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$^{87}Sr/^{86}Sr$ chemostratigraphy of Neoproterozoic Dalradian limestones of Scotland and Ireland: constraints on depositional ages and time scales

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Abstract: New calcite $^{87}Sr/^{86}Sr$ data for 47 limestones from the metamorphosed and deformed Neoproterozoic–Cambrian Dalradian Supergroup of Scotland and Ireland are used to identify secular trends in seawater $^{87}Sr/^{86}Sr$ through the Dalradian succession and to constrain its depositional age. Dalradian limestones commonly have Sr >1000 ppm, indicating primary aragonite and marine diagenesis. Low Mn, Mn/Sr <0.6, $\delta^{18}O$ and trace element data indicate that many $^{87}Sr/^{86}Sr$ ratios are unaltered since diagenesis despite greenschist- to amphibolite-facies metamorphism, consistent with the documented behaviour of Sr and O during metamorphic fluid–rock interaction. Thus, the $^{87}Sr/^{86}Sr$ data are interpreted largely to reflect $^{87}Sr/^{86}Sr$ of coeval seawater. Currently available data show that Neoproterozoic seawater $^{87}Sr/^{86}Sr$ rose from *c*. 0.7052 at 850–900 Ma to *c*. 0.7085 or higher in the latest Neoproterozoic. Temporal changes at *c*. 800 Ma and *c*. 600 Ma bracket the range in $^{87}Sr/^{86}Sr$ values of calcite in Grampian, Appin and lowest Argyll Group (*c*. 0.7064–0.7072) and middle and uppermost Argyll Group (*c*. 0.7082–0.7095) limestones, consistent with a rise in seawater $^{87}Sr/^{86}Sr$ around 600 Ma. $^{87}Sr/^{86}Sr$ data are consistent with the sedimentary affinity of the Islay Subgroup with the underlying Appin Group, and with a possible time interval between deposition of Islay and Easdale Subgroup rocks. They indicate that the Dalradian, as a whole, is younger than *c*. 800 Ma.

Keywords: Dalradian, Neoproterozoic, $^{87}Sr/^{86}Sr$, $\delta^{18}O$, limestone.

The heterolithic Neoproterozoic to Cambrian Dalradian Supergroup of Scotland and Northern Ireland was deposited on the eastern margin of Laurentia as it began to break out of Rodinia (Dalziel 1992, 1994), and was deformed and metamorphosed during the Ordovician Grampian orogeny (Harris *et al*. 1994). Evidence for the maximum age of the Dalradian is ambiguous, and interpretations differ markedly (e.g. Highton *et al*. 1999; Smith *et al*. 1999). However, this age is critically important in constraining tectonic models for the Neoproterozoic evolution of eastern Laurentia through the eastern North American to Ireland–Scotland–Greenland sector (e.g. Soper & England 1995; Bluck & Rogers 1997; Highton *et al*. 1999; Prave 1999*a*; Smith *et al*. 1999; Dalziel & Soper 2001). It also has wider implications for the age of the Neoproterozoic glacigenic Port Askaig Formation and the correlation of this important unit with other Neoproterozoic tillites worldwide.

A key feature of Dalradian lithostratigraphy is the presence of limestones in many parts of the succession. In this paper, we present new $^{87}Sr/^{86}Sr$ and $\delta^{18}O$ data for 47 samples of Dalradian limestones. We compare temporal variations in $^{87}Sr/^{86}Sr$ with those of carbonate rocks from undeformed and unmetamorphosed Neoproterozoic successions worldwide to constrain the depositional age of the Dalradian Supergroup and units within it. Temporal variations in seawater $^{87}Sr/^{86}Sr$ through the Neoproterozoic are comparable in magnitude with those known to have occurred during the Phanerozoic (e.g. Burke *et al*. 1982; Denison *et al*. 1994*a*; Howarth & McArthur 1997). Because the age ranges of most Neoproterozoic sedimentary successions are poorly constrained by radiometric or biostratigraphical dating, $^{87}Sr/^{86}Sr$ data are widely used to constrain such ages and aid correlation of Neoproterozoic sedimentary sequences in widely separated regions (e.g. Derry *et al*. 1989; Narbonne *et al*. 1994; Melezhik *et al*. 2001). Brasier & Shields (2000) recently used the $^{87}Sr/^{86}Sr$ and $\delta^{13}C$ of carbonates beneath the Neoproterozoic glacigenic Port Askaig Formation in the Dalradian of the SW Scottish Highlands to propose a Sturtian (*c*. 720 Ma) age for this unit. Here we report the isotope geochemistry of calcitic limestones throughout the entire Neoproterozoic Dalradian Supergroup. We identify secular variations in $^{87}Sr/^{86}Sr$ and use the data to provide wider age constraints on Dalradian sedimentation, focusing in particular on the age of onset of Dalradian deposition and the evidence for prolonged and continuous sedimentation and rifting.

Geology and age of the Dalradian Supergroup

Lithostratigraphy

The Dalradian Supergroup of Scotland and Ireland (Fig. 1) comprises siliciclastic and carbonate rocks, together with subordinate volcanic and volcaniclastic rocks, deposited on continental crust on the eastern Laurentian margin during the Neoproterozoic and up to at least the early Mid-Cambrian (Harris *et al*. 1994; Stephenson & Gould 1995; Tanner 1995). The Dalradian is divided into four Groups (oldest to youngest): Grampian, Appin, Argyll and Southern Highland. The Grampian Group is dominated by fluvial to marine siliciclastic rocks with very rare limestone units (Glover *et al*. 1995). The base of the Grampian Group beneath the oldest lithostratigraphical unit (Glen Shirra Subgroup) is nowhere exposed and its relationship to gneissose metasedimentary rocks that may constitute basement is unknown (Smith *et al*. 1999).

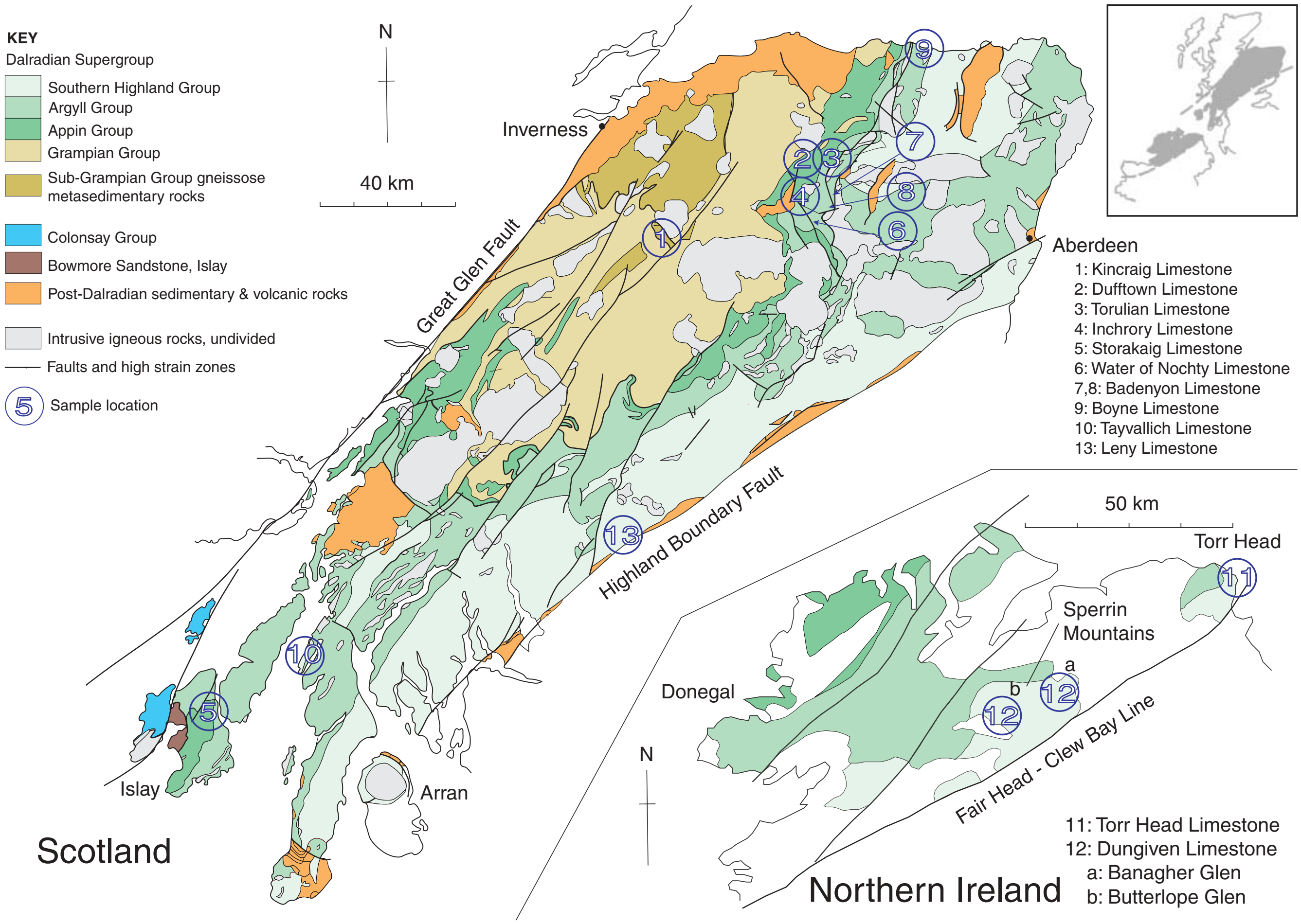


Fig. 1. Summary geological map of the Dalradian geology of the Scottish Grampian Highlands and Northern Ireland and the location of samples from limestone units discussed in the text. Details of specific sample locations are given in Table 1. Geology for the Grampian Highlands based on Stephenson & Gould (1995, fig. 3), and for Northern Ireland and location inset based on Harris *et al.* (1994, fig. 13).

The succeeding Appin Group comprises a cyclic succession of arenites and quartzites, carbonates (chiefly limestones) and semipelitic rocks deposited in generally shallow marine environments. This style of sedimentation continues into the lower part of the overlying Argyll Group (Islay Subgroup), which is traditionally separated from the Appin Group by the glacigenic Port Askaig Formation. The middle to upper parts of the Argyll Group are dominated by coarse siliciclastic and semipelitic to pelitic rocks, with some limestones, deposited in rapidly subsiding, relatively deep marine rift basins (Stephenson & Gould 1995, and references therein) related to the opening of the Iapetus Ocean. Volcanism at the top of the Argyll Group was accompanied by the extensive intrusion of mafic sills into underlying sediments (Graham 1976).

Volcanic rocks in the SW Scottish Highlands overlie the Tayvallich Limestone, whose lithostratigraphical equivalents in northern Ireland and Scotland, (Culdaff, Dungiven, Torr Head, Loch Tay and Boyne Limestones; Harris *et al.* 1994; Stephenson & Gould 1995) form a laterally persistent and important lithostratigraphical marker horizon across much of the Dalradian outcrop. The Southern Highland Group is characterized by coarse siliciclastic and pelitic units containing volcaniclastic horizons (‘Green Beds’). Rare limestones include the graphitic Leny Limestone near the top of the Group (Tanner 1995), which contains an early Mid-Cambrian *Pagetides* trilobite fauna (Pringle 1940; Cowie *et al.* 1972).

Arc collision in the late Cambrian and Ordovician resulted in the Grampian (Taconic) Orogeny of Scotland and Ireland (e.g. Dewey & Mange 1999). Polyphase deformation was accompanied by greenschist- to upper amphibolite-facies metamorphism with local anatexis (Harte 1988; Stephenson & Gould 1995), during which temperatures ranged from *c.* 400 to 600 °C (e.g. Graham *et al.* 1983; Beddoe-Stephens 1990; Skelton *et al.* 1995).

Age of the Dalradian Supergroup

Only two dates constrain Dalradian deposition. U–Pb zircon ages for mafic volcanic rocks in the Tayvallich Volcanic Formation date volcanism and sedimentation at the top of the Argyll Group at 595–600 Ma (Halliday *et al.* 1989; Dempster *et al.* 2002). This date fixes the age of the immediately underlying Tayvallich and lithostratigraphically related limestones at *c.* 600 Ma, providing a lower age limit for deposition of metasedimentary rocks of the Argyll Group. At the exposed top of the overlying Southern Highland Group, adjacent to the Highland Boundary, the *Pagetides* trilobite fauna in the Leny Limestone dates deposition of the limestone and its host pelites to about 510–515 Ma (Cowie *et al.* 1972).

The glacigenic Port Askaig Formation has been correlated with North Atlantic Varangerian tillite sequences (e.g. Hambrey 1983; Fairchild & Hambrey 1995), with estimated ages of 630–560 Ma (Kaye & Zartman 1980; Benus 1988; Krogh *et al*. 1988; Brasier & McIlroy 1998). Although a 630 Ma age for the Port Askaig Formation might provide enough time to deposit the remainder of the overlying Argyll Group (*c*. 35 Ma), Varangerian correlation has been considered by some to be difficult to reconcile with the *c*. 600 Ma age of the Tayvallich Volcanic Formation. Therefore the Port Askaig Formation has recently been correlated with 'Sturtian' tillites (Brasier & Shields 2000; Condon & Prave 2000; Prave 1999*a*, *b*), the latter dated by U–Pb methods on igneous rocks at between *c*. 720 and 740 Ma (Walter *et al*. 2000).

Dalradian sedimentation has been interpreted to result from crustal extension and episodic rifting that occurred largely uninterrupted over 300 Ma (e.g. Soper 1994; Dalziel & Soper 2001). Conversely, Prave (1999*a*) considered this model to be geodynamically improbable, based on Dalradian facies characteristics and problems of timing. He interpreted pre-Easdale Subgroup rocks as flysch and subsequent molasse derived from a Knoydartian (*c*. 800–730 Ma) orogen. Easdale and younger Argyll Group rocks are interpreted as rift deposits arising from Iapetan ocean opening and as being unconformable on Islay Subgroup and older units, whereas rocks of the overlying Southern Highland Group are interpreted as a rift to drift succession.

Current controversy over the maximum age of the Dalradian arises from contrasting interpretations of structural and lithostratigraphical relationships, and differing geological interpretation of chronological data (Highton *et al*. 1999; Smith *et al*. 1999; Tanner & Bluck 1999). In the Central Grampian Highlands of Scotland, gneissose and locally migmatitic rocks underlying the Grampian and Appin Groups (the Glen Banchor and Dava successions; Fig. 1; Smith *et al*. 1999) have been interpreted as basement upon which Grampian and Appin Group rocks were deposited unconformably (e.g. Piasecki & Van Breeman 1979; Piasecki 1980; Robertson & Smith 1999; Smith *et al*. 1999). This interpretation is supported by evidence from regional mapping (Robertson & Smith 1999; Smith *et al*. 1999) and the absence of 800–900 Ma monazite ages in proven Grampian Group rocks (Smith *et al*. 1999). Others have inferred that the Grampian Group and possibly parts of the Appin Group were deformed and metamorphosed along with the sub-Grampian Group rocks by Neoproterozoic tectonothermal activity in the Scottish Central Grampian Highlands dated at between *c*. 800 and *c*. 900 Ma (Noble *et al*. 1996; Highton *et al*. 1999).

Limestone petrography and geochemistry

Sampled limestone units and localities

Forty-seven whole-rock samples of limestone were collected from the main limestone lithostratigraphical units (e.g. Harris *et al*. 1994) at localities across the Dalradian outcrop in Scotland and Northern Ireland (Table 1, Figs 1 and 2). The limestones are mainly pale to very dark grey with variable grain size, the purest limestones being the coarsest. Quartz, feldspar and white mica are the chief siliciclastic impurities, occurring in variable amounts; a number of limestones are graphitic. Only calcitic limestones lacking significant dolomite and/or calc-silicate minerals were analysed, as the presence of these phases can indicate interaction with non-marine fluids that will significantly modify the isotopic composition of the carbonate component. The lithological characteristics are summarized in Table 2 (see Thomas 1989 for more details). Cathodoluminescence of samples shows that dolomite is entirely absent from the grey calcitic limestones with high Sr and low whole-rock MgO (Thomas 1999). Minute traces of dolomite found during electron microprobe analysis in a sample of the Torulian Limestone probably reflect primary high-Mg calcite in the original sediment (Thomas 1999). The low Mg content of the limestones generally precludes the presence of dolomite at the observed metamorphic pressures and temperatures (Goldsmith & Newton 1969; Thomas 1999). The indicative metamorphic grades for sample localities are shown together with sample numbers, localities, sampled units and additional features in Table 1.

Analytical techniques

Sample preparation. Whole-rock samples weighing 1–2 kg were collected from fresh outcrops. Veins and weathered rock were removed. Samples were cleaned and jaw-crushed, and homogeneous aliquots ground in an agate mill. Aliquots were used for preparation of fused beads and pressed powder pellets for major and trace element analysis by standard XRF techniques, and for analysis of $^{87}Sr/^{86}Sr$ and $^{18}O/^{16}O$ of the bulk calcite component.

Analysis of $^{87}Sr/^{86}Sr$. Samples for $^{87}Sr/^{86}Sr$ analysis were leached in 2.5 ml 0.15M ammonium acetate (NH_4OAc) for 2 h prior to dissolution of calcite in 1M acetic acid (HOAc) for a further 2 h at room temperature (see Gorokhov *et al*. 1995; Kuznetsov *et al*. 1997; Shields 1999; Bailey *et al*. 2000). The pre-dissolution leach in NH_4OAc was used to remove non-stoichiometric Sr (Walls *et al*. 1977; Gao 1990), which has been shown to be significantly more radiogenic than Sr bound in lattice sites in carbonate and sufficiently abundant to contaminate the calcite $^{87}Sr/^{86}Sr$ signature (e.g. Gorokhov *et al*. 1995; Kuznetsov *et al*. 1997; Thomas 1999; Bailey *et al*. 2000). Differences in sampling, sample leach and dissolution treatments reported by various workers in other studies of Neoproterozoic carbonate rocks (compare Asmerom *et al*. 1991; Gorokhov *et al*. 1995; Brasier & Shields 2000; Fairchild *et al*. 2001) will yield measurable differences in Sr isotope ratios and need to be considered in any interpretation of carbonate $^{87}Sr/^{86}Sr$ data, particularly where used comparatively and in the determination of temporal variations.

Strontium was separated from the supernatant by standard ion-exchange techniques using resin columns and $^{87}Sr/^{86}Sr$ analysed by thermal ionization mass spectrometry on a VG 54E single collector or a VG Sector 54-30 multiple-collector mass spectrometer. The $^{87}Sr/^{86}Sr$ ratio was corrected for mass fractionation using $^{86}Sr/^{88}Sr = 0.1194$ and an exponential law. Precision on the VG 54E was better than ± 0.00004 (2 SE) and repeat analysis of NBS 987 gave $^{87}Sr/^{86}Sr = 0.71024 \pm 3$ (1 SD, $n = 20$). On the VG Sector 54-30, precision was better than ± 0.00002 (2 SE) and repeat analysis of NBS 987 gave $^{87}Sr/^{86}Sr = 0.710243 \pm 10$ (1 SD, $n = 88$).

Analysis of $^{18}O/^{16}O$. CO_2 was extracted from calcite in each sample by reaction under vacuum of 10–15 mg of powder with 5 ml concentrated H_3PO_4 at 25 °C (McCrea 1950; Rosenbaum & Sheppard 1986). Samples were reacted for 24 h, and extracted CO_2 was purified and analysed for $^{18}O/^{16}O$ in a VG Isogas SIRA 10 mass spectrometer. Errors on individual analyses are ±0.1‰. Results for $^{18}O/^{16}O$ are quoted as $\delta^{18}O$ ‰ relative to V-SMOW and PDB.

Analysis of Sr, Rb, Mn and Al. Data for Inchrory, Dufftown, Torulian and Boyne Limestone samples are taken from the whole-rock XRF dataset of Thomas (1989). Data for the remaining limestones were determined by XRF analysis by staff of the British Geological Survey Analytical Geochemistry Laboratories. Trace element data are not available for the Tayvallich Limestone (*sensu stricto*). Mn and Al data are converted to ppm from wt% oxide data to facilitate comparison with Sr data.

Results

The $^{87}Sr/^{86}Sr$, $\delta^{18}O$, Al, Sr and Mn compositions of the limestones are presented in Table 2. The $^{87}Sr/^{86}Sr$ and $\delta^{18}O$ data are presented graphically with respect to a summary Dalradian lithostratigraphy in Figure 2. Key characteristics of limestone

Table 1. *Location and lithostratigraphical position of samples of Dalradian limestones analysed in this study*

Sampled unit	Subgroup	Locality	Grid reference	Samples	Numbers	Sample group reference no.	Metamorphic grade
Southern Highland Group							
Leny Limestone Member		Leny Quarry, Callander	NN 615 098	2	HY1362, 1364	13	Lower greenschist
Uppermost Argyll Group (Tayvallich Limestone and equivalents)							
Scotland							
Boyne Limestone	Tayvallich	Boyne Bay, Banffshire coast	NJ 616 660	4	HY147–150	9	Amphibolite
Tayvallich Limestone		Port an Sgadain	NR 707 846	7	T1–T6b	10	Greenschist
Northern Ireland							
Torr Head Limestone		Torr Head, Co. Antrim	H 232 406	2	HY1348, 1349	11	Greenschist
Dungiven Limestone		Butterlope Glen, Co. Tyrone	C 493 047	1	HY1350	12	Amphibolite
		Banagher Glen, Co. Tyrone	C 668 047	1	HY1351		
Easdale Subgroup, Argyll Group							
Badenyon Schist and Limestone Formation	Easdale	Ladylea Hill Quarry, Strathdon	NJ 33860 17480	2	HY81–84	8	Amphibolite
		Quillichan Burn	NJ 30240 14600	1	HY89	7	
Islay Subgroup, Argyll Group							
Nochty Semipelite and Limestone Formation	Islay	Water of Nochty, Finlate Hill	NJ 32850 26090	1	HY88	6	
Appin Group							
Islay							
Storakaig Limestone Member	Blair Atholl	Ballygrant Quarry	NR 395 666	5	HY1333–1337	5	Greenschist
Mainland Scotland							
Inchrory Limestone		A939 road section, Tomintoul	NJ 151 194	5	HY56–60	4	Amphibolite
Torulian Limestone (member)	Ballachulish	Bridge of Avon, River Avon section	NJ 1496 2019	1	HY43		Amphibolite
		Carn Daimh, Glenconglass	NJ 1749 2259	1	HY47		
		Glen Suie	NJ 2766 2595	1	HY360		
		Tor Ellick, Glen Fiddich	NJ 3166 3202	1	HY393	3	
			NJ 3186 3205	1	HY394		
Dufftown Limestone		Parkmore Quarry, Dufftown	NJ 334 411	5	HY67–71	2	
Grampian Group							
Coire nan Laogh Semipelite Formation (Kincraig Limestones)	Corrieyairack	Kincraig Quarry	NH 8213 0604	2	HY1072, 73	1	Amphibolite
		Kincraig Farm, Dunnachton track	NH 8214 0577	2	SMS446, 447		
		Allt na Baranachd	NH 7959 0586	2	SMS448, 449		

Grid references are in British National Grid or Northern Irish National Grid. Sample locations are shown in Figure 1. Sample group reference numbers are also given in Table 2 and Figure 2.

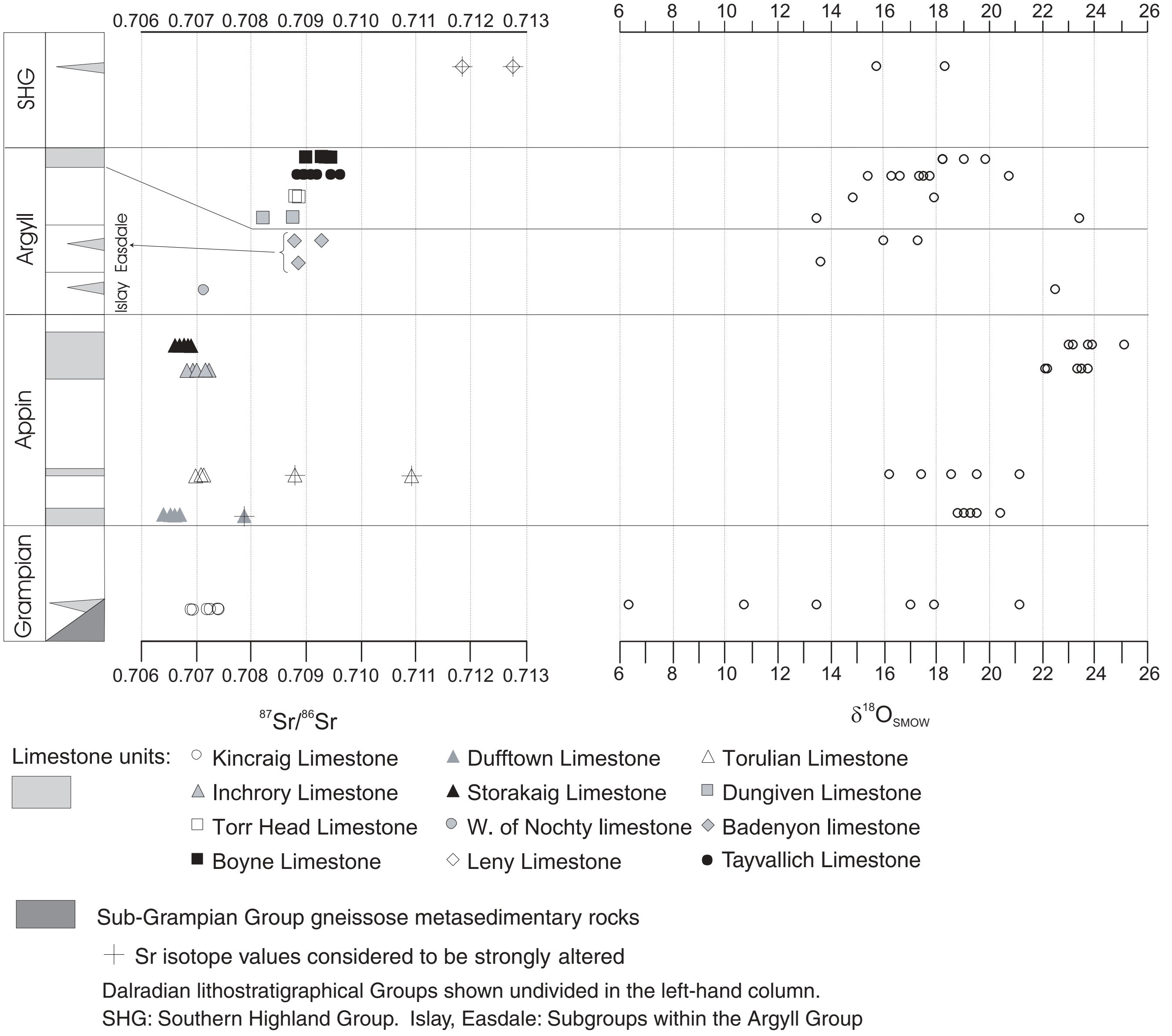


Fig. 2. $^{87}Sr/^{86}Sr$ and $\delta^{18}O$ data for Dalradian limestones, plotted relative to lithostratigraphical position (see also Tables 1 and 2).

geochemistry that help identify diagenetic or metamorphic modification are given in Table 3.

Strontium isotope ratios

The $^{87}Sr/^{86}Sr$ data show systematic variations with lithostratigraphy (Fig. 2). The $^{87}Sr/^{86}Sr$ values for the Kincraig limestones (0.706905–0.707414) are comparable with those for Appin Group samples (*c.* 0.7064–0.7074; three altered samples excluded; see below) and the sample from the Water of Nochty Semipelite and Limestone Formation (Islay Subgroup; Argyll Group). The $^{87}Sr/^{86}Sr$ values in the Dufftown Limestone are the lowest in the study (0.706448–0.706667).

Our data for the Storakaig Limestone (0.706651–0.706902) are lower than those reported by Brasier & Shields (2000; $^{87}Sr/^{86}Sr = 0.706911–0.707252$; their 'Ballygrant Limestone'). This discrepancy may be due to differences in sample preparation, as Brasier and Shields did not pre-leach samples in NH_4OAC, or may reflect temporal variation because of sampling at slightly different stratigraphical levels within the unit.

The values for the Inchrory Limestone samples are slightly higher (0.706863–0.707213). $^{87}Sr/^{86}Sr$ is much more radiogenic in three Appin Group samples, indicating that it has been strongly modified (Fig. 2, Table 2). Limestone in sample HY43 was infiltrated by at least two metamorphic fluids (Thomas 1999) and alteration of $^{87}Sr/^{86}Sr$ is attributed to these events.

The $^{87}Sr/^{86}Sr$ of middle and upper Argyll Group limestones (*c.* 0.7082–0.7096) is significantly more radiogenic than that of the Grampian and Appin Groups and lower Argyll Group. The lowest $^{87}Sr/^{86}Sr$ values occur in the samples from the Torr Head and Dungiven limestones (0.708220–0.708857), whereas those from the Boyne and Tayvallich limestones range from 0.708851 to 0.709637. Three limestones from the Easdale Subgroup (Badenyon Schist and Limestone Formation) have $^{87}Sr/^{86}Sr$

Table 2. *The Sr and O isotope compositions of Dalradian limestones analysed in this study, with selected trace element data*

Sample	Lithology	$^{87}Sr/^{86}Sr$	± Error	Sr	Sr/Ca	Rb	Mn	Mn/Sr	Al	$\delta^{18}O_{SMOW}$	$\delta^{18}O_{PDB}$	Sample group reference number
Southern Highland Group												
Leny Limestone												
HY1362	Black, graphitic and very fine-grained limestone	0.711859	0.000030	1085	0.00369	20	220	**0.20**	11100	15.7	−14.7	13
HY1364		0.712781	0.000017	985	0.00436	31	360	0.37	17100	18.3	−12.2	
Argyll Group												
Boyne Limestone												
HY147	Grey limestone, medium- to coarse-grained with layers of calc-silicates in places	0.709018	0.000016	4607	0.01996	13	310	**0.07**	37000	19.0	−11.6	9
HY148		0.709451	0.000016	2695	0.00886	43	700	0.26	21400	19.8	−10.8	
HY149		0.709305	0.000014	3534	0.01504	23	700	**0.20**	40000	18.2	−12.3	
HY150		0.709297	0.000016	3225	0.01021	52	540	**0.17**	13400	18.2	−12.3	
Tayvallich Limestone												
T1	Grey to dark grey limestone, coarsely crystalline	0.708851	0.000020	No elemental data available						20.7	−9.8	10
T2		0.709203	0.000020							15.4	−15.0	
T3		0.708960	0.000017							16.6	−13.8	
T4		0.709096	0.000018							16.3	−14.1	
T5		0.709467	0.000020							17.5	−13.0	
T6a		0.709637	0.000017							17.7	−12.8	
T6b		0.708969	0.000016							17.3	−13.2	
Torr Head Limestone												
HY1348	Very coarse, dark grey limestone	0.708857	0.000039	1865	0.00544	26	144	**0.08**	16300	14.8	−15.6	11
HY1349		0.708810	0.000032	2115	0.00582	20	144	**0.07**	10400	17.9	−12.5	
Dungiven Limestone												
HY1350	Very coarse, dark grey limestone	0.708220	0.000033	265	0.00089	3	3900	14.72	17700	13.4	−16.9	12
HY1351		0.708745	0.000043	2299	0.00634	12	220	**0.10**	8360	23.4	−7.2	
Badenyon Schist and Limestone Formation												
HY81	Grey limestone, medium grained	0.709268	0.000023	1445	0.00440	11	619	0.43	6774	17.2	−13.3	8
HY84		0.708807	0.000020	1965	0.00495	10	310	**0.16**	7939	16.0	−14.5	
HY89		0.708896	0.000023	1372	0.00356	4	697	0.51	1852	13.6	−16.8	7
Nochty Semipelite and Limestone Formation												
HY88		0.707117	0.000020	1398	0.00399	26	155	**0.11**	8627	22.4	−8.3	6
Appin Group												
Storakaig Limestone, Islay (≈ Inchrory Limestone)												
HY1333	Very dark grey, very fine-grained limestone	0.706902	0.000029	2014	0.00523	6	72	**0.04**	2170	23.2	−7.5	5
HY1334		0.706744	0.000041	2622	0.00672	4	72	**0.03**	1430	23.9	−6.8	
HY1335		0.706854	0.000040	2495	0.00667	4	290	**0.12**	1640	23.0	−7.6	
HY1336		0.706790	0.000019	1937	0.00559	4	360	**0.19**	1480	23.7	−7.0	
HY1337		0.706651	0.000034	1881	0.00505	3	360	**0.19**	847	25.1	−5.6	
Inchrory Limestone												
HY56	Medium 'blue' grey, medium- to coarse-grained limestone, commonly with banded appearance	0.707213	0.000016	1471	0.00447	21	310	0.21	13700	22.1	−8.5	4
HY57		0.706923	0.000018	2104	0.00594	12	77	**0.04**	10500	22.2	−8.4	
HY58		0.706940	0.000016	2135	0.00608	16	160	**0.07**	10800	23.3	−7.3	
HY59		0.706863	0.000016	2211	0.00605	9	160	**0.07**	5560	23.7	−7.0	
HY60		0.706974	0.000021	1880	0.00539	18	77	**0.04**	9580	23.5	−7.2	

Torulian Limestone											
HY43	Coarsely crystalline, white to very pale grey limestone	0.710927	0.000018	776	0.00206	9	310	0.40	2490	16.2	−14.2	3
HY47		0.708813	0.000017	822	0.00248	4	230	0.28	10200	17.4	−13.0	
HY360		0.707131	0.000017	1316	0.00330	4	77	**0.06**	53	21.1	−9.5	
HY393		0.706986	0.000016	593	0.00166	6	160	0.27	9050	18.5	−12.0	
HY394		0.707017	0.000016	2178	0.00546	4	160	**0.07**	1590	19.5	−11.0	
Dufftown Limestone											
HY67	‘Blue’ grey, medium- to coarse-grained limestone	0.706667	0.000017	1253	0.00355	12	310	0.25	5240	19.3	−11.2	2
HY68		0.706583	0.000017	1217	0.00321	7	160	**0.13**	3020	19.0	−11.6	
HY69		0.707884	0.000018	714	0.00191	11	230	0.32	3120	20.4	−10.2	
HY70		0.706448	0.000017	1712	0.00451	4	160	**0.09**	1430	19.5	−11.1	
HY71		0.706576	0.000016	950	0.00269	7	540	0.57	2750	18.8	−11.7	
Grampian Group											
Kincraig Limestone, Coire nan Laogh Semipelite Formation											
HY1072	Very pale grey to medium grey, medium- to coarse-grained limestone	0.706927	0.000018	1785	0.00495	8	155	**0.09**	9160	17.9	−12.5	1
HY1073		0.706905	0.000016	1764	0.00492	9	155	**0.09**	9140	21.1	−9.4	
SMS446		0.707203	0.000016	1948	0.00549	2	432	0.22	8840	13.4	−17.0	
SMS447		0.707177	0.000018	1975	0.00551	1	360	**0.18**	8310	17.0	−13.4	
SMS448		0.707414	0.000017	1545	0.00451	12	576	0.37	9630	6.3	−23.8	
SMS449		0.707256	0.000017	1614	0.00476	16	432	0.27	10300	10.7	−19.6	

Al and Mn, converted from whole-rock wt% oxide to ppm element; Sr and Rb, whole-rock XRF data. Values for Mn/Sr ⩽0.2 are highlighted in bold (see text for discussion).

ranging from *c.* 0.7088 to 0.7093. The Leny Limestone (Southern Highland Group) has the most radiogenic Sr of any limestones ($^{87}Sr/^{86}Sr = 0.711859–0.712781$).

Oxygen isotope ratios

$\delta^{18}O$ values for calcite in the limestones vary from +6.3‰ in sample SMS448 (Kincraig Limestone) to +25.1‰ in HY1337 (Storakaig Limestone) (Table 2, Fig. 2). In general, Appin Group limestones have the highest $\delta^{18}O$ values and most consistent ‘within-sample group’ values. Within-sample group variation is highest in the Kincraig limestones (+6.3−+21.1‰). Argyll and Southern Highland Group limestones generally have $\delta^{18}O$ <+20‰ and the samples from the Boyne Limestone have the most consistent values (+18.2−+19.8‰).

Diagenetic and metamorphic effects on geochemical signatures in Dalradian limestones

The lack of isotopic and trace element equilibrium between primary carbonate rocks and non-marine diagenetic and metamorphic fluids results in modification of pre-metamorphic calcite $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ signatures by metamorphic reactions and fluid–rock interaction. This disequilibrium has been exploited to quantify fluid flow during both diagenesis and metamorphism (Rye *et al.* 1976; Baker *et al.* 1989; Banner & Hanson 1990; Bickle & Baker 1990; Veizer 1992; Graham *et al.* 1997; Lewis *et al.* 1998). $\delta^{18}O$ is commonly modified by metamorphic fluid infiltration over tens of centimetres to metres in carbonate boundary layers. In contrast, $^{87}Sr/^{86}Sr$ is typically modified on scales of <50 cm, even by high cross-layer fluid fluxes, consistent with decoupling of $^{18}O/^{16}O$ and $^{87}Sr/^{86}Sr$ during infiltration (Bickle 1992). Measurable diffusional exchange of Sr between silicates and carbonate sufficient to alter calcite $^{87}Sr/^{86}Sr$ ratios during metamorphism is prevented by very slow volume diffusion of cationic species. None of the samples in this study comes from boundary layers on the scale over which metamorphic modification of $^{87}Sr/^{86}Sr$ has usually been observed. Internal domains that preserve pre-metamorphic geochemical signatures can readily be identified and sampled. The corollary of this limited and quantifiable response of carbonate rocks to metamorphic fluid–rock interaction is that various geochemical signatures in metamorphosed carbonate rocks can be interpreted in terms of their sedimentary and diagenetic history (e.g. Melezhik *et al.* 1997; Thomas 1999; Zachariah 1999).

The limestones in this study are essentially unaffected by decarbonation reactions, indicated by loss-on-ignition values consistent with virtually all Ca being sequestered in calcite. The formation of calc-silicates in all the limestones is limited by low Mg and Al. At metamorphic temperatures (400–600 °C), calc-silicate phases consistent with limestone bulk compositions are stable only in the presence of very water-rich fluids. Their absence implies a lack of hydrous metamorphic fluid infiltration consistent with the low permeability of calcite-rich matrices at most metamorphic temperatures, pressures and likely fluid compositions (Holness & Graham 1995).

Various geochemical criteria have been used to identify by proxy post-depositional modification of $^{87}Sr/^{86}Sr$ in carbonate rocks (e.g. Derry *et al.* 1989; Asmerom *et al.* 1991; Kaufman *et al.* 1993; Denison *et al.* 1994*b*; McArthur 1994; Jacobsen & Kaufman 1999; Fairchild *et al.* 2000). These include low Mn/Sr ratios, low carbonate Rb contents, carbonate Sr contents of 10^2–10^3 ppm and carbonate $\delta^{18}O_{SMOW}$ >+20‰. Published empirical limiting values for these criteria (Table 3) and their range in

Table 3. *Comparison of the geochemistry of Neoproterozoic and Phanerozoic limestones from selected studies with that of Dalradian limestones*

Reference	Sr (ppm)	Rb[*] (ppm)	Rb/Sr	Mn (ppm)	Mn/Sr	$\delta^{18}O_{SMOW}$[†] (‰)
Asmerom *et al.* 1991	32–520	0.006–0897	$\leqslant$0.01	–	$\leqslant$2	>22
Brasier *et al.* 1996	>500	–	–	–	<0.6	–
Denison *et al.* 1994	>900	–	–	<300	<0.5	–
Derry *et al.* 1989	201–2474	0.05–1.49	$\leqslant 5 \times 10^3$[‡]	–	–	–
Fairchild *et al.* 2000	>500	–	–	<100	<0.2	–
Gorokhov *et al.* 1995	–	–	–	–	*c.* 2	–
Kaufman *et al.* 1993	52–3705	–	<0.001[‡]	–	<1.5	>20
Kaufman & Knoll 1995	–	–	–	–	<2–3	>21
Kennedy *et al.* 1998	>200	–	–	–	<1	–
Kuznetsov *et al.*	160–605	–	–	10–50	<0.5	–
Misi & Veizer 1998	>250–300	–	–	–	$\leqslant$0.2	>23
Saylor *et al.* 1998	–	–	–	–	<2	>21
Dalradian limestones in this study						
Range	265–4607	1–52[§]	0.0005–0.0161	72–3890[§]	0.03–14.7	6–25
Median	1825	10	0.006	260	0.17	19

Where values are preceded by > or <, the values quoted are those deemed by the authors to be limiting values with regard to the state of preservation of primary or near-primary ^{87}Sr/^{86}Sr values.

[*] Rb in dissolved carbonate fraction.

[†] To nearest ‰.

[‡] As ^{87}Rb/^{86}Sr.

[§] From whole-rock XRF data.

Dalradian limestones are used together with petrographical and other geochemical data to aid interpretation of the ^{87}Sr/^{86}Sr ratios in the Dalradian limestones.

Calcitic limestones rich in Sr ($\geqslant 10^3$ ppm) are generally considered to have been originally aragonitic, as aragonite can accommodate up to 10^4 ppm Sr (Bathurst 1975). Conversely, calcitic limestones containing $\leqslant 10^2$ ppm Sr either had a primary low-magnesian calcite mineralogy or have undergone extensive diagenesis (e.g. Tucker & Wright 1990). The high Sr content of most Dalradian limestones demonstrates that the primary carbonate mineralogy was chiefly aragonite. Preservation of high Sr values in limestones that now contain only low-Mg calcite indicates that diagenesis was primarily within the marine environment, and that diagenetic fluids were dominated by coeval seawater.

Lack of correlation between Sr content and ^{87}Sr/^{86}Sr (Fig. 3a) suggests that reduction of Sr during diagenetic recrystallization of aragonite to calcite is not associated with measurable contamination of calcite Sr by more radiogenic Sr from external diagenetic fluids. The effect of radiogenic Sr in any infiltrating fluid phase, likely to have low Sr concentrations, will be swamped by the isotopic signature of the abundant Sr released from the recrystallizing aragonite, at least at low fluid fluxes.

Mn and the Mn/Sr ratio are important in interpreting ^{87}Sr/^{86}Sr ratios in carbonate rocks because Mn can act as a tracer for non-marine diagenetic fluids (e.g. meteoric, continental and metamorphic fluids that are commonly enriched in Mn; e.g. Tucker & Wright 1990, fig. 6.10) and radiogenic Sr. Mn/Sr <0.6 has been widely used as a bounding value to identify ‘unaltered’ samples; Mn/Sr <0.2 was considered by Fairchild *et al.* (2000) to be a more stringent test of unaltered state (Table 2, Fig. 3b). Mn/Sr ratios in our samples are, with one exception, <0.6 and 24 samples have Mn/Sr <0.2 (Fig. 3b).

Although δ^{18}O varies widely (Table 2), the relationship between δ^{18}O and ^{87}Sr/^{86}Sr (Fig. 4a) indicates that even where δ^{18}O has been significantly modified (e.g. Kincraig Limestone samples), the ^{87}Sr/^{86}Sr values have been modified much less significantly.

Al acts as a proxy for radiogenic ^{87}Sr contained in feldspars and phyllosilicates, both of which occur in some limestones in trace to small quantities. ^{87}Sr/^{86}Sr in calcite covaries positively with Al in some sample groups (Fig. 4b), suggesting limited contamination of calcite ^{87}Sr/^{86}Sr by radiogenic ^{87}Sr from feldspars and micas. However, although decay of ^{87}Rb will have increased ^{87}Sr/^{86}Sr in the silicates over time, incorporation into the calcite of radiogenic Sr produced in the silicates will have been limited because Sr is preferentially excluded from calcite during recrystallization and the high calcite Sr concentrations will buffer contaminant ^{87}Sr.

Limited contamination of primary carbonate Sr by radiogenic Sr from silicates in some samples results from incorporation of more radiogenic Sr released from silicates into pore fluids during diagenesis when the carbonate mineralogy was most reactive and when there would have been a large and dynamic pore volume.

Discussion

Degree of preservation of primary ^{87}Sr/^{86}Sr signatures

Comparison of the geochemistry of Dalradian limestones with the values of parameters listed in Table 3 considered to indicate a ‘least altered’ state shows that Dalradian limestones lie well within currently accepted limits in almost all cases. The secular trends in ^{87}Sr/^{86}Sr data presented here for metamorphosed Dalradian limestones can therefore be reliably compared directly with ^{87}Sr/^{86}Sr data for unmetamorphosed limestones in other studies, which have been used to establish temporal variation of Neoproterozoic seawater ^{87}Sr/^{86}Sr (as listed in Fig. 5). Nevertheless, covariation between ^{87}Sr/^{86}Sr and other elements shows consistent shifts in ^{87}Sr/^{86}Sr away from some primary value. Most Grampian and Appin Group limestones have retained ^{87}Sr/^{86}Sr close to their primary values and, by implication, that of coeval seawater. The covariation of ^{87}Sr/^{86}Sr with Al suggests approximate ^{87}Sr/^{86}Sr values of coeval seawater of *c.* 0.7065 for the Inchrory and Storakaig limestones and *c.* 0.7064 for the Dufftown Limestone samples, excluding HY69 (Fig. 4b). ^{87}Sr/^{86}Sr is slightly more radiogenic in the Inchrory Limestone than in the Storakaig Limestone, reflecting more abundant phyllosilicate and feldspar. The data suggest that Dalradian seawater during Appin Group times had ^{87}Sr/^{86}Sr of *c.* 0.7064–0.7065. The single limestone sample from the Water of Nochty Semi-

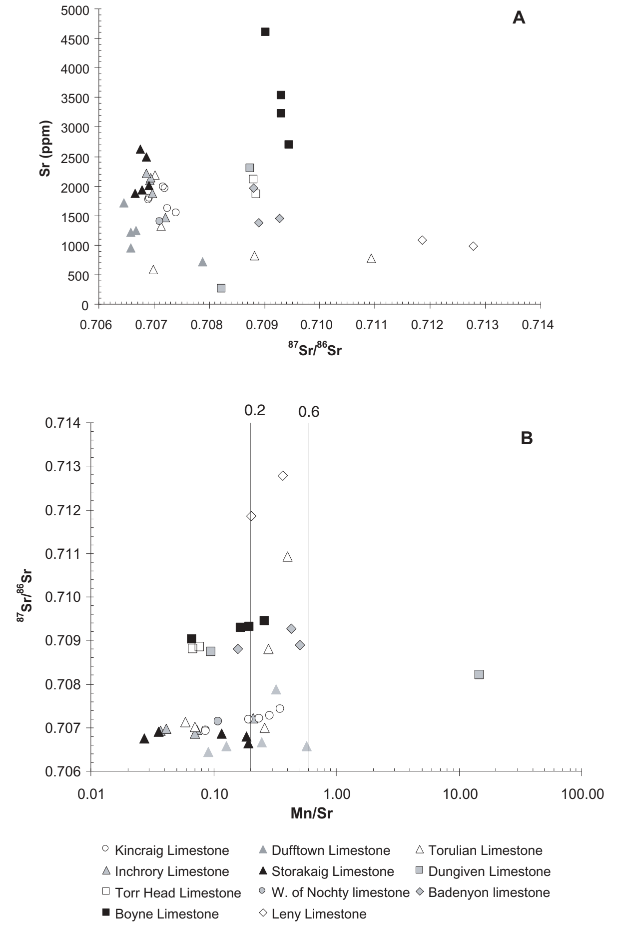


Fig. 3. **(a)** Variation of ^{87}Sr/^{86}Sr with Sr (ppm) for limestones from each of the lithostratigraphical groups in the Dalradian. **(b)** Variation of ^{87}Sr/^{86}Sr with Mn/Sr for Dalradian limestones. It should be noted that most limestones have Mn/Sr $<$0.2 and all but one have Mn/Sr $<$0.6.

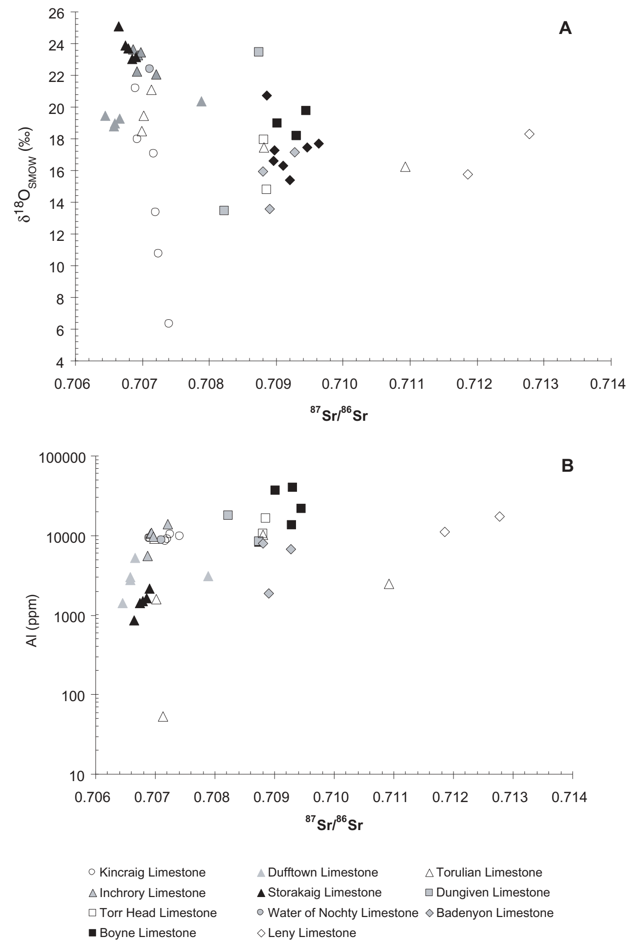


Fig. 4. **(a)** Variation of ^{87}Sr/^{86}Sr with δ^{18}O in Dalradian limestones. The general increase in ^{87}Sr/^{86}Sr with decreasing $\delta^{18}O_{SMOW}$ in Appin and Grampian Group limestones should be noted. **(b)** Variation of Al with ^{87}Sr/^{86}Sr.

pelite Formation has ^{87}Sr/^{86}Sr very similar to values for the Inchrory samples (Figs 2 and 3a).

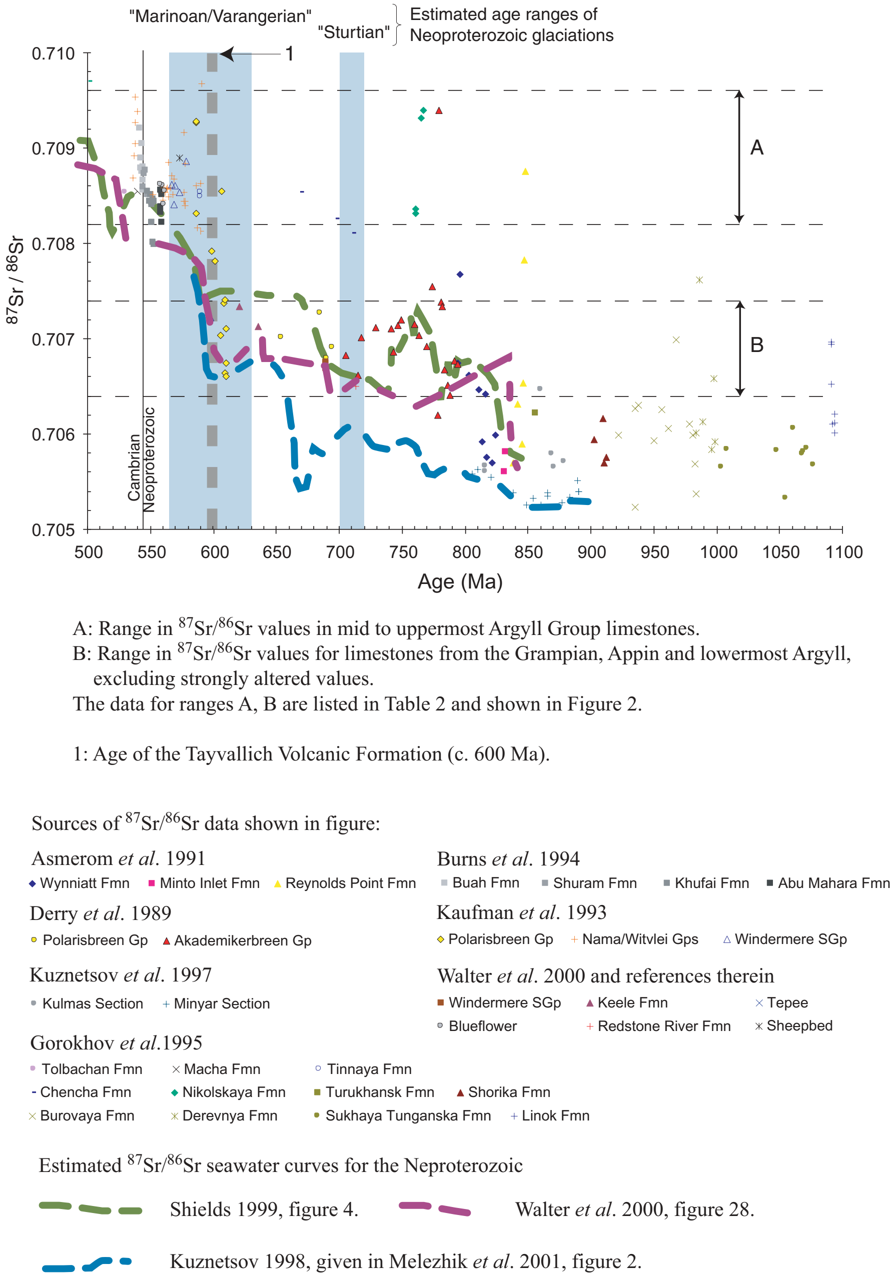
The state of preservation of primary ^{87}Sr/^{86}Sr in middle and upper Argyll Group limestones is less clear, mainly because the wider 'within-group' variation suggests that ^{87}Sr/^{86}Sr has been more disturbed compared with ^{87}Sr/^{86}Sr from the Grampian, Appin and lower Argyll Groups. However, the relationships between ^{87}Sr/^{86}Sr, Sr, Mn, Al and δ^{18}O differ little from those for older Dalradian strata (Figs 3 and 4) and ^{87}Sr/^{86}Sr has a similar relative range (Table 2). The Argyll Group limestone data are consistent internally despite varying degrees of δ^{18}O modification, and are consistently in range with data from non-metamorphosed limestone units of *c*. 600 Ma age (see below). Thus, the upper Argyll Group limestones indicate a temporal change to significantly more radiogenic seawater ^{87}Sr/^{86}Sr than in early Argyll Group times. The Torr Head and Dungiven limestone samples are considered to retain values closest to that of coeval seawater and the best estimate for seawater ^{87}Sr/^{86}Sr from these data at *c*. 600 Ma is *c*. 0.708.

The very radiogenic Sr isotope signature in the Leny Limestone must result largely from diagenetic fluid–rock interaction, despite the low Mn/Sr ratios (0.37, 0.20), as the ^{87}Sr/^{86}Sr ratios of *c*. 0.712 are very high even for Cambrian limestones (*c*. 0.709; see Burke *et al*. 1982). The limestone beds are very thin (*c*. 0.3 m) and diagenetic fluids from the dominant host pelitic units would have swamped the carbonate ^{87}Sr/^{86}Sr with more radiogenic Sr.

Temporal variation of Neoproterozoic seawater ^{87}Sr/^{86}Sr

The temporal variation of ^{87}Sr/^{86}Sr in Neoproterozoic carbonate-bearing successions from around the world has been used to elucidate temporal variation in seawater ^{87}Sr/^{86}Sr for the period from 1100 Ma to the early Cambrian (Derry *et al*. 1989; Asmerom *et al*. 1991; Kaufman *et al*. 1993; Burns *et al*. 1994; Narbonne *et al*. 1994; Gorokhov *et al*. 1995; Kuznetsov *et al*. 1997; Kennedy *et al*. 1998; Misi & Veizer 1998; Saylor *et al*. 1998; Yang *et al*. 1999; Fairchild *et al*. 2000; see also reviews by Jacobsen & Kaufman 1999; Shields 1999; Walter *et al*. 2000; Melezhik *et al*. 2001).

Results of the key studies are summarized in Figure 5, along with recent interpretations of the ^{87}Sr/^{86}Sr seawater curve for the Neoproterozoic (Kuznetsov 1998), given by Shields (1999), Walter *et al*. (2000) and Melezhik *et al*. (2001). Age constraints on these Sr isotope data are limited and rely on: (1) radiometric age determinations of basement or intrusive rocks that uncon-



A: Range in ^{87}Sr/^{86}Sr values in mid to uppermost Argyll Group limestones.
B: Range in ^{87}Sr/^{86}Sr values for limestones from the Grampian, Appin and lowermost Argyll, excluding strongly altered values.
The data for ranges A, B are listed in Table 2 and shown in Figure 2.

1: Age of the Tayvallich Volcanic Formation (c. 600 Ma).

Sources of ^{87}Sr/^{86}Sr data shown in figure:

Estimated ^{87}Sr/^{86}Sr seawater curves for the Neproterozoic

Fig. 5. Estimated limits on the maximum age of the Dalradian, based on the estimated secular variation in the ^{87}Sr/^{86}Sr composition of seawater during the Neoproterozoic and early Cambrian via ^{87}Sr/^{86}Sr in limestones. Data given in Table 2. The estimated seawater ^{87}Sr/^{86}Sr evolution curves for the Neoproterozoic are taken from Kuznetsov (1998, given by Melezhik *et al.* 2001), Shields (1999) and Walter *et al.* (2000).

formably underlie or cut the carbonate-bearing successions; (2) assumed lithostratigraphical correlation (e.g. of tillites, etc.); (3) the presence or absence of soft-bodied or microfaunal assemblages; (4) direct Pb/Pb and K–Ar dates of carbonates and glauconites (Kuznetsov *et al.* 1997, and references therein; Melezhik *et al.* 2001). In some studies, ages for individual samples are interpolated between bounding ages by using the empirical subsidence rate equation of Sleep (1971) or by simple linear interpolation (e.g. Walter *et al.* 2000). Clearly, the accuracy of the estimated ages of individual samples is difficult to assess, given the different methods and lack of independent evidence. Different interpretations of the ages or correlations of key lithostratigraphical units will lead to different age estimates, as shown in Figure 5 by the difference in ages assigned to the Polarisbreen Group (Svalbard) by Derry *et al.* (1989) and Kaufman *et al.* (1993). Nevertheless, there was an overall rise in seawater ^{87}Sr/^{86}Sr during the Neoproterozoic similar to that which has occurred over a similar period of time through the latter part of the Phanerozoic (e.g. Howarth & McArthur 1997).

Neoproterozoic seawater ^{87}Sr/^{86}Sr values were significantly lower than 0.7065 before *c.* 800 Ma (Fig. 5) increasing to values between 0.7065 and 0.7075 at about 800 Ma (e.g. Jacobsen & Kaufman 1999), although data reported by Kuznetsov (1998; see Melezhik *et al.* 2001a, fig. 2) indicate that ^{87}Sr/^{86}Sr values may have remained below about 0.7060 until about 660 Ma, then rapidly increased to values of *c.* 0.7065. Seawater ^{87}Sr/^{86}Sr values further increased from *c.* 0.7070 to >0.7080 between *c.* 600 Ma and the earliest Cambrian. The main shift from *c.*

0.7070 to *c*. 0.7085 apparently occurred over a comparatively short period of time (*c*. 30–50 Ma; Kaufman *et al*. 1993; Jacobsen & Kaufman 1999, fig. 4). This contrasts with the somewhat larger uncertainty attached to the increase in $^{87}Sr/^{86}Sr$ that occurred at or after 800 Ma (Kuznetsov 1998, as reported by Melezhik *et al*. 2001).

The depositional age of the Dalradian

We now map the relative secular variations in $^{87}Sr/^{86}Sr$ of Dalradian limestones onto the temporal variation of $^{87}Sr/^{86}Sr$ in Neoproterozoic carbonate-bearing successions worldwide to provide new constraints on the age and rates of Dalradian sedimentation. These constraints are only as reliable as the data against which they are compared, but they provide hypotheses that may be tested in future geochronological studies.

Maximum age. Accepting that seawater $^{87}Sr/^{86}Sr$ was $\ll 0.7065$ before *c*. 800 Ma, we conclude that the Dalradian cannot be older than *c*. 800 Ma and, indeed, may be significantly younger. This conclusion is consistent with recently published zircon age spectra for Dalradian metasedimentary rocks, which show that there are no detrital zircons younger than *c*. 900 Ma in any Dalradian succession (Cawood *et al*. 2003). Kuznetsov's Neoproterozoic seawater $^{87}Sr/^{86}Sr$ curve implies that the Dalradian could be as young as *c*. 700 Ma, allowing for the fact that the Kincraig limestones lie above the lowest known Grampian Group rocks (Smith *et al*. 1999, fig. 2). This is consistent with the emerging evidence for early and mid-Neoproterozoic tectonothermal events between *c*. 800 and 730 Ma in the Moine Supergroup of the Northern Highlands and the Dava and Glen Banchor successions in the Central Highlands (Strachan *et al*. 2002; Tanner & Evans 2003), as these events represent significant crustal thickening and so are likely to be orogenic in origin. Given the evidence for regional unconformity of Grampian Group rocks on the gneissose rocks of the Dava and Glen Banchor successions (Smith *et al*. 1999), the 'Moinian' metamorphic edifice must have been uplifted and significantly eroded before the Grampian Group was deposited, implying a significant time gap following the tectonothermal events.

Such a young age for the Dalradian has important implications both for the interpretation of Dalradian lithostratigraphy and for the wider tectonic history of the eastern Laurentian margin upon which the Dalradian and Moine Supergroups were deposited (Soper 1994; Prave 1999*a*; Dalziel & Soper 2001). The time scale for all Dalradian sedimentation would have been *c*. 200 Ma; the Grampian, Appin and Argyll Groups would all have been deposited within the period between *c*. 700 Ma and 600 Ma. Noting, by way of comparison, that the whole of the Moine was deposited in just 80 Ma (950–870 Ma; Friend *et al*. 2003), a 100 Ma time scale for deposition of the three lowermost Dalradian groups is feasible and is consistent with the absence of major orogenic unconformities within these lithostratigraphical units (see Highton *et al*. 1999; Prave 1999*a*; Dempster *et al*. 2002).

The corollary of a maximum age for the Dalradian of no more than 700 Ma is that there must have been a significant hiatus in the Neoproterozoic sedimentary record of the Scottish–Irish sector of the Laurentian margin, occupied by thermotectonic events, uplift and erosion. This puts in doubt any model for the development of the eastern Laurentian margin that invokes long-lived, episodic lithospheric extension over the period of time during which the Moine and Dalradian Supergroups were deposited (e.g. Soper 1994; Dalziel & Soper 2001).

Recent arguments for a 'Sturtian' correlation for the Port Askaig Formation (Brasier & Shields 2000; Condon & Prave 2000) are not precluded by a <800 Ma age for the Dalradian. However, a *c*. 700 Ma age for the beginning of Dalradian sedimentation would prohibit the possibility of the Port Askaig Formation being a 'Sturtian' tillite correlative. The Port Askaig Formation could be an 'old' (*c*. 630 Ma) Varangerian 'tillite' (see Gorokhov *et al*. 2001), implying very rapid deposition of all of the Argyll Group between *c*. 630 and 600 Ma (see below). This may not be unreasonable, given the character of middle to upper Argyll Group facies. Alternatively, the Port Askaig Formation may correlate with neither Varangerian nor Sturtian tillites, with major implications for correlation of Neoproterozoic tillites worldwide, their role in current extreme climatic models for the Neoproterozoic, and the use of such tillites as a worldwide lithostratigraphical correlative tool.

The deposition of the Argyll Group. Limestones from the Grampian and Appin Groups and the Islay Subgroup (lower Argyll Group) have $^{87}Sr/^{86}Sr$ values distinct from those for limestones of the middle to upper Argyll Group (Figs 2, 3 and 4). The lithostratigraphically sharp and large shift in $^{87}Sr/^{86}Sr$ in Dalradian limestones between the Islay and Easdale Subgroups coincides with a significant change in Dalradian basin dynamics. Sedimentologically, the Islay Subgroup can be considered as part of the cyclic pelite–limestone–quartzite system that characterizes the Appin Group, deposited on a gently subsiding continental margin. In contrast, successions within the Easdale Subgroup are generally much more restricted geographically (Harris *et al*. 1994), indicating deposition within fault-bounded, restricted basins. Deep-marine sediments, volcanic rocks and synsedimentary mineralization arising from hydrothermal systems active in rift faults (Coats *et al*. 1980) all indicate basin deepening in a rapidly developing rift setting. This instability increases markedly in the Crinan Subgroup with the incoming of pebbly and conglomeratic rocks and turbidites that then dominate sedimentation through into the Southern Highland Group. The apparent marked shift in $^{87}Sr/^{86}Sr$ recorded in limestones between Appin and lowermost Argyll Groups and those in the middle–upper Argyll Group may be an artefact of the absence of a continuous chemostratigraphic record and/or may indicate a very rapid rise in global seawater$^{87}Sr/^{86}Sr$. Alternatively, this shift may indicate a significant time interval between deposition of Islay and Easdale Subgroup rocks. The fact that the more radiogenic seawater $^{87}Sr/^{86}Sr$ values occur globally at *c*. 600 Ma also strongly suggests that the middle and upper parts of the Argyll Group were deposited very rapidly, perhaps no more than 20 Ma before the eruption of the Tayvallich lavas (Fig. 5). Thus the sharp change in $^{87}Sr/^{86}Sr$ observed in Easdale limestones is consistent with the presence of an erosional unconformity at the base of the Easdale Subgroup (Pitcher & Berger 1972; Prave 1999*a*). The length of any such time interval is critical for the interpretation of the age of the glaciation that produced the Port Askaig Formation.

Summary and conclusions

Metamorphosed Dalradian limestones have high Sr concentrations, typically >1000 ppm, wide-ranging calcite $\delta^{18}O$ values, a number of which exceed +20‰, and Mn/Sr ratios of $\leqslant 0.6$. Comparison of limestone trace element and stable isotope data with a number of geochemical criteria used to determine the extent of alteration of $^{87}Sr/^{86}Sr$ in carbonate rocks shows that the $^{87}Sr/^{86}Sr$ ratios of calcite in many of the limestones can be considered to be close to that of coeval seawater. The $\delta^{18}O$, Mn and Sr abundance data indicate that diagenesis occurred wholly within the marine environment, with seawater dominating the diagenetic fluid. We consider that any alteration of primary $^{87}Sr/^{86}Sr$ values occurred essentially during diagenesis and that contaminating ^{87}Sr was derived mainly from phyllosilicates and feldspars in the limestone sediment.

Comparison of Dalradian limestone $^{87}Sr/^{86}Sr$ data with data from other, generally undeformed and unmetamorphosed Neoproterozoic carbonate-bearing successions shows that the Dalradian limestones have similar calcite $^{87}Sr/^{86}Sr$ ratios, with similar or lesser ranges of within-unit variation. Grampian, Appin and lowermost Argyll group limestones have $^{87}Sr/^{86}Sr$ in the range 0.7064–0.7072, excluding three extreme values. Middle to upper Argyll Group limestones have $^{87}Sr/^{86}Sr$ in the range 0.7082–0.7095. A general rise in seawater $^{87}Sr/^{86}Sr$ from *c.* 0.7052 at about 900 Ma to *c.* 0.7085 or more in the very latest Neoproterozoic appears to have been punctuated by sharper increases at *c.* 800 and *c.* 600 Ma that bracket the range in $^{87}Sr/^{86}Sr$ values in Grampian and Appin Group limestones. $^{87}Sr/^{86}Sr$ data for Grampian, Appin and lowest Argyll Group limestones confirm the sedimentary affinity of the Islay Subgroup with the underlying Appin Group, and are consistent with a rapid shift in seawater $^{87}Sr/^{86}Sr$ and/or a signficant time interval between deposition of Islay and Easdale Subgroup rocks. The latter is also consistent with a suggested erosional unconformity at the base of the Easdale Subgroup. Data for middle and upper Argyll Group limestones are consistent with Sr isotope data for other Neoproterozoic limestones of around 600 Ma, and indicate rapid deposition. The $^{87}Sr/^{86}Sr$ data support field evidence from the Scottish Central Highlands for these rocks having been deposited unconformably on gneissose metasedimentary rocks affected by tectonothermal events that occurred some time between *c.* 730 and 900 Ma. The 800–600 Ma bracket in seawater $^{87}Sr/^{86}Sr$ indicates that the Grampian and Appin Groups (and, therefore, the Dalradian as a whole) are younger than *c.* 800 Ma and may be younger than *c.* 700 Ma. If the Grampian and Appin Groups were younger than *c.* 700 Ma, the Port Askaig Formation could not be a Sturtian tillite correlative. The duration of Dalradian sedimentation may have been much shorter than has been envisaged to date. Direct and more precise determination of the age and duration of Dalradian sedimentation and the age of key lithostratigraphical units, such as the Port Askaig Formation, await the application of alternative dating techniques. The results of this study provide broad discrimination between various models for the time scale and age of Dalradian sedimentation, and a focus for future geochronological studies to test competing hypotheses.

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