Prave, A.R. and Fallick, A.E. and Thomas, C.W. and Graham, C.M. (2009) *A composite C-isotope profile for the Neoproterozoic Dalradian Supergroup of Scotland and Ireland.* Journal of the Geological Society, 166 (5). pp. 845-857. ISSN 0016-7649

A composite C-isotope profile for the Neoproterozoic Dalradian Supergroup of Scotland and Ireland

A.R. PRAVE[1], A.E. FALLICK[2], C.W. THOMAS[3] & C.M. GRAHAM[4]

[1]*Geosciences, University of St Andrews, St Andrews, KY16 9AL, UK*
[2]*Scottish Universities Environmental Research Centre, East Kilbride, G75 0QF, UK*
[3]*British Geological Survey, Murchison House, West Mains Road, Edinburgh, EH9 3LA, UK*
[4]*School of Geosciences, Grant Institute, University of Edinburgh, Edinburgh, EH9 3JW, UK*

Abstract: The Neoproterozoic Dalradian Supergroup is a dominantly siliciclastic metasedimentary succession in the Caledonian orogenic belt of the British-Irish isles. Despite polyphase tectonothermal deformation and greenschist to upper amphibolite facies metamorphism, carbonate units distributed throughout the Dalradian record marked $\delta^{13}C_{carbonate}$ excursions that can be linked to those associated with key environmental events of Neoproterozoic time. These include: (i) tentative correlation of the Ballachulish Limestone to the *c*. 800 Ma Bitter Springs anomaly; (ii) the presence of the pre-Marinoan Trezona anomaly and 635 Ma Marinoan-equivalent cap carbonate sequence in rocks of the middle Easdale Subgroup, and (iii) the terminal Proterozoic (*c*. 600-551 Ma) Wonoka-Shuram anomaly in the Girlsta Limestone on Shetland. These linkages strengthen previously inferred correlations of the Stralinchy-Reelan formations and the Inishowen-Loch na Cille-MacDuff ice-rafted debris beds to the, respectively, 635 Ma Marinoan and 582 Ma Gaskiers glaciations and suggest that the oldest Dalradian glacial, the Port Askaig Formation, is one of the *c*. 750 – 690 Ma Sturtian glacial episodes. These $\delta^{13}C$ data and resulting correlations provide more robust constraints on the geological evolution of the Dalradian Supergroup than anything hitherto available and enhance its utility in helping refine understanding of Neoproterozoic Earth history.

The Dalradian Supergroup is a dominantly siliciclastic metasedimentary succession that extends from the Shetland Islands through mainland Scotland and across the northern part of Ireland (Fig. 1). Together with the Torridonian and Moine Supergroups, it forms a major part of the record of Neoproterozoic Earth history in Britain and Ireland, recording deposition on the evolving margin of the Laurentian craton prior to the opening of Iapetus (Anderton 1982, 1985). Like many contemporary successions worldwide, it contains evidence for the hallmark climatic events of the Neoproterozoic, particularly the putative ‘Snowball Earth’ glaciations (Hoffman *et al*. 1998; Hoffman & Schrag 2002). Unlike many other well-studied Neoproterozoic successions, it is polyphase deformed and metamorphosed. In particular, the mid-Ordovician Grampian orogenic event (*c*. 465 Ma; *e.g.* Oliver *et al*. 1998) resulted in greenschist to upper-amphibolite facies metamorphism across much of the Dalradian outcrop. Despite this, the lithostratigraphy of the Dalradian is moderately well established and there is good preservation of primary sedimentological features in many areas. However, the lack of a sufficiently well constrained chronological framework for the Dalradian frustrates efforts to better link it to Neoproterozoic successions elsewhere. This paper rectifies that by establishing a $\delta^{13}C_{carbonate}$ chemostratigraphy for Dalradian carbonate rocks.

Only two depositional ages are known for the entire Dalradian succession: the U-Pb ages of 595 Ma ±4Ma (Halliday *et al*. 1989) for a keratophyre and 601 ±4 Ma (Dempster *et al*. 2002) for an ash bed, both in the Tayvallich Volcanic Formation in the lowermost Southern Highland Group. Syn-deformational monazite and zircon overgrowths from gneissose lithologies in the Central Scottish Highlands have yielded U-Pb ages between *c*. 840 – 800 Ma (*e.g.* Noble *et al*. 1996; Highton *et al*. 1999; Smith *et al*. 1999), but it remains unproven whether the gneissose rocks from which these ages were obtained sit unconformably beneath the base of the Dalradian (thus constraining a maximum age of deposition) or lie within its lowermost part, in which case Dalradian sedimentation would be older still. Thomas *et al*. (2004) compared $^{87}Sr/^{86}Sr$ data obtained from Dalradian carbonate rocks with global, secular Sr-isotopic curves (*e.g.* Melezhik *et al*. 2001), interpreting the data to indicate that the Dalradian Supergroup spans mid- to late-Neoproterozoic time, and suggested that its base could be as young as 750 Ma or even less. The youngest concordant U-Pb ages of detrital zircons from the Dalradian are *c*. 1000 Ma (Cawood *et al*. 2003, 2007), and thus do not offer any refinement on the timing of the onset of deposition. The uppermost part of the Dalradian succession in mainland Scotland includes the Leny Limestone and Slate Member of the Keltie Water Grit Formation (Tanner 1995; recently informally assigned from the Highland Border Complex to the new Trossachs Group by Tanner & Sutherland 2007). The Leny Limestone contains trilobites of the early Cambrian *Bonnia-Olennelus* Zone (Pringle 1940; Fletcher & Rushton 2007) and Tanner & Sutherland (*op. cit*.) consider that Dalradian sedimentation continued into the early Ordovician. Consequently, the Dalradian Supergroup spans at least 200 – 300 millions of years.

In recent years, a global C-isotopic data set for Neoproterozoic carbonate rocks has been compiled and used to correlate $\delta^{13}C$ profiles worldwide (*e.g.* Kaufman *et al.* 1997; Walter *et al.* 2000; Halverson *et al.*, 2005, 2007a, and references therein). Here we report new $\delta^{13}C$ data for Dalradian carbonate rocks and use them to construct a composite C-isotope profile spanning most of the succession. When these data are integrated with their positions relative to Dalradian glacigenic deposits, there is remarkably strong correspondence with the established $\delta^{13}C$ curve and main glacial deposits for the Neoproterozoic. The key correlations include: (i) a potential correlative of the *c*. 800 Ma Bitter Springs anomaly (Hill & Walter 2000; Halverson *et al.* 2007b); (ii) the pre-Marinoan Trezona anomaly and the 635 Ma Marinoan glacial-cap carbonate sequence (Kennedy 1996; Kennedy *et al.* 1998; Hoffman *et al.* 1998; Hoffmann & Schrag 2002; Hoffmann *et al.* 2004; Halverson *et al.* 2002, 2005; Condon *et al.* 2005; Zhang *et al.* 2008); and (iii) the late Neoproterozoic Wonoka-Shuram anomaly (Burns & Matter 1993; Calver 2000; McKirdy *et al.* 2001; Fike *et al.* 2006; Le Guerroué *et al.* 2006; Rieu *et al.* 2007). Our data provide, for the first time, globally comparative C-isotope events through the Dalradian. This permits comparison with better dated, less deformed Neoproterozoic sections elsewhere, enhancing the contribution the Dalradian succession can make towards understanding Earth System behaviour during a time of profound geological and environmental change.

Background

The Dalradian Supergroup is divided into four main groups: from oldest to youngest, the Grampian, Appin, Argyll and Southern Highland (Harris *et al.* 1978; 1994); each is further divided into subgroups containing numerous formations (Fig. 1). The Dalradian succession contains generally thin and subordinate, but regionally persistent, carbonate units. Their stratigraphical value has long been recognized and various workers have used whole-rock geochemistry to discriminate amongst them and aid in regional correlation (Hickman & Wright 1983; Rock 1986; Thomas 1989; Thomas & Aitchison 2006). Our work builds on and significantly extends this previous work.

Critical to this study is the presence in the Dalradian of glacial deposits. For many years, the Port Askaig Formation, recognised in discontinuous outcrop across mainland Scotland and Ireland, was the only glacial deposit identified within the Dalradian (Spencer 1971; Eyles & Eyles 1983; Arnaud & Eyles 2006; Benn & Prave 2006). However, three distinct glacigenic intervals are now documented (McCay *et al.* 2006). The Port Askaig

Formation at the base of the Argll Group is the oldest of the glacial deposits. The Easdale Subgroup contains the glacial-cap carbonate couplet of the Stralinchy Conglomerate and Cranford Limestone (McCay *et al.* 2006), both best developed near their eponymous villages in Donegal, Ireland. The youngest glacigenic interval in the Dalradian occurs low in the Southern Highland Group and above rocks correlated with the *c.* 600 Ma Tayvallich Volcanics. It is preserved in discontinuous 'boulder beds' interpreted as ice-rafted debris (IRD), including the Inishowen IRD in Donegal, Ireland, and the Loch na Cille and MacDuff Boulder Beds in SW and NE Scotland, respectively (Sutton & Watson 1954; Stoker *et al.* 1999; Condon *et al.* 2000, 2002).

The timing and number of Neoproterozoic glacial events remain a matter of debate, thus an unequivocal chronostratigraphy of Dalradian glacial deposits cannot yet be established. However, integration of a variety of datasets including δ^{13}C isotopic profiles, ^{87}Sr/^{86}Sr isotopes, a sparse but growing set of radiometric age constraints, and lithostratigraphy, shows that a globally correlative framework of key Neoproterozoic environmental events can be exploited as proxies for chronostratigraphy (*e.g.* Halverson *et al.* 2005, 2007a, and references therein). For the Dalradian, Brasier & Shields (2000) used C and Sr isotope data to suggest that the Port Askaig Formation is best correlated to the Ghubrah glacial in Oman, now known to be *c.* 713 Ma in age (Bowring *et al.* 2007). McCay *et al.* (2006) concluded that the Stralinchy Conglomerate – Cranford Limestone pairing is equivalent to the 635 Ma Marinoan glacial – cap carbonate sequence in Namibia (Hoffmann *et al.* 2004; Condon *et al.* 2005; Zhang *et al.* 2008). The Inishowen-Loch na Cille – MacDuff beds can be reasonably linked to the 582 Ma Gaskiers glaciation geochronologically constrained in Newfoundland (Bowring *et al.* 2007).

Sampling

449 carbonate samples were obtained from outcrops of the main carbonate units exposed in Donegal, Ireland, mainland Scotland and Shetland, and used to construct the composite C-isotope profile for the Dalradian succession. Samples were cut, cleaned and polished, and thin sections made from representative samples and examined to assess textures. Powders for 413 samples were obtained using a Sherline microdrill. The remaining samples were taken from powders prepared for whole rock analysis. Carbon and oxygen isotope analysis was undertaken at the Scottish Universities Environmental Research Centre using an automated triple-collector gas source mass spectrometer (Analytical Precision AP2003) linked to an automated gas-preparation device. In the latter, *c.* 1 mg of the powdered sample is reacted

with 103% phosphoric acid to produce carbon dioxide which is then purified before analysis. Precision and accuracy are monitored by reference to long-term analysis of laboratory and international standards. Precision is better than 0.2‰ at 1σ for carbon and oxygen. Data are reported as δ‰ values relative to V-PDB (Table 1).

Interpretation of $\delta^{13}C_{carbonate}$ signatures in Dalradian carbonate rocks

All studies of variations in $\delta^{13}C_{carbonate}$ in Neoproterozoic carbonate rocks are based on the premise that these variations reflect closely those in the $\delta^{13}C$ of contemporary seawater. The results of the large number of studies undertaken to date on those rocks show that this premise is largely justified. However, in order to interpret with confidence correlations of C-isotope profiles of metacarbonate rocks to unmetamorphosed successions, the possible effects of diagenetic and/or metamorphic processes modifying C-isotope compositions (*e.g.* Veizer 1992; Melezhik *et al*. 2005) of the Dalradian carbonate rocks must be considered.

Thomas *et al*. (2004) have shown that diagenetic effects on $\delta^{13}C$ in most Dalradian limestones were likely minor. Part of the evidence for reaching this conclusion is the relatively high Sr contents for most of these limestones (~1 to 2 x 10^3 ppm; Hickman & Wright 1983; Rock 1986; Thomas 1989; Thomas *et al*. 2004) which has been used to infer that the original carbonate phase was largely aragonite and that diagenetic pathways were rather simple, consistent with transition from aragonite to calcite in the presence of a fluid dominated by broadly contemporaneous seawater away from the influence of meteoric and other exotic fluids. Regarding metamorphism, the metamorphic fluids passing through the Dalradian rocks are known to have been poor in C-bearing phases (*e.g.* CO_2, CO, CH_4) relative to calcite, thus the isotopic composition of the carbonate carbon was largely buffered (Holness & Graham 1995; Graham *et al*. 1997; Thomas 2000) and that any alteration of the $\delta^{13}C$ of Dalradian limestones would have been small relative to the amplitude of secular changes in Neoproterozoic seawater. Micro-analytical (ion microprobe) analyses of calcite grains in amphibolite facies limestone (Lewis *et al*. 1998, 2000) strongly supports this conclusion and shows that, while $\delta^{18}O$ in the edges of calcite grains is depleted by up to 20‰ by grain boundary fluid infiltration, $\delta^{13}C_{carbonate}$ is unmodified. This indicates a decoupling of $\delta^{18}O$ and $\delta^{13}C$ signatures in terms of response of these isotopic systems to metamorphic fluid infiltration. The relationship between the $\delta^{13}C$ and $\delta^{18}O$ data in this study also reveals no systematic covariation (see data in Table 1); detailed discussion of $\delta^{18}O$ variations in Dalradian carbonate rocks will be the subject of another paper by the two junior authors.

Even given the potential mechanisms for altering primary C-isotopic compositions, the remarkable similarity of the Dalradian's C-isotopic profile to the global curve (see below) is the strongest line of evidence that primary signals have been preserved. This gives us confidence in interpreting the $\delta^{13}C$ data in terms of secular changes in seawater during Dalradian deposition, and in comparing these data with those for other Neoproterozoic successions. Thus the caveats highlighted by Fairchild & Kennedy (2007) regarding a-critical acceptance of Neoproteorozic $\delta^{13}C_{carbonate}$ data have been considered, assessed, and accounted for in our samples of the Dalradian carbonate rocks.

Results

Figures 2 and 3 show the $\delta^{13}C_{carbonate}$ trend for the composite stratigraphic column of the Dalradian Supergroup, compared to the currently proposed global curve of Halverson *et al.* (2005, 2007a).

Grampian Group Limestones. Only one interval of carbonate rocks occurs in the Grampian Group, a 10 – 20 m thick limestone unit in the Kincraig Formation (Corrieyairack Subgroup). The limestone is sandwiched between thick successions of fine-grained psammite and semi-pelite and, at the eponymous type locality in the central Scottish Highlands, occurs a few tens of metres above the inferred base of the Grampian Group (Smith *et al.* 1999). The rocks are at upper amphibolite facies and, although psammitic rocks retain sedimentary structures, pelitic units have developed gneissose textures. The limestone unit, though, is surprisingly coherent and displays well-developed carbonate-siliciclastic cycles. These consist of 0.5 – 2 m thick, sharp-based calcitic marbles separated by thinner psammite-pelite beds. The upward vertical trend is for carbonate:psammite-pelite ratios to decrease. Given that there is only one well-developed section of the Kincraig Limestone, inferring depositional settings is speculative, but the stratigraphic trend implies deepening-upward peritidal cycles, an inference supported by the fact that overlying units consist of siliciclastic turbidites (Smith *et al.* 1999). Each limestone bed was sampled. The resulting $\delta^{13}C_{carbonate}$ values are mostly positive, ranging between 3‰ and 9‰, but the data are too limited in number to establish the presence or otherwise of systematic trends.

Appin Group Limestones. The Appin Group contains several major carbonate units. The oldest is the Ballachulish Limestone and its equivalents (*e.g.* the Dufftown and Sandend members of the Mortlach Graphitic Schist Formation) that occur at the base of the Ballachulish Subgroup (Appin Group). The next is the Appin Limestone and its equivalents (various carbonate units in the Ailnack, Cockburn and Tarnash formations) that define the top of that Subgroup. The overlying Blair Atholl Subgroup contains the thickest and most extensive sequence of carbonate rocks in the Dalradian, the Lismore, Fordyce, Ballygrant, Islay and Lossit formations.

The Ballachulish Limestone comprises 0.2 – 5 m thick dark-grey beds of fine- to medium-crystalline limestone interbedded with thinner dark-grey pelites. It occurs abruptly above a thick sequence of light-coloured, locally calcareous, quartz-mica schists and pelites (*e.g.* Leven Schist and Cairnfield formations). It appears to grade upward into the overlying pyritiferous and carbonaceous (graphitic at higher grades) Ballachulish Slate Formation. In NE Scotland, the limestone forms a discontinuous member within the base of the Mortlach Graphitic Schist Formation. The Ballachulish Limestone (and its correlatives) varies in thickness along strike, typically between many tens to as much as two hundred metres in thickness. Intimate association of the carbonate rocks with dark-grey, fine-grained siliciclastic units suggests deposition in a relatively deep-water setting, although an exact assessment of the depositional environment is limited because of overprinting by amphibolite facies metamorphism across much of its outcrop. Nevertheless, the $\delta^{13}C_{carbonate}$ profile is striking, with values revealing a sharp, monotonic decline from *c.* 5‰ down to -7‰.

The Appin Limestone and equivalents are white and light grey to pastel coloured units many metres to several tens of metres in thickness. They consist of 0.1 – 0.5 m thick beds of fine-grained limestone, limestone rhythmite and thin resedimented beds and were probably deposited in a suite of shallow to deeper marine environments. The $\delta^{13}C_{carbonate}$ values of the Appin Limestone are between *c.* 2‰ and 4‰, indicating a return to positive values from the low values of the Ballachulish Limestone.

The carbonate units of the Blair Atholl Subgroup record the next dramatic excursions in C-isotopic trends. These rocks consist of a variety of carbonate lithologies, thin-bedded allodapic limestone, thicker dark grey units containing resedimented oolites, to even thicker-bedded lighter-coloured units locally containing chert and peritidal features such as enterolithic bedding, tepee structures and microbial mats. The overall vertical facies succession displays interbedded thin carbonate-pelite units passing upward into carbonate rocks many tens of metres thick with only minor siliciclastic intervals, implying development of a prograding carbonate shelf off which material was shed into a deeper basin. Starting with the oldest units (limestones of the Lismore, Inchrory and Fordyce formations), $\delta^{13}C_{carbonate}$ values begin at *c.* 3‰ then rise sharply to peak at *c.* 9‰. An abrupt downturn occurs in the Ballygrant and Lossit formations (and equivalents) to values as low as *c.* -6‰, followed by a similarly sharp recovery to values of 0‰ to 1‰ beneath the sharp and erosive base of the Port Askaig Formation.

Argyll Group Limestones. Carbonate rock units are less common in the overlying Argyll Group. Many are regionally discontinuous, mainly reflecting original lateral facies changes and/or erosional truncation. Nevertheless, distinguishable $\delta^{13}C_{carbonate}$ trends persist. The oldest carbonate rocks in the Argyll Group occur in the upper part of the Bonahaven Dolomite Formation, a mixed siliciclastic and carbonate unit. These carbonate rocks are some of the best-studied in the Dalradian because they contain well-preserved sedimentary features, including microbial lamination and desiccation cracks, and an origin as shallow-water deposits is certain (*e.g.* Spencer & Spencer 1972; Fairchild 1980). The Bonahaven Dolomite has also been considered as a potential cap carbonate on the Port Askaig Formation (*e.g.* Brasier & Shields 2000), but the thick carbonate-bearing units in the Bonahaven Dolomite (Members 3 and 4 of Fairchild 1980, 1991) do not cap glacigenic rocks and are separated from the last diamictite-bearing units by many tens of metres of strata. These strata record deposition in intertidal and shallow-marine settings (Spencer & Spencer 1972; Fairchild 1991), and possibly even more restricted shoreline settings (Fairchild 1980, 1985). Our $\delta^{13}C_{carbonate}$ data vary from -8‰ to -4‰, with a trend of upwards-increasing $\delta^{13}C_{carbonate}$ values. Strongly positive values have been reported for the topmost beds of the Bonahaven (Brasier & Shields 2000) but our sampling must have inadvertently missed those.

The third set of well-defined C-isotope excursions in the Dalradian occurs in carbonate rocks in the deep-water Easdale Subgroup, the Degnish, Ardrishaig, Badenyon, Portaleen, Termon and equivalent units. These units are from a few to many tens of metres in thickness and consist of 0.1 – 0.5 m thick beds of allodapic limestones, grainstones, rhythmites and micrites in various shades of grey. The salient feature of $\delta^{13}C$ in these rocks is that values rise from around 0‰ to a peak of *c.* 6‰ and then plunge to values as low as -12‰. From this deep nadir, there is a steady recovery to values between around 0‰ and 2‰. This recovery occurs in rocks that immediately underlie units correlated with the Marinoan-equivalent glacial – cap carbonate couplet of McCay *et al.* (2006). The cap carbonate (Cranford Limestone; McCay *et al.* 2006) is best developed in the Dalradian succession in Donegal, Ireland (Pitcher & Berger 1972); equivalent rocks have now been documented elsewhere in the Dalradian (*e.g.* Kilbride Limestone, data herein; the Whiteness Limestone on Shetland, Prave *et al.* 2009). These rocks define a C-isotope trend that starts with basal values mostly around 0‰ to -3‰ then decline to a low of *c.* -7‰, before rising to values oscillating by about ±2‰ around 0‰. More positive values, to as high as 4‰, are recorded in the youngest carbonate units in the topmost parts of the Easdale Subgroup.

The youngest major carbonate unit in the Argyll Group is the Tayvallich – Loch Tay Limestone and equivalents. It crops out across northern Ireland and mainland Scotland and is one of the most laterally continuous units in the Dalradian. At the eponymous type locality, the 600 Ma Tayvallich Volcanic Formation lies immediately above the limestone. The Loch na Cille Boulder Bed, the uppermost glacigenic interval in the Dalradian, occurs several kilometers south of the same locality and some 500 m stratigraphically above the dated volcanic rocks. The Tayvallich – Loch Tay Limestone is several tens of metres thick and consists of 0.2 – 2 m thick beds of medium to dark grey and locally black limestone. Where sedimentary features are preserved, calcitic grainstones and siltstones are observed interbedded with thinner and subordinate fine-grained siliciclastic interbeds. These lithologies are inferred to have formed in shelf settings below fairweather wave base. The black lithology can be coarsely crystalline, with single calcite crystals up to 1 cm across and containing abundant graphite inclusions. The C-isotope trend rises stratigraphically from values of *c.* -2‰ to 0‰ to values as high as *c.* 7‰.

Southern Highland Group Limestones on Shetland On mainland Scotland and Ireland, Southern Highland Group rocks are largely psammitic and pelitic, with intervening mafic volcanic units that locally include pillow lavas. Carbonate rocks are rare and limited to the lowermost parts of the Group. Those that are present have $\delta^{13}C_{carbonate}$ values from 3‰ to 6‰, similar to the values in the underlying Tayvallich Subgroup. However, on Shetland, several thick carbonate units are present in rocks interpreted to be equivalent to the Southern Highland Group (Flinn 1985). These limestones contain the last major excursion in $\delta^{13}C$ observed in the Dalradian succession.

Because of their geographical isolation, the lithostratigraphy of the Dalradian of Shetland is not easily correlated with that in mainland Scotland and Ireland. However, Prave *et al.* (2009) have shown that the Whiteness Limestone is a Marinoan-equivalent cap carbonate. This establishes a firmer link between Shetland and sections elsewhere, indicating that post-Whiteness-Limestone rocks are broadly correlative with the upper part of the Easdale Subgroup and the Southern Highland Group succession. Several kilometres stratigraphically above the Whiteness Limestone on Shetland is the 700 – 900 m thick Girlsta Limestone (Flinn 1985). Amphibolite facies metamorphism has obliterated primary sedimentary structures, but the thickness of the Girlsta Limestone suggests it would have been part of an extensive carbonate platform (note that there is no evidence to suggest that significant tectonic thickening has occurred). What is striking is that it records a remarkably deep, and persistent negative $\delta^{13}C_{carbonate}$ excursion, with values as low as -9‰ to -11‰ for the entire unit (Prave *et al.* 2009). The profound negative excursion recovers sharply to values of *c.* 3‰ in marbles of the Fulgarth Limestone, which occurs above a 100 m thick psammite-pelite interval developed between it and the top of the Girlsta Limestone. Lithologically, the Fulgarth is similar to the Girlsta Limestone, comprising pastel-coloured banded marble with no discernable sedimentary features preserved. The youngest carbonate unit on Shetland is the 400 – 500 m thick Laxfirth Limestone; it is 1-2 km above the Girlsta Limestone and separated from it by pelitic and psammitic rocks. Metamorphism has also destroyed sedimentary features in the Laxfirth Limestone, but its thickness also implies that it would have been part of a carbonate bank/platform. $\delta^{13}C_{carbonate}$ values in the Laxfirth Limestone start at *c.* -2‰ and rise to average around 0‰. Although the Laxfirth Limestone could be as young as Cambrian in age, we follow others (*e.g.* Flinn 1985) in assuming that all the Dalradian rocks on Shetland predate the Cambrian Leny Limestone.

Discussion: Global C-isotopic trends and the Dalradian

In lieu of other chronometric techniques, C-isotope stratigraphy has provided a means of ‘telling Neoproterozoic time’ (Knoll 2000). Over the past few years, papers have synthesised C-isotope profiles from numerous well-exposed and -documented Neoproterozoic successions and have constructed a global C-isotope stratigraphy tied to as many absolute geochronological constraints as are currently available (*e.g.* Halverson *et al.* 2005, 2007a). It is against this composite $\delta^{13}C$ curve that we have evaluated our data for the Dalradian. The comparisons are striking and the overall trends of the Dalradian $\delta^{13}C$ profile matches closely with the global curve (Figs. 2, 3): there are three stratigraphically discrete glacigenic intervals, the two older ones are sandwiched between sharp negative excursions and intervening carbonate rocks have strongly positive $\delta^{13}C$ excursions.

The four significant negative $\delta^{13}C$ excursions in the Dalradian can be correlated to those known for Neoproterozoic sections worldwide. The youngest of these, the deep and persistent negative excursion recorded in the Girlsta Limestone, is interpreted as the Shuram-Wonoka anomaly (Prave *et al.* 2009). No other known negative $\delta^{13}C$ excursion in Earth history is as dramatic. Published age constraints and determinations place it between *c*. 600 Ma and 551 Ma (Condon *et al*. 2005; Le Guerroué *et al*. 2006; Bowring *et al.* 2007; Rieu *et al*. 2007; Melezhik *et al*. 2008), consistent with the *c*. 600 Ma age for the Tayvallich Volcanics (Halliday *et al*. 1989; Dempster *et al.* 2002). The link is supported further by the documentation of the Shuram-Wonoka anomaly in similar rocks in the Scandinavian Caledonides (Melezhik *et al*. 2008).

The next two negative $\delta^{13}C$ excursions bracket the glacigenic Stralinchy Conglomerate and its correlative intervals in Scotland. These excursions occur immediately before and after the glacial unit. This sandwich of negative excursion – glacial unit – negative excursion, its position several kilometers stratigraphically beneath the 600 Ma Tayvallich volcanic rocks, and the physical similarity of the Cranford Limestone (and its correlatives) to cap carbonates known elsewhere (see McCay *et al*. 2006), strongly suggest correlation with the Trezona and cap carbonate excursions associated with the Marinoan glaciation (Kennedy *et al.* 1998; Hoffman & Schrag 2002; Halverson *et al*. 2002, 2005). U-Pb zircon ages on ash beds that date the meltback phase and the formation of the cap carbonate of this glaciation yield an age of 635 Ma for these events (Hoffmann *et al.* 2004; Condon *et al*. 2005; Zhang *et al*. 2008).

The Port Askaig Tillite Formation is the oldest of the Dalradian glacial deposits. Four aspects are informative: (i) it occurs sandwiched between positive isotope excursions of 5‰ to 10‰; (ii) it is underlain by a sharp negative excursion (the term ‘Islay anomaly’ has been proposed; G. Halverson, pers comm., 2009); (iii) $^{87}Sr/^{86}Sr$ for associated carbonate rocks is *c*. 0.706 (Brasier & Shields 2000; Thomas *et al.* 2004); and (iv) it contains several thin (5-10 cm thick) Fe-rich layers. These data match well those which characterise deposits of the Sturtian icehouse episodes (Halverson *et al.* 2005, 2007a). The number and timing of Sturtian glaciations is far from being resolved; antecedent to the varying ages that have been obtained on ‘Sturtian’ deposits, the Port Askaig was considered to be correlative with the Ghubrah glacial in Oman (Condon & Prave 2000; Brasier & Shields (2000), now known to be *c*. 713 Ma (Bowring *et al*. 2007). This correlation is possible but remains unproven. Initially, the deeply negative $\delta^{13}C$ values of the overlying Bonahaven Formation puzzled us because they stand out from the global trends and could have been interpreted as recording a diagenetically modified and/or restricted marine signal and thereby potentially compromising its utility for global correlations (Fairchild, pers. comm. 2009). However, recent work by Macdonald *et al*. (2009) has documented a deep negative $\delta^{13}C$ excursion (values as low as -7.5‰), termed by them the Tayshir anomaly, in the inter-glacial Tsagaan Oloom Formation in southwestern Mongolia. The Bonahaven Dolomite and the Tsagaan Oloom Formation occupy compatible stratigraphic positions relative to the two main phases of Neoproteorzoic glaciations and the amplitude of C-isotopic decline is similar in both formations. Thus, we interpret the $\delta^{13}C$ values of the Bonahaven Formation as recording a global depositional signal, rather than one of locally nuanced depositional conditions and/or diagenetic resetting.

The oldest $\delta^{13}C$ excursion that is recorded in Dalradian rocks, and which can be correlated to a global event, is that in the Ballachulish Limestone and equivalents. We tentatively correlate this excursion with the *c*. 800 Ma Bitter Springs anomaly (Hill & Walter 2000; Halverson *et al.* 2007b), documented in the Amadeus Basin, central Australia. The Ballachulish Limestone (and its equivalents) occurs well below the Port Askaig Formation and, like the Bitter Springs anomaly, exhibits a negative excursion that punctuates a profile marked by positive C-isotopic values (5‰ or higher). The decline in $\delta^{13}C_{carbonate}$ values in the Ballachulish Limestone to *c*. -7‰ is lower than those documented elsewhere for the Bitter Springs anomaly (down to *c.* -4‰; Halverson *et al.* 2007a,b), but this can be attributed to basinal gradient effects (*e.g*. Jiang *et al.* 2007; Giddings & Wallace 2009). The base of the Dalradian is well below the Ballachulish Limestone thus, if our correlation with the 800 Ma Bitter Springs anomaly is correct, the onset of Dalradian sedimentation must be older than 800 Ma. However, $^{87}Sr/^{86}Sr$ data for the Kincraig Formation (Thomas *et al.* 2004), which is stratigraphically older than the Ballachulish Limestone, are consistent with an age of c. 750 – 800 Ma when compared with the latest compilation of Neoproterozoic $^{87}Sr/^{86}Sr$ data (Halverson *et al*. 2007b). Thus the age of the base of the Dalradian is still uncertain and further work is required to resolve this issue, including a circumspect consideration of the basement-cover relationships and the 800 – 840 Ma age dates for the sheared gneissose rocks in the Central Highlands of Scotland (Highton *et al*., 1999; Noble *et al.* 1996).

Discussion: Geological implications for the Dalradian

The Dalradian Supergroup is one of three major Neoproterozoic supracrustal successions within the Scottish-Irish Highlands (the Moine and Torridonian Supergroups being the other two). If the age constraints on the global C-isotope excursions are correct and if we are correct in our interpreted correlations, the C isotope data can be used to provide first-order estimates of the time spans of large sections of Dalradian lithostratigraphy: the time encompassed in the Grampian and Appin Groups would be on the order of more than 100 Myr, in the Islay and mid Easdale Subgroups some 80 Myr, and in the Stralinchy Conglomerate to the Leny Limestone some 50 Myr.

The need remains for obtaining independent radiometric age control on these C-isotopic excursions, as well as improved age constraints for the initiation of Dalradian sedimentation, but these correlations provide a better temporal framework than anything that has existed previously for the Dalradian. Combined with sedimentological studies, this ‘chronostratigraphy’ can be used to test and refine models for the geological evolution of the Dalradian and thus a means for reconstructing more accurate and precise Neoproterozoic palaeogeographies. In addition, given the likelihood of such long time spans, the Dalradian must contain significant unconformities. One such proposed unconformity at the base of the Easdale Subgroup (Pitcher & Berger 1972) is supported by a step-increase in $^{87}Sr/^{86}Sr$ on carbonate rocks (Thomas *et al*. 2004). The discovery and documentation of such surfaces should spur the next major research effort to advance understanding of Dalradian geology.

Summary and Conclusion

Carbon isotope data for the major carbonate units in the Dalradian Supergroup exhibit a composite profile that matches well with the global $\delta^{13}C$ composite trend established from numerous Neoproterozoic sections worldwide. The Ballachulish Limestone records a negative excursion that is tentatively linked to the *c*. 800 Ma Bitter Springs anomaly, but we acknowledge the issue that this correlation raises for the age of the onset of Dalradian sedimentation. Carbonate rocks in the Bonahaven Dolomite and Easdale Subgroup have C-isotope trends compatible with the Tayshir and Trezona anomalies, respectively, which predate the global Marinoan glaciation, and the Easdale rocks contain the 635 Ma Marinoan cap-carbonate sequence. This places the Cryogenian – Ediacaran boundary within the mid-Easdale Subgroup at the base of the Cranford Limestone and its equivalents. We correlate the $\delta^{13}C$ excursion in the Girlsta Limestone on Shetland with the Shuram-Wonoka negative $\delta^{13}C$ excursion, known to have occurred between *c*. 600 – 551 Ma. The $\delta^{13}C$ data also support correlations of the Dalradian glacigenic units to those known worldwide: the Port Askaig Formation to the *c*. 750-690 Ma Sturtian episodes of glaciation, the Stralinchy

Conglomerate to the 635 Ma Marinoan glaciation, and the Inishowen-Loch na Cille-MacDuff IRD beds to the 582 Ma Gaskiers glaciation. For the first time, chronostratigraphic constraints can be established for the lithostratigraphy of the Dalradian Supergroup. Thus, we infer that the base of the Dalradian to the Port Askaig Tillite Formation likely spans over 100 Myr, the interval containing the three glacial units (Port Askaig Formation, Stralinchy Conglomerate, Inishowen-Loch na Cille-MacDuff IRD beds, and their equivalents) lasted a minimum of some 130 Myr, and the succession from there to the Leny Limestone (and correlatives) was of *c.* 50 Myr duration. After more than a century of study, the Dalradian is approaching a state whereby the timing, rates and durations of the processes forming, rather than deforming, the rocks can be brought more clearly into focus.

Acknowledgements

ARP and AEF acknowledge support from the Carnegie Trust to the Universities of Scotland. CWT published with the permission of the Executive Director, British Geological Survey. CWT thanks the BGS, Edinburgh University and the Scottish Universities Environmental Research Centre for support. Thanks are extended to I. Fairchild and G. Shields whose comments on an earlier version much improved this manuscript.

References

ANDERTON, R. 1982. Dalradian deposition and the late Precambrian-Cambrian history of the North Atlantic region: a review of the early evolution of the Iapetus Ocean. *Journal of the Geological Society, London* **139**, 421-431.

ANDERTON, R. 1985. Sedimentation and tectonics in the Scottish Dalradian. *Scottish Journal of Geology* **21**, 407-436.

ARNAUD, E. & EYLES, C. H. 2006. Neoproterozoic environmental change recorded in the Port
Askaig Formation, Scotland: climatic and tectonic controls on sedimentation. *Sedimentary Geology* **183**, 99-124.

BAKER, A. J. & FALLICK, A. E. 1989. Evidence from Lewisian limestone for isotopically heavy carbon in two–thousand–million–year–old sea water. *Nature* **337**, 352-354.

BANKS, C. J. & WINCHESTER, J.A. 2004. Sedimentology and stratigraphic affinities of Neoproterozoic coarse clastic successions, Glenshirra Group, Inverness-shire, Scotland. *Scottish Journal of Geology* **40**, 159-174.

BANNER, J. L. & HANSON, G. N. 1990. Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis. *Geochimica et Cosmochimica Acta* **54**, 3123-3137.

BENN, D. I. & PRAVE, A. R. 2006. Subglacial and proglacial glacitectonic deformation in the Neoproterozoic Port Askaig Formation, Scotland. *Geomorphology* **75**, 266-280.

BOWRING, S.A., GROTZINGER, J., CONDON, D.J., RAMEZANI, J. & NEWALL, M. 2007. Geochronologic constraints on the chronostratigraphic framework of the Neoproterozoic Huqf Supergroup, Sultanate of Oman. *American Journal of Earth Science* **307**, 1097-1145.

BRASIER, M.D. & SHIELDS, G. 2000. Neoproterozoic chemostratigraphy and correlation of the Port Askaig glaciation, Dalradian Supergroup of Scotland. *Journal of the Geological Society London*, **157**, 909-914.

BURNS, S.J. & MATTER, A. 1993. Carbon isotopic record of the latest Proterozoic from Oman. *Eclogae Geologicae Helvetiae* **86**, 595-607.

CALVER, C.R. 2000. Isotope stratigraphy of the Ediacaran Neoproterozoic III of the Adelaide Rift Complex, Australia, and the overprint of water column stratification. *Precambrian Research* **100**, 121-150.

CAWOOD, P.A., NEMCHIN, A.A., SMITH, M. & LOEWY, S. 2003. Source of the Dalradian Supergroup constrained by U-Pb dating of detrital zircon and implications for the East Laurentian margin. *Journal of the Geological Society, London* **160**, 231-246.

CAWOOD, P.A., NEMCHIN, A. A., STRACHAN, R., PRAVE, A. & KRABBENDAM, M., 2007. Sedimentary basin and detrital zircon record along East Laurentia and Baltica during the assembly and breakup of Rodinia. *Journal of Geological Society, London* **164**, 257-275

CONDON, D.J. & PRAVE, A.R. 2000. Two from Donegal: Neoproterozoic glacial episodes on the northeast margin of Laurentia. *Geology* **28**, 951–954.

CONDON, D.J., PRAVE, A.R. & BENN, D. 2002. Neoproterozoic glacial–rainout intervals: observations and implications. *Geology* **30**, 35-38.

CONDON, D., ZHU, M., BOWRING, S., WANG, W., YANG, A. & JIN, Y. 2005. U–Pb ages from the Neoproterozoic Doushantuo Formation, China. *Science* **308**, 95-98.

DEMPSTER, T.J., ROGERS, G., TANNER, P.W.G., BLUCK, B.J., MUIR, R.J., REDWOOD, S.D., IRELAND, T.R. & PATERSON, B.A. 2002. Timing of deposition, orogenesis and glaciation within the Dalradian rocks of Scotland: Constraints from U-Pb zircon ages. *Journal of the Geological Society, London* **159**, 83-94.

EYLES, C. H. & EYLES, N. 1983. Glaciomarine model for upper Precambrian diamictites of the
Port Askaig Formation, Scotland. *Geology*, **11**, 692-696.

FAIRCHILD, I. 1980. Sedimentation and origin of a late Precambrian ‘dolomite’ from Scotland. *Journal of Sedimentary Petrology* **50**, 423-446.

FAIRCHILD, I.J. 1985. Petrography and carbonate chemistry of some Dalradian metasediments: preservation of diagenetic textures. *Journal of the Geological Society, London* **142**, 167-185.

FAIRCHILD, I.J. 1991. Itinerary II and III. Topmost Islay Limestone (Appin Group), Port Askaig and Bonahaven Formations (Argyll Group), Port Askaig area, Islay, and Bonahaven Formation (Argyll Group) north coast of Islay, *In*: Hambrey, M.J., Fairchild, I.J., Glover, B.W., Stewart, A.D., Treagus, J.E. & Winchester, J.A. (eds) The Late Precambrian Geology of the Scottish Highlands and Islands. Geologists Association Guide, London, 33-52.

FAIRCHILD, I. & KENNEDY, M.J. 2007. Neoproterozoic glaciation in the Earth System. *Journal of the Geological Society, London* **164**, 895-921.

FIKE, D.A., GROTZINGER, J.P., PRATT L.M. & SUMMONS, R.E. 2006. Oxidation of the Ediacaran Ocean. *Nature* **444**, 744-747.

FLETCHER, T.P. & RUSHTON, A.W.A. 2007. The Cambrian fauna of the Leny Limestone, Perthshire. *Earth and Environmental Science Transactions of the Royal Society of Edinburgh* **98**, 199-218.

FLINN, D. 1985. The Caledonides of Shetland. *In*: Gee, D.G. & Sturt, B.A. (eds) The Caledonide Orogen – Scandinavia and Related Areas. Wiley, Chichester, 1158-1171.

GIDDINGS, T. AND WALLACE, M.W. 2009. Facies-dependent $\delta^{13}C$ variation from a Cryogenian platform margin, South Australia: Evidence for stratified Neoproterozoic oceans? *Palaeogeography, Palaeoclimatology, Palaeoecology* **271**, 196-214.

GRAHAM, C. M., SKELTON, A. D. L., BICKLE, M. & COLE, C. 1997. Lithological, structural and deformation controls on fluid flow during regional metamorphism. In: *Deformation-enhanced Fluid Transport in the Earth's Crust and Mantle* (edited by Holness, M. B.). *Mineralogical Society Series* **8**. Chapman and Hall, London, 196-226.

HALLIDAY, A., GRAHAM, C.M., AFTALION, M. & DYMOKE, P. 1989. The depositional age of the Dalradian Supergroup: U-Pb and Sm-Nd studies of the Tayvallich Volcanics, Scotland. *Journal of the Geological Society, London* **146**, 3-6.

HALVERSON, G.P., HOFFMAN, P.F., SCHRAG, D.P. & KAUFMAN, A.J. 2002. A major perturbation of the carbon cycle before the Ghaub glaciation (Neoproterozoic) in Namibia: Prelude to snowball Earth? *Geochemistry, Geophysics, Geosystems* **3**, 24 p.

HALVERSON, G.P., HOFFMAN, P.F., SCHRAG, D.P., MALOOF, A.C. & RICE, A.H.N. 2005. Towards a Neoproterozoic composite carbon isotope record. *Geological Society of America Bulletin* **117**, 1181-1207.

HALVERSON, G.P., DUDAS, F.O., MALOOF, A.C. & BOWRING, S.A. 2007a. Evolution of the $^{87}Sr/^{86}Sr$ composition of Neoproterozoic seawater. *Palaeogeography, Palaeoclimatology, Palaeoecology* **256**, 103-129.

HALVERSON, G.P., MALOOF, A.C., SCHRAG, D.P., DUDAS, F.O. & HURTGEN, M. 2007b. Stratigraphy and geochemistry of a ca 800 Ma negative carbon isotope interval in northeastern Svalbard. *Chemical Geology* **237**, 23-45.

HARRIS, A. L., BALDWIN, C. T., BRADBURY, H. J., JOHNSON, H. D. & SMITH, R. A. 1978. Ensialic sedimentation: the Dalradian Supergroup. In: *Crustal Evolution in Northwest Britain and adjacent regions* (edited by Bowes, D. R. & Leake, B. E.). *Special Report* **6**. Geological Society, London, 52-75.

HARRIS, A.L., HASELOCK, P.J., KENNEDY, M. & MENDUM, J.R. 1994. The Dalradian Supergroup in Scotland, Shetland and Ireland. *In*: Gibbons, W. & Harris, A.L. (eds) *A revised correlation of Precambrian rocks in British Isles.* Geological Society, London, Special Report 22, 33-53.

HICKMAN, A.H. AND WRIGHT, A.E. 1983. Geochemistry and chemostratigraphical correlation of slates, marbles and quartzites of the Appin Group, Argyll, Scotland. *Transactions Royal Society Edinburgh: Earth Sciences* **73**, 251-278.

HIGHTON, A.J., HYSLOP, E.K. & NOBLE, S.R. 1999. U-Pb zircon geochronology of migmatisation in the northern-central Highlands: evidence for pre-Caledonian (Neoproterozoic) tectonometamorphism in the Grampian block, Scotland. *Journal of the Geological Society London*, **156**, 1195–1204.

HILL, A.C. & WALTER, M.R. 2000. Mid-Neoproterozoic (830–750 Ma) isotope stratigraphy of Australia and global correlation. *Precambrian Research* **100**, 181–211.

HOFFMAN, P.F., KAUFMAN, A.J., HALVERSON, G.P. & SCHRAG, D.P. 1998. A Neoproterozoic snowball Earth. *Science* **281**, 1342-1346.

HOFFMAN, P.F. & SCHRAG, D.P. 2002. The snowball Earth hypothesis: Testing the limits of global change. *Terra Nova* **14**, 129-155.

HOFFMANN, K.H., CONDON, D.J., BOWRING, S.A. & CROWLEY, J.L. 2004. A U-Pb zircon date from the Neoproterozoic Ghaub Formation, Namibia: constraints on Marinoan glaciation. *Geology* **32**, 817-820.

HOLNESS, M. B. & GRAHAM, C. M. 1995. P-T-X effects on equilibrium carbonate-H_2O-CO_2-NaCl dihedral angles: constraints on carbonate permeability and the role of deformation during fluid infiltration. *Contributions to Mineralogy and Petrology* **119**, 301-313.

JIANG, G., KAUFMAN, A.J., CHRISTIE–BLICK, N., ZHANG, S. & WU, H. 2007. Carbon isotope variability across the Ediacaran Yangtze platform in South China: Implications for a large surface-to-deep ocean $\delta^{13}C$ gradient. *Earth and Planetary Science Letters* **261**, 303-320.

KAUFMAN, A.J., KNOLL, A.H. & NARBONNE, G.M. 1997. Isotopes, ice ages, and terminal Proterozoic Earth history. *Proceedings of the National Academy of Sciences of the United States of America* **94**, 6600-6605.

KENNEDY, M.J. 1996. Stratigraphy, sedimentology, and isotopic geochemistry of Australian Neoproterozoic postglacial cap dolostones; deglaciation, $\delta^{13}C$ excursions, and carbonate precipitation. *Journal of Sedimentary Research* **66**, 1050-1064.

Kennedy, M.J., Runnegar, B., Prave, A.R., Hoffmann, K.H. & Arthur, M. 1998. Two or four Neoproterozoic glaciations? *Geology* **26**, 1059-1063.

Kessler, L.G. & Gollop, I. G. 1988. Inner shelf/shoreface—intertidal transition. Upper Precambrian, Port Askaig Tillite, Isle of Islay, Argyll, Scotland. *In*: De Boer, P.L. *et al*. (eds) *Tide-influenced Sedimentary Environments and Facies,* D. Reidel, 341–358.

Knoll, A.H. 2000. Learning to tell Neoproterozoic time. *Precambrian Research* **100**, 3-20.

Le Guerroué, E., Allen, P.A., Cozzi, A., Etienne, J.L. & Fanning, M. 2006. 50 Myr recovery from the largest negative ^{13}C excursion in the Ediacaran ocean. *Terra Nova* **18**, 147-53.

Lewis, S., Graham, C., Thomas, C. W., Bond, C. & Holness, M. 2000. Time-scales and mechanisms of metamorphic fluid flow from integrated textural and ^{18}O/^{16}O micro-analysis studies of metacarbonates: evidence for transient flow events. *Goldschmidt 2000, Journal of Conference Abstracts* **5**(2), 641.

Lewis, S., Holness, M. & Graham, C. M. 1998. Ion microprobe study of marble from Naxos, Greece: Grain-scale fluid pathways and stable isotope equilibration during metamorphism. *Geology* **26**, 935-938.

Macdonald, F.A., Jones, D.S. & Schrag, D.P. 2009. Stratigraphic and tectonic implications of a newly discovered glacial diamictite-cap carbonate couplet in southwestern Mongolia. *Geology* **37**, 123-126.

McCay, G.A., Prave, A.R., Alsop, G.I. & Fallick, A.E. 2006. Glacial trinity: Neoproterozoic Earth history within the British–Irish Caledonides. *Geology* **34**, 901-912.

McKirdy, D.M., Burgess, J.M., Lemon, N.M., Yu, X., Cooper, A.M., Gostin, V.A., Jenkins, R.J.F. & Both, R.A. 2001. A chemostratigraphic overview of the late Cryogenian interglacial sequence Adelaide Fold–Thrust Belt, South Australia. *Precambrian Research* **106**, 149-186.

Melezhik, V.A., Gorokhov, I.M., Kuznetsov, A.B. & Fallick, A.E. 2001. Chemostratigraphy of Neoproterozoic carbonates: implications for 'blind dating'. *Terra Nova* **13**, 1-11.

Melezhik, V.A., Roberts, D., Fallick, A.E. & Gorokhov, I.M. 2008. The Shuram–Wonoka event recorded in a high-grade metamorphic terrane: insight from the Scandinavian Caledonides. *Geological Magazine* **145**, 161-172.

Melezhik, V.A., Roberts, D. Fallick, A.E. Gorokhov I.M. and Kuznetsov A.B. 2005. Geochemical preservation potential of high–grade calcite marble versus dolomite marble: implication for isotope chemostratigraphy. *Chemical Geol*ogy **216**, 203-224.

NOBLE, S. R., HYSLOP, E. K. & HIGHTON, A. J. 1996. High precision U-Pb monazite geochronology of the *c.* 806 Ma Grampian Shear Zone and implications for the evolution of the Central Highlands of Scotland. *Journal of the Geological Society London*, **153**, 511-514.

OLIVER, G.J.H., CHEN, F., BUCHWALD, R. & HEGNER, E. 1998. Fast tectonometamorphism and exhumation in the type area of the Barrovian and Buchan zones. *Geology* **28**, 459-462.

PITCHER, W.S. & BERGER, A.R. 1972. *The geology of Donegal: a study of granite emplacement and unroofing*. New York, Wiley Interscience, 435 p.

PRAVE, A. R. 1999. The Neoproterozoic Dalradian Supergroup of Scotland: an alternative hypothesis. *Geological Magazine* **136**, 609-617.

PRAVE, A.R., STRACHAN, R.A. & FALLICK, A.E. 2009. Global C cycle perturbations recorded in marbles: a record of Neoproterozoic Earth history within the Dalradian succession of the Shetland Islands, Scotland. *Journal of the Geological Society, London* **166**, 129-135.

PRINGLE, J. 1940. The discovery of Cambrian trilobites in the Highland Border rocks near Callander, Perthshire (Scotland). *The Advancement of Science* **1**, 252.

RIEU, R. ALLEN, P.A., COZZI, A., KOSLER, J. & BUSSY, F. 2007. A composite stratigraphy for the Neoproterozoic Huqf Supergroup of Oman: integrating new litho–, chemo– and chronostratigraphic data of the Mirbat area, southern Oman. *Journal of the Geological Society, London* **164**, 997-1009.

ROCK, N.M.S. 1986. Chemistry of the Dalradian (Vendian–Cambrian) metalimestones, British Isles. *Chemical Geology* **56**, 289-311.

SMITH, M., ROBERTSON, S. & ROLLIN, K.E. 1999. Rift basin architecture and stratigraphical implications for basement-cover relationships in the Neoproterozoic Grampian Group of the Scottish Caledonides. *Journal of the Geological Society, London* **156**, 1163-1174.

SPENCER, A.M. 1971. *Late Pre-Cambrian glaciation in Scotland.* Geological Society of London, Memoir 6, 100 p.

SPENCER, A.M., & SPENCER, M.O. 1972. The Late Precambrian/Lower Cambrian Bonahaven Dolomite of Islay and its stromatolites. *Scottish Journal of Geology* **8**, 269–282.

STOKER, M.S., HOWE, J.A. & STOKER, S.J. 1999. Late Vendian-? Cambrian glacially influenced deepwater sedimentation, MacDuff Slate Formation (Dalradian), NE Scotland. *Journal of the Geological Society, London* **156**, 55-61.

SUTTON, J. & WATSON, J.V. 1954. Ice-borne boulders in the MacDuff Group of the Dalradian of Banffshire. *Geological Magazine* **91**, 391-398.

TANNER, P.W.G. 1995. New evidence that the Lower Cambrian Leny Limestone at Callender, Perthshire, belongs to the Dalradian Supergroup, and a reassessment of the 'exotic' status of the Highland Border Complex. *Geological Magazine* **132**, 473–483.

TANNER, P.W.G. & SUTHERLAND, S. 2007. The Highland Border Complex, Scotland: a paradox resolved. *Journal of the Geological Society, London* **164**, 111-116.

THOMAS, C.W. 1989. Application of geochemistry in the stratigraphic correlation of Appin and Argyll Group carbonate rocks from the Dalradian of northeast Scotland. *Journal of the Geological Society, London* **146**, 631-647.

THOMAS, C.W. 2000. The petrology and isotope geochemistry of Dalradian carbonate rocks. Unpublished PhD thesis, University of Edinburgh.

THOMAS, C.W. & ATCHINSON, J. 2006. Log-ratios and geochemical discrimination of Scottish Dalradian limestones: a case study. *In*: Buccianti, A., Mateu-Figueras, G. & Pawlowsky-Glahn, V. (eds) *Compositional Data Anaylsis in the Geosciences: From Theory to Practice*. Geological Society, London, Special Publications 264, 25-41.

THOMAS, C.W., GRAHAM, C.M., ELLAM, R.M. & FALLICK, A.E. 2004. $^{87}Sr/^{86}Sr$ chemostratigraphy of Neoproterozoic Dalradian limestones of Scotland and Ireland: constraints on depositional ages and time scales. *Journal of the Geological Society, London* **161**, 229-242.

VEIZER, J. 1992. Depositional and diagenetic history of limestones: Stable and radiogenic isotopes. In: Clauer, N. & Chaudhuri, S. (eds.) *Isotopic Signatures and Sedimentary Records.* Springer-Verlag, Berlin, 13-48.

WALTER, M.R., VEEVERS, J.J., CALVER, C.R., GORJAN, P. & HILL, A.C. 2000. Dating the 840–544 Ma Neoproterozoic interval by isotopes of strontium, carbon, and sulfur in seawater, and some interpretative models. *Precambrian Research* **100**, 371-433.

ZHANG, S., JIANG, G & HAN, Y. 2008. The age of the Nantuo Formation and Nantuo glaciation in south China. *Terra Nova* **20**, 289-294.

Table caption

Table 1. C and O isotopic data for Dalradian carbonate units. (CT) denotes whole rock data of C. Thomas; Cranford Limestone data from McCay *et al*. (2006); Girlsta, Fulgarth and Laxfirth limestone data from Prave *et al*. (2009); all other data Prave & Fallick. L = limestone, D = dolostone. British and Irish National grid references are listed in brackets and denote location of start of section.

Figure captions

Fig. 1. Highly simplified geological map and composite stratigraphic column focusing on the main carbonate rock units of the Dalradian Supergroup in the British-Irish isles. Abbreviations of map localities for the glacigenic deposits: C – Cranford; LC – Loch na Cille; M – MacDuff; PA – Port Askaig; S – Stralinchy. Faults on inset map: HBF – Highland Boundary Fault; GGF – Great Glen Fault; MT – Moine Thrust. Note that the glacigenic rocks are shown in upper case in the stratigraphic column.

Fig. 2. $\delta^{13}C_{carbonate}$ trends for the major carbonate units in the Dalradian Supergroup. The siliciclastic units are much reduced in order to focus attention on the C-isotopic excursions. The profiles are plotted on a composite section that includes localities scattered across the length of the Dalradian outcrop belt from Donegal, Ireland, through mainland Scotland and from there northward to Shetland. The Cambrian Leny Limestone, which rests depositionally on the youngest beds of the Dalradian on mainland Scotland, has not been recognised on Shetland thus its position above the Laxfirth Limestone is inferential. Position of main stratigraphic units is noted. See text for discussion.

Fig. 3. Composite C-isotopic profile of the Dalradian (open large triangles) compared to the proposed global Neoproterozoic curve (grey background symbols; this version of the global curve was provided by G. Halverson, pers. comm. 2009). Placement of the Dalradian data on the global curve is based on the stratigraphic position of carbonate rock units and their associated C-isotopic trends relative to the correlation of the Dalradian glacial rocks with those of the global curve. See text for discussion. Note that this version of the global curve places the Shuram-Wonoka anomaly antecedent to the Gaskiers glaciation.

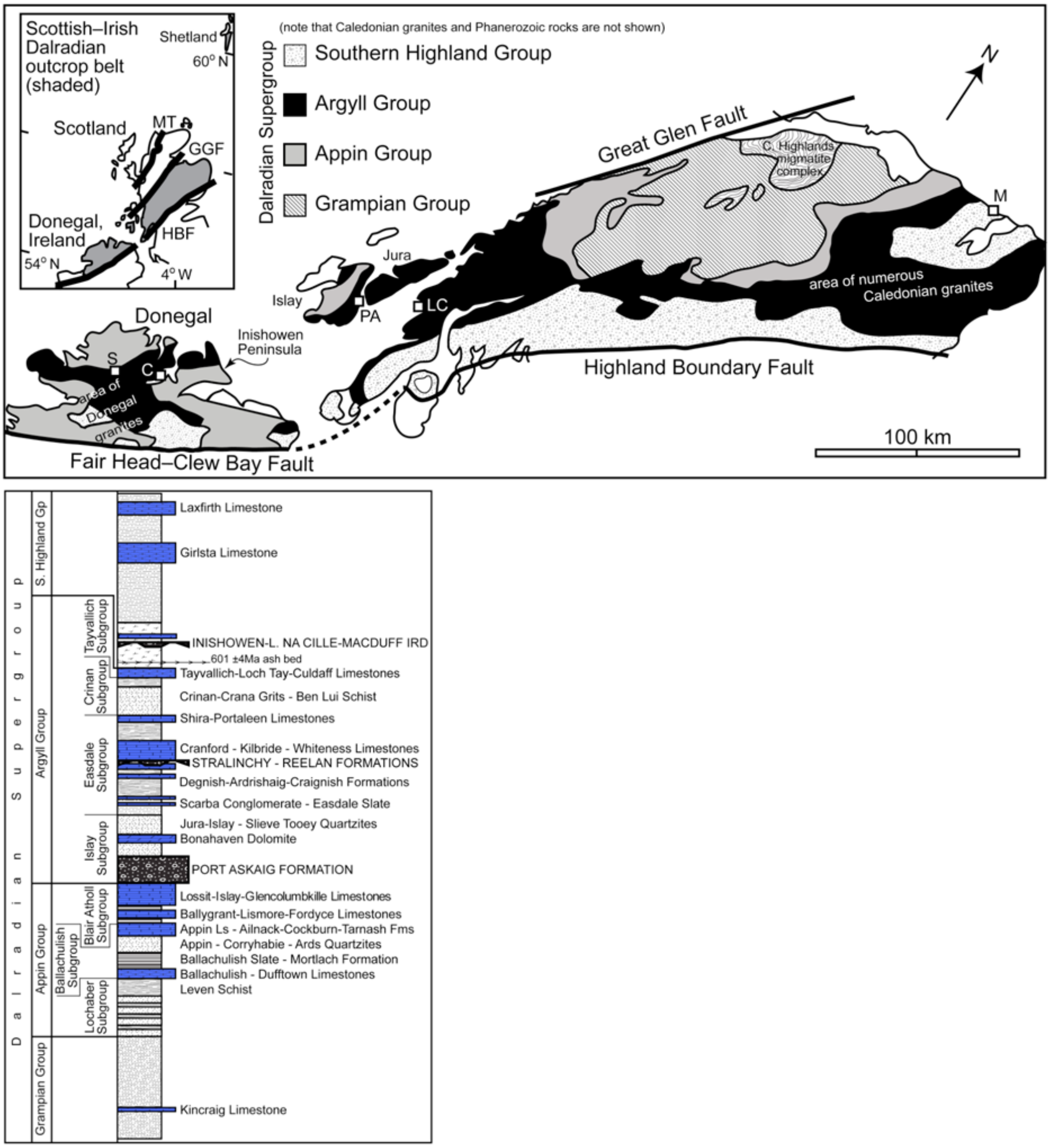
Scottish–Irish Dalradian outcrop belt (shaded)
Shetland
60° N
Scotland
MT
GGF
Donegal, Ireland
HBF
54° N
4° W
(note that Caledonian granites and Phanerozoic rocks are not shown)
Dalradian Supergroup
Southern Highland Group
Argyll Group
Appin Group
Grampian Group
N
Great Glen Fault
C. Highlands migmatite complex
M
Jura
Islay
PA
LC
area of numerous Caledonian granites
Donegal
Inishowen Peninsula
S
C
area of Donegal granites
Highland Boundary Fault
100 km
Fair Head–Clew Bay Fault
Dalradian Supergroup
S. Highland Gp
Argyll Group
Appin Group
Grampian Group
Tayvallich Subgroup
Crinan Subgroup
Easdale Subgroup
Islay Subgroup
Blair Atholl Subgroup
Ballachulish Subgroup
Lochaber Subgroup
Laxfirth Limestone
Girlsta Limestone
INISHOWEN-L. NA CILLE-MACDUFF IRD
601 ±4Ma ash bed
Tayvallich-Loch Tay-Culdaff Limestones
Crinan-Crana Grits - Ben Lui Schist
Shira-Portaleen Limestones
Cranford - Kilbride - Whiteness Limestones
STRALINCHY - REELAN FORMATIONS
Degnish-Ardrishaig-Craignish Formations
Scarba Conglomerate - Easdale Slate
Jura-Islay - Slieve Tooey Quartzites
Bonahaven Dolomite
PORT ASKAIG FORMATION
Lossit-Islay-Glencolumbkille Limestones
Ballygrant-Lismore-Fordyce Limestones
Appin Ls - Ailnack-Cockburn-Tarnash Fms
Appin - Corryhabie - Ards Quartzites
Ballachulish Slate - Mortlach Formation
Ballachulish - Dufftown Limestones
Leven Schist
Kincraig Limestone

Figure 1.

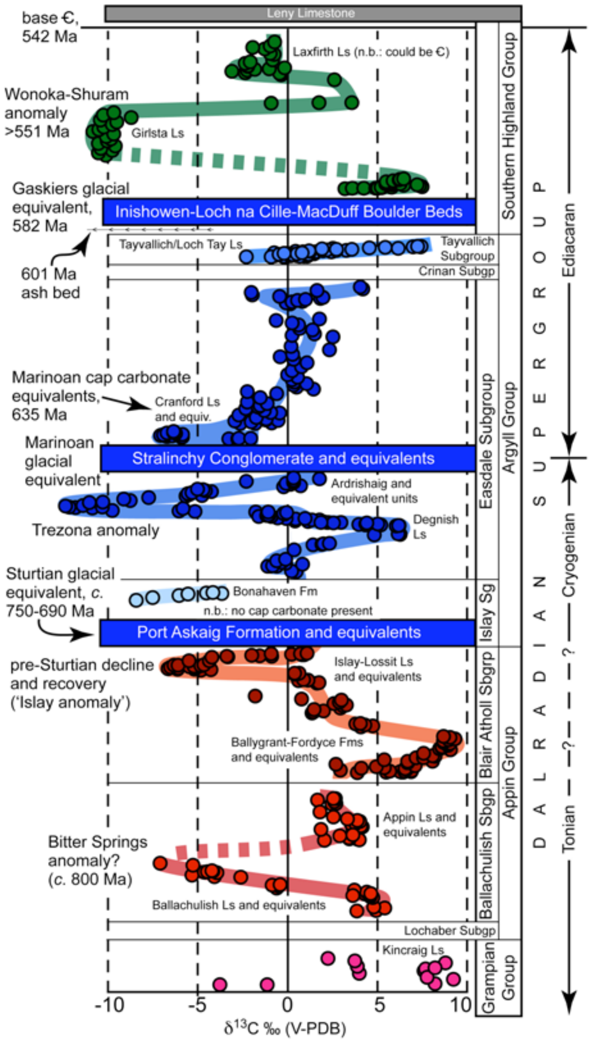
Leny Limestone
base Є, 542 Ma
Laxfirth Ls (n.b.: could be Є)
Wonoka-Shuram anomaly >551 Ma
Girlsta Ls
Gaskiers glacial equivalent, 582 Ma
Inishowen-Loch na Cille-MacDuff Boulder Beds
Tayvallich/Loch Tay Ls
Tayvallich Subgroup
Crinan Subgp
601 Ma ash bed
Marinoan cap carbonate equivalents, 635 Ma
Cranford Ls and equiv.
Marinoan glacial equivalent
Stralinchy Conglomerate and equivalents
Ardrishaig and equivalent units
Trezona anomaly
Degnish Ls
Sturtian glacial equivalent, c. 750-690 Ma
Bonahaven Fm
n.b.: no cap carbonate present
Port Askaig Formation and equivalents
pre-Sturtian decline and recovery ('Islay anomaly')
Islay-Lossit Ls and equivalents
Ballygrant-Fordyce Fms and equivalents
Appin Ls and equivalents
Bitter Springs anomaly? (c. 800 Ma)
Ballachulish Ls and equivalents
Lochaber Subgp
Kincraig Ls
-10
-5
0
5
10
δ13C ‰ (V-PDB)
Southern Highland Group
Easdale Subgroup
Argyll Group
Islay Sg
Blair Atholl Sbgrp
Ballachulish Sbgp
Appin Group
Grampian Group
DALRADIAN SUPERGROUP
Ediacaran
Cryogenian
?
Tonian
?

Figure 2

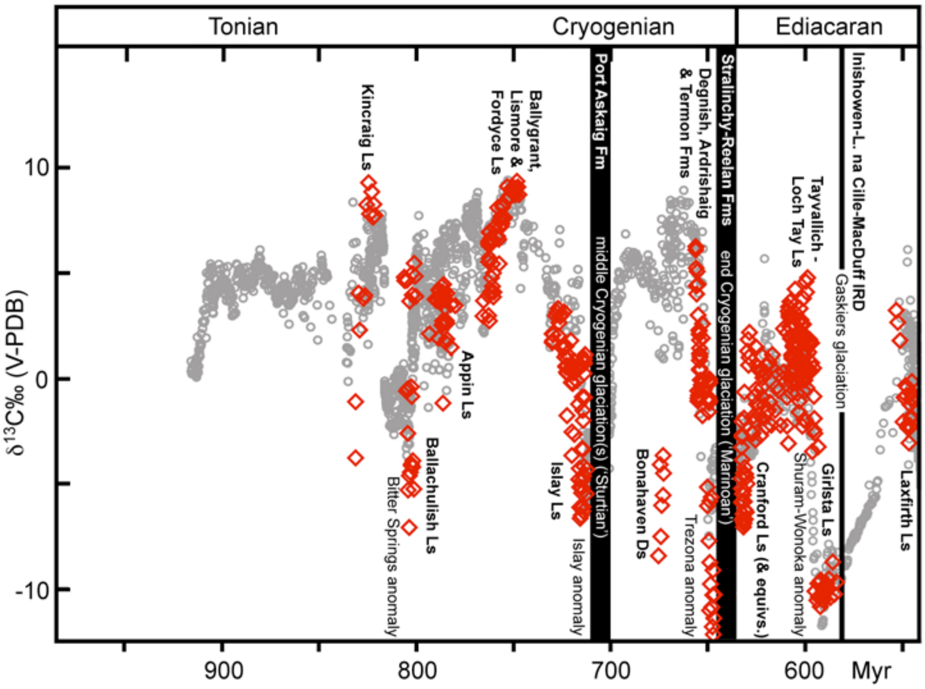
Tonian
Cryogenian
Ediacaran
10
0
-10
$\delta^{13}C$‰ (V-PDB)
900
800
700
600
Myr
Kincraig Ls
Ballygrant, Lismore & Fordyce Ls
Port Askaig Fm
Degnish, Ardrishaig & Termon Fms
Stralinchy-Reelan Fms
Tayvallich - Loch Tay Ls
Inishowen-L. na Cille-MacDuff IRD
Gaskiers glaciation
Appin Ls
Ballachulish Ls
Bitter Springs anomaly
Islay Ls
Islay anomaly
middle Cryogenian glaciation(s) ('Sturtian')
Bonahaven Ds
Trezona anomaly
end Cryogenian glaciation ('Marinoan')
Cranford Ls (& equivs.)
Shuram-Wonoka anomaly
Girlsta Ls
Laxfirth Ls

Figure 3