The Palaeoproterozoic global carbon cycle: insights from the Loch Maree Group, NW Scotland

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Abstract: Two Palaeoproterozoic events have particularly interested Earth scientists. These are the global Lomagundi–Jatuli Event, the greatest magnitude positive carbonate carbon isotope excursion in Earth history, and the Shunga Event, the world’s largest organic carbon burial event. Analysis of newly acquired high-resolution C–O isotope data and U–Pb zircon geochronology refine understanding of carbon isotope characteristics and timing of deposition of the Palaeoproterozoic Loch Maree Group of NW Scotland. Petrographic examination reveals a basal unconformity between the Loch Maree Group and Archaean basement, permitting a stratigraphy and younging direction to be assigned. Detrital zircon ages from immediately above the unconformity are dated at c. 2.3 Ga. δ13Ccarbonate data on two temporally discrete carbonate packages range from c. +15 to 2‰ in the older unit and c. 2 to −5‰ in the younger carbonate unit. Current age constraints indicate that the Loch Maree Group is too young to be fully coeval with the Lomagundi–Jatuli Event but is within the age range of the Shunga Event. This revives consideration of a straightforward mass-balance process involving burial of organic carbon as an explanation for at least some of the C-cycle perturbations of Palaeoproterozoic time.

Supplementary Material: Sample descriptions from the Loch Maree Group, geochemical data, sample preparation and geochronology data are available at http://www.geolsoc.org.uk/SUP18865.

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Some of the most profound modifications of the Earth system occurred during early Palaeoproterozoic time (c. 2500–2000 Ma), not least of which was oxygenation of Earth’s atmosphere and upper oceans followed by two unparalleled excursions in the global carbon cycle, the Lomagundi–Jatuli and Shunga Events (Schidlowski et al. 1975; Baker & Fallick 1989a,b; Karhu & Melezhik 1992; Buick et al. 1998; Maheshwari et al. 1999; Bekker et al. 2004, 2006; Kump et al. 2011; Prétat et al. 2011). The former is the greatest magnitude and longest lasting positive carbonate carbon isotope excursion in Earth history (Canfield 2001; Melezhik et al. 2005; Holland 2006; Martin et al. 2013a). The latter, at least in the Shunga type area in NW Russia, is considered to be the world’s oldest, largest organic carbon burial episode (Melezhik et al. 1999; Martin et al. 2015). In so far as the global carbon cycle is commonly viewed as an isotopic mass-balance process (i.e. burial of light organic matter drives oceanic compositions to higher δ13Ccarbone values, it was first assumed that the two events were synchronous (Karhu & Holland 1996). However, later work on the geology of the Fennoscandian Shield showed that the rocks recording the Shunga Event post-dated those recording the Lomagundi–Jatuli Event; this temporal diachronieity led to it being termed the ‘Palaeoproterozoic Paradox’ (Melezhik & Fallick 1996). Recently published and summarized geochronological constraints confirm that the Lomagundi–Jatuli Event at c. 2220–2060 Ma mostly predates the Shunga Event at c. 2100–2000 Ma (Martin et al. 2013a,b).

Explaining the genesis of these events has stimulated creative ideas about the functioning of the global carbon cycle in deep time. The most recent include an enhanced weathering-derived flux of P-rich nutrients into the world’s oceans to trigger global bacterial blooms (Bekker & Holland 2012), worldwide subaerial oxidative breakdown of organic-rich rocks lowering the value of the 63C input into oceans (Kump et al. 2011; although this model has been questioned by Weber & Gauthier-Lafaye 2013), and a global enhancement in the precipitation of isotopically light diagenetic carbonate (Melezhik et al. 2012; Schrag et al. 2013).

Here we report on new carbon isotope data and U–Pb zircon geochronology that refine understanding of the carbon isotope characteristics and timing of deposition of the Palaeoproterozoic Loch Maree Group of NW Scotland. The Loch Maree Group is noteworthy because data derived from these rocks were used to first postulate that the Lomagundi–Jatuli Event was global in extent (Baker & Fallick 1989a,b). Our new data reveal that the Group is younger than c. 2300 Ma, and permissibly as young as c. 2000 Ma (based on U–Pb detrital zircon data; Whitehouse et al. 1997a) but older than c. 1900 Ma (the age of intrusive granodioritic bodies; Park et al. 2001; Park 2002), and confirm that it records δ13Ccarbonate values typical of those commonly assigned to the Lomagundi–Jatuli Event. The depositional age window is broad but based on several lines of inference (see below) is arguably coeval with the Shunga Event. If correct, then a straightforward, mass-balance process driven by organic carbon burial can be resurrected as a viable mechanism for at least some Palaeoproterozoic C-isotope excursions.

Geological setting

The Loch Maree Group is part of the Lewesian Complex of the NW Highlands of Scotland (Fig. 1) and consists of intercalated
amphibolites, arc- and continental-derived siliciclastic rocks, thin calcitic and dolomitic carbonates, and rare banded quartz–magnetite rocks and graphitic schists. Park et al. (2001) interpreted those rocks as a Palaeoproterozoic subduction–accretion complex that experienced two major deformations (referred to as Early, c. 1.9 Ga, and Late, c. 1.7 Ga, Laxfordian structures) defined by widespread penetrative planar-linear fabric, large-scale upright folds and the near-vertical NW–SE-trending Gairloch shear zone (Park 2010; Fig. 1). Because there are no obvious large-scale early folds and given the new discovery of a probable unconformity at the base of the Loch Maree Group (see below), it might be assumed that the stratigraphic framework is overall right-way-up. However, narrow shear zones (see Fig. 1), such as the Ialltaig–Mill na Claise and Flowerdale shear zones (Park 2010), transect the stratigraphy and even though many of the rock units on either side of these zones look similar their presence demands circumspection regarding the stratigraphic integrity of the Loch Maree Group. Thus, it is useful to consider the Loch Maree Group in terms of three tectonostratigraphic packages separated by the Ialltaig–Mill na Claise and Flowerdale shear zones (Park 2010, transect the stratigraphy and even though many of the rock units on either side of these zones look similar their presence demands circumspection regarding the stratigraphic integrity of the Loch Maree Group. Thus, it is useful to consider the Loch Maree Group in terms of three tectonostratigraphic packages separated by the Ialltaig–Mill na Claise and Flowerdale shear zones (Fig. 1): the Cloiche sequence, with the unconformity at its base and containing the strongly positive δ13Ccarbonate carbonate rocks; the Kerrysdale sequence, typified by the carbonate–graphite schist-quartzite-bearing marine succession containing plateau basalt or primitive-arc volcanic rocks; and the Flowerdale sequence, consisting of inferred deltaic to flysch deposits.

Carbonate rocks of the Loch Maree Group

The carbonate rocks of the Loch Maree Group comprise two main types (Rock et al. 1987; Baker & Fallick 1989a, Park 2002). The first, termed the Cloiche-type, occur along the southern margin of the southwestern segment of the Loch Maree outcrop belt (Fig. 1) and are dominantly calcitic in places marked by quartz, tremolite, actinolite, talc and chlorite. Strikingly similar carbonates occur along the NE margin of that segment (termed the Creag Bhan carbonates after Park 2002) and in the northwestern segment of the Loch Maree Group north of Loch Maree (Fig. 1). At each locality, these carbonate rocks are close to the contact with the underlying Archaean basement. The second type, termed the Kerrysdale type (note that these carbonate rocks were originally classified as ‘Flowerdale-type’ by Park 2002), occupy a position broadly coincident with the central portion of the southwestern segment of the Loch Maree Group outcrop belt (Fig. 1) and consist of centimetre-to decimetre-thick dolomircite beds interbedded with metapsammitic and metapelitic rocks. As noted above, they are associated with rare banded iron formations (banded quartz–magnetite), graphic schists and amphibolites (Park 2002; Williams 1986).

Chemostratigraphy and geochronology

Baker & Fallick (1988, 1989a,b) showed that the carbonate-carbon isotope values preserved in the Loch Maree Group metacarbonate rocks (and broadly coeval units in Norway) were depositional and not altered to any great extent by later amphibolite-facies metamorphism (see those papers for details). Our efforts have focused on obtaining a higher resolution C-isotope dataset than those published previously and on establishing stratigraphic constraints to assess those data.

Carbon and oxygen isotopes: methods

Carbon and oxygen isotope analysis was carried out at the Scottish Universities Environmental Research Centre (SUERC), East Kilbride, UK. A total of 82 carbonate rock samples were analysed: 34 from the Cloiche belt, 27 from the Kerrysdale belt, seven from the Creag Bhan belt and 14 from exposures north of Loch Maree (Fig. 1). Two samples were collected from graphic schists associated with the Kerrysdale-type rocks for organic carbon isotope analysis. In addition, the original 18 samples analysed by Baker & Fallick (1989a) were reanalysed to assess consistency between datasets.
Samples were drilled using a Sherline microdrill and collected in plastic vials. Analyses were performed at 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. Reproducibility of standards is ±0.2‰ and ±0.3‰ for carbon and oxygen respectively at 1σ; calibration was via NBS 19. C-isotope ratios were calibrated to Vienna Pee Dee Belemnite (VPDB). Oxygen isotopes were calibrated to Vienna Standard Mean Ocean Water (VSMOW) and values were corrected to account for dolomite–calcite oxygen fractionation during the sample acidification process (McCrea 1950).

**Geochronology: methods**

One sample (LMG111) was collected in the southern segment of the Loch Maree Group, 1 km above the contact with the Archaean basement (Fig. 1); this was to constrain a maximum age of deposition from detrital zircons. In hand specimen LMG111 is a quartzofeldspathic rock with a ‘sandy’ texture (see below). Recovered zircons occur as subrounded grains, fragments of grains, equant crystals and optically clear elongated crystals with euhedral face terminations. Grain sizes are between 40 and 80 µm and cathodoluminescence (CL) images show growth zoning typical of magmatic crystals.

Zircons were isolated from 2 kg of sample using conventional mineral separation techniques. LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry) was performed at the NERC Isotope Geosciences Laboratory, Keyworth, UK, using a Nu Plasma HR multi-collector ICP-MS system and ablation was conducted using a New Wave Research UP193SS (193 nm), Nd:YAG LA system.

**Carbon and oxygen isotopes: results**

The original Baker & Fallick (1989a) study showed a wide range in C-isotope values for the Loch Maree Group rocks. Our work builds on their findings and reveals that the data can be clustered into two main groups (Fig. 2): the petrologically similar Cloiche and Creag Bhan rocks have δ13C values from 15 to 2‰ and the Kerrysdale-type rocks have values from −2 to −5‰. Along the outcrop belt north of Loch Maree, the lowermost carbonate rocks from near the contact with the Archaean basement display δ13C values from 14 to 11‰ in their basal units and then fall to c. 0‰ in carbonate units tens of metres above that contact. The two graphitic schist samples collected from the Kerrysdale sequence have δ13Corg values of −20.8 and −21.7‰. Values for δ18O for all samples typically fall between +18 and +2‰, with no correlation to C isotopic values or to the rock units (Fig. 2).

**Geochronology: results**

Eighty zircon grain cores and two rims analysed by LA-ICP-MS were ≤5% discordant (Fig. 3). Two populations are evident from analysis of zircon cores: 39 analyses plot around 2.7 Ga with 207Pb/206Pb ages between 2742 and 2650 Ma (Fig. 3a) and 15 analyses plot around 2.3 Ga with 207Pb/206Pb ages between 2354 and 2246 Ma (Fig. 3b). Thirteen analyses have 207Pb/206Pb ages spread between 2647 and 2462 Ma and 12 analyses have 207Pb/206Pb ages older than 2750 Ma. Grain z32 plots off concordia and has most probably undergone some open-system behaviour; we do not consider its age further.

Two grains (z41 and z193) had analyses from the core and one rim. The z41 core yields a 2666 Ma 207Pb/206Pb age and the matching rim yields a 2375 Ma 207Pb/206Pb age. The z193 core yields a 2657 Ma 207Pb/206Pb age and the rim yields a 2694 Ma 207Pb/206Pb age. If during analysis the laser spot overlapped a core–rim pair with ages similar to those seen in grain z41 the result would plot somewhere between the c. 2.7 and 2.3 Ga populations; this may explain some of the 13 analyses that plot within this age range (Fig. 3a), although this problem should have been avoided by using CL imaging to target analysis.

The younger c. 2.3 Ga age population cannot be explained by age mixing between core–rim ages such as seen in grain z41 and the 15 analyses of the younger population specifically targeted the cores of grains, guided by CL analysis. Zircon data from this study (Fig. 3a) and previous studies (e.g. Whitehouse et al. 1997a; Park et al. 2001) suggest that a Laxfordian Pb-loss event is unlikely in Loch Maree rocks. A non-zero Pb-loss event younger than Laxfordian would slightly increase the age of the 2.3 Ga population; for example, a 1 Ga Pb disturbance would increase the upper intercept age to 2344 ± 19 Ma (2σ errors). Given the above considerations we prefer to interpret the maximum age at the stratigraphic level sampled as c. 2.3 Ga.

There may be several age equivalent sources for the c. 2.3 Ga zircon found at Loch Maree. For example, the Tilden Granite in Michigan’s Marquette Range (Great Lakes area) is dated at 2345 ± 20 Ma (Hammond 1976). The maximum detrital zircon age from the Enchantment Lake Formation overlying the Tilden Granite is 2317 ± 6 Ma (Vallini et al. 2006) and a 2306 ± 9 Ma
maximum detrital zircon age is derived for the correlative Sturgeon Quartzite (Vallini et al. 2006). A significant and well-characterized east–west-trending series of Fe-tholeite dykes from Fennoscandia yield c. 2.3 Ga ages; for example, 2331 ± 33 Ma in Finland’s Lisalmi block (Paavola 1988), 2306 ± 6 and 2332 ± 18 Ma in Finland’s Taivalkoski block (Vuollo et al. 2000; Vuollo & Huhma 2005), and c. 2.3 Ga dykes from the Karelia Craton (Stepanova et al. 2015). Examples of 2.3 Ga maximum detrital zircons ages are also recorded in Greenland paragneisses (Kalsbeek & Nutman 1996; Whitehouse et al. 1997b). The age of the NW Scotland Scourie dyke swarm is currently restricted to between c. 2418 and 2375 Ma (Davies & Heaman 2014).

Contact between the Loch Maree Group and Archaean basement

Tectonothermal overprinting of the Loch Maree Group combined with a lack of well-preserved sedimentary structures has confounded efforts to determine stratigraphic younging directions. However, to maximize the value of our C-isotope data for assessing ideas about the Palaeoproterozoic C cycle it is important to place those data within a stratigraphic context. The detrital zircon age data come from what we have identified as a patchily developed, variably thick (from a few tens of centimetres to a few metres) micaceous quartzo-feldspathic metasandstone occurring between the Archaean gneissic basement and the overlying basal metasedimentary units of the Loch Maree Group. Although the contact between the Loch Maree Group and basement is in many places tectonized (e.g. Park 2002), petrographic examination of samples reveals clearly an original sedimentary origin for the metasandstone, and we interpret it as a metamorphosed palaeo-grus preserved along a palaeoweathered surface; that is, this interval records an original unconformity surface showing that the lower part of the Loch Maree Group was depositional on the Archaean basement. Further, the Palaeoproterozoic-age detrital zircons confirm that the metasandstone is not simply tectonized or reworked Archaean Lewisian gneiss. These findings, combined with the mapping of Park (2002), indicate that the synform–antiform structures of the outcrop belt are a syncline–anticline couplet. Hence, the structural stratigraphy of the Loch Maree Group is reflecting an original, albeit tectonized, stratigraphy. It is this basis that allows us to construct the composite C-isotopic profile shown in Figure 4.

Discussion and conclusion

There are two new conclusions about the Loch Maree Group rocks that can be drawn from the above. First, the new maximum date of c. 2300 Ma combined with the c. 2000 Ma detrital zircon ages (Whitehouse et al. 1997a) from the overlying Flowerdale schists allows the placing of the Group’s δ13C data broadly within the time window for the Lomagundi–Jatuli and Shunga Events. Second, the fact that the base of the Loch Maree Group sits unconformably on Archaean basement confirms that at least the lower part of the Group is autochthonous, not an exotic Palaeoproterozoic terrane. Further, the carbonate rocks that form that portion of the Group, the Cloiche and Creug Bhan Belts and the outcrop belt sampled north of Loch Maree, are all isotopically heavy (mean δ13C = 9.2 ± 0.9‰). The outcrop belt north of Loch Maree yields heavy δ13C values in the lowermost part and lighter values in the upper part (see Fig. 4b). The younger, overlying Kerrysdale-type carbonate rocks have isotopically lighter values, with a mean δ13C = −0.8 ± 0.6‰. However, the narrow shear zones noted above disrupt the stratigraphic continuity of the Group. This requires assessing whether the composite stratigraphy shown in Figure 4a is a reasonable reconstruction of a once more coherent and contiguous stratigraphic succession, or whether the shear zones are bounding geologically unrelated terranes, thereby making comparisons of C-isotopic trends suspect.

The Loch Maree Group is considered to represent a subduction–accretionary complex, comparable, for example, with the Rhodopes of southeastern Europe and the Shimanto Belt of Japan (Park et al. 2001). Reassuringly, these better-preserved and constrained younger examples reveal that, although they are structurally complex, at the scale of the Loch Maree Group outcrop belt their internal stratigraphies remain reasonably coherent (e.g. Taira et al. 1982; Marchev et al. 2004, 2005; Aoki et al. 2008). What adds further confidence to our proposed stratigraphic framework is that the inferred older carbonate units exposed at the north shore of Loch Maree have strongly positive C-isotope values in their basal portions and these become lighter in their upper parts. Then, in the next package of carbonate rocks, which in our model are stratigraphically younger, values are relatively normal (see Fig. 4a and b). This pattern is comparable with the overall C-isotopic composite profiles exhibited by many stratigraphically coherent Palaeoproterozoic successions elsewhere; that is, strongly positive values declining towards normal values (e.g. Weber & Gauthier-Lafaye 2013; Črne et al. 2014).

Given the above and combining it with the age constraints for the Loch Maree Group two inferences can be made. First, the
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Archaean gneiss

Flowerdale sequence

Kerrysdale sequence

Cloiche sequence, incl. Creag Bhan & North Shore carbonates

Fig. 4. (a) Simplified composite stratigraphy of the Loch Maree Group and corresponding C-isotope profile (b); thicknesses are schematic. Creag Bhan and North Shore δ¹³C_carbonate data have been included in the Cloiche sequence.
strongly positive C-isotope values are limited to the lower part of the Loch Maree Group because normal values return in the younger Kermadec-type carbonate rocks. Second, the 2.3 Ga detrital zircon ages provide evidence that the Loch Maree Group is resting unconformably on Archean gneissic rocks and given the inference that there is stratigraphic continuity between the lower carbonate units and the Flowerdale Schist, then the depositional age of those carbonate rocks is likely to be constrained to between c. 2000 Ma, the age of detrital zircons recovered from the Flowerdale schists, and the c. 1900 Ma intrusive ages. This time window makes the Loch Maree Group rocks too young to be fully coeval with the Lomagundi–Jatuli Event recognized elsewhere but within the age range known for the Shunga Event (see references cited above). Consequently, the Loch Maree Group data permit consideration of an isotopic mass-balance mechanism involving the coeval burial of organic carbon as a viable explanation for at least some of the positive C-cycle perturbations of Palaeoproterozoic time.

In summary, the Loch Maree Group preserves large-magnitude positive carbonate-isotope values (δ13C values as high as +15‰) that have the character of the Lomagundi–Jatuli Event. However, current age constraints imply that the Group is unlikely to be temporally coeval with other Lomagundi–Jatuli-bearing successions elsewhere but permissibly albeit not conclusively linked to the organic carbon burial episode of the Shunga Event. This possibility revives consideration of a straightforward, carbon cycle mass-balance process as a potential explanation for the large C-isotope excursions of Palaeoproterozoic time. Our findings also urge circumspection before adopting a view that those excursions (the Lomagundi–Jatuli and Shunga ‘events’) are temporally distinct singularities, but certainty and resolution await better geochronology.

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