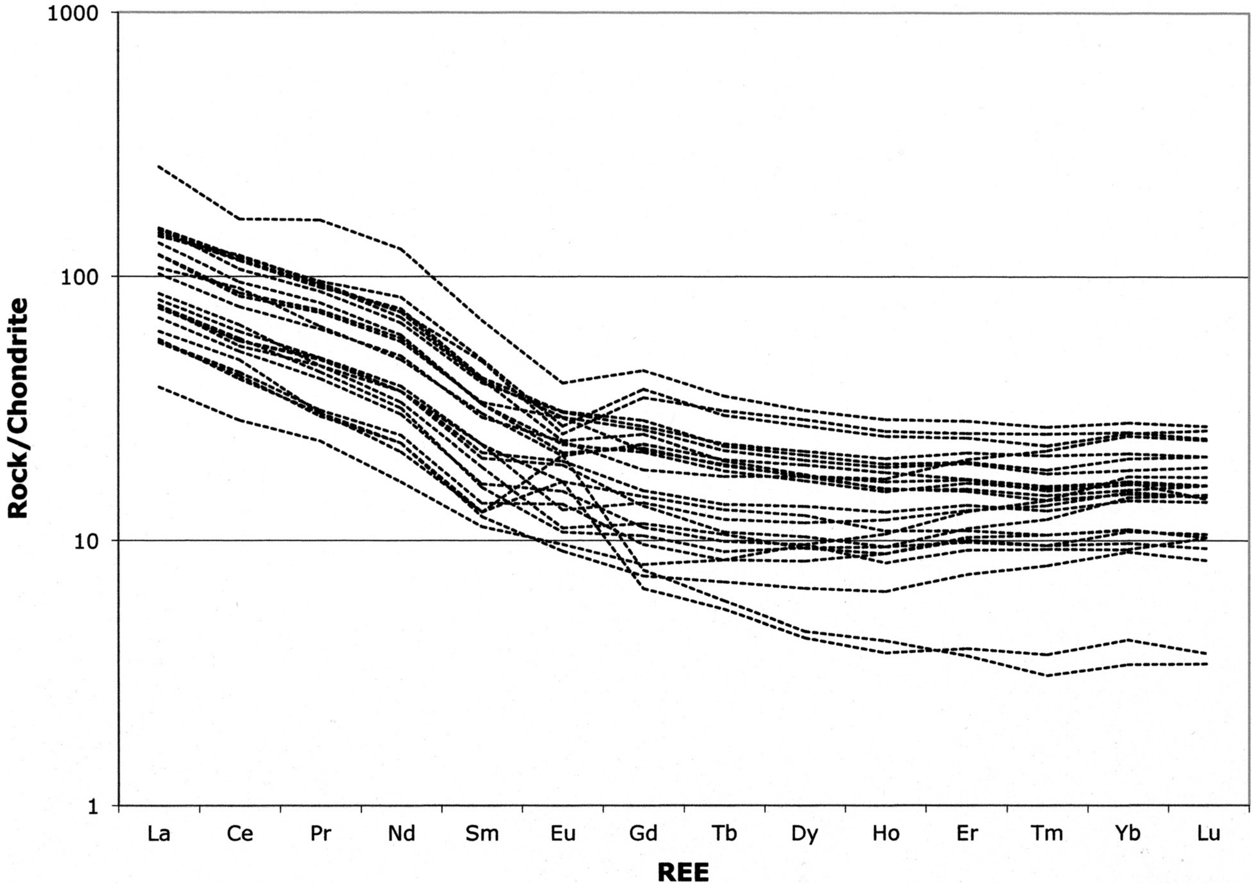

**Figure 7** Chondrite-normalised rare earth elements (REE) for all calc-silicate rocks.

Extensional magmatism has been described within the Moine Supergroup of Scotland in which metagabbros and tholeiitic metadolerite dykes were emplaced in the Glenfinnan and Loch Eil groups. The metagabbros have been dated at 873 ± 6 Ma (Millar 1999). In general, andesitic tholeiites occur in continental flood basalt provinces whose mineral composition is typically plagioclase feldspar ± clinopyroxene + quartz + FeTi oxides, with plagioclase occurring as phenocrysts and in the groundmass. The abundance of plagioclase feldspar explains the low value or total absence of a negative Eu anomaly.

Calc-silicate rocks have traditionally been described as metamorphosed marls or calcareous muds. Based on the geochemical evidence presented, it is proposed that they should be considered as metamorphosed tuffs. The arguments to support this proposal are given below:

- Arkoses, which contain high levels of feldspar, are commonly coarse grained (1–5 mm) proximal deposits, and are unlikely to form thin fine-grained beds with sharp upper and lower contacts;
- Feldspar in metamorphosed clastic rocks tends to be fine-grained albite;
- Plagioclase feldspar is less common in clastic rocks that K-feldspar;
- Lamellar-twinning in plagioclase feldspar is an igneous characteristic;

- Feldspar concentrations in mudrocks are generally <5 %, as opposed to 20–50 % in the grey tuffs and calc-silicate rocks;
- Zr, Ti, Ni plots support an orthoamphibolite (igneous) affinity (Winchester 1984);
- High concentrations of Zr (up to 800 ppm) could be generated by alkaline trachytic magmas (Wilson 1989);
- Isolated populations of thin beds which differ from their host is typical of tuffs which represent episodic phases of volcanism;
- If part of the Moine Supergroup (Upper Morar Psammite) had been deposited in braided river plains (Bonsor & Prave 2008), it is hard to conceive how a lime-rich marl could be formed and deposited in such an environment, except by invoking a marine or lagoon incursion on a regular basis and an equally rapid regression. In contrast, an ash cloud could dump a layer of volcanic ash instantaneously.

Another key issue in this debate relates to the relative rarity of carbonate deposits in the Palaeo-, Meso- and early Neoproterozoic. Marbles are described in the Lewisian Loch Maree Group, in association with banded ironstones, and in the Lewisian inlier near Dornie. Carbonates are known in the Stoer Group, lower Torridonian Supergroup, but these are associated with algal mats and stromatolitic structures, while other deposits indicate that calcite pseudomorphed gypsum in what are described as evaporite lake deposits (Stewart 2002). Earlier reports of marbles in the Moine succession (Read *et al.* 1926) were later considered to be thrust slices and infolds of Lewisian basement (Holdsworth *et al.* 1994). No mention is made of carbonates in Moine sequences by Mendum *et al.* (2009). In other words, widespread carbonate precipitation was not a common feature of the Torridonian and Moine supergroups. Significant carbonate deposition doesn't appear until the early Dalradian, when the Ballachulish Limestone is deposited in the middle of the Appin Group. Age constraints on this are provided by a date of 806 Ma for the Grampian Shear Zone (Noble *et al.* 1996) and the 720 Ma-old Port Askaig Tillite (basal Argyll Group) (Condon & Prave 2000). These dates would suggest an age of *c.*750 Ma for the first significant limestone deposit in the Neoproterozoic, 120 million years later than the youngest Moine rocks.

## 5. Conclusion

Consideration of field relationships, mineralogy and geochemistry suggest that calc-silicates could represent altered tuffs derived from tholeiitic sources of intermediate compositions erupted from extensional tectonic environments. Given the paucity of datable zircons, attention should be given to matching calc-silicate assemblages in terms of stratigraphy, relative thicknesses and abundance, which would allow correlation of the barren Moine metasedimentary sequences of Scotland and contemporary deposits elsewhere. Unique REE signatures of calc-silicates rocks could be used to refine or even re-appraise existing ideas of Moine stratigraphy. This hypothesis could help to explain the apparent paucity of volcanic rocks over some 220 Myr of geological time during the Proterozoic, when Torridonian and Moine rocks were being deposited in an active extensional basin.

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