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The stable isotope (C, O, S) record of Paleoproterozoic marbles, Scotland

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Abstract: Paleoproterozoic marbles occur widely in NW Scotland. The isotopically heavy carbonate carbon ($\delta^{13}C$ >3‰) in marbles that characterizes the worldwide Lomagundi–Jatuli Event (2.3–2.05 Ga) is recognized in the Laurentian Foreland, the Moine Nappe and the Sgurr Beag Nappe, over a 150 km transect across the Caledonian thrust belt. A light oxygen isotope composition distinguishes marbles that have been sheared and retrogressed by ingress of meteoric water, possibly during both Laxfordian and Caledonian orogenesis. The shearing of marbles also contributed to graphite formation (mean $\delta^{13}C$ −7.2‰). Pyrite in the marbles contains isotopically heavy sulfur, typical of Paleoproterozoic diagenetic sulfides precipitated from low-sulfate seawater. These data show that the *c.* 2 Ga marbles in Scotland are a high-quality archive of information on their depositional and post-depositional history. The data emphasize a continuum of a Paleoproterozoic marble–graphite–sulfide-bearing assemblage from eastern Canada and Greenland through Scotland to Scandinavia.

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The record of Paleoproterozoic sedimentation includes an anomalous globally extensive development of shallow-water carbonate platform deposits (Condie *et al.* 2000), which now occur as marbles. The marbles, and associated sediments, are a repository for information about the Earth's surface at *c.* 2 Ga, including ocean salinity (Parnell *et al.* 2022), atmospheric composition (Prave *et al.* 2021), the sedimentary carbon budget (Kerr *et al.* 2016; Canfield 2021), palaeobiology (Kamennaya *et al.* 2018), metallogeny (Partin *et al.* 2021) and contribution to plate-tectonic processes (Parnell and Brolly 2021). Studies of the marbles are therefore important to an understanding of planetary development during the Paleoproterozoic. Paleoproterozoic marbles crop out widely in the North Atlantic region, including in NW Scotland (Figs 1 and 2). The Scottish rocks are a mixed package of metasediments and metavolcanic rocks, which form outliers younger than the predominant Archean tonalitic gneisses (Park 2002; Mason *et al.* 2004*a*, *b*). The Paleoproterozoic marbles in NW Scotland have a mineralogical and geochemical signature of deposition from evaporative seawater (Parnell *et al.* 2022). Globally, the carbon isotope record of Paleoproterozoic marbles is central to documenting a worldwide episode of anomalously heavy carbon deposition, known as the Lomagundi–Jatuli Event, and concomitant inferences about oxygenation of the atmosphere (Martin *et al.* 2013; Eguchi *et al.* 2020; Prave *et al.* 2021). The contribution to the isotopic record from Scotland hitherto is based on data from marbles at Gairloch (Baker and Fallick 1989; Kerr *et al.* 2016). However, many other localities in Scotland (Fig. 2) include Paleoproterozoic (*c.* 2 Ga) marbles that hitherto have not been measured. We show here that isotopic studies of the marbles have the potential to improve our understanding of stratigraphic age, sedimentary environment and structural history of some of the oldest rocks in Britain.

Some marble horizons, but not all, were also a focus of deformation, including isoclinal folding and mylonite formation (Park 2002). Six marble occurrences stand out as associated with shearing. Three are within the Laurentian foreland to the (west of the) Caledonian thrust belt, and they are assumed to record deformation in the late Paleoproterozoic Laxfordian Orogeny. The other three are within the thrust belt, and their proximity to thrust planes juxtaposing supracrustal rocks and the Neoproterozoic Wester Ross and Loch Ness supergroups (Krabbendam *et al.* 2021) implies that they could record Caledonian deformation. The occurrence of marble indicates potential for deformation, but does not discriminate between minor movement and much more intense shearing that could support thrusting. We sought to test a possible means of making this distinction by analysis of the oxygen isotope composition of the marble. In several other datasets from marbles (Baker *et al.* 1989; Buick *et al.* 1997; Pili *et al.* 1997; Famin *et al.* 2004), retrogression along sheared surfaces caused a shift to a lighter isotope composition. One locality at Gott, Tiree, contains abundant graphite in the sheared marble.

This study reports the carbon and oxygen isotopic compositions of Paleoproterozoic marbles from 21 localities in NW Scotland (Figs 2 and 3), carbon isotopic compositions of associated marble and graphite at Gott (Fig. 4) and sulfur isotopic compositions of pyrite in seven marbles.

The objectives of the study are as follows:

(1) determination of the record of the Lomagundi–Jatuli Event in the carbon isotope composition;

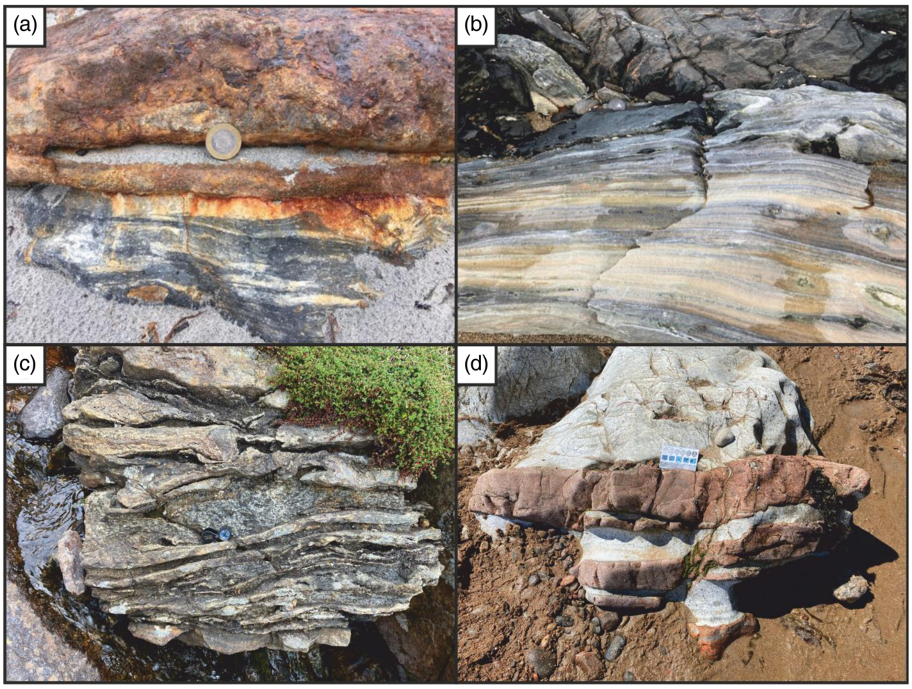

Fig. 1. Outcrops of Paleoproterozoic marbles, NW Scotland. (**a**) Marble layered with dark graphitic matter, below ironstone, Gott, Tiree. (**b**) Marble layered with silicate porphyroblasts and quartzite laminae, Bay Steinigie, South Harris (field width 1 m). (**c**) Lens of marble (with lens for scale) within bedded quartzites, Armadale. (**d**) Marble intruded by pegmatites (brown, horizontal), Rosemarkie.

(2) interpretation of variations in the oxygen isotope composition; in particular, marbles were analysed to test if they might indicate selected involvement in orogenic deformation;
(3) measurement of the carbon isotope composition in coupled marble and graphite at Gott to test for any relationship between them;
(4) measurement of the sulfur isotope composition of pyrite in marbles;
(5) incorporation of the isotopic record from Scotland into a broader record in the Paleoproterozoic of the North Atlantic region from Canada to Scandinavia.

Methods

Geological setting and sampling

Paleoproterozoic marbles were sampled from 21 localities in NW Scotland (Figs 2 and 4). Details of the localities are given in Table 1. Marbles occur in the Laurentian foreland, and in nappes in the Caledonian thrust pile. Most samples in the Moine Thrust Zone are located in the Moine Nappe and Sgurr Beag Nappe (Table 1). The basement east of the Moine Thrust Zone was formerly regarded as Lewisian Complex of the Northern Highlands Terrane (Friend *et al.* 2008). Recently, the eastern basement has been attributed to a terrane in Baltica that was juxtaposed against Lewisian rocks of Laurentia along the Grenvillian suture, now marked by the Moine Thrust Zone (Strachan *et al.* 2020). Notwithstanding this model in which basement rocks from two terranes are now juxtaposed, they both include supracrustal outliers with marbles. The marbles are consistently calcite, with porphyroblasts predominantly of phlogopite and fosterite (Table 1). Three of the largest marble-bearing outcrops, including 11 of the localities, in South Harris, Gairloch and Glenelg, have each been interpreted to represent accretionary complexes (Park *et al.* 2001; Baba 2002; Storey 2008*b*). It is likely that marbles in the smaller outcrops were deposited in a similar context, in carbonate platforms prior to accretion. The larger outcrops are each dated at 2.0–1.9 Ga. The Loch Maree Group at Gairloch is dated at 1.9–2.0 Ga, based on Nd crustal ages (O'Nions *et al.* 1983), minimum ages of detrital zircons (Kerr *et al.* 2016) and a 1.90 Ga intrusive gneiss (Park *et al.* 2001). The metasediments in South Harris are dated at 1.8–1.9 Ga, by detrital zircons (Whitehouse and Bridgwater 2001) and associated *c.* 1.9 Ga arc rocks (Mason *et al.* 2004*a*). Eclogites at Glenelg–Loch Duich, whose protoliths were possibly synchronous with metasediments, yield Hf_{TDM} ages around 2.0 Ga (Brewer *et al.* 2003; Storey 2008*a*). Individual marble beds are typically of 0.5–3 m thickness, modified by local shearing and thrusting. The marbles are isoclinally folded, tectonically interleaved with other lithologies, and marble-bearing horizons include mixed cataclasite–mylonite (Park *et al.* 2001). Associated lithologies include quartzose sandstones (psammites), graphitic schists and ironstones (Table 1). The mineral assemblage, recorded particularly in studies on Tiree samples, indicates metamorphism at granulite facies, followed by retrogression to amphibolite and greenschist facies associated with shearing (Westbrook 1972; Beach 1980; Cartwright 1992).

Six marbles in shear zones were identified:

(1) Armadale, at the thrust margin of the Strathy Complex, where the marble is a suggested control on deformation (Moorhouse and Moorhouse 1983);
(2) Gleann Meinich, mapped along a thrust contact between the Neoproterozoic Loch Ness Supergroup and the Archean–Paleoproterozoic basement, within the Scardroy Inlier, a ductile thrust slice along the Sgurr Beag Thrust (Holdsworth 1989);
(3) Glen Shiel, along the thrust eastern margin of the Glenelg–Loch Duich Inlier, identified as the Sgurr Beag Thrust (Harris and Strachan 2010);
(4) Bay Steinigie, a sedimentary package along the sheared contact between the Leverburgh and

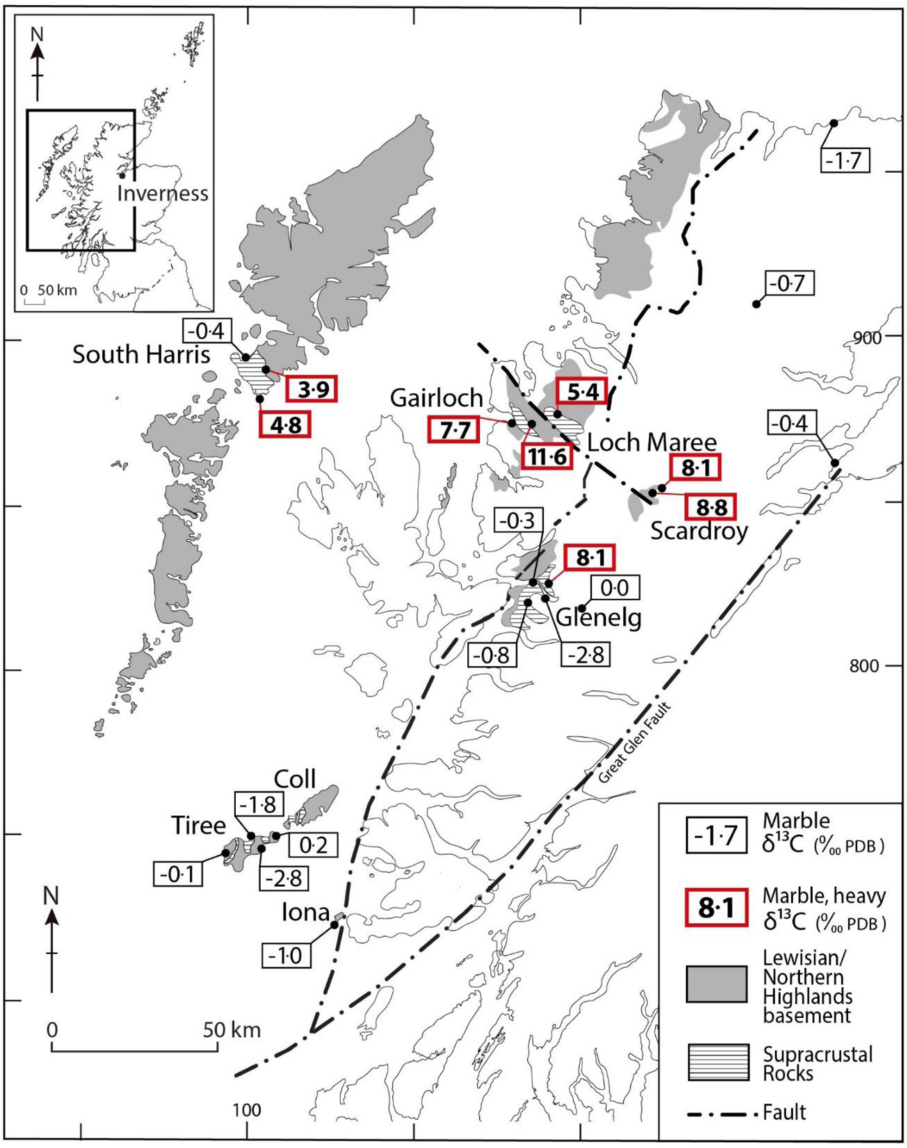

Fig. 2. Map of NW Scotland, showing localities for Paleoproterozoic supracrustal marble, with mean carbon isotope compositions.

Langavat belts of the South Harris Complex (Mason *et al.* 2004*b*);

(5) Gott, Tiree, a sedimentary package with an intense shear fabric (Cartwright 1992);

(6) Meal Aundury, along a ductile shear zone in the Loch Maree Group at Gairloch (British Geological Survey 1999).

The shear zone at Gott additionally contains graphite in the marble. The locality also includes graphitic schists for comparison (Westbrook 1972; Parnell *et al.* 2021*a*).

Analysis

Samples of marble were drilled using a Sherline microdrill and collected in plastic vials. Analyses were performed at the Scottish Universities Environmental Research Centre, East Kilbride (SUERC) on an automated continuous flow VG Prism Series II Isotope Ratio Mass Spectrometer using international standard IAEA-CO-8 (calcite) and internal standard MAB2C. Carbon isotope ratios were calibrated to Vienna Pee Dee Belemnite (VPDB). Oxygen isotopes were calibrated to Vienna Standard Mean Ocean Water (VSMOW). Reported analyses are each the mean of four values.

Stable carbon isotope analysis was conducted on graphitic samples digested in 10% HCl to remove trace carbonate. Samples were analysed by standard closed-tube combustion method by reaction *in vacuo* with 2 g of wire form CuO at 800°C overnight. Marble samples were crushed to a powder, then 1 mg of each powdered sample was dissolved in phosphoric acid at 70°C before measurement of isotope ratios was carried out at SUERC. Data are reported in per mil (‰) using the δ notation v. Vienna Pee Dee Belemnite (V-PDB). Repeat analysis gave $\delta^{13}C$ reproducibility around ±0.2‰ (1σ).

Pyrite was sampled from millimetre-scale crystal masses in the marbles. For sulfur isotope analysis, pyrite samples were combusted with excess Cu_2O at 1075°C to liberate the SO_2 gas under vacuum conditions. Liberated SO_2 gases were analysed on a VG Isotech SIRA II mass spectrometer, with standard corrections applied to raw $\#^{66}SO_2$ values to produce true $\#^{34}S$. The standards employed were the international standard NBS-123, IAEA-S-3 and SUERC standard CP-1. Reproducibility of standards is ±0.2‰ and ±0.3‰ for carbon and oxygen respectively at 1σ.

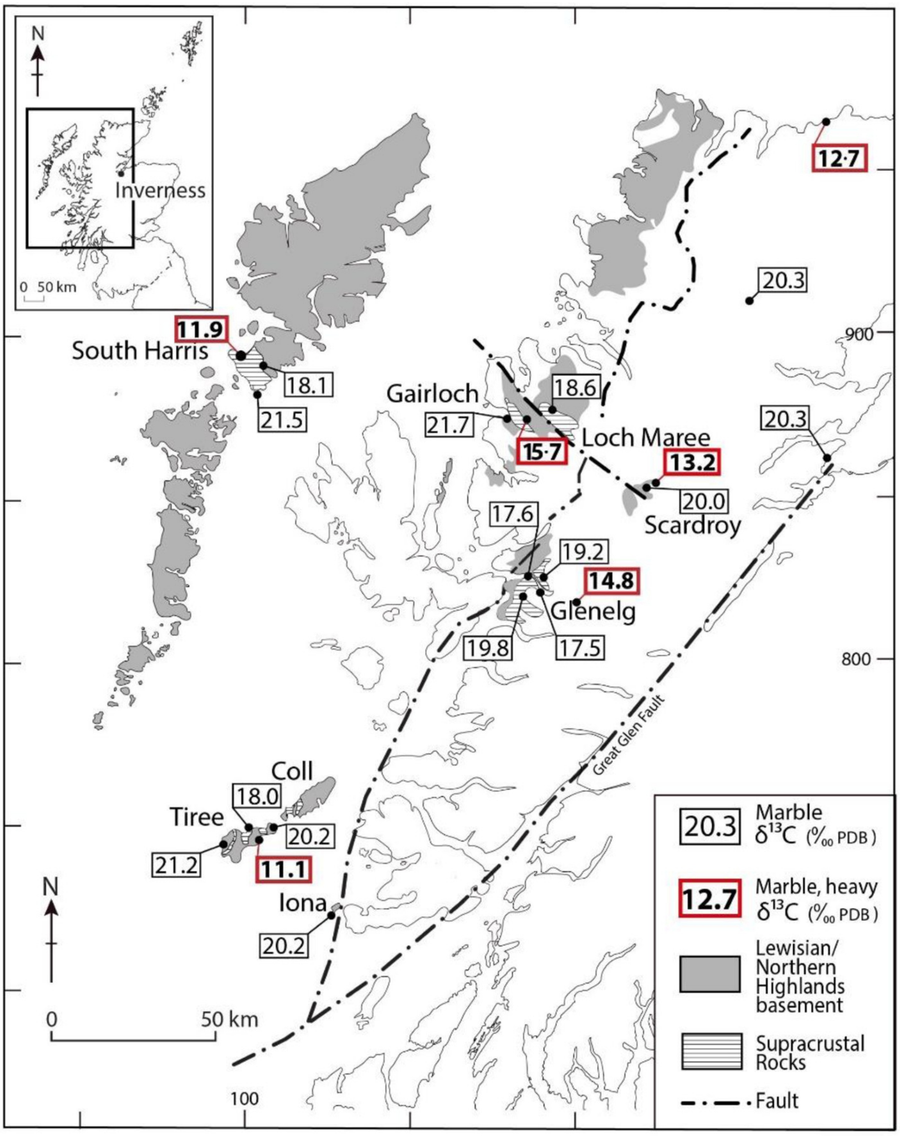

Fig. 3. Map of NW Scotland, showing localities for Paleoproterozoic supracrustal marble, with mean oxygen isotope compositions.

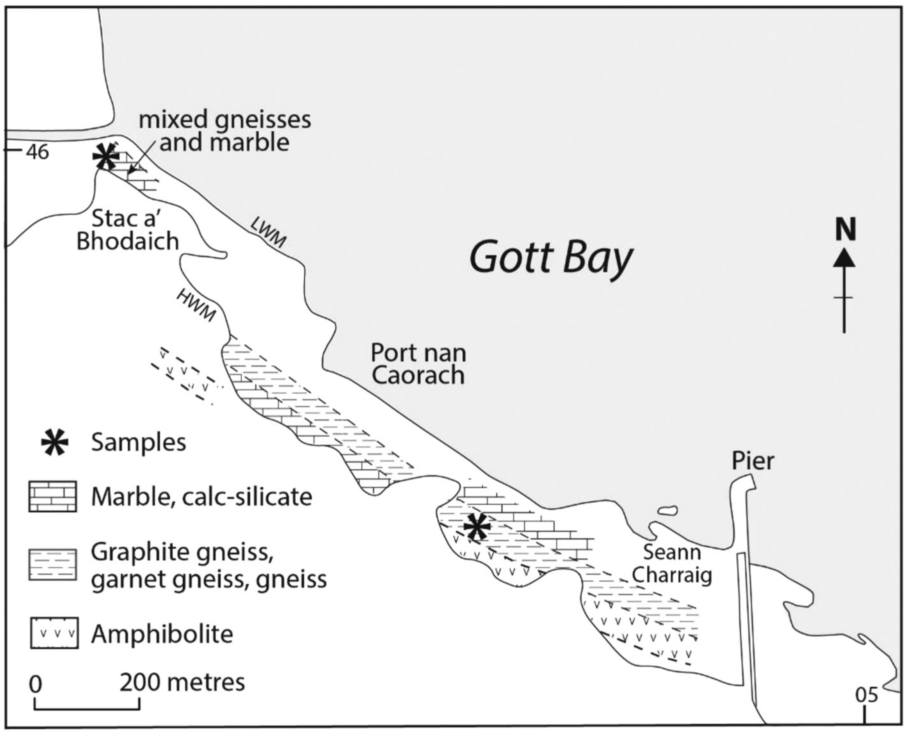

Fig. 4. Map of Gott Bay, Island of Tiree, showing location of graphite-bearing marble and graphitic gneiss. LWM, low water mark; HWM, high water mark.

Table 1. *Mean values for δ18O, δ13C and δ34S isotope data (‰) in Paleoproterozoic marbles, NW Scotland*

Locality	Grid reference	Structural level	Description, associated facies	Reference	$\delta^{18}O$ (SMOW)	$\delta^{13}C$ (PDB)	$\delta^{34}S$ (CDT)
Sheared							
Armadale	NC 774655	Naver Nappe	Layered with quartzite lenses; sulfidic (pyrite); minor ironstone	Strachan *et al.* (2010)	12.7	−1.7	6.3, 9.9
Gleann Meinich	NH 235545	Sgurr Beag Nappe	Massive, phlogopite-rich	Sutton and Watson (1951)	13.2	**8.1**	
Glen Shiel	NH 007136	Sgurr Beag Nappe	Massive, phlogopite–diopside-rich	Harris and Strachan (2010)	14.8	0.0	
Bay Steinigie	NG 019939	Foreland	Layered, much detrital matter; minor graphite	Fettes *et al.* (1992)	11.9	−0.4	
Gott, Tiree	NM 045456	Foreland	Layered, graphitic laminae; sulfidic (pyrite); graphitic schist, ironstone	Cartwright (1992)	11.1	−2.8	11.7, 11,7, 11.7, 11.9, 12.3
Meall Aundrary	NG 855722	Foreland	Pure calcite, recrystallized?	Park (2002)	15.7	**11.6**	
Non-sheared							
Loch Shin	NC 521139	Moine Nappe	Layered, amphibole-rich; sulfidic (pyrrhotite)	Parnell *et al.* (2021*b*)	20.3	−0.7	8.0
Rosemarkie	NH 745594	Sgurr Beag Nappe	Massive, phlogopite-rich; pegmatite veins	Garson *et al.* (1984)	20.3*	−0.4	
Scardroy	NH 223523	Sgurr Beag Nappe	Massive, phlogopite-rich; sulfidic (pyrite); minor graphite, ironstone	Sutton and Watson (1951)	20.0	0.4, **8.8**†	−0.2, −0.3, −0.4, −1.2, −1.3
Glenelg	NG 840201	Moine Nappe	Massive, forsterite-rich	May *et al.* (1993)	19.8	−0.8	
Ratagain	NG 905210	Moine Nappe	Massive, phlogopite-rich	May *et al.* (1993)	17.5	−2.8	
Totaig	NG 875253	Moine Nappe	Massive, phlogopite-rich; sulfidic (pyrite); graphitic schist	May *et al.* (1993)	17.6	−0.3	7.7
Carr	NG 901245	Moine Nappe	Massive, phlogopite–forsterite-rich	May *et al.* (1993)	19.2	**8.1**	
Rodel	NG 048832	Foreland	Massive, phlogopite-rich; sulfidic (pyrrhotite); graphitic schist	Fettes *et al.* (1992)	21.5	**4.8**	11.3, 11.4, 11.6
Loch Langavat	NG 052890	Foreland	Massive, phlogopite-rich; sulfidic (pyrite)	Fettes *et al.* (1992)	18.1	**3.9**	10.2
Kilkenneth, Tiree	NL 933454	Foreland	Massive, phlogopite-rich	Cartwright (1992)	21.2	−0.1	
Balphetrish, Tiree	NM 010475	Foreland	Massive, talc-rich, pink	Cartwright (1992)	18.0	−1.8	
Caolas, Tiree	NM 094490	Foreland	Massive, phlogopite-rich	Cartwright (1992)	20.2	0.2	
Iona	NM 265216	Foreland	Massive, forsterite-rich; graphitic schist, ironstone	Bailey *et al.* (1925)	20.2	−1.0	
Shieldaig	NG 812725	Foreland	Layered, phlogopite-rich	Park (2002)	21.7	**7.7**	
Letterewe	NG 952720	Foreland	Massive, phlogopite-rich; ironstone	Robertson *et al.* (1949)	18.6	**5.4**	

Bold type indicates anomalously heavy carbon.*Excludes one aberrant result.
†Two populations.

Scanning electron microscopy (SEM) was conducted in the Aberdeen Centre for Electron Microscopy, Analysis and Characterisation (ACEMAC) facility at the University of Aberdeen using a Carl Zeiss Gemini SEM 300 VP Field Emission instrument equipped with an Oxford Instruments NanoAnalysis Xmax80 Energy-Dispersive Spectroscopy (EDS) detector, and AZtec software suite.

Structural ordering of graphite was measured using a Renishaw inVia reflex Raman spectrometer, with a back-scattering geometry in the range of 700–3200 cm^{-1}, a 2400 l mm^{-1} spectrometer grating and charge-coupled device (CCD) detector. Microscopic observations were carried out with a ×100 optical power objective. A 514.5 nm diode laser was used for excitation with an output of 50 mW. The laser power was reduced by using a 10% filter. The Raman system was calibrated against the 520.7 cm^{-1} band of silica. Raman band deconvolution was calculated using LabSpec6 software by Horiba, and maximum temperatures were calculated from the R2 ratio (Schito *et al.* 2017).

Results

The mean $\delta^{13}C$ and $\delta^{18}O$ values for marbles do not show a mutual dependence (Fig. 5), and they are treated as two distinct datasets.

The C $\delta^{13}C$ values fall into two groups, in the ranges −3 to 0‰ and +3 to +12‰. Anomalously heavy isotope compositions are recorded in marbles from Rodel, Loch Langavat, Carr, Letterewe, Meall Aundrary, Shieldaig, Scardoy and Gleann Meinich (Figs 3 and 6). These localities are in the Laurentian Foreland, and the Moine and Sgurr Beag nappes (Fig. 7). In the supracrustal outcrops in South Harris and Glenelg, there are both localities with and without anomalous compositions.

The $\delta^{18}O$ values also fall into two groups, of six and 15 localities (Fig. 8) in the ranges 11–16‰ and 17–22‰ respectively.

The graphite in marble at Gott is finely interlaminated with chlorite, and they are both deformed by the shearing motion (Fig. 9). In some beds the streaks are linked to form a laminar

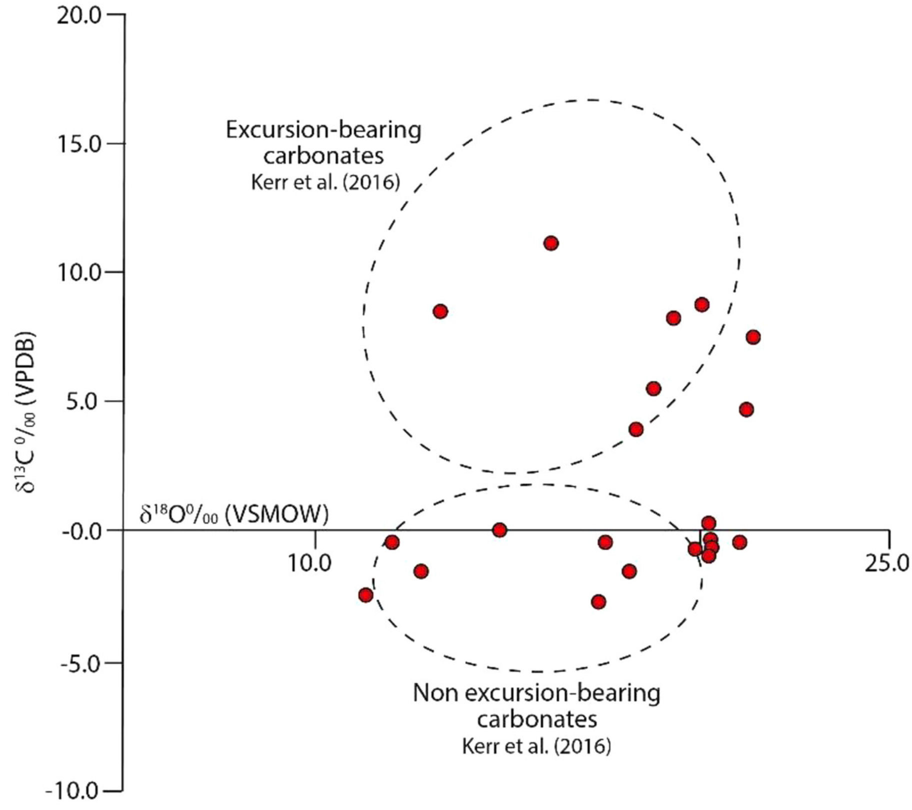

Fig. 5. Cross-plot of oxygen and carbon isotope compositions for new marble samples (red), plotted relative to data fields measured previously in the Gairloch district, interpreted as unrelated to, or related to, the isotopic excursion of the Lomagundi–Jatuli Event. Source: Gairloch district data fields from Kerr *et al.* (2016).

fabric that accentuates a mylonitic texture, similar to that in younger deformed marbles (Carlson *et al.* 1990). The Raman spectra from the graphite in marble and in the associated schists are distinct, despite their close proximity. Graphite in the schist is fully ordered and shows a well-defined order (G) peak, but graphite in the marble additionally shows a pronounced disorder (D) peak (Fig. 10). The marble graphite also shows a broad S band peak in the second-order region (Fig. 10), which is split into two bands upon complete graphitization. Peak intensity ratios (I_D/I_G) for marble graphite range from 0.34 to 0.46 ($n = 6$), and for schist graphite are zero owing to complete order. The carbon isotope composition of the schist graphite (−17.4 to −24.0‰, mean −20.0 ± 2.01‰, $n = 6$) is also distinct from the composition of the marble graphite (−6.4 to −9.0‰, mean −7.2 ± 0.86‰, $n = 6$). The composition of the carbonate in the graphite-bearing marble is typical of marine limestones (−2.4 to −3.3‰, mean −2.87 ± 0.29‰, $n = 6$), as recorded in the majority of the marbles.

Measurements of $\delta^{34}S$ determined in pyrite–pyrrhotite in the marbles (Table 2) are consistently positive over six localities spanning the whole region, in the range 6.3–12.3‰, and near-zero at Scardroy (Fig. 11).

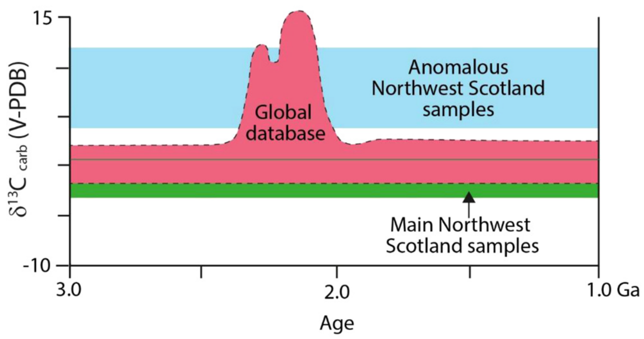

Fig. 6. Global compilation of carbon isotopic compositions for marbles through the early Proterozoic, showing anomalously heavy isotope compositions during the *c.* 2.2–2.1 Ga Lomagundi–Jatuli Event. Data range for isotopically heavy samples from NW Scotland indicates that they are products of this event. Scottish samples plotted to show composition, not age, for clarity, and some are independently dated at 2.0–1.9 Ga. Source: after Prave *et al.* (2021).

Discussion

Carbon isotope composition of marbles

The carbon isotope data fall into two groups, which plot with ranges measured previously in the Gairloch district (Fig. 5), interpreted as either unrelated to, or related to, the Lomagundi–Jatuli Event (Kerr *et al.* 2016). The significance of the Lomagundi–Jatuli Event is open to interpretation, although this does not affect its value as a time marker. It has been regarded as a perturbation of the global carbon cycle linked to oxygenation of the atmosphere (Martin *et al.* 2013; Eguchi *et al.* 2020; Mänd *et al.* 2020), but recently has been reasoned instead to be a facies-dependent consequence of shallow-water deposition (Prave *et al.* 2021). The isotope compositions from Scotland do not bear on the interpretation, but they add to the global database that records isotopically heavy carbonate carbon in marbles in the mid-Paleoproterozoic (Fig. 6). The event is dated at 2.3–2.05 Ga (Martin *et al.* 2013), which implies that the marbles with anomalous compositions in Scotland were deposited as limestones at this time. The dates measured at 2.0–1.9 Ga in the main outcrops are partly dates of early metamorphism of the sediments and are not inconsistent with

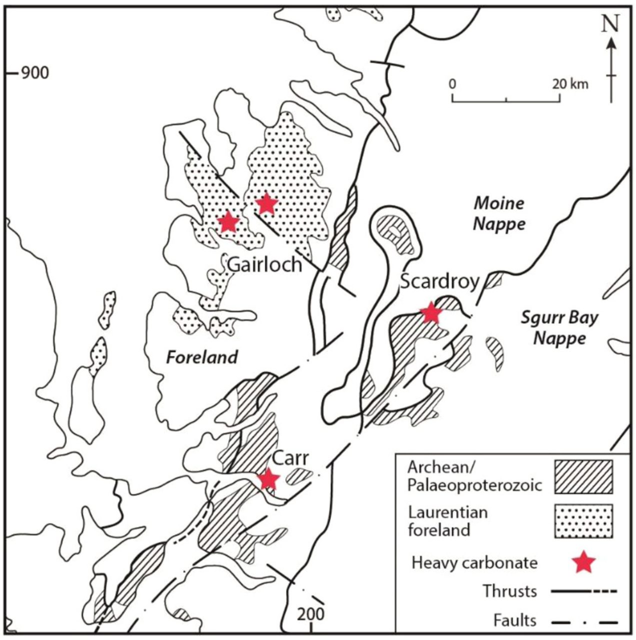

Fig. 7. Simplified structural map of NW Scotland mainland, showing occurrence of Lomagundi–Jatuli signature in Laurentian foreland (Gairloch district), and Moine Nappe (Carr) and Sgurr Beag Nappe (Scardroy district).

deposition at 2.3–2.05 Ga. Evidence from Gairloch shows that the succession records a transition from marble bearing the anomaly to marble without anomaly, and that it could therefore include dates from both the Lomagundi–Jatuli Event and slightly younger sedimentation (Kerr *et al.* 2016). The new data from South Harris and Glenelg show similar transitions, although the sediment 'way up' cannot be proven. There is no evidence that the carbon isotope compositions were modified in the samples from shear zones, and they can be considered as reliable records of the marine composition during deposition.

The localities that record the Lomagundi–Jatuli Event are in the Laurentian Foreland, and the Moine and Sgurr Beag nappes (Fig. 7); that is, they occur on both sides of the Moine Thrust Zone. Correlation of a stratigraphic horizon (i.e. the marble containing the Lomagundi–Jatuli signature) between different structural levels supports the model of structural repetition by Caledonian thrusting, but the relationship between the localities is complicated by uncertainty about how and when the terranes on either side of the thrust zone were juxtaposed, and we do not interpret this further.

Oxygen isotope composition: Laxfordian and Caledonian deformation

The carbon and oxygen compositions do not show any mutual relationship (Fig. 5); that is, the oxygen compositions are not controlled by primary variations in the carbon composition. Rather, the data fall into two groups. The composition of the larger group matches the range 17–22‰ that is characteristic of marine carbonate rocks at about 2 Ga (Shields and Veizer 2002). The smaller group, with a lighter isotopic composition, consists of the six localities where marked shearing is observed (Fig. 8). This match strongly suggests that the context allowed modification of the original isotopic signature. The tightly clustered nature of the data for individual marbles shows that there was wholescale alteration of the primary composition, rather than millimetre-scale fluctuations. Retrogressive mineralogy was identified at several of the sheared localities, including Armadale (Burns *et al.* 2004), at Gott, Tiree (Cartwright 1992), and in the shear zones at Gairloch (Shihe and Park 1992) and South Harris (Mason *et al.* 2004*b*). The ingress of meteoric water during or after shearing would explain a shift to a lighter composition by isotopic exchange between the water and the minerals. There is no evidence of hydrothermal alteration such as mineralization along fractures, which might have indicated an alternative source of water. Data are available for other case studies showing the effects on isotopic composition of retrogressive metamorphism by water-rich fluids along shear zones through marbles. Marbles from Naxos, Greece (Baker *et al.* 1989), Tinos, Greece (Famin *et al.* 2004), the Reynolds Range, Australia (Buick

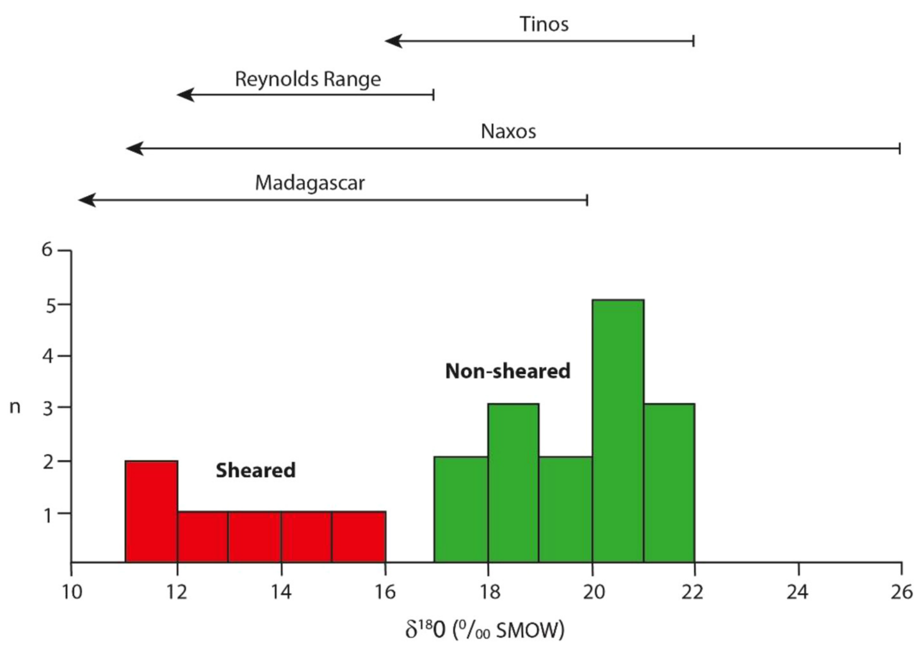

Fig. 8. Oxygen isotope compositions of Paleoproterozoic supracrustal marbles, NW Scotland, distinguishing sheared and non-sheared localities. For comparison, published data trends are shown for marbles in shear zones, becoming lighter with retrogression. Sources: Baker *et al.* (1989), Buick *et al.* (1997), Pili *et al.* (1997) and Famin *et al.* (2004).

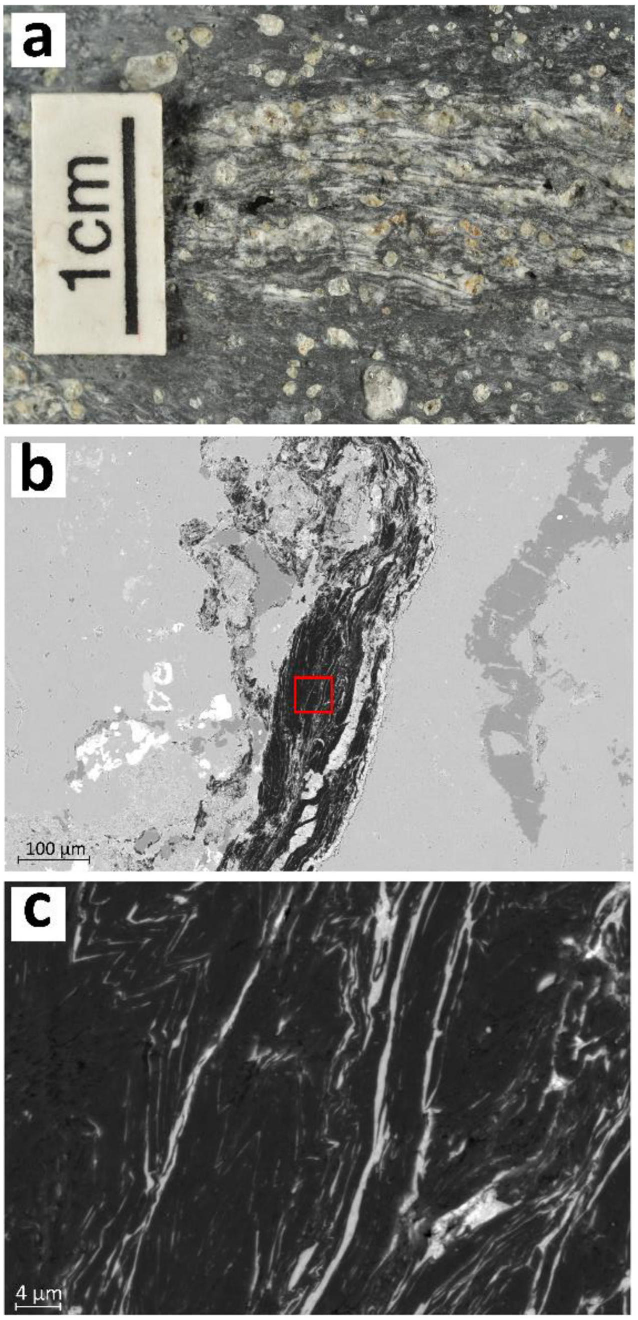

Fig. 9. Petrography of graphitic marble, Gott, Tiree. (**a**) Mylonitic fabric, defined by graphitic streaks (dark) and porphyroblasts. (**b**) Backscattered electron micrograph, showing graphitic streak (black) and pyrite (white) in calcite matrix. Red box marks position of (**c**). (**c**) Close-up of graphite in (**b**), showing interlaminated chlorite.

et al. 1997) and Madagascar (Pili *et al.* 1997) all show increasingly light isotope data with retrogression as they interacted with isotopically lighter water-rich fluids (Fig. 8). The starting composition was wide-ranging among these examples, but all reached a lightest composition comparable with those of the sheared Paleoproterozoic marbles.

Retrogression in NW Scotland is attributed to several orogenic episodes, including the Laxfordian (Shihe and Park 1992), Grenvillian (Storey *et al.* 2005), Knoydartian and Caledonian (Friend *et al.* 2008) orogenies. The Moine Thrust Zone in the region is a classic representation of imbricate thrust stacking, during the Caledonian Orogeny (Watkins *et al.* 2014; Searle *et al.* 2019). Detachment of the thrust slices occurred especially on the Cambrian An-t-Sron Formation (Butler 2004), which is carbonaceous, carbonate-rich and evaporite-bearing. However, the Moine Thrust Zone is superimposed upon rocks recording older orogenic events, including the Laxfordian Orogeny, and Mesoproterozoic faulting (Hardman *et al.* 2023), which deformed the Archean–Paleoproterozoic Lewisian Complex. The marbles that show shearing and retrogression possibly record both Laxfordian and Caledonian deformation.

The Paleoproterozoic age of the sheared marbles places them at the advent of 'modern' plate tectonics at about 2 Ga (Brown and Johnson 2019; Wan *et al.* 2020) and widespread detachment on carbonaceous shales and carbonate-rich rocks (Parnell and Brolly 2021). The detachment surfaces that slipped during Paleoproterozoic orogenies were reactivated during younger orogenies superimposed at the same locations (Parnell and Brolly 2021). Conceivably, marbles sheared during the Laxfordian could have been reactivated during the Caledonian thrusting.

Carbon isotope composition in graphite

The heavy isotope composition of the marble-hosted graphite in Tiree implies that its origin was distinct from the graphite in the adjacent schist, and also from graphite elsewhere in the Lewisian Complex (Parnell *et al.* 2021*a*). The graphite is therefore attributed to decarbonation of the marble during deformation, rather than from organic matter as in the graphitic schist, as recorded in other studies (Luque *et al.* 2012) The greater disorder also suggests that the marble-hosted graphite formed at a younger time, before fully graphitizing conditions occurred. Regardless of its mode of formation, it does not appear to have experienced the granulite-facies metamorphism that fully graphitized the schist. The temperature equivalents for marble graphite and schist graphite calculated from the R2 parameter (Beyssac *et al.* 2002) are 449–477°C and >600°C respectively. The timing post-peak metamorphism is corroborated by detailed petrographic examination. The graphite on the slip planes is intricately accompanied by chlorite, both intensely deformed into tight folds (Fig. 9c). The chlorite was a product of retrogression, so the deformation must have been no older than this event. There is widespread evidence for retrogression to greenschist facies in the Lewisian Complex, especially associated with shear structures (Beach 1980; Cartwright 1992), formed by Laxfordian deformation during the latest Paleoproterozoic and early Mesoproterozoic.

Graphite formation was associated with deforming marble during post-collision relaxation (orogenic collapse) (Jamtveit *et al.* 2019). The relaxation phase was an opportunity for the ingress of fluid, including meteoric water, which caused hydration to a retrograde mineralogy (Jamtveit *et al.* 2019). Reaction weakening enhanced shear deformation, and thus slip is associated with orogenic collapse. Fluid ingress and shearing are mutually enhancing and would have been focused by slices of supracrustal sediment interleaved with the Archean gneisses.

Paleoproterozoic sulfides

Hitherto, sulfur isotope data from sulfides in the Paleoproterozoic supracrustal inliers have been from the

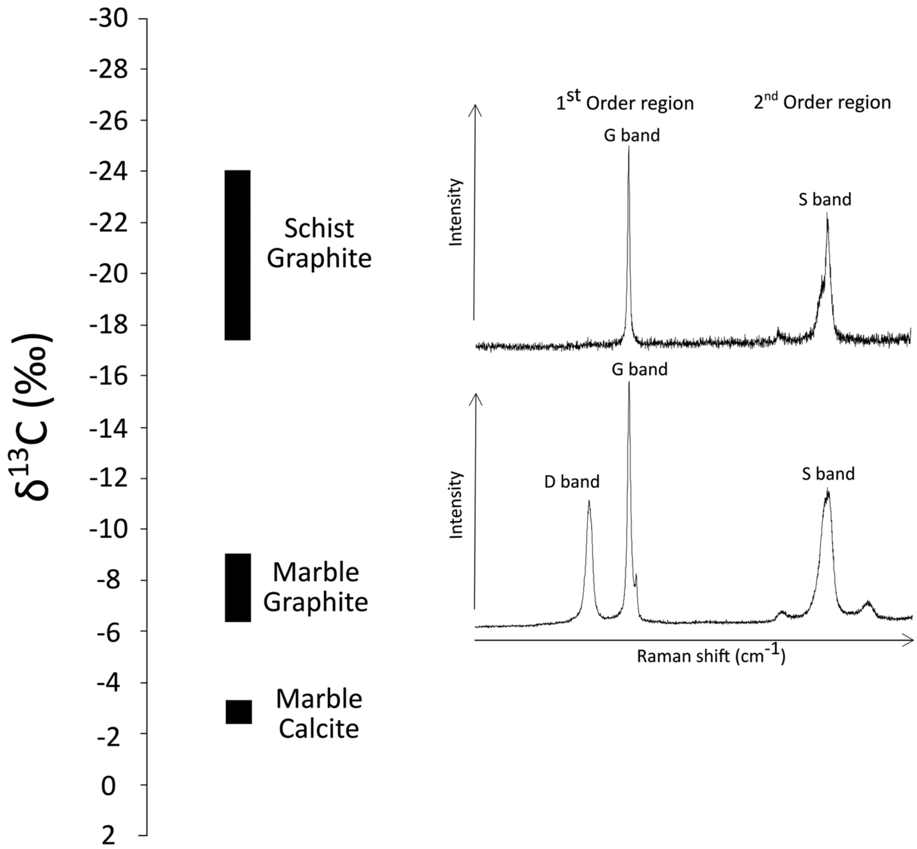

Fig. 10. Carbon isotope compositions (‰) and Raman spectra for schist graphite, marble graphite and marble carbonate, Tiree. Marble graphite is isotopically heavier than schist graphite, and more similar to marble carbonate. Marble graphite is more disordered than schist graphite, shown by the D (disorder) peak, and preservation of minor S band peaks.

volcanic massive sulfide ore prospect at Kerry Road, Gairloch (Jones *et al.* 1987; Drummond *et al.* 2020). The Kerry Road data are tightly grouped around 0‰, and they were assumed to represent fluids of magmatic–hydrothermal origin (Jones *et al.* 1987; Drummond *et al.* 2020). With the exception of the pyrite from Scardroy, which also has a near-zero composition, the pyrite–pyrrhotite measured here in marbles at six other localities (Table 2) is markedly heavier (13 samples measuring 6.3–12.3‰). The values are comparable with those of mid-Paleoproterozoic sulfides in sedimentary rocks elsewhere that are attributed to an origin in seawater (Fig. 11). The isotopically heavy sulfur isotopic composition, which contrasts with younger diagenetic pyrite with a light isotope composition, reflects derivation from Paleoproterozoic seawater with a relatively limited sulfate content (Scott *et al.* 2014). The similarity of the Scardroy and Kerry Road data suggests that Scardroy may host unrecognized hydrothermal mineralization.

Table 2. *Determinations of $\delta^{34}S$ for sulfides in Paleoproterozoic marbles, NW Scotland*

Locality	Grid reference	Mineral	$\delta^{34}S$ (‰ CDT)
Rodel, Harris	NG 048832	Pyrrhotite	11.3, 11.4, 11.6
Loch Langavat, Harris	NG 052890	Pyrite	10.2
Gott, Tiree	NM 045456	Pyrite	11.7, 11,7, 11.7, 11.9, 12.3
Totaig	NG 875253	Pyrite	7.7
Scardroy	NH 223523	Pyrite	−0.2, −0.3, −0.4, −1.2, −1.3
Loch Shin	NC 521139	Pyrrhotite	8.0
Armadale	NC 774655	Pyrite	6.3, 9.9

The North Atlantic context

Paleoproterozoic marbles occur also in terranes adjacent to Scotland, in eastern Canada, Greenland and Scandinavia. Isotope data for these marbles show similar trends to the Scottish data, including a signature of the Lomagundi–Jatuli Event in Labrador (Melezhik *et al.* 1997; Hodgskiss *et al.* 2020), the Superior region (Bekker *et al.* 2006) and north Sweden (Melezhik and Fallick 2010). The Canadian and Scandinavian localities also contain isotopically heavy carbon in graphite formed by the decarbonation of marble (Parnell *et al.* 2021*a*), and isotopically heavy sulfur in diagenetic pyrite (Motomura *et al.* 2018). Together with similar facies associations between marble and ironstones and graphitic beds (e.g. St-Onge *et al.* 2020; Rosa *et al.* 2023), the commonalities in data add weight to a picture of a continuum in Paleoproterozoic orogenic belts (Fig. 12) from Canada to Scotland to Scandinavia (Park *et al.* 2001; Tuisku *et al.* 2012; Bagas *et al.* 2020).

Conclusions

Twenty-one Paleoproterozoic marbles from distinct localities in NW Scotland yielded stable isotope data that have helped to improve our understanding of their stratigraphic age, sedimentary environment and structural history. Anomalies in the data contribute to an understanding of their history. In particular,

(1) isotopically heavy carbonate carbon at eight localities indicates deposition during the Lomagundi–Jatuli Event, dated elsewhere at 2.3–2.05 Ga;
(2) isotopically light oxygen at six localities reflects shearing, and isotopic exchange after ingress of

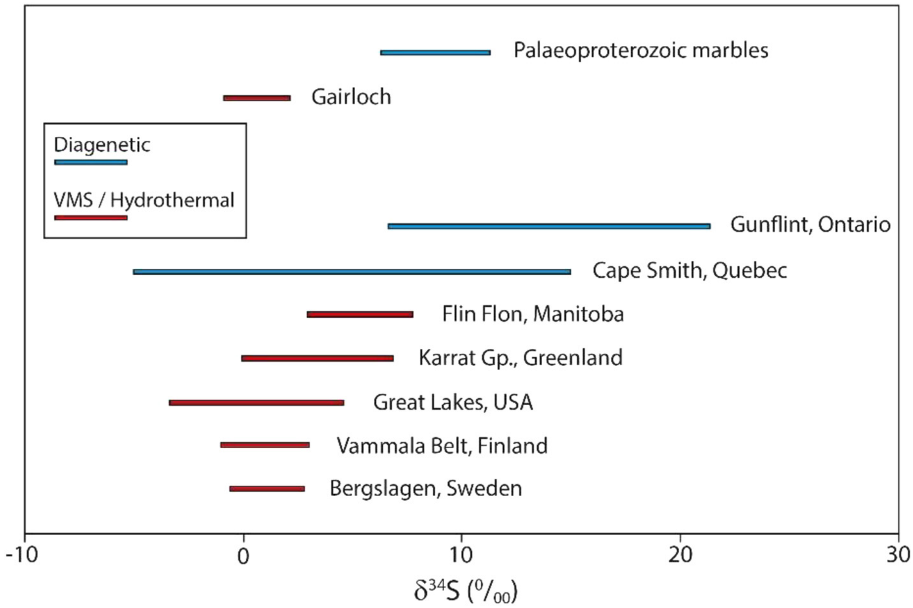

Fig. 11. Range of isotopically heavy (positive) sulfur isotope compositions of sulfides in six Paleoproterozoic supracrustal marbles. Near-zero data for Scardroy are omitted as an atypical outlier. Sulfur isotope compositions of sulfide deposits of mid-Paleoproterozoic (1.9–1.8 Ga) age from the wider North Atlantic region are shown for comparison. Gairloch (Kerry Road) deposit plots near zero like other volcanogenic massive sulfide (VMS) deposits. Marble-hosted data plot with other diagenetic pyrite representing seawater sources. Sources: data from Papunen and Mäkelä (1980), Wagner *et al.* (2005), Wacey *et al.* (2013), Moleski *et al.* (2018), Motomura *et al.* (2018, 2020), Drummond *et al.* (2020) and Partin *et al.* (2021).

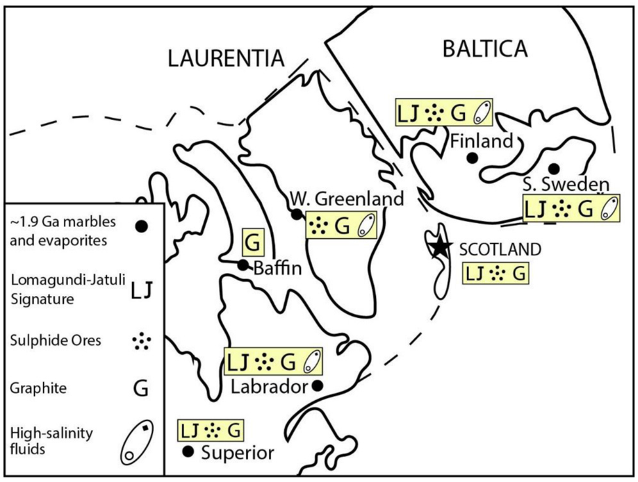

Fig. 12. Map of North Atlantic region, reconstructed for early Proterozoic time, showing occurrences of marbles with evaporites, graphite and sulfides and evidence for the Lomagundi–Jatuli signature. Source: after Park (2002); details of localities modified from Parnell *et al.* (2022).

meteoric water; shearing may have been variably Laxfordian and/or Caledonian;

(3) shearing of marble at Gott, Tiree, caused the formation of graphite by decarbonation, distinct from graphite that represents metamorphosed organic matter;
(4) isotopically heavy sulfur in pyrite–pyrrhotite in six of seven marbles, in contrast to isotopically light diagenetic pyrite in younger rocks, may indicate precipitation from relatively low-sulfate Paleoproterozoic seawater.

A comparison of the compositions with known trends in isotopic fractionation in Paleoproterozoic and other marbles suggests that the Scottish Paleoproterozoic marbles yield data that can be successfully interpreted in terms of age, environment and subsequent deformation.

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Data availability All data generated or analysed during this study are included in this published article.

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