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Seawater signatures in the supracrustal Lewisian Complex, Scotland

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Abstract

Marble in the supracrustal rocks of the Lewisian Complex, Tiree, includes chlorine-bearing amphiboles, chlorine-rich apatite, sulphur-rich scapolite, albite and phlogopite, all of which are regarded as evidence for evaporites in other metamorphosed sequences. Titanite yields U–Pb ages of ~1.6 Ga, i.e. late Laxfordian, which excludes a younger imprint of sodium metasomatism. Traces of anhydrite, and isotopically heavy pyrite, also indicate deposition from seawater. Elsewhere in the Hebrides, tourmaline in Lewisian Complex marbles may represent seafloor exhalative deposits. Combined, the evidence suggests Lewisian Complex supracrustal marbles formed in an evaporative environment, like other Palaeoproterozoic successions across the North Atlantic region.

1. Introduction

The Lewisian Complex of northern Britain has been very extensively studied for over 200 years (MacCulloch, 1819; Peach *et al.* 1907; Park & Tarney, 1987; Mendum *et al.* 2009). The complex consists particularly of tonalitic gneisses of Archaean age, derived from an igneous protolith. In common with Precambrian basement elsewhere in the North Atlantic region (Fig. 1), the Lewisian Complex also includes local supracrustal successions of metasediment (Fig. 2). The supracrustal successions contain a range of chemical sediments, including graphitic schists, ironstones and marbles, which where dated (Whitehouse & Bridgwater, 2001; Park, 2002) are mid-Palaeoproterozoic (~1.9–2.0 Ga). Across the region, from North America to Russia (Fig. 1; Table S1 in the Supplementary Material available online at https://doi.org/10.1017/S0016756822000474), these successions have evidence of former evaporites in the form of surviving sulphate minerals, metamorphic minerals with a signature of evaporitic seawater, and sulphur isotope data. To date, however, no such evidence is reported from Britain. Here we report evidence for signatures that would be consistent with evaporitic facies in the Lewisian Complex of Scotland. The uniformity of facies assemblage across the region, together with a setting related to an accretionary plate boundary (Park, 2002), implies that evaporitic facies were marine rather than lacustrine.

## 2. Geological setting and methods

Samples were collected from supracrustal rocks in the Lewisian Complex on the island of Tiree (Fig. 2). The supracrustal rocks on Tiree include garnet schists, graphitic schists, sandstones, ironstones and marbles (Westbrook, 1972; Whitehouse & Russell, 1997). The best exposed sections are at Vaul (National Grid Reference NM 048490), Balephetrish (NM 014473) and Gott (NM 044459). They are metamorphosed to amphibolite facies and sheared, but they preserve detrital mineralogy. Estimated *P–T* conditions are 10.5 ± 1.5 kbar and $810 \pm 50\,°C$ (Cartwright, 1992).

Mineral phenocrysts are especially abundant in the Tiree marbles (Fig. 3). The inclusions were investigated using scanning electron microscopy, conducted in the ACEMAC facility at the University of Aberdeen.

The mineralogy of the Lewisian Complex elsewhere in Scotland is affected by sodium metasomatism which also affected the Neoproterozoic Moine Supergroup (Sutton & Watson, 1951; May *et al.* 1993). An imprint by Neoproterozoic or younger fluids would exclude interpretations of a Lewisian protolith, and must be tested. Accordingly, the assemblage of mineral phenocrysts was dated using U–Pb analysis of titanite crystals. U–Pb isotope analyses were done using the laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS) laboratory at Lund University, where a Teledyne Photon Machines G2 laser is coupled to a Bruker Aurora Elite quadrupole ICP-MS. The laser is equipped with a HelEx two-volume sample cell with an energy meter. Instrument tuning, using NIST612, was aimed at obtaining high and stable signal counts on lead isotopes, on low oxide production (below 0.5 % monitoring $^{238}U/^{238}U^{16}O$ and $^{232}Th/^{232}Th^{16}O$)
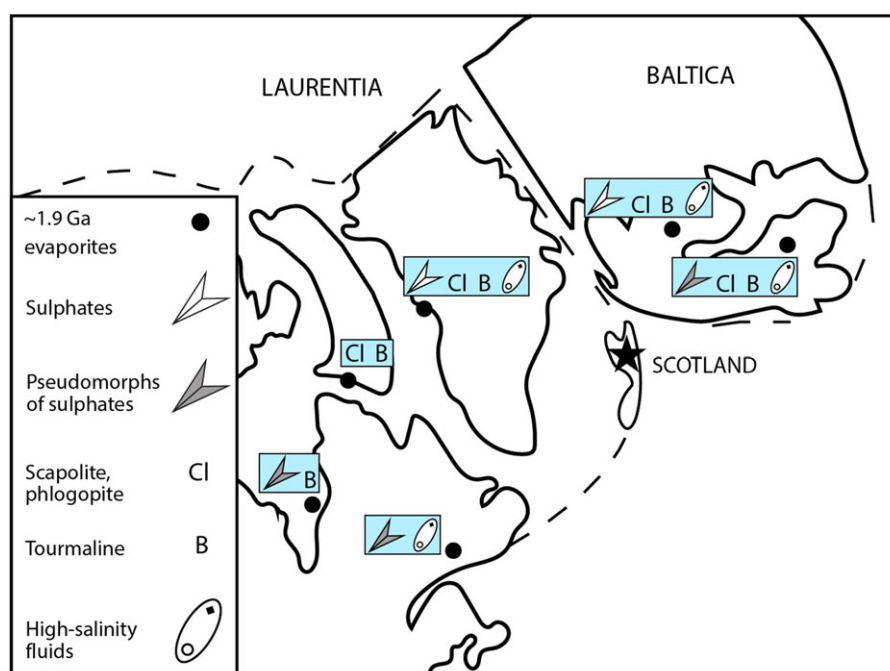
Fig. 1. (Colour online) Map of North Atlantic region, reconstructed for early Proterozoic time (after Park, 2002), showing inferred occurrences of evaporites and types of evidence. Details in Table S1, in the Supplementary Material available online at https://doi.org/10.1017/S0016756822000474.

and on Th/U ratios around 1. Standard-sample-standard bracketing incorporated the natural titanite MKED1 (Spandler *et al.* 2016) as primary reference material, and natural titanite ONT2 (Spencer *et al.* 2013) as a secondary standard. Each analysis was made with 300 shots at 10 Hz with a fluence of 1.5 J cm^{-2}. Baseline compositions were measured for 30 s before each measurement, and subtraction was done with a step-forward approach. Common Pb was monitored by measuring ^{202}Hg and mass 204 (^{204}Hg + ^{204}Pb). Baseline levels on mass 204 were *c.* 440 cps with a standard error (SE) around 20 cps (5–6 %). Data reduction was done with iolite using the X_U_Pb_Geochron4 DSR (Paton *et al.* 2010, 2011), and the common Pb correction was done using the VizualAge DRS (Petrus & Kamber, 2012). Plotting and final age calculations were done with Isoplot(R); intercept ages are based on 'model 1' calculations, and errors confidence levels are 95 % with overdispersion (Vermeesch, 2018).

For sulphur isotope analysis, pyrite samples were combusted with excess Cu$_2$O at 1075 °C in order 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 δ^{66}SO$_2$ values to produce true δ^{34}S. The standards employed were the international standard NBS-123, IAEA-S-3 and SUERC standard CP-1.

3. Criteria

Several criteria have been proposed for the identification of replaced evaporites in Precambrian successions (Warren, 2016). The criteria are based particularly on the chemistry of mineral phenocrysts that developed during metamorphism up to hundreds of millions of years after sedimentation (Moine *et al.* 1981; Warren, 2016; Hammerli & Rubenach, 2018). The evidence is most convincing where there are multiple positive criteria. The most direct evidence is:

(i) The survival of evaporite minerals anhydrite, gypsum or halite.
(ii) Pseudomorphs of evaporite minerals, most distinctively gypsum and halite (e.g. Ririe, 1989; Zentmyer *et al.* 2011).

Evidence for former evaporites also includes the growth of specific minerals containing chlorine or boron derived from seawater:

(iii) Phlogopite mica, which contains a high magnesium content and traces of chlorine (Schreyer *et al.* 1980; Moine *et al.* 1981).
(iv) Minerals indicative of sodium metasomatism, including albite and especially scapolite, which contains traces of sulphur and/or chlorine (Mora & Valley, 1989). High sulphur levels in particular reflect assimilation of sulphate evaporites (Morrissey & Tomkins 2020; Zeng *et al.* 2020), while high chlorine levels are also measured in scapolite from skarn deposits (Mora & Valley, 1989).
(v) Tourmaline, which is the major reservoir of boron in meta-evaporitic rocks (Henry *et al.* 2008; Riehl & Cabral, 2018). Tourmaline is often restricted to beds containing scapolite assumed to be derived from saline fluids (Mora & Valley, 1989).

Corroborative evidence includes:

(vi) Chlorine-rich apatite, which could be derived from a magmatic source or seawater, and which is positive evidence where a magmatic input is lacking (Mao *et al.* 2016).
(vii) Sulphur isotope compositions of pyrite, which are comparable to the heavy composition of evaporites/seawater rather than the near-zero composition of magmatic sulphur (Golani *et al.* 2002; Johnston *et al.* 2006).
(viii) High-salinity fluids, especially in ore deposits that formed during or shortly after sedimentation (e.g. Conliffe *et al.* 2013).

4. Results

Mineral phenocrysts in the Tiree marbles (Figs 3 and 4) are dominated by pyroxenes (enstatite, diopside), amphiboles (tremolite), olivine (forsterite), micas and feldspars, and also scapolite, titanite (sphene), apatite, epidote, pyrite and quartz.
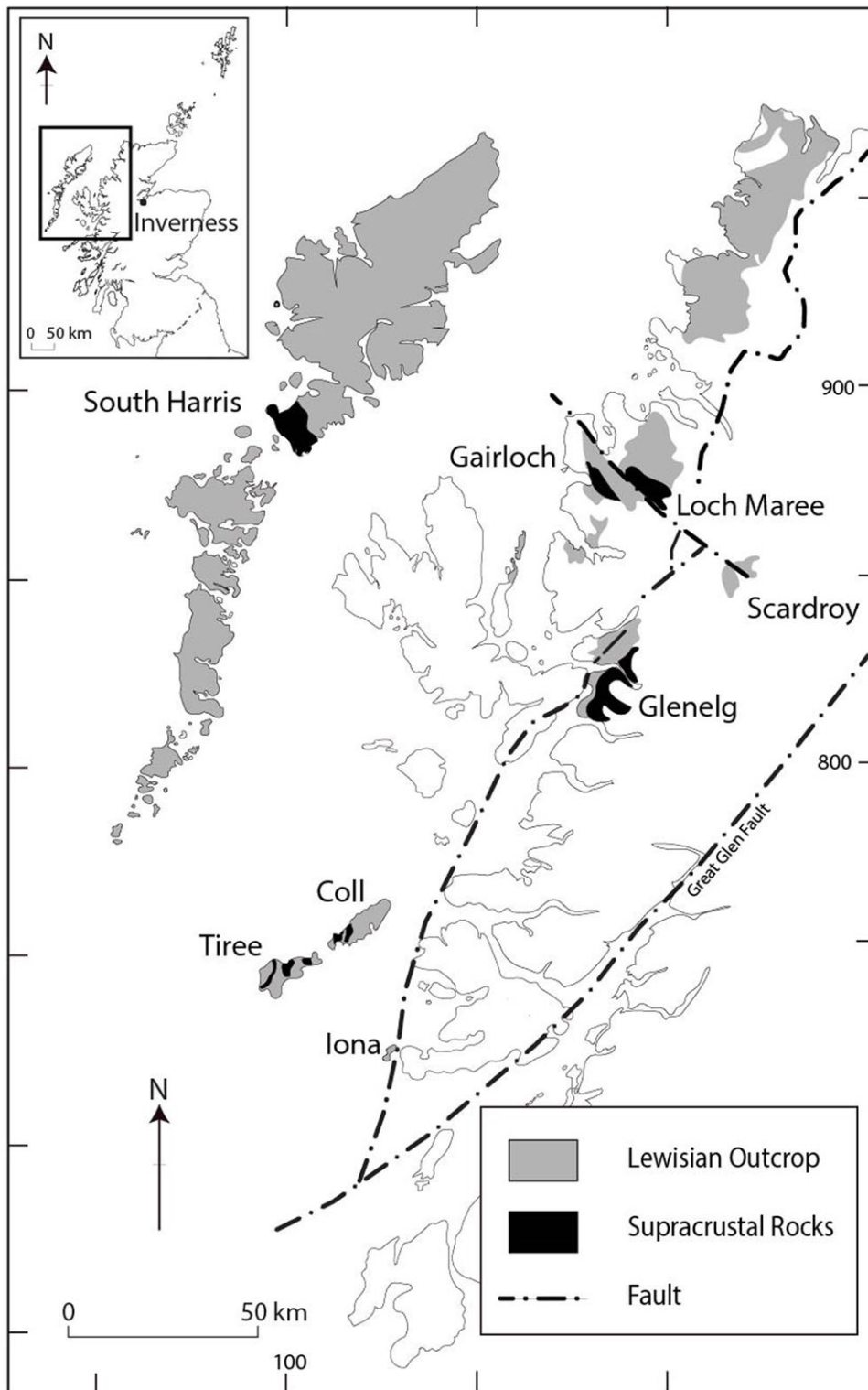
Fig. 2. Map of NW Scotland, showing distribution of Lewisian supracrustal inliers.

Minerals present in trace amounts include the sulphates anhydrite and barite. Anhydrite occurs as crystal fragments up to 15 µm size, in a calcite-rich groundmass. Barite occurs as a disseminated overprint on phenocrysts of pyroxene and amphibole. Measurements of the sulphur isotope composition of five pyrite crystals in marble at Gott yielded closely clustered values of 11.7, 11.7, 11.7, 11.9 and 12.3 ‰ (Fig. 5).

Sodium metasomatism is represented by replacive albite and scapolite. Scapolite has been recognized in the Tiree marble since the first petrographic studies (Coomaraswamy, 1903; Hallimond, 1947), and the Lewisian supracrustal rocks are conspicuously richer in scapolite than other rocks in Britain (Flett, 1907). The anion chemistry of scapolite includes variable combinations of −Cl, −F, −S and −OH, where proportions of −Cl and −S are interpreted to suggest
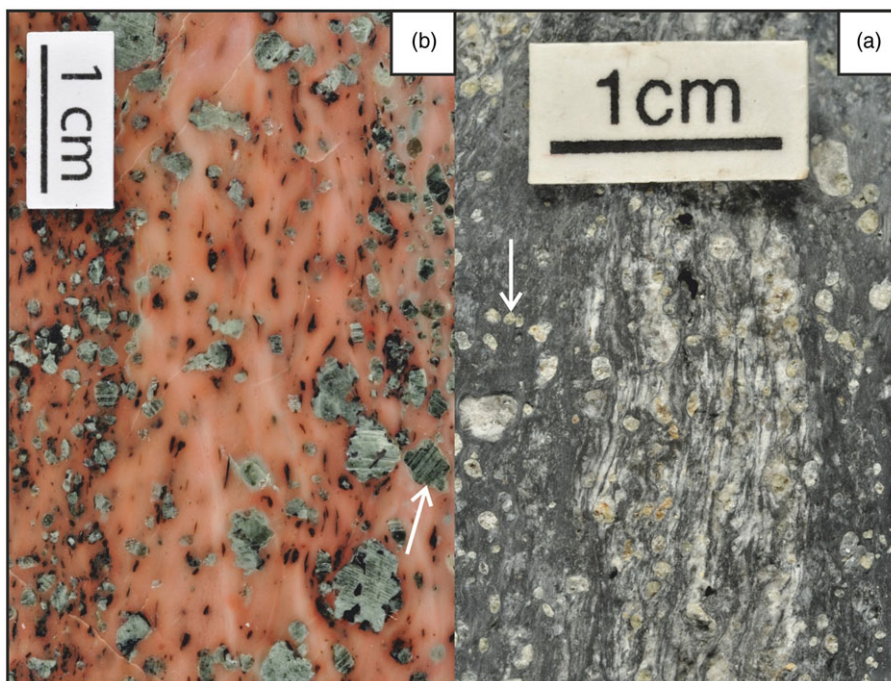
Fig. 3. (Colour online) Phenocryst-bearing marble, Palaeoproterozoic, Tiree. (a) Gott, rich in olivine (arrowed), pyroxenes, amphiboles, K-feldspar and streaks of graphite; (b) Balephetrish, rich in pyroxenes (arrowed) and amphiboles. Pink colour due to talc groundmass.
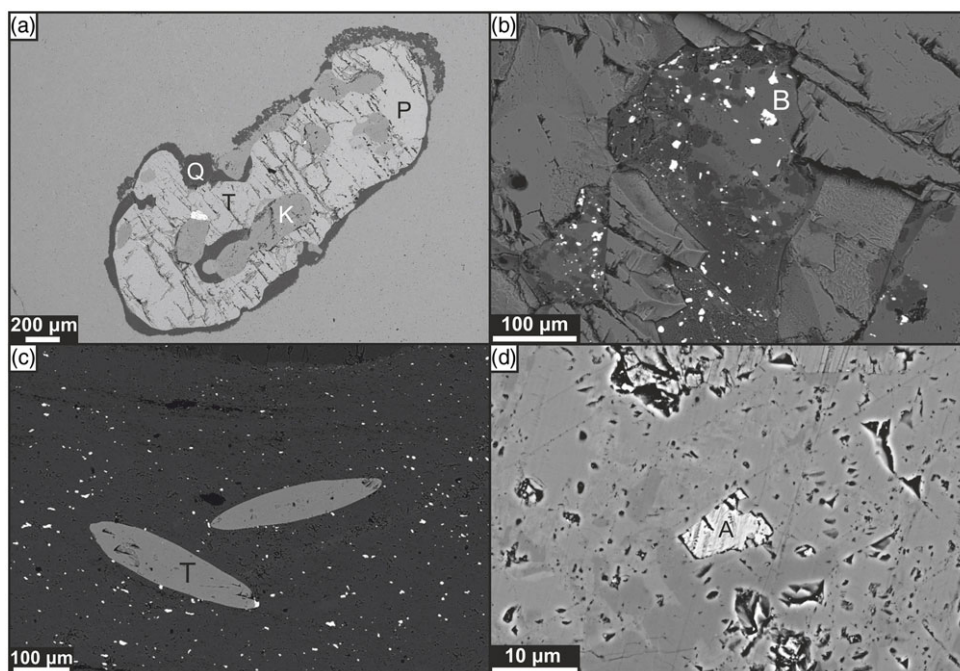

Fig. 4. (Colour online) Backscattered electron images of mineral phases in marble, Gott, Tiree. (a) Multi-phase phenocryst pf pyroxene (light grey, P) with potassium feldspar (grey, K) and titanite (bright, T), all coated with veneer of quartz (black, Q). (b) Abundant small barite (bright, B) within potassium feldspar and pyroxene. (c) Two crystals of titanite (T) within calcite, and abundant small pyrite (bright). (d) Crystal of anhydrite (A), showing characteristic cubic cleavage.

relative contributions from replaced halite and gypsum (Warren, 2016). Sulphur and chlorine were measured up to 2.30 % and 0.93 % respectively in the scapolite (Table S2, in the Supplementary Material available online at https://doi.org/10.1017/S0016756822000474). The higher sulphur contents occur in scapolite with the lower chlorine contents, as expected when both contribute to the same atomic sum. The marble at Gott, and to a lesser extent in other Tiree marble, is partially altered to masses of albite.

Phlogopite occurs pervasively through the supracrustal marbles on Tiree and in other Scottish localities. The phlogopite
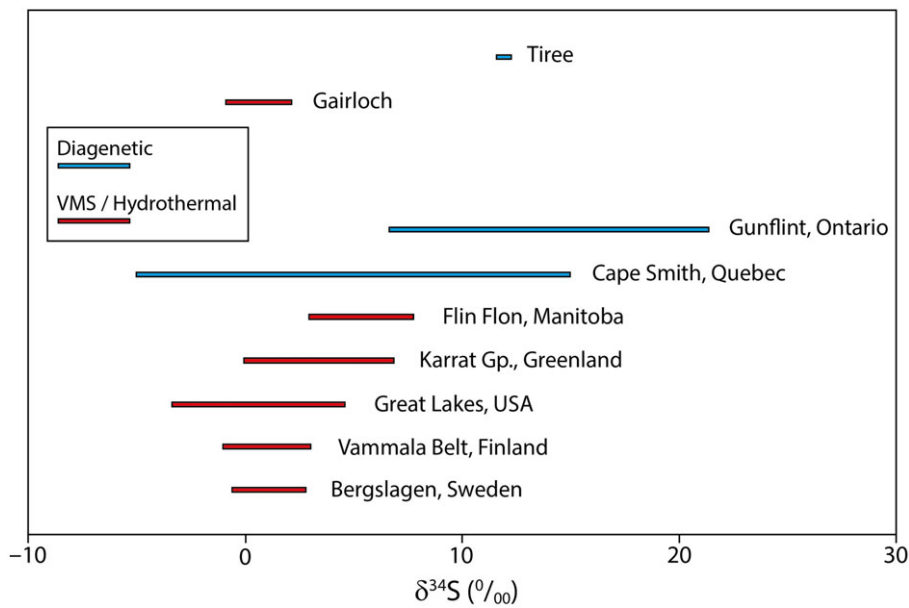
consistently contains 0.15 to 0.25 wt % chlorine. Apatite crystals are chlorine-bearing, up to 2.8 wt % where measured (Table S3, in the Supplementary Material available online at https://doi.org/10.1017/S0016756822000474). The marble is not spatially related to any magmatic deposits. Tourmaline is not recorded in Tiree marble, but it does occur in marbles in several other Lewisian supracrustal outcrops in Harris (Coward *et al.* 1969), Iona (Rock, 1987) and Gairloch – Loch Maree (Robertson *et al.* 1949).

Analyses for dating of the titanite in marble from Gott, Tiree, were made *in situ* on 13 titanite grains in polished rock slabs (Fig. 4), ranging in size from *c.* 100×50 µm to 700×200 µm. A total of 30 spots were analysed; the largest grain was targeted with seven analyses. No age differences are observed between the different grains. All analysed domains are common-Pb (PbC)-rich, with $^{206}Pb/^{204}Pb$ ratios ranging from 500 to 18 000. On a Wetherill Concordia diagram, uncorrected data fan out from being 90 % to 102 % concordant, with a larger spread along the Concordia. Pb corrected data are from 95 % to 103 % concordant, and plot on a relatively well-defined Discordia line (Fig. 6) with a lower intercept at 330 ± 157 Ma and an upper intercept at 1593 ± 7 Ma ($n = 30$; MSWD = 5.4). This indicates that the applied PbC works well, and age data are therefore obtained from the PbC data. Deselecting all reverse discordant analyses yields an upper intercept age of 1593 ± 11 Ma ($n = 17$; MSWD = 3.0) (Fig. 6), and selecting only 100 % concordant analyses yields a Concordia age of 1586 ± 7 ($n = 4$; MSWD = 2.2). The best age estimate for the titanite crystallization is 1593 ± 11 Ma (MSWD = 3.0).

5. Discussion

5.1 Sulphates and sulphides

The anhydrite in Tiree is the first recorded in the Lewisian Complex. In Palaeoproterozoic supracrustal successions in the North Atlantic region, anhydrite is preserved in Greenland (Horn *et al.* 2019), Sweden (Martinsson *et al.* 2016) and Russia (Serdyuchenko, 1975). Together with well-preserved pseudomorphs after gypsum in many regions including Sweden (Lager, 2001) and Canada

(Bell & Jackson, 1974; Zentmyer *et al.* 2011; Hodgskiss *et al.* 2019), there is extensive evidence for sulphate-bearing seawater, at ~2.0–1.9 Ga. In several cases, sulphur isotope data are available and are strongly positive, in accord with an evaporative origin for the anhydrite. The occurrence of anhydrite in the Lewisian Complex is therefore not anomalous, and rather is consistent with the global picture of widespread evaporites in the Palaeoproterozoic. Evidence for pseudomorphs in Tiree may be obscured by shearing focused on the metasediments.

The temporal relationship between anhydrite and barite cannot be proven, but the overprinting pattern of the barite suggests that it is most likely to be later, in which case the barite sulphur could have been remobilized from the anhydrite and precursor gypsum. In the Hudson Bay region, pseudomorphs of ~2.0 Ga gypsum are similarly overprinted by barite (Hodgskiss *et al.* 2019).

The sulphur-bearing scapolite from Tiree suggests derivation from a sulphate-rich sedimentary environment (Morrissey & Tomkins 2020; Zeng *et al.* 2020). Several other Palaeoproterozoic successions contain scapolite attributed to metamorphism of evaporites, but only one of five data sets has a sulphur content as high as the range for the Tiree scapolite (Table S2, in the Supplementary Material available online at https://doi.org/10.1017/S0016756822000474).

Globally, sulphide deposits of the mid-Palaeoproterozoic that have been characterized by sulphur isotopic composition fall into two main groups. Volcanic massive sulphides derived from magmatic-hydrothermal fluids have a composition of ~0 ‰, while sulphides attributed to derivation from seawater sulphate have a heavy (positive $\delta^{34}S$) composition. This could include volcanic massive sulphides in which the hydrothermal fluids were recycled from seawater rather than purely magmatic. Mid-Palaeoproterozoic (1.9–1.8 Ga) diagenetic pyrite is characterized by positive $\delta^{34}S$ values, reflecting derivation from seawater with a relatively limited sulphate content, notwithstanding the occurrence of sulphate evaporites (Scott *et al.* 2014). In the North Atlantic region, Palaeoproterozoic volcanic massive sulphides and diagenetic sulphidic shales have distinct compositions (Fig. 5). Sulphur isotope data from sulphides in the Lewisian supracrustal inliers have hitherto been limited to the volcanic massive sulphide deposit at Kerry Road, Gairloch, are tightly grouped
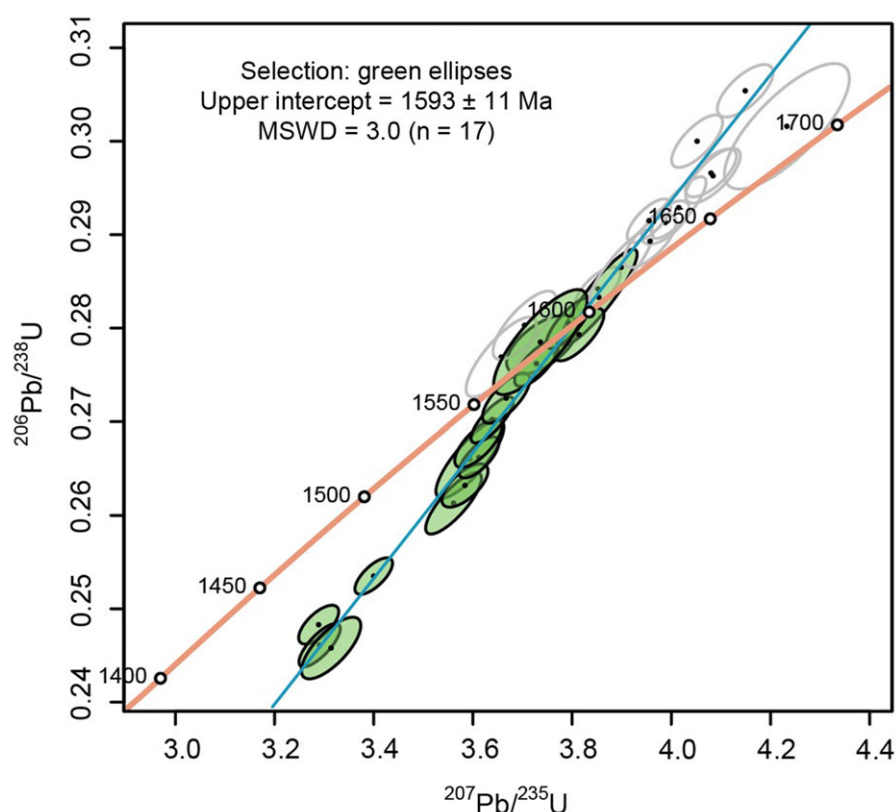
Fig. 6. (Colour online) Wetherill Concordia diagram with Pb corrected data. Data points plot along a relatively well-defined Discordia line. Data points shown as green ellipses outline the selection of data used for the final age calculation. Error ellipses are shown with a 95 % confidence level.

around 0 ‰ and probably represent fluids of magmatic-hydrothermal origin (Drummond *et al.* 2020). In contrast, the pyrite measured here from the Tiree marble is markedly positive (mean 11.9 ‰), comparable to those of mid-Palaeoproterozoic sulphides attributed to an origin in seawater (Fig. 5).

5.2 Phenocryst assemblage

The phenocryst assemblage in the Tiree marble is found in many other Lewisian Complex marbles of northern Scotland, from South Harris to Scardroy (Fig. 2). A core assemblage of pyroxene, amphibole, olivine, mica, titanite, epidote and quartz phenocrysts is consistent across the region (Rock, 1987). The uniformity implies that the marble-hosted phenocrysts represent the metamorphic overprint on the original mineralogy, rather than local effects.

The ~1600 Ma dates for the Tiree titanite record mineral growth in the Palaeoproterozoic–Mesoproterozoic, and show no contribution from the much younger episodes of sodium metasomatism found elsewhere in northern Scotland. The sodium, chlorine and sulphur recorded in the mineral assemblage can therefore be confidently attributed to the chemistry of the depositional environment of the marble in the Palaeoproterozoic.

The titanite dates are comparable with the younger ages determined for reworking of the Lewisian Complex. They show no evidence of the 2500–2000 Ma reworking ages (Crowley *et al.* 2015) determined for Archaean gneisses in the bulk of the Lewisian Complex. The age is also younger than the ~1.8–1.7 Ga date ascribed to the main phase of Laxfordian deformation and metamorphism that widely affects the Lewisian Complex in NW

Scotland (Goodenough *et al.* 2013). However, there is increasing evidence for an event in Scotland in the range 1.6–1.55 Ga, described by some workers as 'Late Laxfordian'. This includes a ~1.6 Ga 'cooling' date for hornblende in a shear zone (Sherlock *et al.* 2008), a 1.55 Ga Re–Os date for copper mineralization (Holdsworth *et al.* 2020), a major magnetizing event 1.7 to 1.5 Ga (Piper, 1992) and a 1.6–1.4 Ga age for cooling of granite on the Stanton Banks west of Tiree (Scanlon & Daly, 2001). Holdsworth *et al.* (2020) point out that an event of this age in Scotland links activity in Canada and Scandinavia at the time, which saw the later stages of the Labradorian and Gothian orogenies respectively.

5.3 Chlorine-bearing phases

Apatite in the Tiree marble commonly contains above 1 wt % chlorine, and up to 2.8 wt % (Table S3, in the Supplementary Material available online at https://doi.org/10.1017/S0016756822000474). These contents are higher than those in many other marbles (Table S3), or apatite in granites and iron deposits which mostly contain <0.5 % (Ishihara & Moriyama, 2015). The Tiree apatite is thus considered to be chlorine-rich. This would be consistent with a seawater origin for the apatite, and there are no associated magmatic rocks which might indicate an alternative origin. However, phosphatic rocks were widespread globally at *c.* 1.9 Ga (Papineau, 2010), and we regard the chlorine-rich apatite as supporting rather than critical evidence.

The chlorine content of the phlogopite in the marble is not exceptional, but is comparable with the content in micas from other suspected metamorphosed evaporites (Moine *et al.* 1981;

Mora & Valley 1989; Opletal et al. 2007). The role of micas as a residence for seawater-derived chlorine is in their relative abundance rather than the content per mineral.

The assemblage of chlorine-bearing mineral phases, in particular scapolite and phlogopite, is typical of metamorphosed evaporites (Moine et al. 1981; Mora & Valley, 1989; Warren, 2016). The combination of scapolite and phlogopite is encountered in several Palaeoproterozoic supracrustal successions in the North Atlantic region, including in Bergslagen, Sweden (Oen & Lustenhouwer, 1992), Finland (Reinikainen, 2001) and Baffin Island, Canada (Belley et al. 2017), and in each case has been interpreted as evidence of former evaporites. It would therefore be consistent to interpret the Lewisian Complex geochemistry as further evidence of Palaeoproterozoic evaporite deposition.

Saline fluids from chlorine-bearing mineral phases are important for transport of metals and creation of ore deposits (Yardley & Graham, 2002; Riehl & Cabral, 2018; Morrissey & Tomkins, 2020). Coeval supracrustal rocks in adjacent Greenland and Scandinavia contain ore deposits in which evaporites are implicated as a source of mineralizing fluids (Frietsch et al. 1997; Horn et al. 2019). Metalliferous ores and mineral showings in the Lewisian supracrustals (Coats et al. 1997; Drummond et al. 2020; Parnell et al. 2021) suggest that there may also be potential deposits in Scotland, to which evaporite-derived fluids could have contributed.

5.4 Sodium metasomatism and tourmaline

The albite in Tiree marbles is further evidence of sodium metasomatism. The albite is part of the mineral assemblage which dates to the latest Palaeoproterozoic – early Mesoproterozoic. This distinguishes it from episodes of sodium metasomatism in other parts of northern Scotland, which affect Mesoproterozoic and Neoproterozoic metasediments (Sutton & Watson 1951; May et al. 1993; Van de Kamp & Leake, 1997), and which must be of younger age. Albitization occurs in Palaeoproterozoic rocks contiguous to Scotland, in Greenland and Scandinavia. This albitite in the North Atlantic region is argued to be derived from evaporites or seawater (Kalsbeek, 1992; Frietsch et al. 1997; Gleeson & Smith, 2009), and there is not a clear alternative in Scotland that would preclude a similar origin.

The lack of recorded tourmaline in the Tiree marble may reflect the relatively quiescent nature of Palaeoproterozoic sedimentation there. While tourmaline is increasingly recognized as evidence for metamorphosed evaporite sequences, in many cases the environments included exhalative brines on the sea floor (e.g. Oen & Lustenhouwer, 1992; Jiang et al. 1997). Where tourmaline is reported most abundantly in the Scottish marbles, at Loch Maree (Robertson et al. 1949), the marbles occur in a section that also hosts exhalative sulphide mineralization and iron formation (Drummond et al. 2020). The tourmaline in Lewisian marble thus conforms to evidence in other successions for an association with meta-exhalites. Tourmaline-bearing metasediments across the North Atlantic region of c. 1.9 Ga age, from Quebec (Chown, 1987) to Hudson Bay (Ricketts, 1978), Greenland (Thomassen, 1992) and Sweden (Hellingwerf et al. 1994), are all attributed to former evaporites.

6. Conclusions

Combinations of criteria have contributed to a picture of evaporites in Palaeoproterozoic supracrustal successions across the North Atlantic region (Fig. 1; Table S1 in the Supplementary Material available online at https://doi.org/10.1017/S0016756822000474). The aspects that are consistent with an evaporitic facies in the Lewisian Complex of Tiree include anhydrite, scapolite, phlogopite, chlorine-rich apatite, and pyrite with a positive sulphur isotope signature. The attribution is not definitive, but it represents multifaceted evidence in support of a role for fluids derived from seawater. The evidence of pseudomorphs is currently lacking. Nonetheless, it seems likely that the supracrustal rocks of the Lewisian Complex included evaporitic facies, like their counterparts in many other parts of the North Atlantic.

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