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Basic volcanism contemporaneous with the Sturtian glacial episode in NE Scotland

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ABSTRACT: The Dalradian Supergroup contains three distinct glacigenic units, formerly termed 'Boulder Beds', which are correlated with widespread Neoproterozoic glaciations. The oldest and thickest unit, the Port Askaig Formation, marks the Appin–Argyll group boundary of the Dalradian Supergroup and has been correlated with the Middle Cryogenian (Sturtian) glaciation. The Auchnahyle Formation, a diamictite-bearing sequence near Tomintoul in NE Scotland, exhibits strong lithological similarities to the Port Askaig Formation. Both these glacigenic 'Boulder Bed' units contain abundant dolomite clasts in their lower parts and more granitic material at higher levels. Both metadiamictite units are overlain by thick shallow-marine quartzite units. C isotope data from Appin Group carbonate strata below the Auchnahyle Formation support this correlation. U–Pb laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) detrital zircon data from the Auchnahyle Formation metadiamictite differ slightly from the Port Askaig Formation, but are similar to detrital zircon spectra obtained from the Macduff Formation, a diamictite unit in the younger Southern Highland Group of the Dalradian Supergroup; both apparently reflect derivation from local basement rocks. No detritus younger than 0·9 Ga is observed, so the data do not constrain significantly the depositional age of the glacial strata. A thin tholeiitic pillow basalt unit in the lower part of the Auchnahyle Formation is geochemically distinct from pre-tectonic metadolerite sills and from basic metavolcanic rocks up-section. A Sturtian (c. 720–700 Ma) age for the Auchnahyle Formation metadiamictite would imply that this basaltic volcanism represents the oldest recorded volcanic activity in the Dalradian Supergroup and is inferred to represent an early, local phase of proto-Iapetan rifting within the Rodinian supercontinent.

KEY WORDS: C isotopes, Cryogenian, Dalradian, geochronology, U–Pb, zircon

The 'Boulder Beds' of the Dalradian Supergroup of Scotland and NW Ireland are schistose dominantly metasiltstone units containing angular to rounded granitic and carbonate clasts. They were recognised as distinctive lithologies in the early nineteenth century (e.g. Jameson 1800; MacCulloch 1819) and a glacigenic origin was suggested in the latter part of the nineteenth century (e.g. Thomson 1871, 1877). Kilburn *et al.* (1965) compiled all known exposures of the 'Boulder Bed' localities in Scotland and NW Ireland, and demonstrated that they formed part of a uniform succession for over 600 km along strike. The best exposed sections of 'Boulder Bed', the Port Askaig Formation, crop out on the Garvellach Islands and Islay in western Scotland (Fig. 1), where a combined thickness of over 750 m of metadiamictite and related metasandstone is exposed. These sections have been described in detail in the classic memoir of Spencer (1971).

With the exception of the Early Cambrian trilobites and inarticulate brachiopods of the Leny Limestone (Pringle 1939; Fletcher & Rushton 2008), the Dalradian Supergroup is unfortunately almost entirely devoid of fossils. Lithostratigraphical correlation of this diverse series of Laurentian margin metasedimentary and mafic volcanic rocks is also hampered by complex polyphase deformation and locally by rapid lateral facies changes. Despite these difficulties, a coherent lithostratigraphy from western Ireland to the Shetland Islands has been established (e.g. Harris *et al.* 1978, 1994). It comprises four Groups – the Grampian, Appin, Argyll and Southern Highland – with the Port Askaig Formation and its stratigraphical equivalent units in the lowermost Argyll Group forming a key marker horizon in the Dalradian succession (Fig. 2). McCay *et al.* (2006) and Brasier & Shields (2000) suggest that this formation is best correlated with the global Sturtian glacial episode. Other studies (e.g. Condon & Prave 2000; McCay *et al.* 2006) demonstrate the presence of two further possible glacigenic units within the Dalradian Supergroup (Fig. 2). The Stralinchy 'Boulder Bed' occurs within the Easdale Subgroup in Donegal (Hutton & Alsop 2004) and has been interpreted as a glacigenic diamictite and correlated with the global Marinoan glaciation (McCay *et al.* 2006). The Stralinchy 'Boulder Bed' is overlain by a 6 m-thick dolostone that exhibits a pronounced negative C isotopic trend (McCay *et al.* 2006), characteristic of Neoproterozoic cap carbonates (e.g. Hoffman & Schrag 2002). The Loch na Cille and Inishowen 'Boulder Beds' occur within the uppermost Argyll Group and basal Southern Highland Group strata respectively, and are correlated with the more restricted Gaskiers glacial event (Condon & Prave 2000; Bowring *et al.* 2003). A glacial affinity for the Stralinchy 'Boulder Bed' is based on the presence of ice-rafted debris, although this is harder to prove for the Loch na Cille 'Boulder Bed'. The precise stratigraphical position of other glacial units within the Dalradian, such as those within the Macduff Formation on the Banffshire coast, remains uncertain.

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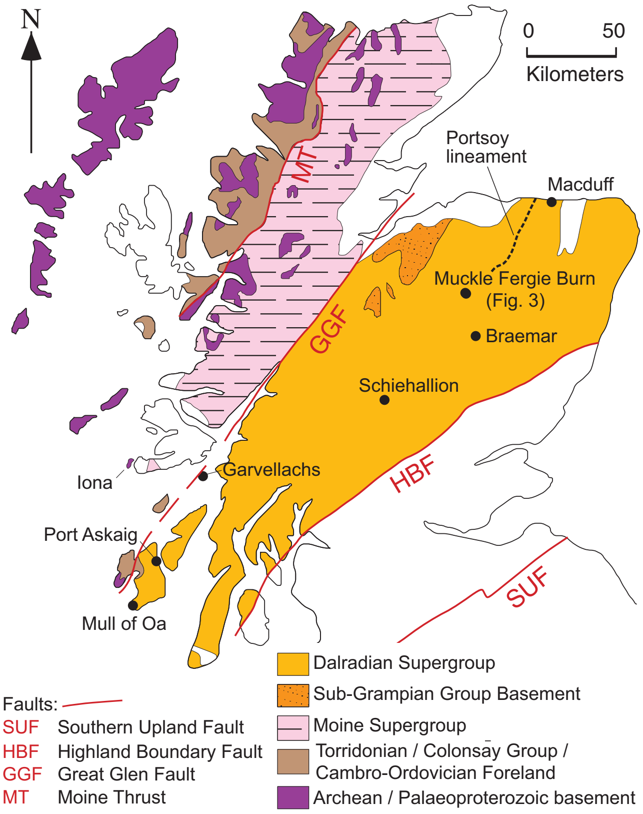

Figure 1 Geological map of Scotland. The Port Askaig Formation, its stratigraphical equivalents and the Macduff Formation (of uncertain stratigraphical affinity) are marked.

The earliest phase of widespread extrusive magmatic activity in the Dalradian Supergroup occurs within the Easdale Subgroup (Fig. 2). This volcanism was focused within the central Southern Highlands (Stephenson & Gould 1995) and the volcanic products consist mainly of tholeiitic basic lavas and tuffs such as the Laoigh Metabasites and Farragon Beds (Goodman & Winchester 1993). The occurrence of possible metavolcanic units immediately beneath Port Askaig Formation equivalents in NE Scotland (Stephenson & Gould 1995) is important, as it predates the first major phase of volcanism in the Easdale Subgroup. This study aims to aid correlation of these metadiamictite horizons in NE Scotland with the Port Askaig Formation by using C isotope data from interbedded carbonate rocks, and to characterise geochemically the metavolcanic units immediately beneath the metadiamictites. U–Pb Pb laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) detrital zircon data are also presented, with the aim of constraining the depositional age of these metadiamictite horizons in NE Scotland.

1. Regional geology of the Tomintoul region

North of Braemar (Fig. 1), the lower parts of the Islay Subgroup consist of a prominent quartzite, termed the Kymah Quartzite Formation. The Kymah Quartzite Formation is underlain in parts by psammitic and semipelitic units that contain thin metadiamictite units and also thin metacarbonate beds which are commonly dolomitic. These diamictite-bearing units are markedly lenticular and are found on Upper Donside, in the Muckle Fergie Burn area (4·8 km south of Tomintoul), and in the Ladder Hills. In the Muckle Fergie Burn this basal unit has been termed the Auchnahyle Formation (British Geological Survey 1996). The formation consists of micaceous and quartzose psammite with subsidiary semipelite and thin metalimestone, metadolostone and metadiamictite beds. The Auchnahyle Formation has a maximum thickness of c. 150 m. Farther ENE, the correlative Ladder Hills Formation and laterally equivalent more pelitic and metacarbonate-rich unit, the Nochty Semipelite and Limestone Formation, reach some 500 m in thickness, apparently representing localised basinal deposition (British Geological Survey 1995; Stephenson & Gould 1995). In the Ladder Hills Formation the metadiamictite horizons are exposed near the top of the formation and commonly overlain by a thin metadolostone bed (Fig. 3). In the Muckle Fergie Burn, a stream section east of the River Avon, an across-strike section of the Auchnahyle Formation is exposed. The 'Boulder Bed' was first recorded here by Gregory (1931) and later documented by Morgan (1966) and Spencer & Pitcher (1968). Carbonate rocks of the Appin Group occur below the Auchnahyle Formation and are well exposed in the Allt Bheithachan stream section west of the River Avon (Fig. 3).

This study presents C isotope data from the carbonate rocks below the diamictite (Fig. 3). Geochemical data from basic metavolcanics and metadolerite intrusions adjacent to the diamictite are also presented from the Islay–Easdale Subgroup rocks of the Muckle Fergie Burn section (Fig. 5). Further to the east, correlation of the Argyll and Southern Highland group rocks is difficult, as sequences cannot readily be correlated across the Portsoy Lineament, a major tectonic dislocation (Fettes *et al.* 1991). This means that the stratigraphical positions of key horizons east of the lineament, such as the basic and ultrabasic metavolcanic rocks of the Blackwater Formation (MacDonald *et al.* 2005; Fig. 2) and the metadiamictite units in the Macduff Formation on the Banffshire coast (Fig. 1) remain uncertain. This study also presents U–Pb LA-ICP-MS detrital zircon data from the metadiamictites of the Auchnahyle Formation and the Macduff Formation in an attempt to clarify regional stratigraphical correlations (Fig. 6).

2. Geology of the Allt Bheithachan and Muckle Fergie Burn stream sections

The lithostratigraphy of the Allt Bheithachan and Muckle Fergie Burn stream sections is outlined in Figure 3 and represents a complete section from the Ballachulish Subgroup to the Easdale Subgroup. The formation names closely follow the Glenlivet (75W) 1:50 000 geological map of the region (British Geological Survey 1996). The regional metamorphic grade is lower amphibolite facies. Typical assemblages in metabasites are hornblende + epidote + biotite + plagioclase ± quartz, while pelitic rocks contain quartz + biotite + muscovite + plagioclase ± garnet. The regional strike of bedding is NNW–SSE, with dips moderate to shallow to the ENE (Fig. 3). The amount of stratigraphical repetition due to folding in the Allt Bheithachan and Muckle Fergie Burn sections is relatively minor, although in some portions of the sections it does locally repeat the stratigraphy.

In the Allt Bheithachan stream section, the first prominent metalimestone bands appear within the Ailnack Phyllite and Limestone Formation, a predominantly semipelitic and pelitic unit with thin metalimestones and psammite beds (Fig. 3). The overlying Neilead Semipelite Formation is a blue-grey semipelite with minor limestone beds. The Neilead Semipelite Formation passes gradationally up over some 15 m into the Inchory Limestone Formation, a blue-grey crystalline metalimestone with individual beds over 50 cm thick. The overlying Glenfiddich Pelite Formation is a thinly laminated graphitic pelite which contains a relatively pure metalimestone (the Glenfiddich Pelite Limestone Member), a 5 m-thick unit exposed on the cusp of a waterfall.

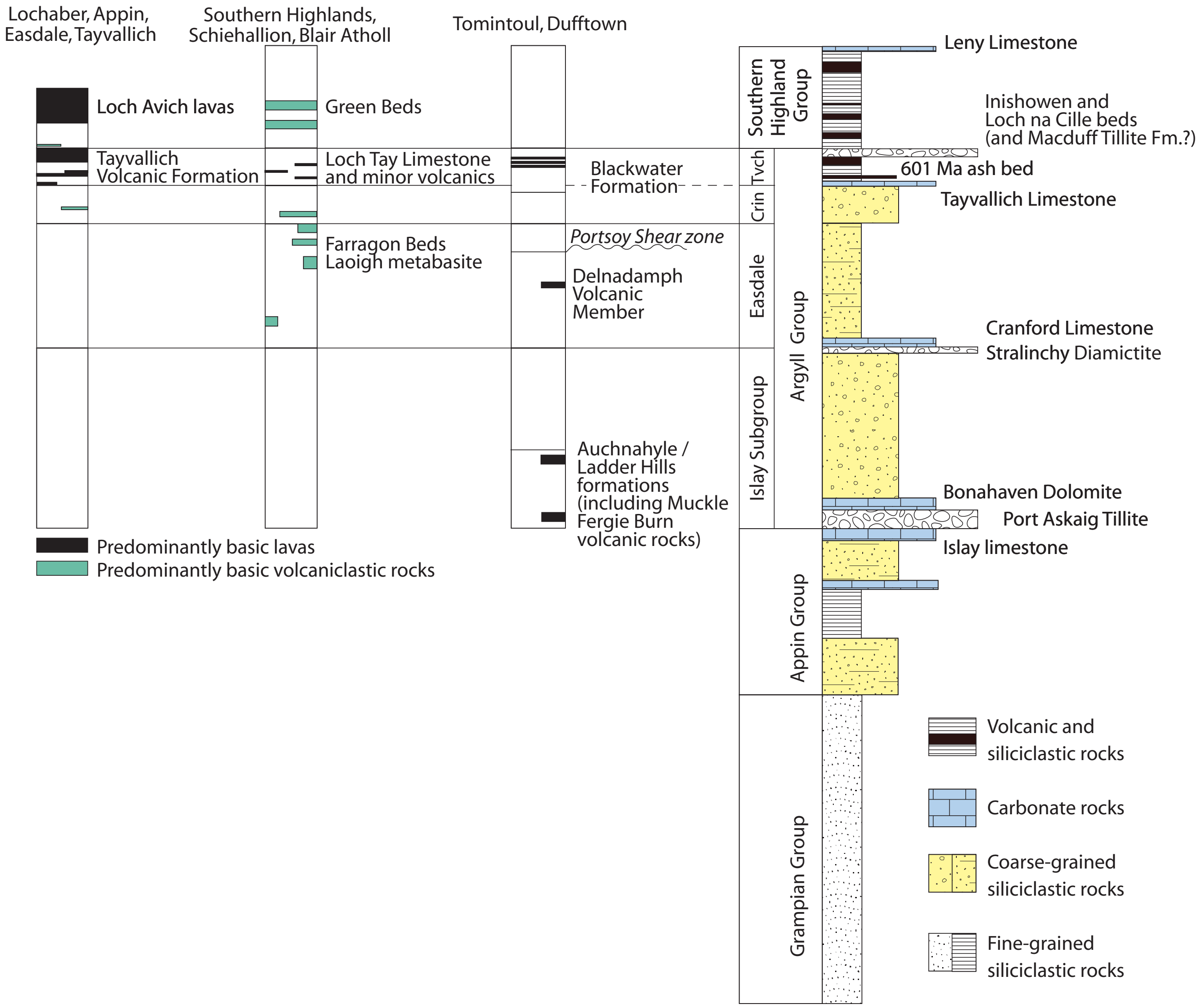

Figure 2 Occurrences of basic meta-igneous rocks within the Argyll and Southern Highland Groups (based on Stephenson & Gould 1995) combined with the composite Dalradian stratigraphy showing the three glacigenic units recognised by McCay *et al.* (2006).

The Muckle Fergie Burn section commences east of the River Avon. The lower part of the burn section exposes the Auchnahyle Formation which consists mainly of psammitic and semi-pelitic rocks. Near the base of the formation, a basic metavolcanic unit with pillow structures is exposed (Fig. 4). Further up-section, the sequence becomes more semipelitic and a thin metalimestone (4 m thick) and meta-dolostone (5 m thick) crop out. The lowest metadiamictite bed is about 20 m thick and crops out directly above the meta-dolostone. The basal portions of the metadiamictite, interpreted as a tillite, have a pale to mid-grey-green, carbonate-rich, highly micaceous psammite matrix with elongate ochreous yellow-brown clasts of dolomite up to 10 cm in length, which commonly weather back. Small (<1 cm) quartz clasts are also visible, but only a very low proportion of granitic clasts (<1 cm) are present. Nearing the top of the metadiamictite bed, metadolostone and granitic clasts occur in approximately equal abundance. No evidence of dropstones or ice rafted debris was observed. Overlying the 'Boulder Bed' is a c. 10 m-thick quartzite sequence with its lower beds rich in pyrite. Higher up the burn section further 'Boulder Beds' are exposed in a predominantly psammite sequence. The lowest one forms a prominent waterfall at [NJ 1657 1396] and contains scattered small granitic and metadolostone clasts in an unbedded grey-grey schistose semipelite matrix. The higher occurrence, some 5 m thick, occurs at [NJ 1661 1395]; again, small quartz, granite and rare metadolostone clasts lie in a highly micaceous psammite matrix.

Although unexposed in the Muckle Fergie Burn section, the Auchnahyle Formation is interpreted as passing up with apparent conformity into the overlying Kymah Quartzite Formation, as seen in the Ladder Hills and on Upper Donside. The Kymah Quartzite Formation is a white to cream, blocky to massive quartzite and psammitic unit with well developed cross bedding. Younging directions are consistently to the east. A thin, schistose chlorite-rich amphibolitic bed is encountered near the top of the formation and may be of volcanic origin (British Geological Survey 1996). The overlying Culchavie Striped Formation is a laminated micaceous psammite and semipelite with occasional coarse garnet-bearing layers. There is a gradational contact into the overlying graphitic pelites of the Glenbuchat Graphitic Schist Formation. This formation contains a thick unit of pale to dark green amphibolitic metavolcanic rocks, the Delnadamph Volcanic Member (British Geological Survey 1996; Fig. 3). Pillow structures and weathered out vesicles (Fig. 3b), which are moderately flattened due to regional tectonism, are well developed in this unit.

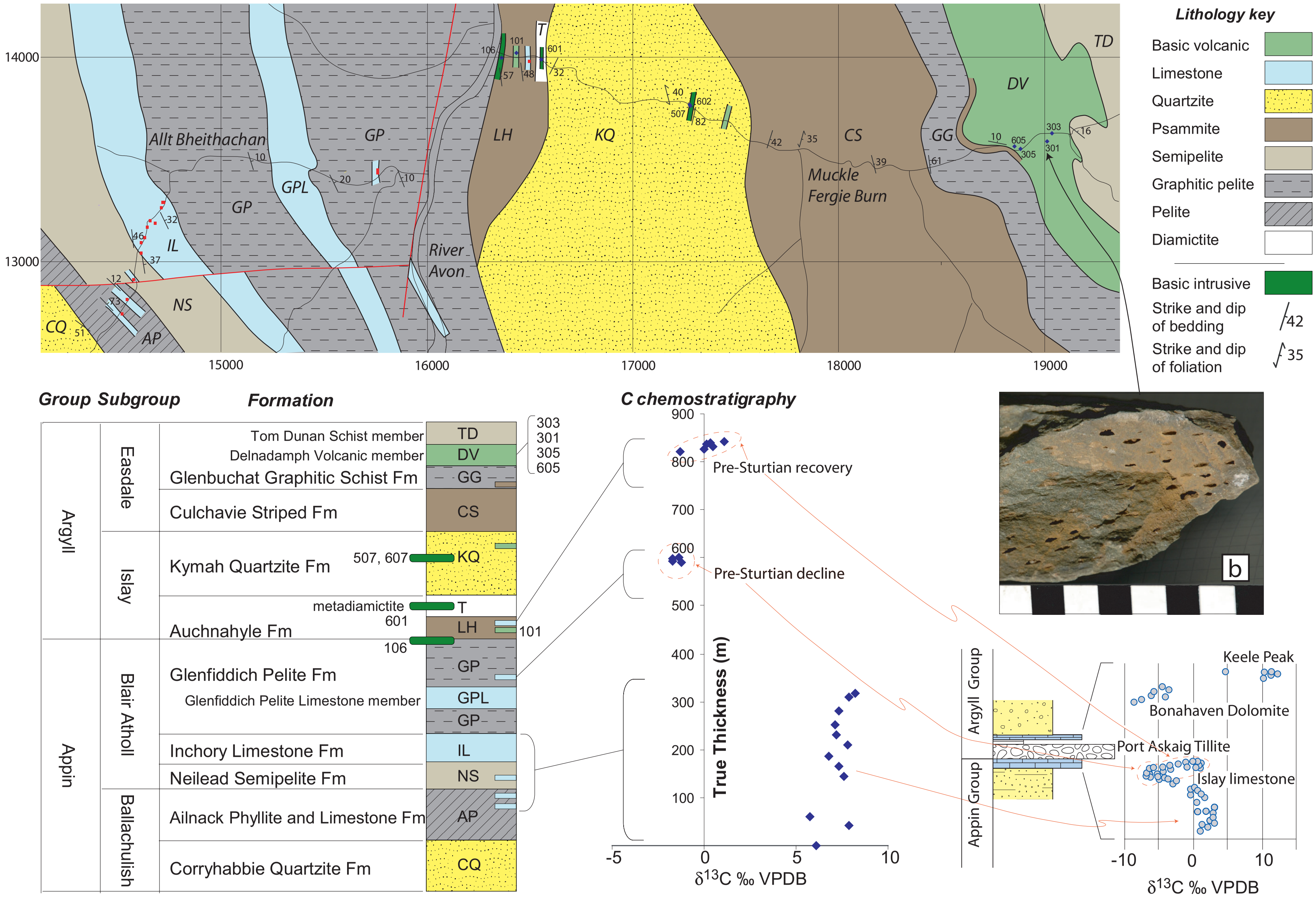

Figure 3 Geological map, regional lithostratigraphy and C isotope data for the Allt Bheithachan and Muckle Fergie Burn stream sections south of Tomintoul. Outcrop data from the stream sections come from the present authors' own field mapping; extrapolation of the formation boundaries and formation names are taken from the Glenlivet 1:50 000 geological map of the region (British Geological Survey 1996). The C isotope data from above and below the Port Askaig Formation of McCay *et al.* (2006) are illustrated for comparison. Inset (b) illustrates flattened, weathered-out vesicles from the outer rind of a pillow in the Delnadamph Volcanic Member. Scale bar: each square=1 cm.

Figure 4 Photograph of the Muckle Fergie Burn volcanic unit, a tholeiitic pillow lava immediately below the metadiamictite of the Auchnahyle Formation.

In addition to the two metavolcanic units described above in the Auchnahyle Formation and the Delnadamph Volcanic Member, a series of coarse-grained, massive metadolerite bodies have also been recorded in the Muckle Fergie Burn section (Fig. 3). These mafic bodies share the same pervasive regional foliation as the metasedimentary country rocks, are aligned parallel to the regional strike of bedding and appear to predate all regional deformation and metamorphism. Cross-cutting relationships with the country rocks are difficult to observe due to the poor exposure, but the presence of coarse-grained relict plagioclase phenocrysts in these massive bodies, combined with the absence of any pillows or vesicles, suggests they represent sills. It is possible, however, that some units mapped as sills may represent volcanic horizons which do not exhibit clear extrusive characteristics. The stratigraphically lowest sill intrudes the basal portion of the Auchnahyle Formation, close to where the Muckle Fergie Burn enters the River Avon (Fig. 3). Additional sills are common within the formation and also occur within the overlying Kymah Quartzite (Fig. 3). The thick sill within the Auchnahyle Formation contains relict phenocrysts of plagioclase up to 1 cm in length, which have been replaced by fine-grained epidote+albite.

3. Geology of the Macduff region

The tillite unit within the Macduff Formation lies near the top of the exposed Southern Highland Group succession on the Banffshire coast (Fig. 1). It is best seen 1 km east of Macduff Harbour, where it consists of about 20 m of predominantly turbiditic arenites and pelitic units containing scattered clasts ranging from granule to boulder size. The glacial affinity of the succession was first recognised by Sutton & Watson (1954) and confirmed by Hambrey & Waddams (1981). Hambrey & Waddams (1981) described seven units, with an upper unit of massive diamictite overlying six units of graded greywackes. Clast types are typically less than 10 cm across, but range up to a metre. The clasts comprise syenite, trondhjemite and granodiorite with local pegmatite and vein quartz, with the exception of the uppermost graded greywacke (unit 6), where the stones are comprised chiefly of pale grey metalimestone. Hambrey & Waddams (1981) interpret the majority of the tillite unit as deep water turbidites with abundant ice rafted debris, and suggested the uppermost unit of massive diamictite may have been deposited by a grounded ice sheet. Stoker *et al.* (1999) reinterpreted the sequence as of distal glaciomarine origin, as evidenced by ice-rafted dropstones, glacigenic debris-flow diamictites and an allochthonous slumped unit. They suggested that the uppermost diamictite bed was an integral part of the deep-water succession and rejected the lodgement-till interpretation of Hambrey & Waddams (1981).

The age of the underlying Macduff Formation has proved controversial. Lithostratigraphical correlation of the Dalradian succession is difficult, as sequences cannot be correlated at subgroup level across the Portsoy–Duchray Hill Lineament (Goodman 1994; Fettes *et al*. 1991). Graptolites collected by Hugh Miller in the 19th century were identified by Skevington (1971) as *Monograptus priodon*, which indicates a late Llandovery–Wenlock age. This identification has now been discredited, as the specimen lithology is atypical of the Macduff Formation, and the sample is thought to have been mislabelled. Possible Ordovician chitinozoa were recorded by Downie *et al*. (1971) from the Macduff Formation, but subsequent workers have discounted these findings (Bliss 1977; Molyneux 1998). Downie *et al*. (1971) also recorded Ordovician acritarchs collected by Lister from the Macduff Formation. Two specimens were identified, *Veryhachium* cf. *lairdii* and ?*Veryhachium trispinosum*. The specimen of ?*V. trispinosum* has since been lost, but the acritarch specimen identified as *V.* cf. *lairdii* was located and its identity confirmed by Molyneux (1998). The sample from which the acritarchs were purportedly obtained came from Tarlair Bay, about 1·5 km east of Macduff at [NJ 719 647], in some of the uppermost exposed units of the Macduff Formation. However, the specimens were processed as a batch that also included samples from known Ordovician rocks of Northern England, making it possible that contamination occurred (J. Mendum, pers. comm. 2009). The Ordovician date is based on a single acritarch specimen and attempts to replicate the occurrence at Tarlair Bay have not been successful. Its implied age is difficult to reconcile with evidence that the Dalradian Supergroup experienced Early Ordovician deformation and metamorphism during the Grampian Orogeny (Soper *et al*. 1999).

4. Analytical methods

4.1. Volcanic whole-rock geochemistry

Whole-rock samples were analysed for major oxides and trace elements by X-ray fluorescence (XRF) spectroscopy using a Phillips PW 1400 at the Centre d'Analyses Minérale, University of Lausanne, Switzerland. Samples were fused with lithium borate and analysed for their rare-earth element and trace element concentrations by inductively coupled plasma mass spectrometry (ICP-MS) using a Thermo X-Series ICP-MS at OMAC Laboratories, Co. Galway, Ireland.

4.2. Stable isotope analyses – sampling methodology, preparation and analytical method

Twenty-two analyses and seven replicate analyses were obtained from fresh hand specimens of metacarbonate rocks carefully selected in the field. Each specimen was sliced and powders (0·5–5 mg) were extracted using a microdrill. Diagenetic overprinting of original seawater isotopic signatures is a concern in Neoproterozoic carbonates, and every analysed sample has probably experienced some degree of alteration during diagenesis, dolomitisation or metamorphic recrystallisation. However, due to the high concentration of C in carbonate rocks relative to meteoric fluids, the $\delta^{13}C$ composition of carbonate rocks is far more resistant to chemical overprinting than $\delta^{18}O$. Many previous studies have addressed the reliability of $\delta^{13}C$ signatures in Neoproterozoic carbonates, and the consensus is that even clearly diagenetically altered and dolomitised carbonates appear to preserve their original $\delta^{13}C$ composition (e.g., Kaufman *et al*. 1991; see detailed discussion in Halverson *et al*. 2005).

Due to the extreme depletion of ^{13}C in organic matter, one process that can potentially substantially alter primary carbonate $\delta^{13}C$ compositions is the incorporation of carbon from the oxidation of organic matter or methane during diagenesis (e.g. Irwin *et al*. 1977). Due to the low content of organic matter in the hand samples and in the Allt Bheithachan and Muckle Fergie Burn sections as a whole, it is felt that the samples used in the present study are not significantly affected by this type of isotopic alteration.

Samples were run on a Thermo Delta^{plus} Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS) at Trinity College Dublin. For $\delta^{13}C$ and $\delta^{18}O$ analysis of carbonates, a CTC Analytics CombiPal Autosampler with a thermostatic hot block and FMI acid pump was interfaced to the Delta^{plus} via a Thermo GasBench II. Each sample of 0·6 mg was weighed into a clean, dry round-bottomed Exetainer® screw-capped borosilicate glass vial using a Sartorius MC5 microbalance. The vial was capped with a new septum and racked in the hot-block. Each sample vial was flush-filled with 100 ml/min flow of helium for 5 min and then a double needle configuration was set up on the autosampler. Each sample was dosed with five drops of phosphoric acid by the acid needle and allowed to equilibrate for 91 min at 72 °C before the sample needle filled a 100 μl loop on the valco valve in the Gas Bench. Ten sequential aliquots of CO_2 were introduced to the Delta^{plus} and the first and the last peaks discarded. Average $\delta^{13}C$ and $\delta^{18}O$ values of the eight peaks were recorded.

The International Atomic Energy Authority standard CO-1 was used to correct each batch of unknown samples to primary standard values (V-PDB for $\delta^{13}C$ and V-PDB and SMOW for $\delta^{18}O$). An internal standard (Cranford dolomite) was run with each batch of samples and is used as a cross-check and to monitor machine stability. Two hundred and thirty-nine replicates of Cranford dolomite run in 20 sample batches gave a 1 SD of 0·06‰ for $\delta^{13}C$ and 0·11‰ for $\delta^{18}O$. These values are consistent with the stated precision recorded by Thermo for the GasBench II Carbonate option, which is 0·06‰ for $\delta^{13}C$ and 0·10‰ for $\delta^{18}O$.

4.3. U–Pb LA-ICP-MS detrital zircon dating

U–Pb dating of detrital zircons has proven to be a powerful tool for stratigraphical correlation, providing identification of sediment sources and constraints on depositional ages (e.g. Kosler *et al*. 2002). Metadiamictite samples of several kilograms in weight were collected from the Auchnahyle Formation (sample TL 104 [NJ 1654 1400]) and the Macduff Formation (sample MD-8 [NJ 7137 6489]). The Auchnahyle Formation sample comes from the basal portion of the metadiamictite unit, which contains abundant metadolostone clasts. The Macduff Formation sample comes from the massive metadiamictite in the uppermost portion of the sequence (Unit 7 of Hambrey & Waddams 1981). Zircons were separated from the crushed samples by conventional means. The sub-300 μm fraction was processed using a Gemeni (Rogers) mineral separation table, and then the heavy fraction was passed through a Frantz magnetic separator at 1 A. The non-paramagnetic portion was then placed in a filter funnel with di-iodomethane and the resulting heavy fraction passed again through the Frantz magnetic separator at full current. All zircons were then hand picked in ethanol using a binocular microscope, mounted in an epoxy resin disk, and polished to reveal their grain interiors.

Table 1 XRF major and trace element data.

Sample		Muckle Fergie volcanic	Metadolerite sills				Delnadamph Volcanic Member			
		TL101	TL106	TL507	TL601	TL602	TL301	TL303	TL305	TL605
SiO_2	%	48·43	47·03	44·63	46·12	45·66	52·84	53·18	44·44	47·76
TiO_2	%	3·01	2·01	1·91	1·52	1·90	1·76	1·49	1·50	1·52
Al_2O_3	%	14·50	14·35	13·39	17·10	14·29	15·34	14·99	16·69	16·75
Fe_2O_3	%	16·84	12·40	11·44	9·04	11·48	9·58	9·73	13·60	13·12
MnO	%	0·16	0·16	0·17	0·13	0·17	0·13	0·15	0·15	0·17
MgO	%	6·23	6·44	6·31	5·61	6·78	7·66	6·80	5·12	7·14
CaO	%	5·29	7·52	9·85	9·96	7·94	5·92	6·66	9·58	5·94
Na_2O	%	2·11	2·22	1·89	2·68	2·76	5·09	5·28	4·38	3·73
K_2O	%	0·18	1·02	1·04	0·98	0·53	0·07	0·10	0·17	0·16
P_2O_5	%	0·35	0·23	0·22	0·16	0·21	0·31	0·23	0·20	0·21
LOI	%	2·26	6·74	8·63	6·17	6·97	1·52	0·81	4·38	2·05
Cr_2O_3	%	0·01	0·02	0·03	0·02	0·04	0·05	0·06	0·06	0·05
NiO	%	0·00	0·00	0·01	0·01	0·01	0·02	0·02	0·03	0·02
Sum	%	99·36	100·14	99·53	99·51	98·73	100·29	99·49	100·30	98·61
Nb	ppm	18·2	12	10·9	9·4	11	10·4	9·3	12·1	10·9
Zr	ppm	199	149	113	103	114	156	136	102	119
Y	ppm	35·3	25·1	23·1	18·8	23·2	25·4	19·1	24·9	24·7
Sr	ppm	176	445	135	448	139	403	311	168	465
U	ppm	<2<	<2<	<2<	<2<	<2<	<2<	<2<	<2<	<2<
Rb	ppm	2·7	64·3	44·7	29·5	19·6	<1·0<	<1·0<	1·1	2·8
Th	ppm	5	2	2	3	3	3	3	3	4
Pb	ppm	3	14	3	4	2	4	4	<2<	3
Ga	ppm	26	20	19	18	19	17	18	21	19
Zn	ppm	149	134	72	81	93	93	89	91	141
Cu	ppm	15	9	24	50	36	5	11	18	17
Ni	ppm	28	33	50	61	57	161	211	266	200
Co	ppm	61	59	53	51	57	58	72	73	68
Cr	ppm	63	103	216	157	229	357	442	419	371
V	ppm	344	269	247	205	238	159	164	183	188
Ce	ppm	32	20	15	11	15	18	15	19	18
Nd	ppm	11	15	16	19	17	14	6	8	8
Ba	ppm	<9<	104	60	161	30	54	31	58	80
La	ppm	16	9	6	6	7	11	8	13	10
S	ppm	722	920	848	1149	1565	144	131	234	181
Hf	ppm	10	2	2	<1<	12	5	4	<1<	3
Sc	ppm	81	49	29	31	50	42	39	44	46
As	ppm	<3<	<3<	3	<3<	<3<	4	3	3	<3<

U–Pb zircon analyses were determined by LA-MC-ICP-MS at the NERC Isotope Geosciences Laboratory using procedures outlined by Horstwood *et al.* (2003). The correction for common Pb was based on the measurement of ^{204}Pb, using an ion counter. Analyses were carried out using a Nu-Plasma MC-ICP-MS system coupled to a New Wave Research solid-state NdYAG laser ablation system (UP193SS). A spot size of 25 μm was selected. Dwell time was 60 s, the first 15 s of which was disregarded in order to avoid any elevated common Pb from surface contamination. The pit depth was approximately 15 μm. A ^{205}Tl/^{235}U solution was aspirated during analysis, using a Cetac Technologies Aridus desolvating nebuliser, to correct for instrumental mass bias and plasma-induced inter-element fractionation. Data were reduced and errors propagated using an in-house spreadsheet calculation package, with ages determined using the Isoplot 3 macro of Ludwig (2003). Between five and ten analyses of the zircon standard 91500 were performed every hour and used to normalise the data. Zircon standards GJ-1 and Mud Tank were run as unknown samples at the start and finish of each analytical session to assess overall accuracy and precision. Analytical data are listed in Table 4 and illustrated graphically in Figure 6. Only data with less than 10% discordance are represented. The quoted 2σ uncertainty on the ^{207}Pb/^{206}Pb and the ^{206}Pb/^{238}U ages employs a minimum uncertainty of 1% and 1·5% respectively. All age data illustrated in the probability density diagrams (Fig. 6c, d) use the ^{207}Pb/^{206}Pb ages.

5. Results

5.1. Volcanic geochemistry results

Major, trace and rare earth element (REE) geochemical data for the Dalradian basic metavolcanic and intrusive rocks are presented in Tables 1 and 2, and selected trace element and REE plots are illustrated in Figure 5. Samples have been divided into three separate groups (Table 1): the Muckle Fergie Burn volcanic unit in the lower part of the Auchnahyle Formation (sample TL101), the Delnadamph Volcanic Member (samples TL301, TL303, TL305 and TL605), and the pre-tectonic metadolerite sills (samples TL106, TL507, TL601 and TL602). Based on their major element geochemistry, the

Table 2 ICP-MS rare earth element data.

Sample		TL101	TL106	TL507	TL601	TL602	TL301	TL303	TL305	TL605
La	ppm	14·9	10·7	8·2	7·1	8·7	11·3	9·1	10·5	10·3
Ce	ppm	41·4	29·8	22·4	20·1	24·2	27·5	24·1	26·8	26·2
Pr	ppm	5·9	4·2	3·2	2·9	3·5	4·1	3·3	3·5	3·7
Nd	ppm	26·0	19·6	15·2	12·9	16·4	18·6	14·1	14·3	15·2
Sm	ppm	6·6	4·9	4·0	3·6	4·6	5·0	3·7	3·8	3·8
Eu	ppm	2·1	1·6	1·4	1·3	1·5	1·3	1·2	1·3	1·3
Gd	ppm	5·8	4·7	4·3	3·4	4·0	4·8	3·5	3·8	4·0
Tb	ppm	1·2	0·9	0·8	0·6	0·8	0·9	0·7	0·8	0·8
Dy	ppm	6·8	4·8	4·2	3·7	4·5	4·6	3·7	4·5	4·6
Ho	ppm	1·3	1·0	0·9	0·7	0·9	1·0	0·7	1·0	1·0
Er	ppm	3·9	2·8	2·4	2·0	2·5	2·6	1·9	2·6	2·6
Tm	ppm	0·5	0·4	0·3	0·3	0·3	0·3	0·3	0·4	0·4
Yb	ppm	3·3	2·2	2·2	1·8	2·4	2·1	1·7	2·4	2·3
Lu	ppm	0·5	0·4	0·3	0·3	0·4	0·3	0·3	0·3	0·4
La/Sm		2·27	2·18	2·08	1·99	1·90	2·27	2·49	2·73	2·76
La/SmN*		1·42	1·36	1·30	1·24	1·18	1·42	1·56	1·70	1·72
ΣREE	ppm	120·2	88·0	69·8	60·6	74·7	84·2	68·3	75·9	76·5

*Normalised to the carbonaceous chondrite values of McDonough & Sun (1995).

Muckle Fergie Burn volcanic unit (TL101) and all the metadolerite samples plot as sub-alkali basalts, both on the total alkali versus silica (TAS) diagram (not illustrated) and using the CIPW norm algorithm of Verma *et al.* (2002) and Fe_2O_3/FeO ratio procedure of Middlemost (1989). The Delnadamph Volcanic Member exhibits some variations in major element chemistry, with two samples of intermediate composition (TL301 and TL303) plotting in the basaltic andesite field. The Muckle Fergie Burn and Delnadamph Volcanic Member samples are both depleted in CaO relative to the metadolerite suite (Table 1), possibly as a result of seafloor hydrothermal metamorphism and spilitisation. The Delnadamph Volcanic Member samples are also enriched in Na_2O, again probably as a result of these processes.

Figure 5a, b and d, illustrate the relationship between fluid-immobile, high field strength elements such as Nb, Y, Zr and Ti in a series of bivariate diagrams. These elements, along with the REE (Fig. 5e) are generally considered to be stable under conditions of hydrothermal alteration and metamorphism up to medium metamorphic grades. Figure 5a and b illustrate Nb *vs.* Zr and Y *vs.* Zr diagrams for the entire suite of analyses. Both the Delnadamph metavolcanic rocks and the metadolerite sills have restricted ranges of concentrations for Nb (between 9 and 12 ppm), Y (between 19 and 25 ppm) and Zr (between 102 and 156 ppm). In contrast, the Muckle Fergie Burn volcanic sample (TL101) exhibits elevated Nb (18 ppm), Y (35 ppm) and Zr (199 ppm) concentrations (Fig. 5a–b). Hence, on a Zr *vs.* TiO_2 diagram (Fig. 5d), sample TL101 (199 ppm Zr, 3·01% TiO_2) falls significantly outside the field defined by the Delnadamph Volcanic Member and the metadolerite sills (102–156 ppm Zr, 1·5–2·01% TiO_2). Figure 5d illustrates N-MORB normalised REE patterns of the entire metabasic-igneous rock suite. All samples illustrate very similar REE patterns with a conspicuous LREE enrichment, with a pattern similar to E-MORB. The Muckle Fergie Burn volcanic sample (TL101) is more enriched in REE (ΣREE= 120 ppm) than the Delnadamph Volcanic Member and metadolerite sills (ΣREE ranging between 61 and 88 ppm).

Whereas the field relationships and geochemical data presented demonstrate that the Muckle Fergie Burn volcanic unit and the Delnadamph Volcanic Member are discrete volcanic episodes, we have added for comparison the petrogenetic scheme of Graham (1976) for the Tayvallich Volcanic Formation and the related suite of intrusive metabasic rocks (metadolerites and metagabbros) in SW Scotland (Fig. 5c). Although the Tayvallich Volcanics are younger than both volcanic suites described here (Fig. 2), the tectonic setting and eruptive products (predominantly tholeiitic basalt) are probably similar. Graham (1976) envisaged that the more Fe- and Ti-rich magmas were subject to *in situ* differentiation involving fractionation of olivine, clinopyroxene, plagioclase and Fe–Ti oxide. Magmas were drawn off to produce thin high-level sills and lavas enriched in incompatible trace elements, while complementary cumulate magmas enriched in Fe- and Ti-oxides were also produced. The differing geochemical characteristics of the Muckle Fergie Burn volcanic unit, the Delnadamph Volcanic Member and the metadolerite sills could therefore be explained as a result of *in situ* differentiation within a single high-level sill and lava complex. However, this interpretation does not accord well with the observed field relationships, which imply there are two discrete volcanic horizons.

The Delnadamph Volcanic Member has been assigned to the Easdale Subgroup based on lithostratigraphic arguments (British Geological Survey 1996). Additionally, on a Y *vs.* Zr bivariate diagram (Fig. 5b) and a Y/P_2O_5 *vs.* Zr diagram (Fig. 5c), the Delnadamph Volcanic Member samples plot inside the field of Easdale Subgroup volcanics, based on data from the NW Mayo Dalradian of western Ireland (Winchester *et al.* 1987) and the Farragon Beds of the central Southern Highlands (Goodman & Winchester 1993), and are geochemically distinct compared to the younger (595 ± 4 Ma, Halliday *et al.* 1989) Tayvallich Volcanic Formation of SW Scotland. It is not certain if the metadolerite sills are related to the Delnadamph Volcanic Member or if they are feeder sills to younger volcanic units, such as the Blackwater Formation (MacDonald *et al.* 2005), found to the east of the Portsoy Lineament. However it should be noted that the metadolerite sills and the Delnadamph Volcanic Member overlap on all the discriminant diagrams presented, and in terms of their REE profiles (Fig. 5a–e).

5.2. C isotope results

Carbon isotope results are listed in Table 3 and illustrated graphically next to the regional stratigraphical column in Figure 3. Samples from the lowermost units in the Allt

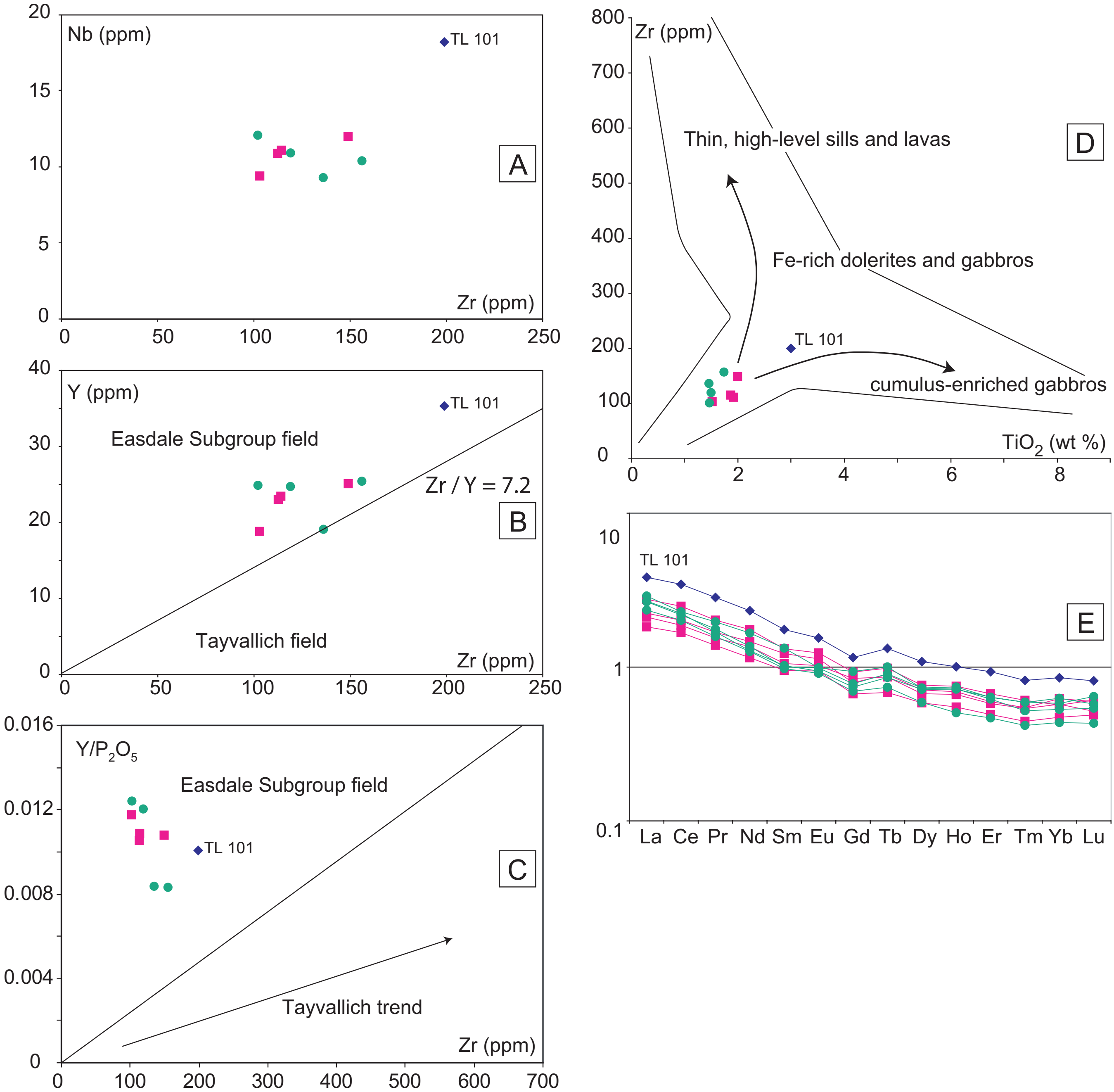

Figure 5 Incompatible trace element (Nb, Zr, Y and Ti) and REE plots for the basic meta-igneous rocks analysed in this study. Analyses from the Delnadamph Volcanic Member are denoted by circles, metadolerite sills by squares and the Muckle Fergie Burn volcanic unit by a diamond (TL101): (A) Nb *vs.* Zr bivariate diagram; (B) Y *vs.* Zr bivariate diagram, Tayvallich field from Winchester *et al.* (1987); (C) Y/P_2O_5 *vs.* Zr diagram, Tayvallich field from Winchester *et al.* (1987); (D) Zr *vs.* TiO_2 bivariate diagram with the petrogenetic scheme of Graham (1976) for the Tayvallich Volcanics superimposed; (E) N–MORB normalised REE plots for all samples. Normalising factors after Hart *et al.* (1999).

Bheithachan stream section from the Ailnack Phyllite and Limestone, Neilead Semipelite and Inchory Limestone formations, yield $\delta^{13}C$ values of between 5·8‰ and 8·2‰, with a slight increase in $\delta^{13}C$ values up section. There is a marked change in $\delta^{13}C$ values in the overlying Glenfiddich Pelite Formation, where a small metalimestone band yields a restricted range in $\delta^{13}C$ values of between −1·2‰ and −1·7‰. The thin metadolostone unit that immediately underlies the metadiamictite unit in the Auchnahyle Formation also yields a restricted range of $\delta^{13}C$ values between −1·3‰ and 1·1‰.

5.3. U–Pb LA-ICP-MS detrital zircon results

Sample TL-104 from the Auchnahyle Formation metadiamictite exhibits U–Pb age peaks at c. 0·95, 1·2, 1·85, 2·1, 2·5, 2·7, 2·9 and 3·2 Ga, with the bulk of detrital ages between c. 1·3 Ga and 1·7 Ga (Fig. 6a, c). Sample MD-8 exhibits U–Pb age peaks at c. 0·9, 1·2, 1·8, 2·1, 2·3, 2·7 and 2·9 Ga, with a broad range of detrital ages between c. 1·3 Ga and 1·6 Ga (Fig. 6b, d). The youngest detrital zircon in each sample is c. 0·89 Ga.

Overall, the U–Pb zircon age spectra of both units are similar, but they differ in several respects from published data from the Port Askaig Formation (Fig. 6e, f; Cawood *et al.* 2003). The Auchnahyle and Macduff formation data are dominated by zircon ages in the 0·9–1·8 Ga range. A similar distribution is also evident in sample IS03A from the Port Askaig Tillite (Fig. 6f; Cawood *et al.* 2003), although the amount of Archean detritus in this Islay sample is greater than that found in the NE Scotland samples. The second Port

Table 3 Stable isotope data.

Sample number	Grid reference*		Height above base (m)	Unit	$\delta^{13}C$ VPDB	$\delta^{18}O$ VPDB	$\delta^{18}O$ SMOW
103a	16491	13979	841·0	Ladder Hills Fm	1·11	− 15·01	15·44
103b	16491	13979	838·5	Ladder Hills Fm	0·32	− 14·65	15·81
103d	16491	13979	836·0	Ladder Hills Fm	0·16	− 14·69	15·77
103e	16491	13979	831·0	Ladder Hills Fm	0·50	− 15·16	15·28
103f	16491	13979	826·0	Ladder Hills Fm	0·00	− 14·15	16·32
103g	16491	13979	821·0	Ladder Hills Fm	− 1·31	− 14·99	15·46
902	15757	13451	600·0	Glenfiddich Pelite Fm	− 1·35	− 12·71	17·81
903	15757	13451	597·0	Glenfiddich Pelite Fm	− 1·72	− 10·81	19·77
904	15755	13438	594·0	Glenfiddich Pelite Fm	− 1·70	− 11·70	18·85
905	15755	13438	591·0	Glenfiddich Pelite Fm	− 1·23	− 11·06	19·51
710b	14723	13292	317·5	Inchory Limestone Fm	8·20	− 9·28	21·34
710c	14709	13267	310·0	Inchory Limestone Fm	7·91	− 8·82	21·82
710d	14682	13187	280·0	Inchory Limestone Fm	7·35	− 6·93	23·77
710e	14640	13171	252·2	Inchory Limestone Fm	7·14	− 7·38	23·30
710f	14628	13122	230·5	Inchory Limestone Fm	7·22	− 8·87	21·77
710i	14657	13204	208·8	Inchory Limestone Fm	7·78	− 9·49	21·13
710j	14716	13289	187·1	Inchory Limestone Fm	6·75	− 12·63	17·89
712	14612	13047	165·4	Inchory Limestone Fm	7·33	− 8·41	22·24
711	14615	13093	143·7	Inchory Limestone Fm	7·62	− 9·00	21·63
801	14563	12913	60·0	Neilead Semipelite Fm	5·76	− 12·36	18·16
803	14543	12815	43·0	Ailnack Phyllite Fm	7·91	− 8·80	21·84
804	14523	12748	0·0	Ailnack Phyllite Fm	6·09	− 11·17	19·39

*National grid square NJ.

Askaig sample from the Garvellach Islands (GA03A) has a more restricted Grenvillian (c. 1 Ga) sub-population, with prominent peaks at c. 1·8 Ga and 2·7 Ga (Fig. 6e).

6. Discussion: regional stratigraphical correlation and implications

Regional lithostratigraphical correlation supports correlation of the Auchnahyle Formation with the Port Askaig Formation (Stephenson & Gould 1995). Both units overlie lithologically similar, diverse pelite/limestone successions assigned to the Blair Atholl Subgroup, and are in turn overlain by shallow marine quartzites of the Islay Subgroup. Basal portions of the main metadiamictite units in both formations contain abundant dolomite clasts, while higher strata record the incoming of granitic detritus.

6.1. Stratigraphical correlations based on the C isotope data

The C isotope data from below the Auchnahyle Formation are consistent with previously published data from the SW Highlands of Scotland. Brasier & Shields (2000) and McCay *et al.* (2006) document strongly positive $\delta^{13}C$ values ($\sim$5‰) from stratigraphically equivalent Blair Atholl Subgroup metalimestones beneath the Port Askaig Formation, consistent with the values reported here from the Inchory Limestone and Neilead Semipelite formations (5·8–8·2‰). In the Islay Limestone Formation, there is a sharp decrease in $\delta^{13}C$ values to about − 4‰ before recovering to $\delta^{13}C$ values of around 0 immediately beneath the Port Askaig Tillite (Brasier & Shields 2000; McCay *et al.* 2006). A similar marked decline in $\delta^{13}C$ values is evident in our dataset from the Glenfiddich Pelite Formation ($\delta^{13}C$ values of between − 1·2‰ and − 1·7‰). The 'pre-tillite recovery' in $\delta^{13}C$ values is also present ($\delta^{13}C$ values immediately underlying the Auchnahyle Formation range from − 1·3‰ to 1·1‰), but it is not as marked as in the SW Highlands.

$^{87}Sr/^{86}Sr$ values from Appin Group and basal Argyll Group limestones in the SW Highlands (Brasier & Shields 2000) range from 0·7064 to 0·7072 and can be matched with $^{87}Sr/^{86}Sr$ values from limestone units (e.g. the Inchory Limestone) in the Tomintoul region (Thomas *et al.* 2004). In contrast, Argyll Group strata overlying the Port Askaig Formation (Brasier & Shields 2000) and Easdale Subgroup strata overlying the Auchnahyle/Ladder Hills Formation (Thomas *et al.* 2004) typically yield $^{87}Sr/^{86}Sr$ values >0·7085. There appears to be a steady rise in the marine strontium $^{87}Sr/^{86}Sr$ values throughout the Neoproterozoic (e.g. Halverson *et al.* 2007), with pre- and immediately post- Sturtian $^{87}Sr/^{86}Sr$ values of <0·7070. $^{87}Sr/^{86}Sr$ values of carbonates which post-date the Marinoan glaciation range from 0·7070 to 0·7075, rising rapidly to 0.7090 (Halverson *et al.* 2007). Hence, lithostratigraphical correlation of the Auchnahyle and Port Askaig formations is supported by the C and Sr isotope data, which is also in accord with a Sturtian age for this event.

6.2. Stratigraphical correlations based on the volcanic geochemistry data

The thin tholeiitic pillow basalt unit that underlies the metadiamictite sequence in the Auchnahyle Formation was extruded in earliest Islay Subgroup times, effectively contemporaneous with the Sturtian glacial episode. It is enriched in Fe, Ti and fluid-immobile, high field strength elements such as Nb, Zr and Y compared to the younger volcanics (the Delnadamph Volcanic Member and possibly related metadolerite sills) which are encountered further up-section. An Easdale Subgroup affinity is thought likely for the Delnadamph Volcanic Member and occurs only a few hundred metres up-section from the Kymah Quartzite (the Islay Quartzite equivalent), and it thus likely represents a time equivalent of Easdale Subgroup volcanic rocks such as the Laoigh Metabasites

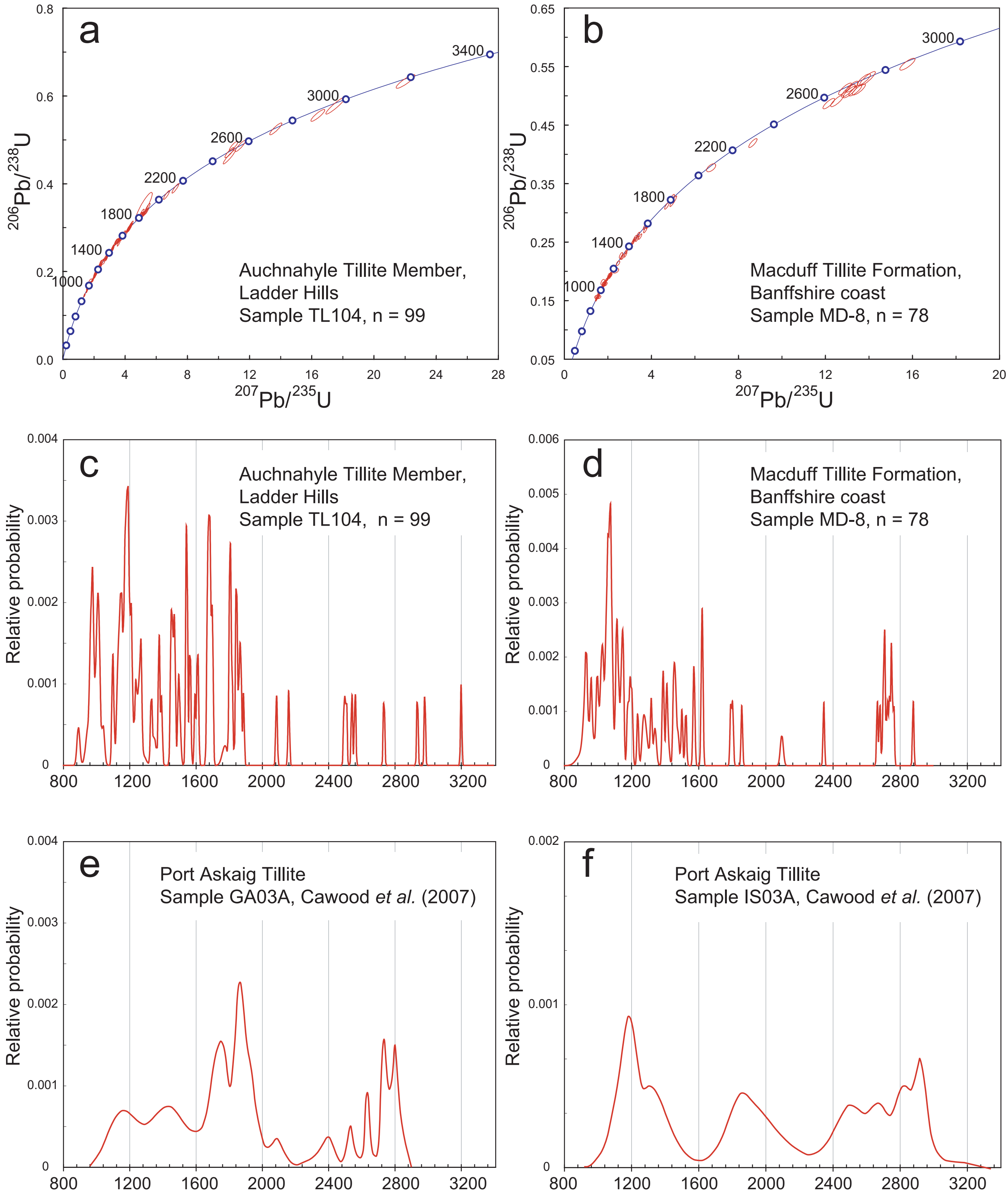

Figure 6 U–Pb Concordia diagram of the LA-ICP-MS detrital zircon data from the meta-diamictite units in the Auchnahyle Formation (a) and the Macduff Formation (b). Probability density diagrams of the U–Pb LA-ICP-MS detrital zircon data from the Auchnahyle Formation (c) and the Macduff Formation (d). Probability density diagrams of detrital zircon U–Pb SHRIMP data from the Port Askaig Formation (e, f) from Cawood *et al.* (2007).

and Farragon Beds. Additionally, the geochemistry of the Delnadamph Volcanic Member is similar to Easdale Subgroup volcanic rocks in the central Southern Highlands and western Ireland and geochemically distinct compared to the younger Tayvallich Volcanic Formation of SW Scotland.

Although the pillow basalt unit that underlies the meta-diamictite sequence in the Auchnahyle Formation is restricted to one outcrop in the Muckle Fergie Burn section, tuffaceous amphibolitic beds have been documented in the upper parts of the correlative Ladder Hills Formation, while mafic lavas with possible pillows are found locally at the base of the quartzite in the Kymah Burn section at the northeast end of the Ladder Hills (British Geological Survey 1995). Combined, this phase of basaltic volcanism in the earliest Islay Subgroup represents the oldest recorded phase of volcanic activity in the Dalradian Supergroup. It is interpreted as reflecting a very early stage of rifting in the Rodinian supercontinent, recording its embryonic stages of break-up that finally resulted in the development of the Iapetus Ocean. There is abundant evidence to suggest that that the final rifting event took place during the late Neoproterozoic, e.g. the voluminous rift-related magmatism that lasted from c. 620 Ma to 550 Ma (e.g. Kamo *et al.* 1989; Cawood *et al.* 2001, Kinny *et al.* 2003). However, recent palaeomagnetic studies suggest that the Iapetus Ocean may have commenced opening as early as ca. 750 Ma (McCausland *et al.* 2007). No primary igneous phase (e.g. baddeleyite or zircon) has been recovered from the Muckle Fergie Burn metavolcanic sample that is suitable for geochronology, and hence any age estimates for this volcanic episode must be based on correlations with global glacial episodes. Temporal constraints for Sturtian glaciation are presently controversial, but fall within a 740–660-Ma time span (see Fairchild & Kennedy 2007 for a review). This early minor phase of proto-Iapetan rifting in northeast Scotland may be contemporaneous with earlier pulses of magmatism along Laurentia's proto-Iapetan margin, such as the dominantly A-type felsic magmatism in the southern Appalachians that is dated at 760–680 Ma (Aleinikoff *et al.* 1995; Tollo *et al.* 2004).

6.3. Stratigraphic correlations based on the U–Pb detrital zircon data

The lithostratigraphical and chemostratigraphical arguments presented above imply that the Auchnahyle Formation can be readily correlated with the Port Askaig Formation. The Macduff Formation (Southern Highland Group) lies significantly above the metavolcanic rocks of the Upper Argyll Group, such as the basic and ultrabasic metavolcanic rocks of the Blackwater Formation (MacDonald *et al.* 2005; Fig. 2). Hence, it must represent a significantly younger glacial event than the Port Askaig Tillite, despite the similarity of the U–Pb zircon age spectra for the detrital zircon populations in both units. One of the goals of this present study was to constrain further the depositional ages of the Auchnahyle and Macduff formations. However, as neither unit yields U–Pb zircon ages younger than 0·89 Ga (Table 4; Fig. 4a–d), the depositional ages of the glacigenic rocks remain poorly constrained.

Local sources of Late Neoproterozoic zircon are likely to have been restricted during deposition of the glacigenic rocks. The pillow lava underlying the metadiamictite in the Auchnahyle Formation is basaltic in composition and unlikely to be a significant source of zircon, unless there were related local phases of acidic magmatism (see Hoskin & Schaltegger 2003). Late Neoproterozoic (c. 600 Ma) zircon grains associated with the opening of the Iapetus Ocean are only a minor component in the Early Palaeozoic detrital record on eastern Laurentia (e.g. Cawood *et al.* 2007). Their absence in the diamictite unit of the Macduff Formation may be a sampling artefact, but a relatively large number of grains (78) were analysed. It seems more likely that the c. 600-Ma magmatic event on this segment of Laurentia was not accompanied by extrusive felsic igneous activity, and that the c. 600-Ma plutonic bodies (e.g. Ben Vuirich, Keith–Portsoy) remained buried during deposition of the turbiditic Macduff Formation. Dempster *et al.* (2001) quote emplacement depths of 8–10 km for the 590 ± 2-Ma Ben Vuirich granite (Rogers *et al.* 1989) based on the pressure estimates of Ahmed-Said & Tanner (2000), which would require significant amounts of exhumation for the limited c. 600-Ma intrusions to be available as a source in Southern Highland Group times.

The similarities between the detrital signatures of the Neoproterozoic glacial sequences in the NE Scottish Highlands, and the slight differences with the Port Askaig Formation data of Cawood *et al.* (2003), likely reflect differences in the underlying basement geology. The ice-rafted granitic clasts found in both units are clearly extra-basinal, but a substantial proportion of the detritus may still have been derived from local sources. In particular, the Garvellach sample (GA03A) of Cawood *et al.* (2003), which yields the restricted Grenvillian (c. 1 Ga) sub-population and prominent detrital peaks at c. 1·8 Ga and 2·7 Ga, suggests local derivation from the Palaeoproterozoic Rhinns Complex (Marcantonio *et al.* 1988; Muir *et al.* 1992). A local source for the Archean detritus could be the Lewisian Gneiss Complex, which occurs offshore and is exposed on the island of Iona a short distance to the northwest (Fig. 1). However, such a correlation ignores Palaeozoic movements on the intervening Great Glen Fault, which may well be substantial.

The glacial sequences in the NE Highlands with their strong c. 1–1·2-Ga peak, variable amounts of detritus from c. 1·3–1·7 Ga and restricted amounts of older detritus, do not seem to have been proximal to the Lewisian Gneiss Complex (Fig. 1). Their detrital zircon age distribution is much more consistent with the magmatic history of the NE Grenville sequence in Labrador (cf. Cawood *et al.* 2003). It is uncertain whether these glacial units were directly sourcing this segment of the Grenville orogen, or if they are second cycle sediments derived from the Moine Supergroup and/or Grampian Group. The U–Pb age spectra closely resemble those of the Loch Eil and Glen Urquhart successions of the Sgurr Beag nappe (Cawood *et al.* 2004) and the Moine and Naver nappes of the Moine Supergroup (Friend *et al.* 2003) and the Strathtummel succession of the Grampian Group (Cawood *et al.* 2003). Most published U–Pb detrital zircon data from the Argyll Group and Southern Highland Groups in Scotland comes from the SW and Central Scottish Highlands (e.g. Cawood *et al.* 2003). It may be the case that the Moine Supergroup and basal Grampian Group clastic wedges, which thicken substantially to the NE, were important sediment sources to the Argyll Group and Southern Highland Group sequences in NE Scotland.

7. Conclusions

Field observations and geochemistry have identified an early ($\sim$700 Ma?) stage of tholeiitic basaltic volcanism within the Dalradian Supergroup of NE Scotland. These pillow basalts immediately underlie the glacigenic Auchnahyle Tillite Member. This unit is correlated with the Port Askaig Formation, which is generally assumed to represent the global Middle Cryogenian (Sturtian) glaciation (e.g. McCay *et al.* 2006). The correlation is based on strong similarities in clast type and the presence of a thick shallow-marine quartzite above both units, and is supported by carbon isotope data from carbonate strata below the Auchnahyle Tillite Member. U–Pb LA-ICP-MS detrital zircon data from the Auchnahyle Formation metadiamictite and the younger diamictites of the Macduff Formation to the NE reflect derivation from local basement rocks. As no detritus younger than 0·9 Ga is observed, the data do not significantly constrain the depositional age of the glacial strata. A Sturtian ($\sim$700 Ma) age for the Auchnahyle Tillite Member implies that this relatively local phase of basaltic volcanism represents the oldest volcanic activity in the Laurentian margin rocks of the Dalradian Supergroup, and is inferred to have resulted from an early phase of proto-Iapetan rifting within the Rodinian supercontinent.

Table 4 LA-MC-ICPMS U–Pb zircon data, samples MD-8 and TL104.

Zircon ID	^{207}Pb/^{206}Pb	1σ%	^{207}Pb/^{235}U	1σ%	^{206}Pb/^{238}U	1σ%	ρ	Age (Ma)						% discordance
								^{207}Pb/^{206}Pb	2σ	^{206}Pb/^{238}U	2σ	^{207}Pb/^{235}U	2σ	
MD_Z1	0·07652	0·61	2·03519	0·97	0·19290	0·75	0·776	1108·7	24·3	1137·0	15·6	1127·4	13·1	−2·6
MD_Z2	0·09476	0·50	3·33942	0·90	0·25558	0·75	0·832	1523·4	18·8	1467·2	19·7	1490·3	14·0	3·7
MD_Z3	0·07713	0·50	1·99376	0·90	0·18747	0·75	0·832	1124·6	19·9	1107·7	15·2	1113·4	12·1	1·5
MD_Z4	0·08922	0·50	2·80929	0·90	0·22838	0·75	0·832	1408·8	19·1	1326·0	18·0	1358·0	13·4	5·9
MD_Z5	0·09175	0·50	3·17021	0·90	0·25060	0·75	0·832	1462·2	19·0	1441·6	19·3	1449·9	13·8	1·4
MD_Z6	0·07314	1·02	1·69892	1·27	0·16847	0·76	0·598	1017·8	41·4	1003·7	14·2	1008·1	16·2	1·4
MD_Z7	0·06990	0·94	1·47232	1·35	0·15276	0·96	0·713	925·5	38·8	916·4	16·4	919·1	16·1	1·0
MD_Z8	0·18504	0·50	12·53277	0·96	0·49122	0·82	0·854	2698·6	16·5	2575·9	34·8	2645·2	17·9	4·5
MD_Z9	0·09139	0·52	3·17697	1·04	0·25214	0·90	0·866	1454·7	19·8	1449·5	23·4	1451·6	16·0	0·4
MD_Z10	0·09987	0·50	3·84165	0·96	0·27899	0·82	0·854	1621·6	18·6	1586·3	23·0	1601·5	15·4	2·2
MD_Z10	0·09987	0·50	3·84165	0·96	0·27899	0·82	0·854	1621·6	18·6	1586·3	23·0	1601·5	15·4	2·2
MD_Z11	0·07142	1·38	1·60865	1·57	0·16335	0·75	0·477	969·6	56·4	975·4	13·6	973·6	19·5	−0·6
MD_Z12	0·09709	0·50	3·70016	0·90	0·27642	0·75	0·832	1568·9	18·7	1573·3	20·9	1571·4	14·3	−0·3
MD_Z13	0·11016	0·50	4·94441	0·91	0·32553	0·76	0·835	1802·0	18·2	1816·7	24·0	1809·9	15·2	−0·8
MD_Z15	0·08357	1·04	2·46543	1·28	0·21396	0·75	0·586	1282·6	40·4	1249·9	17·0	1262·0	18·3	2·6
MD_Z16	0·20641	0·50	15·76604	0·90	0·55398	0·75	0·832	2877·5	16·2	2841·7	34·4	2862·7	17·1	1·2
MDA_Z1	0·19224	0·50	13·53573	0·90	0·51068	0·75	0·832	2761·4	16·4	2659·5	32·6	2717·8	16·9	3·7
MDA_Z2	0·07104	0·50	1·55189	0·90	0·15843	0·75	0·832	958·7	20·4	948·0	13·2	951·2	11·1	1·1
MDA_Z3	0·07760	0·50	2·02972	0·91	0·18970	0·76	0·836	1136·7	19·9	1119·7	15·6	1125·5	12·3	1·5
MDA_Z4	0·07520	0·50	1·85642	0·90	0·17904	0·75	0·832	1073·9	20·1	1061·7	14·7	1065·7	11·8	1·1
MDA_Z5	0·19046	0·50	13·36883	0·90	0·50907	0·75	0·832	2746·2	16·4	2652·7	32·5	2706·1	16·9	3·4
MDA_Z6	0·08950	0·90	2·97889	1·17	0·24141	0·75	0·640	1414·8	34·5	1394·0	18·8	1402·2	17·7	1·5
MDA_Z7	0·09360	0·50	3·38344	0·90	0·26216	0·75	0·832	1500·1	18·9	1500·9	20·1	1500·6	14·0	−0·1
MDA_Z8	0·06894	2·68	1·48671	2·78	0·15641	0·75	0·270	896·9	111	936·8	13·1	925·0	33·2	−4·4
MDA_Z9	0·10949	0·50	4·70767	0·90	0·31185	0·75	0·832	1790·9	18·2	1749·8	22·9	1768·6	15·0	2·3
MDA_Z10	0·18610	0·50	13·04878	1·00	0·50854	0·87	0·866	2708·0	16·5	2650·4	37·5	2683·2	18·7	2·1
MDA_Z12	0·18784	0·50	13·12305	0·96	0·50670	0·82	0·855	2723·3	16·5	2642·5	35·6	2688·5	18·0	3·0
MDA_Z14	0·07419	0·50	1·79518	0·90	0·17550	0·75	0·832	1046·6	20·2	1042·3	14·4	1043·7	11·7	0·4
MDA_Z15	0·07813	0·50	2·08807	0·90	0·19383	0·75	0·832	1150·2	19·9	1142·1	15·7	1144·9	12·3	0·7
MDA_Z16	0·12977	1·03	6·74633	1·27	0·37705	0·75	0·589	2094·8	36·2	2062·5	26·4	2078·7	22·3	1·5
MDA_Z17	0·07565	0·50	1·89117	0·90	0·18130	0·75	0·832	1085·9	20·0	1074·1	14·8	1078·0	11·9	1·1
MDA_Z18	0·07460	0·67	1·82381	1·02	0·17731	0·77	0·755	1057·8	26·9	1052·2	14·9	1054·1	13·3	0·5
MDA_Z19	0·07654	1·62	1·88361	1·78	0·17847	0·75	0·421	1109·3	64·6	1058·6	14·6	1075·3	23·4	4·6
MDA_Z20	0·07678	0·50	1·99142	0·90	0·18812	0·75	0·832	1115·4	20·0	1111·2	15·3	1112·6	12·1	0·4
MDA_Z21	0·09962	0·50	3·71878	0·90	0·27075	0·75	0·832	1616·9	18·6	1544·6	20·6	1575·4	14·3	4·5
MDA_Z22	0·07519	0·50	1·85499	0·90	0·17893	0·75	0·832	1073·5	20·1	1061·1	14·7	1065·2	11·8	1·2
MDA_Z23	0·18114	0·50	12·15290	0·90	0·48660	0·75	0·833	2663·3	16·6	2555·9	31·7	2616·3	16·8	4·0
MDA_Z25	0·18286	0·50	12·90211	0·95	0·51174	0·80	0·849	2678·9	16·5	2664·1	35·0	2672·5	17·7	0·6
MDA_Z26	0·07427	0·79	1·79028	1·09	0·17482	0·75	0·687	1048·8	32·0	1038·6	14·4	1041·9	14·1	1·0
MDA_Z28	0·18602	0·50	13·22211	0·90	0·51551	0·75	0·832	2707·3	16·5	2680·1	32·8	2695·6	16·9	1·0
MDA_Z29	0·09238	0·86	3·27527	1·14	0·25713	0·75	0·659	1475·2	32·5	1475·2	19·7	1475·2	17·6	0·0
MDA_Z30	0·07325	0·60	1·76272	0·96	0·17454	0·75	0·782	1020·8	24·3	1037·1	14·4	1031·8	12·4	−1·6
MDA_Z31	0·14989	0·50	8·66353	0·90	0·41919	0·75	0·832	2344·7	17·1	2256·8	28·5	2303·3	16·3	3·7
MDA_Z32	0·07523	1·27	1·84545	1·48	0·17791	0·75	0·508	1074·8	51·1	1055·5	14·6	1061·8	19·3	1·8
MDA_Z33	0·09734	0·50	3·48181	0·90	0·25941	0·75	0·832	1573·9	18·7	1486·8	19·9	1523·1	14·1	5·5
MDA_Z34	0·07519	0·55	1·88387	0·93	0·18170	0·75	0·804	1073·7	22·3	1076·3	14·9	1075·4	12·3	−0·2
MDA_Z35	0·07359	0·56	1·76253	0·93	0·17371	0·75	0·803	1030·2	22·5	1032·5	14·3	1031·8	12·0	−0·2
MDA_Z36	0·07812	0·57	2·09870	0·94	0·19484	0·75	0·796	1149·9	22·6	1147·6	15·7	1148·4	12·9	0·2
MDA_Z37	0·07974	0·50	2·10482	0·90	0·19144	0·75	0·832	1190·6	19·7	1129·2	15·5	1150·4	12·3	5·2
MDA_Z38	0·07482	0·63	1·86318	0·98	0·18060	0·75	0·767	1063·7	25·3	1070·3	14·8	1068·1	12·8	−0·6
MDA_Z39	0·07460	0·50	1·77684	0·90	0·17275	0·75	0·832	1057·7	20·1	1027·3	14·2	1037·0	11·6	2·9
MDA_Z40	0·07356	1·74	1·82098	1·89	0·17953	0·75	0·397	1029·5	70·2	1064·4	14·7	1053·0	24·5	−3·4
MDA_Z41	0·08608	0·85	2·66698	1·17	0·22470	0·80	0·685	1340·1	32·8	1306·7	18·9	1319·4	17·1	2·5
MDA_Z43	0·07656	0·53	1·99608	0·92	0·18910	0·75	0·819	1109·7	21·0	1116·5	15·4	1114·2	12·3	−0·6
MDA_Z44	0·07063	2·15	1·52922	2·39	0·15704	1·05	0·438	946·6	88·1	940·3	18·3	942·2	29·0	0·7
MDA_Z45	0·07786	0·50	2·06691	0·90	0·19254	0·75	0·832	1143·2	19·9	1135·1	15·6	1137·9	12·3	0·7
MDA_Z46	0·18918	0·50	13·76549	0·90	0·52773	0·75	0·832	2735·1	16·5	2731·9	33·3	2733·7	16·9	0·1
MDA_Z47	0·07543	0·77	1·92058	1·07	0·18466	0·75	0·698	1080·1	30·9	1092·4	15·1	1088·3	14·2	−1·1
MDA_Z48	0·08163	0·50	2·30209	0·90	0·20454	0·75	0·832	1236·6	19·6	1199·7	16·4	1212·9	12·7	3·0
MDA_Z49	0·08506	0·50	2·63384	0·90	0·22458	0·75	0·832	1316·9	19·4	1306·0	17·7	1310·1	13·2	0·8

Table 4 *Continued.*

Zircon ID	$^{207}Pb/^{206}Pb$	1σ%	$^{207}Pb/^{235}U$	1σ%	$^{206}Pb/^{238}U$	1σ%	ρ	Age (Ma)						% discordance
								$^{207}Pb/^{206}Pb$	2σ	$^{206}Pb/^{238}U$	2σ	$^{207}Pb/^{235}U$	2σ	
MDA_Z50	0·07508	0·89	1·72536	1·30	0·16666	0·95	0·731	1070·7	35·8	993·7	17·6	1018·0	16·6	7·2
MDA_Z52	0·08454	2·38	2·34667	2·54	0·20132	0·88	0·348	1305·0	92·4	1182·4	19·1	1226·5	35·5	9·4
MDA_Z53	0·07229	0·56	1·68162	1·10	0·16872	0·94	0·861	994·0	22·6	1005·1	17·5	1001·6	13·9	− 1·1
MDA_Z54	0·11353	0·50	5·00559	1·27	0·31976	1·17	0·919	1856·7	18·1	1788·6	36·3	1820·3	21·3	3·7
MDA_Z55	0·07005	0·53	1·49916	1·13	0·15521	1·00	0·884	930·0	21·7	930·1	17·3	930·0	13·7	0·0
MDA_Z56	0·08300	0·88	2·60058	1·25	0·22725	0·89	0·711	1269·2	34·3	1320·1	21·2	1300·8	18·2	− 4·0
MDA_Z57	0·07244	0·79	1·77543	1·21	0·17775	0·91	0·756	998·4	32·1	1054·7	17·7	1036·5	15·5	− 5·6
MDA_Z58	0·06966	1·26	1·59263	1·50	0·16581	0·81	0·543	918·5	51·7	989·0	14·9	967·3	18·5	− 7·7
MDA_Z60	0·19084	0·50	13·93250	1·06	0·52949	0·93	0·881	2749·4	16·4	2739·3	41·4	2745·1	19·8	0·4
MDA_Z61	0·08023	0·50	2·25304	0·90	0·20368	0·75	0·832	1202·6	19·7	1195·0	16·3	1197·7	12·6	0·6
MDA_Z62	0·07978	0·95	2·12816	1·21	0·19346	0·75	0·619	1191·6	37·6	1140·1	15·7	1158·0	16·6	4·3
MDA_Z63	0·07917	0·50	2·12376	0·90	0·19454	0·75	0·832	1176·5	19·8	1145·9	15·7	1156·6	12·4	2·6
MDA_Z64	0·07441	1·96	1·71000	2·11	0·16668	0·78	0·370	1052·5	78·9	993·8	14·3	1012·3	26·7	5·6
MDA_Z65	0·08809	0·50	2·84025	0·90	0·23383	0·75	0·832	1384·5	19·2	1354·6	18·3	1366·2	13·4	2·2
MDA_Z66	0·09112	0·50	3·10843	0·90	0·24741	0·75	0·832	1449·2	19·0	1425·1	19·1	1434·8	13·8	1·7
MDA_Z67	0·07337	2·28	1·58006	2·41	0·15618	0·77	0·318	1024·3	92·4	935·5	13·3	962·4	29·5	8·7
MDA_Z69	0·08836	0·50	2·89933	0·90	0·23797	0·75	0·832	1390·4	19·2	1376·1	18·6	1381·7	13·5	1·0
MDA_Z71	0·07474	0·59	1·82951	0·96	0·17753	0·75	0·785	1061·6	23·8	1053·5	14·6	1056·1	12·5	0·8
TL104P_Z1	0·07991	0·98	2·30850	1·35	0·20951	0·92	0·683	1194·8	19·4	1226·2	20·5	1214·9	18·9	− 2·6
TL104P_Z2	0·07904	0·50	2·06170	1·06	0·18918	0·94	0·883	1173·2	9·9	1116·9	19·2	1136·2	14·4	4·8
TL104P_Z3	0·08122	0·99	2·29656	1·54	0·20507	1·18	0·764	1226·8	19·5	1202·5	25·8	1211·2	21·6	2·0
TL104P_Z4	0·07156	0·61	1·53044	1·11	0·15511	0·92	0·834	973·5	12·5	929·5	16·0	942·7	13·5	4·5
TL104P_Z5	0·08300	0·50	2·42438	1·06	0·21184	0·94	0·882	1269·2	9·8	1238·6	21·1	1249·9	15·2	2·4
TL104P_Z6	0·07889	0·57	2·20505	1·11	0·20271	0·96	0·859	1169·5	11·3	1189·8	20·7	1182·6	15·4	− 1·7
TL104P_Z7	0·07270	0·90	1·67040	1·89	0·16664	1·66	0·879	1005·7	18·3	993·6	30·6	997·3	23·8	1·2
TL104P_Z8	0·07600	0·50	1·89893	1·08	0·18122	0·96	0·887	1095·0	10·0	1073·6	18·9	1080·7	14·3	2·0
TL104P_Z9	0·09227	0·50	3·18816	1·02	0·25061	0·89	0·872	1472·9	9·5	1441·6	22·9	1454·3	15·6	2·1
TL104P_Z10	0·07905	0·53	2·17683	1·07	0·19973	0·93	0·871	1173·3	10·4	1173·9	20·0	1173·7	14·8	0·0
TL104P_Z11	0·08228	0·50	2·41945	1·07	0·21326	0·94	0·884	1252·2	9·8	1246·2	21·4	1248·4	15·2	0·5
TL104P_Z13	0·07057	1·31	1·57014	1·60	0·16137	0·92	0·576	945·0	26·7	964·4	16·5	958·5	19·6	− 2·1
TL104P_Z14	0·11540	0·50	5·36717	1·06	0·33731	0·93	0·881	1886·2	9·0	1873·7	30·3	1879·6	18·0	0·7
TL104P_Z15	0·08776	0·50	2·87005	1·06	0·23719	0·94	0·882	1377·2	9·6	1372·1	23·1	1374·1	15·9	0·4
TL104P_Z16	0·07112	1·42	1·60559	1·76	0·16374	1·03	0·589	960·8	29·0	977·5	18·7	972·4	21·8	− 1·7
TL104P_Z17	0·16491	0·50	10·70962	1·12	0·47102	1·00	0·895	2506·6	8·4	2488·0	41·2	2498·3	20·6	0·7
TL104P_Z18	0·09836	0·50	3·58250	1·07	0·26415	0·95	0·885	1593·3	9·3	1511·0	25·6	1545·7	16·9	5·2
TL104P_Z19	0·07114	0·50	1·57136	1·14	0·16019	1·02	0·898	961·5	10·2	957·9	18·1	959·0	14·0	0·4
TL104P_Z20	0·06872	0·84	1·38489	1·31	0·14617	1·00	0·765	890·2	17·4	879·5	16·5	882·5	15·3	1·2
TL104P_Z21	0·10329	0·50	4·24177	1·07	0·29784	0·94	0·883	1684·1	9·2	1680·6	27·8	1682·1	17·4	0·2
TL104P_Z22	0·08170	0·50	2·39534	1·05	0·21264	0·92	0·879	1238·3	9·8	1242·9	20·8	1241·2	14·9	− 0·4
TL104P_Z23	0·10411	0·50	4·33596	1·06	0·30205	0·94	0·883	1698·7	9·2	1701·5	28·0	1700·2	17·4	− 0·2
TL104P_Z24	0·25233	0·50	22·02592	1·12	0·63309	1·00	0·895	3199·4	7·9	3161·8	49·9	3184·9	21·5	1·2
TL104_Z1	0·11023	0·50	4·96961	1·12	0·32699	1·00	0·894	1803·1	9·1	1823·8	31·7	1814·2	18·7	− 1·1
TL104_Z2	0·07175	0·86	1·58749	1·27	0·16046	0·94	0·739	978·9	17·4	959·4	16·7	965·3	15·7	2·0
TL104_Z2	0·11267	0·50	5·05161	1·17	0·32517	1·06	0·904	1842·9	9·0	1814·9	33·3	1828·0	19·6	1·5
TL104_Z2	0·07174	0·85	1·58555	1·27	0·16030	0·95	0·743	978·5	17·3	958·4	16·8	964·6	15·7	2·1
TL104_Z3	0·11267	0·50	5·05161	1·17	0·32517	1·06	0·904	1842·9	9·0	1814·9	33·3	1828·0	19·6	1·5
TL104_Z3	0·11268	0·50	5·03687	1·15	0·32420	1·04	0·901	1843·1	9·0	1810·2	32·7	1825·5	19·3	1·8
TL104_Z4	0·09936	0·50	3·79469	1·07	0·27699	0·94	0·883	1612·2	9·3	1576·2	26·3	1591·6	17·0	2·2
TL104_Z5	0·18900	0·50	13·68238	1·17	0·52505	1·06	0·904	2733·5	8·2	2720·6	46·7	2728·0	21·9	0·5
TL104_Z6	0·08294	2·26	2·52906	2·47	0·22115	1·00	0·403	1267·8	44·2	1288·0	23·2	1280·4	35·4	− 1·6
TL104_Z7	0·08040	0·50	2·25280	1·06	0·20323	0·93	0·881	1206·7	9·8	1192·6	20·2	1197·7	14·7	1·2
TL104_Z8	0·07961	0·56	2·17752	1·12	0·19839	0·97	0·868	1187·3	11·0	1166·6	20·7	1173·9	15·5	1·7
TL104_Z9	0·16821	0·50	10·69479	1·51	0·46111	1·42	0·943	2540·0	8·4	2444·5	57·6	2497·0	27·6	3·8
TL104_Z10	0·10415	0·50	4·28719	1·15	0·29854	1·03	0·900	1699·4	9·2	1684·1	30·5	1690·9	18·7	0·9
TL104_Z11	0·08772	0·50	2·83425	1·19	0·23435	1·08	0·907	1376·3	9·6	1357·2	26·4	1364·6	17·7	1·4
TL104_Z12	0·07261	0·61	1·68451	1·22	0·16826	1·06	0·867	1003·1	12·4	1002·5	19·7	1002·7	15·5	0·1
TL104_Z14	0·10367	0·50	4·40155	1·06	0·30794	0·94	0·882	1690·8	9·2	1730·6	28·3	1712·6	17·4	− 2·4
TL104_Z15	0·07921	0·50	2·22111	1·11	0·20338	1·00	0·894	1177·3	9·9	1193·4	21·6	1187·7	15·5	− 1·4
TL104_Z16	0·08844	0·50	2·80406	1·05	0·22994	0·92	0·878	1392·2	9·6	1334·2	22·1	1356·6	15·5	4·2

Table 4 *Continued.*

Zircon ID	$^{207}Pb/^{206}Pb$	1σ%	$^{207}Pb/^{235}U$	1σ%	$^{206}Pb/^{238}U$	1σ%	ρ	Age (Ma)						% discordance
								$^{207}Pb/^{206}Pb$	2σ	$^{206}Pb/^{238}U$	2σ	$^{207}Pb/^{235}U$	2σ	
TL104_Z17	0·07289	0·50	1·73914	1·11	0·17305	0·99	0·893	1010·8	10·1	1028·9	18·8	1023·1	14·2	− 1·8
TL104_Z18	0·07248	0·89	1·68703	1·33	0·16882	0·98	0·739	999·4	18·2	1005·6	18·3	1003·6	16·8	− 0·6
TL104_Z19	0·08276	0·50	2·54692	1·11	0·22320	0·99	0·893	1263·6	9·8	1298·7	23·3	1285·6	16·1	− 2·8
TL104_Z20	0·11023	0·50	5·06895	1·19	0·33352	1·08	0·908	1803·2	9·1	1855·4	34·8	1830·9	20·0	− 2·9
TL104_Z21	0·11038	0·50	4·94981	1·12	0·32525	1·00	0·895	1805·6	9·1	1815·3	31·6	1810·8	18·7	− 0·5
TL104_Z22	0·07994	0·50	2·15584	1·15	0·19560	1·04	0·901	1195·4	9·9	1151·7	21·8	1166·9	15·8	3·7
TL104_Z23	0·07317	0·50	1·73757	1·04	0·17222	0·91	0·877	1018·8	10·1	1024·3	17·3	1022·6	13·3	− 0·5
TL104_Z34	0·08562	0·50	2·73956	1·06	0·23207	0·94	0·883	1329·6	9·7	1345·3	22·8	1339·3	15·7	− 1·2
TL104_Z35	0·07156	0·60	1·59444	1·08	0·16159	0·90	0·832	973·5	12·3	965·6	16·2	968·0	13·4	0·8
TL104_Z36	0·07966	0·50	2·16493	1·12	0·19710	1·00	0·895	1188·6	9·9	1159·7	21·3	1169·9	15·5	2·4
TL104_Z37	0·07807	0·50	2·06759	1·16	0·19207	1·04	0·902	1148·8	9·9	1132·6	21·6	1138·1	15·7	1·4
TL104_Z38	0·07391	0·88	1·76138	1·27	0·17284	0·91	0·718	1039·0	17·9	1027·7	17·3	1031·4	16·3	1·1
TL104_Z40	0·09559	0·50	3·57243	1·05	0·27105	0·93	0·880	1539·7	9·4	1546·1	25·5	1543·4	16·6	− 0·4
TL104_Z41	0·07961	0·50	2·35879	2·06	0·21490	2·00	0·970	1187·2	9·9	1254·9	45·4	1230·2	29·0	− 5·7
TL104_Z42	0·09690	0·50	3·69969	1·23	0·27692	1·13	0·914	1565·2	9·4	1575·8	31·5	1571·3	19·5	− 0·7
TL104_Z43	0·21991	0·50	17·52351	1·45	0·57794	1·36	0·939	2980·0	8·1	2940·3	63·9	2963·9	27·5	1·3
TL104_Z44	0·08642	1·22	2·73555	1·57	0·22957	0·99	0·627	1347·6	23·6	1332·3	23·7	1338·2	23·1	1·1
TL104_Z45	0·21385	0·50	16·38885	1·11	0·55583	0·99	0·893	2934·9	8·1	2849·4	45·6	2899·8	21·1	2·9
TL104_Z46	0·11120	0·50	4·94480	1·11	0·32251	0·99	0·892	1819·1	9·1	1802·0	31·0	1809·9	18·5	0·9
TL104_Z47	0·13463	0·50	7·22920	1·24	0·38946	1·14	0·915	2159·2	8·7	2120·3	40·9	2140·1	21·9	1·8
TL104_Z48	0·07777	0·76	2·09823	1·29	0·19569	1·04	0·806	1140·9	15·1	1152·1	21·8	1148·2	17·5	− 1·0
TL104_Z49	0·08023	0·79	2·29239	1·47	0·20722	1·24	0·843	1202·7	15·6	1214·0	27·4	1209·9	20·6	− 0·9
TL104_Z50	0·09174	0·76	3·17085	1·30	0·25067	1·05	0·809	1462·0	14·5	1441·9	27·1	1450·1	19·9	1·4
TL104_Z51	0·17019	0·50	11·40860	1·19	0·48618	1·08	0·907	2559·5	8·4	2554·1	45·2	2557·1	21·9	0·2
TL104_Z52	0·07864	0·50	2·06972	1·25	0·19088	1·15	0·917	1163·1	9·9	1126·1	23·7	1138·8	17·0	3·2
TL104_Z53	0·07720	0·61	1·92536	1·17	0·18089	1·00	0·856	1126·3	12·1	1071·8	19·8	1089·9	15·5	4·8
TL104_Z54	0·11068	0·50	5·00084	1·08	0·32770	0·95	0·885	1810·6	9·1	1827·2	30·2	1819·5	18·0	− 0·9
TL104_Z55	0·09584	0·50	3·69077	1·56	0·27929	1·48	0·947	1544·7	9·4	1587·8	41·4	1569·4	24·6	− 2·8
TL104_Z56	0·16367	0·50	10·97213	1·03	0·48622	0·90	0·874	2493·9	8·4	2554·3	37·8	2520·8	18·9	− 2·4
TL104_Z57	0·09911	0·50	3·90256	1·18	0·28558	1·07	0·906	1607·4	9·3	1619·4	30·5	1614·2	18·9	− 0·7
TL104_Z58	0·10311	0·50	4·31927	1·12	0·30381	1·01	0·895	1680·9	9·2	1710·2	30·1	1697·0	18·3	− 1·7
TL104_Z59	0·11350	0·50	5·17536	1·06	0·33070	0·94	0·882	1856·2	9·0	1841·8	29·9	1848·6	17·9	0·8
TL104_Z60	0·10253	0·50	4·19613	1·11	0·29683	0·99	0·893	1670·4	9·2	1675·5	29·3	1673·3	18·1	− 0·3
TL104_Z60	0·09585	0·50	3·65687	1·15	0·27672	1·04	0·901	1544·7	9·4	1574·8	28·9	1562·0	18·2	− 1·9
TL104_Z60	0·10263	0·50	4·21032	1·11	0·29754	0·99	0·893	1672·2	9·2	1679·1	29·3	1676·0	18·1	− 0·4
TL104_Z61	0·09573	0·50	3·65323	1·07	0·27678	0·94	0·883	1542·5	9·4	1575·1	26·3	1561·2	16·9	− 2·1
TL104_Z62	0·07838	0·50	2·18362	1·17	0·20206	1·05	0·904	1156·5	9·9	1186·4	22·8	1175·8	16·1	− 2·6
TL104_Z63	0·09328	0·58	3·44865	1·22	0·26813	1·07	0·879	1493·6	11·0	1531·3	29·1	1515·6	19·0	− 2·5
TL104_Z64	0·10229	0·50	4·08670	1·14	0·28977	1·02	0·898	1666·0	9·3	1640·4	29·5	1651·7	18·4	1·5
TL104_Z65	0·09204	0·50	3·37723	1·28	0·26612	1·18	0·920	1468·3	9·5	1521·1	31·8	1499·1	19·8	− 3·6
TL104_Z66	0·11441	0·50	5·27625	1·08	0·33447	0·96	0·887	1870·6	9·0	1860·0	31·0	1865·0	18·4	0·6
TL104_Z67	0·07720	1·16	2·07430	1·76	0·19487	1·32	0·751	1126·4	23·2	1147·7	27·8	1140·4	23·9	− 1·9
TL104_Z68	0·07622	0·50	2·01777	1·22	0·19200	1·11	0·912	1100·9	10·0	1132·2	23·0	1121·5	16·4	− 2·8
TL104_Z69	0·09121	0·50	3·11202	1·17	0·24747	1·06	0·904	1450·9	9·5	1425·4	27·0	1435·7	17·8	1·8
TL104_Z70	0·09364	0·75	3·44741	1·21	0·26701	0·95	0·783	1500·9	14·3	1525·6	25·7	1515·3	18·9	− 1·6
TL104_Z71	0·10850	1·83	5·20307	4·24	0·34780	3·83	0·902	1774·4	33·4	1924·1	126·2	1853·1	69·8	− 8·4
TL104_Z72	0·07760	0·50	2·09774	1·34	0·19606	1·24	0·928	1136·6	9·9	1154·1	26·2	1148·1	18·2	− 1·5
TL104_Z73	0·12907	0·50	6·66068	1·21	0·37429	1·10	0·911	2085·3	8·8	2049·5	38·6	2067·4	21·2	1·7
TL104_Z74	0·07802	0·50	2·11977	1·18	0·19705	1·06	0·905	1147·4	9·9	1159·4	22·6	1155·3	16·1	− 1·0
TL104_Z75	0·07943	0·50	2·34426	1·29	0·21404	1·19	0·921	1182·9	9·9	1250·3	26·9	1225·8	18·1	− 5·7
TL104_Z76	0·09152	0·50	3·19012	1·39	0·25281	1·29	0·933	1457·4	9·5	1452·9	33·6	1454·8	21·2	0·3
TL104_Z77	0·10322	0·50	4·27161	1·42	0·30013	1·33	0·936	1682·9	9·2	1692·0	39·4	1687·9	23·1	− 0·5
TL104_Z78	0·07252	2·22	1·77937	2·52	0·17795	1·19	0·471	1000·6	45·1	1055·8	23·1	1037·9	32·2	− 5·5
TL104_Z79	0·09101	0·50	3·18187	1·30	0·25356	1·20	0·924	1446·9	9·5	1456·8	31·3	1452·8	20·0	− 0·7
TL104_Z80	0·10290	0·50	4·21949	1·29	0·29741	1·19	0·921	1677·0	9·2	1678·5	34·9	1677·8	20·9	− 0·1
TL104_Z81	0·09672	0·50	3·62076	1·29	0·27149	1·19	0·922	1561·9	9·4	1548·4	32·7	1554·1	20·3	0·9
TL104_Z82	0·11409	0·50	5·43760	1·25	0·34566	1·14	0·916	1865·6	9·0	1913·9	37·8	1890·8	21·2	− 2·6
TL104_Z83	0·08063	0·50	2·32157	1·51	0·20882	1·42	0·943	1212·5	9·8	1222·5	31·6	1218·9	21·2	− 0·8

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