Redox condition of the late Neoproterozoic pelagic deep ocean: 57Fe Mössbauer analyses of pelagic mudstones in the Ediacaran accretionary complex, Wales, UK

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A B S T R A C T

We report geological and geochemical analysis of Neoproterozoic pelagic deep-sea mudstones in an accretionary complex in Lleyn, Wales, UK. Ocean plate stratigraphy at Porth Felen, NW Lleyn, consists of mid-ocean ridge basalt (>4 m), bedded dolostone (2 m), black mudstone (5 m), hemipelagic siliceous mudstone (1 m), and turbiditic sandstone (15 m), in ascending order. The absence of terrigenous clastics confirms that the black and siliceous mudstone was deposited in a pelagic deep-sea. Based on the youngest U-Pb age (564 Ma) of detrital zircons separated from overlying sandstone, the deep-sea black mudstone was deposited in the late Ediacaran. The 5 m-thick black mudstone contains the following distinctive lithologies: (i) black mudstone with thin pyritic layers (0.8 m), (ii) alternation of black mudstone and gray/dark gray siliceous mudstone (2.4 m), (iii) thinly-laminated dark gray shale (1 m), and (iv) black mudstone with thin pyritic layers (1 m). 57Fe Mössbauer spectroscopy confirms that these black mudstones contain pyrite without hematite. In contrast, red bedded claystones (no younger than 542 Ma) in the neighboring Braich section contain hematite as their main iron mineral. These deep-sea mudstones in the Lleyn Peninsula record a change of redox condition on the pelagic deep-sea floor during the Ediacaran. The black mudstone at Porth Felen shows that deep-sea anoxia existed in the late Ediacaran. The eventual change from a reducing to an oxidizing deep-sea environment likely occurred in the late Ediacaran (ca. 504–542 Ma).

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1. Introduction

Oxidation of the deep ocean has been generally considered to have occurred in a stepwise manner in the late Neoproterozoic, almost at the same time as the metazoan diversification often called the “Cambrian Explosion” (e.g., Canfield et al., 2007; Fike et al., 2006; Och and Shields-Zhou, 2012). In order to estimate the ambient redox conditions, the geochemistry of Neoproterozoic sedimentary rocks have been well studied (e.g., Anbar and Knoll, 2002; Canfield et al., 2007; Canfield et al., 2008; Lenton et al., 2014; Li et al., 2010; Lyons et al., 2014; Och and Shields-Zhou, 2012). The key representative redox indicator is iron speciation (ratio of highly reactive iron in total iron; Fe3+ / Fe2+) used, for example, by Canfield et al. (2007), Shen et al. (2008), Johnston et al. (2013). However, the precise timing and the process of the oxidation and its link with animal evolution remain controversial. A major problem has been that most previous studies investigated only epicontinental shallow-ocean sedimentary rocks or epicontinental basinal sedimentary rocks, and have never analyzed mid-oceanic deep-sea sedimentary rocks. Pelagic deep-sea sedimentary rocks in ancient accretionary complexes (ACs) are essential for analyzing and understanding past global deep-oceans, as shown in studies of Paleozoic and Mesozoic ACs (e.g., Isozaki, 1997), because they provide the only record of pelagic deep-sea environments older than 200 Ma (Matsuda and Isozaki, 1991; Isozaki, 1997, 2014). Thus, ACs are more useful to understand global signals than epicontinental sedimentary rocks that tend to reflect local, continental fluctuations. Such deep-sea sedimentary rocks occur solely in subduction-accretion complexes exposed on land, as emphasized by Japanese geologists since the 1990s.

In Phanerozoic deep-sea cherts in Japan the iron minerals quantitatively reflect the redox level of the deep-sea water during deposition (Kubo et al., 1996; Matsuo et al., 2003; Nakao and Isozaki, 1994; Sato et al., 2009, 2012). Hematite-bearing red chert and pyrite-bearing black chert are deposited under oxic and anoxic condition, respectively.
The Neoproterozoic AC with black carbonaceous pelagic mudstones on Anglesey Island and Lleyn Peninsula in Wales, UK, recorded the Neoproterozoic subduction zone along the Avalonian margin of the Iapetus Ocean (Kawai et al., 2007; Maruyama et al., 2010). Sato et al. (2009) reported red hematite-bearing chert/siliceous claystone, from Llanddwyyn Island in Anglesey (Fig. 1), which formed under oxidizing conditions in the late Neoproterozoic (namely in the Ediacaran or possibly in the Cryogenian) deep-sea.

This article reports the occurrence of Ediacaran deep-sea black mudstones and red bedded claystones in Lleyn, which provide a new dataset of Neoproterozoic redox changes in deep ocean, in particular the timing of the first deep-sea oxidation in Earth history.

2. Geological setting

The Gwna Group on Anglesey Island and Lleyn Peninsula was first described by the pioneering geologist, Greenly (1919). The Gwna Group is composed predominantly of basaltic greenstones/ greenschists, in places pillow-bearing that have a low-K tholeiitic composition (Thorpe, 1972), and volumetrically minor chert, claystone, quartzite, graphitic phyllite, limestone, and greywacke. No index fossils have been reported from the red-bedded cherts of the Gwna Group except for poorly preserved acritarchs (Muir et al., 1979). The term “mélange” was coined by Greenly (1919) for spectacular examples in northern Anglesey, Wales (see Wood, 2012). The Gwna Group underwent blueschist to epidote amphibolite facies metamorphism at ~600 Ma (Dallmeyer and Gibbons, 1987; Kawai et al., 2006, 2007). Wood (1974) and Barber and Max (1979) first suggested that the Gwna Group formed in a subduction zone in the Neoproterozoic, and this was likely on the western margin of Avalonia (Kawai et al., 2007, 2008).

The Gwna Group crops out sporadically for over 200 km across the NE-SW strike from the western side of the Lleyn Peninsula to northern Anglesey (Fig. 1). Maruyama et al. (2010) confirmed that the Gwna Group is a subduction-accretion complex based on the presence of ocean plate stratigraphy (OPS) constrained by the mode of occurrence, lithology, and zircon chronology. Asanuma et al. (2015) described the detailed geological setting of our study area, located on the southern part of the Lleyn Peninsula (Fig. 2). The ocean-floor sedimentary rocks comprise red-bedded claystones at Braich, and black mudstones at Porth Felen. In some outcrops, terrigenous sandstones overlie MORB without intercalation of pelagic sedimentary rocks, possibly because of the short distance between the mid-oceanic ridge and the trench.

The AC containing the deep-sea chert formed earlier than underlying high-pressure blueschists, which have a controversial metamorphic age of 560–550 Ma (Dallmeyer and Gibbons, 1987), but no index fossils or zircon U-Pb ages were available in the AC. However, Asanuma et al. (2015) reported many new zircon ages from Anglesey-Lleyn, and suggested that the depositional age of the relevant red bedded cherts was probably as young as 526 Ma.

3. Ediacaran OPS of the Gwna Group

The Ediacaran ocean-floor rocks crop out on the well-exposed coast at Porth Felen, SW Lleyn (Figs. 1, 2). Each thrust-bounded block shows a portion of characteristic Ocean Plate Stratigraphy (OPS) that is composed of pillow basalt, carbonate, black mudstone, siliceous mudstone, and turbidite in ascending order (Fig. 2). The most complete stratigraphy can be observed in a hanging-wall outcrop (Fig. 3) near the boundary between the Gwna Group and a Schist Unit (Kawai et al., 2007). The tectonic slices with the OPS are bounded by many layer-parallel thrusts, which belong to a stacked duplex structure. The stratigraphy of each slice and the overall compressional structures are typical of ACs worldwide (Isozaki et al., 1990; Kusky et al., 2013), and therefore we were able to reconstruct the original stratigraphy (Fig. 4). The stratigraphic bottom is occupied by pillow basalt (~4 m thick) that is overlain by a 2 m-thick bedded dolostone, which in turn is overlain by ca. 5 m-thick black mudstones that are capped by 15 m-thick turbidites of mudstone and sandstone. The black mudstones are rich in organic carbon (ca. 6–10 wt%) and contain fine-grained pyrites.

The black mudstone is divisible into ~4 subunits; (i) black mudstone with thin pyritic layers (0.8 m), (ii) an alternation of black mudstone and gray/dark gray siliceous mudstone (2.4 m), (iii) thinly-laminated dark gray shale (1 m), and (iv) black mudstone with thin pyritic layers (1 m). The uppermost black mudstone changes upwards gradually into coarser-grained clastic sedimentary rocks, which in ascending order include greenish gray siliceous mudstone (2 m), greenish gray mudstone (1 m), greenish gray mudstone with sandstone pebbles (1 m), sandstone (3 m), greenish gray mudstone with sandstone pebbles (1 m), greenish gray claystone (5 m), and red claystone (1 m). The fact that the black mudstones are stratigraphically sandwiched between underlying pillow-bearing basalt with mid-ocean ridge chemical affinity (Saito et al., 2015) and overlying coarse-grained terrigenous pebbly sandstone-mudstone is typical of OPS worldwide (Isozaki, 2014; Kusky et al., 2013).

The black mudstones are thinly laminated and contain pyritic layers (Figs. 4, 5). Microscopic observations reveal that these black mudstones have very fine matrices and contain no terrigenous clastic and carbonate minerals; these relations indicate that they were primarily deposited in the low-energy environment of a pelagic deep-sea floor. The black mudstones contain frambooidal pyrite (Fig. 5D) that is typically deposited when an overlying water column is anoxic, as shown by Algeo et al. (2010) for the Superanoxia at the Permian-Triassic boundary.
A second outcrop of deep-sea sedimentary rocks is at Braich, 1 km northwest of Porth Felen (Fig. 2), where prominent red-bedded siliceous claystones, and turbidite sandstones occur without underlying basalts. The red-bedded claystones at Braich contain a clear rhythmic alternation of siliceous and argillaceous layers (Fig. 6) with no terrigenous clastic or carbonate minerals, indicating that they were deposited on a pelagic deep-sea floor. Siliceous fossils such as radiolarians or siliceous sponges are missing. The red-bedded claystones are similar, and equivalent, to the red-bedded cherts on Llanddwyn Island in Anglesey described by Sato et al. (2009).

Detrital zircon grains separated from a turbiditic sandstone bed at Porth Felen (LLY464) have the youngest U-Pb age of 564 ± 14 Ma (Asanuma et al., 2015). The depositional age of the underlying black mudstone is therefore no younger than late Ediacaran, and estimated to be approximately 580–570 Ma.

4. Analysis

$^{57}$Fe Mössbauer spectroscopy is one of the most useful analytical methods to identify the chemical states of iron in powdered samples and to quantify their relative abundances, and it is far simpler and more reliable than classical wet analyses. We investigated 5 deep-sea sedimentary rock samples by $^{57}$Fe Mössbauer spectroscopy: 3 black mudstones (LLY489, 494, 500) from Porth Felen and 2 red-bedded claystones (LLY 326, 359) from Braich. The fresh, best-preserved parts of the samples were cut with a diamond saw and hand-picked under the microscope to avoid weathered surfaces and veins. The sample chips were ground to 100-mesh powder in an agate mortar. Mössbauer spectra were measured with an Austin Science S-600 Mössbauer spectrometer at the University of Tokyo using a 1.11 GBq $^{57}$Co/Rh source at room temperature. By comparing the Mössbauer parameters (isomer shift, quadrupole splitting, and inner magnetic field) to standard data, we identified the constituent iron species and calculated their relative abundances. Mössbauer spectra were calculated by a least-square method with restrictions of intensity and half-width of peaks. All doublets were treated as symmetric. Peak positions of pyrite were constrained as in previous studies. The presence of pyrite crystals was also checked under the microscope.

5. Results

The Mössbauer spectra of the samples are shown in Fig. 7, and the Mössbauer parameters for all the analyzed samples are given in Table 1. The Mössbauer analyses of the 5 samples identified the
following 5 iron species: hematite, paramagnetic Fe$^{3+}$ (high spin; h.s.), paramagnetic Fe$^{2+}$ (h.s.)II, pyrite, and paramagnetic Fe$^{2+}$ (h.s., outer). Fe$^{3+}$ (h.s.) and Fe$^{2+}$ (h.s., outer) are typically found in clay minerals such as illite or chlorite. Fe$^{3+}$ (h.s.)II is an unidentified iron species. The red claystones (LLY 326, 359) from Braich contain hematite as the main iron mineral (more than 60 % total iron) with smaller amounts of Fe$^{2+}$ (h.s., outer) and Fe$^{3+}$ (h.s.), outer). The black mudstones (LLY489, 494, 500) from Porth Felen contain pyrite (no more than 30 %), Fe$^{2+}$ (h.s., outer), and occasionally Fe$^{3+}$ (h.s.)II.

6. Discussion

6.1. Chemical state of iron in deep-sea sedimentary rocks

The iron species in the 3 black mudstones (LLY404, 489, 500) from Porth Felen are composed of pyrite, paramagnetic Fe$^{2+}$ (h.s., outer), and occasionally Fe$^{3+}$ (h.s.)II. The existence of pyrite without hematite suggests that these mudstones were deposited and consolidated under reducing conditions. The Fe$^{2+}$ (h.s., outer) is commonly a component of clay minerals such as chlorite and illite. LLY494 contains large amounts of Fe$^{3+}$ (h.s.)II, a newly identified iron species among our series of Mössbauer analyses of deep-sea cherts, that is likely formed during secondary alteration because of LLY494’s shaley lithology. The iron species in the 2 red claystones (LLY326, 359) from Braich are mainly composed of hematite without secondary iron-hydroxide or pyrite. These relations suggest that these claystones were deposited and consolidated under oxidizing conditions. These hematite-bearing claystones also contain small amounts of Fe$^{2+}$ (h.s.), which is assumed to be a component of clay minerals such as chlorite and illite.

The types and compositions of iron minerals in pelagic deep-sea sedimentary rocks are widely considered to reflect the redox condition of the interstitial water during early diagenesis (e.g. Isozaki, 1997; Sato et al., 2011; Thurston, 1972). An anoxic water column and/or an elevated flux of organic matter could have caused the reducing condition during the consolidation of the deep-sea sedimentary rocks. If the sedimentary rocks have not undergone secondary high-grade metamorphism or alteration, the redox condition of the deep-sea

Fig. 3. Outcrop photo and annotated sketch of the sub-vertical outcrop (ca. 8 m height by 20 m width) of OPS with black mudstone at Porth Felen, Lleyn Peninsula, Wales. Note that the OPS is imbricated by many layer-parallel thrusts and duplex structures. The outcrop can be divided into sub-horses A and B by a layer-parallel thrust in the middle of the outcrop; the lower one (A) consists of basalt continuously overlain by dolostone and black mudstone; the upper one (B) is siliceous mudstone and sandstone/mudstone. Short stratigraphic columns (A-1 ~ 11 and B-1 ~ 11) are united into the composite OPS (Fig. 4) by schematically sliding them on layer-parallel thrusts.
water at the time of deposition is approximately and reliably indicated by the iron species. In the classic studies of Mössbauer spectroscopy of deep-sea cherts (Kubo et al., 1996; Matsuo et al., 2003; Sato et al., 2009, 2011, 2012), the iron minerals in pelagic cherts from ACs were used as a proxy for the palaeo-deep-sea environment. These studies determined the redox potential of the Fe(III)/Fe(II) transition (Berner, 1981) for the threshold between “oxidizing” and “reducing” conditions, which describes the redox potentials higher than and lower than that of the Fe(III)/Fe(II) transition, respectively.

It is noteworthy that the ratio of FeHR/FeT is not an absolute indicator of the oxic/anoxic condition. The proxy was not specifically in pelagic deep-sea sedimentary rocks, but in black shales deposited in the Black Sea and epicontinental basins (Raiswell and Canfield, 1998). It is questionable that the empirical threshold of FeHR/FeT (~0.38) can be influenced by an influx of terrigenous material. Bearing this in mind, the Mössbauer analysis of deep-sea sedimentary rocks is a simple and reliable method to determine oxidizing/reducing conditions.

In this study, we utilized black mudstones and red-bedded claystones, instead of pelagic deep-sea cherts. The Ediacaran ocean floor sedimentary rocks in Anglesey and Lleyn include red-bedded cherts (Maruyama et al., 2010), but they do not contain radiolaria as in Phanerozoic OPS, possibly owing to the lack of silica-secreting plankton such as radiolaria in the Ediacaran ocean. The black mudstones at Porth Felen have siliceous layers as shown in the stratigraphic column (Fig. 4), although the amount of SiO2 is much less than that in Phanerozoic cherts. The oldest known

![Figure 4](image)

**Fig. 4.** Stratigraphic column of reconstructed OPS at Porth Felen, Lleyn; composed of pillow basalt, dolostone, black mudstone, siliceous mudstone, and sandstone/mudstone in ascending order. The youngest detrital zircon age of sandstone in the OPS (*) is 526 ± 14 Ma (Asanuma et al., 2015). The 5 m-thick black mudstone is divisible into 4 subunits. (i) Black mudstone with thin pyritic layers (0.8 m), (ii) an alternation of black mudstone and gray/dark grey siliceous mudstone (2.4 m), (iii) thinly-laminated dark gray shale (1 m), and (iv) jet-black mudstone with thin pyritic layers (1 m).
Radiolarian fossils are in earliest Cambrian strata in South China (Braun et al., 2007). However, the red-bedded claystones and black mudstones in the Ediacaran OPS occupy exactly the same stratigraphic position as the red-bedded cherts and gray-black cherts in Phanerozoic OPS, and their constituent iron minerals are likewise used as a proxy for their paleo-deep sea environment.

When considering a paleo-redox environment, it is necessary to pay attention to the difference between jasper and bedded chert. The British Geological Survey map of Anglesey of Greenly (1919) shows many outcrops of ‘jasper’; over 40 localities alone in Anglesey. Some of these are not hydrothermal jasper in modern terminology, but red-bedded chert that overlies pillow basalt. Bedded chert and jasper have different meanings in the modern reconstruction of a paleo-environment. Bedded cherts are deposited on an open-ocean floor and they have a long sedimentation time, whereas jaspers are precipitated on MORB and are associated with hydrothermal activity. The iron redox of bedded

Fig. 5. Black mudstone in the OPS at Porth Felen, SW Lleyn Peninsula. A. outcrop; B. polished slab; C. thin section view; and D. microscopic image of frambooidal pyrite. Note that the black mudstone is thinly laminated and contains pyrite, suggesting a reducing depositional condition.

Fig. 6. Red bedded claystone in the OPS at Braich, SW Lleyn Peninsula. A. outcrop; B. close-up view of the outcrop (alternation of siliceous and argillaceous layers); C. polished slab; and D. thin section view.
chert represents a more global deep-sea environment than jasper. The two sedimentary rocks can be easily distinguished; bedded cherts are rhythmically bedded, whereas jaspers tend to be massive, and occur in inter-pillows or over-pillows. Moreover, sedimentological textures (thin-lamination) and color (smoky purplish red or vivid red) can be used to distinguish bedded chert from jasper, respectively.

The present results suggest that the black mudstones from Porth Felen (late Ediacaran; ca. 560–542 Ma) were deposited on a reducing pelagic deep-sea floor.

6.2. Redox of the Ediacaran deep ocean

Using present and previously-published Mössbauer analyses, Fig. 8 shows the secular changes in relative pelagic deep-sea redox conditions with time in Lleyn and Anglesey. The preliminary data in Sato et al. (2009) support the idea that oxidizing conditions in the pelagic deep ocean persisted throughout the Phanerozoic except for some extreme anoxic events, such as the P-T boundary Superanoxia (Isozaki, 1997; Matsuo et al., 2003) and the Toarcian oceanic anoxic event in the Jurassic (Hori, 1993; Sato et al., 2012). Previous studies of Neoproterozoic ocean redox conditions (e.g. Canfield et al., 2007; Canfield et al., 2008; Och and Shields-Zhou, 2012) suggested a gradual oxidation during the Ediacaran before the appearance of the Ediacaran Biota in epicontinental basin sedimentary rocks. However, in this study we report the first direct or specific evidence for a reducing pelagic deep-ocean in the late Ediacaran. Although the depositional age of the Neoproterozoic cherts at Llanddwyin in Anglesey Island is still uncertain due to lack of index fossils or zircon ages, the deep ocean was already oxygenated enough for the deposition of hematite in the latest Neoproterozoic (>560 Ma). The deep-sea redox conditions during the Ediacaran are estimated in Fig. 8.

The Neoproterozoic Oxidation Event (NOE) may have triggered the evolution of multicellular animals, because aerobic respiration became possible after the rise of oxygen during the NOE (e.g. Canfield et al., 2007; Och and Shields-Zhou, 2012; Runnegar, 1982). The black mudstones in the Lleyn Peninsula probably represent Ediacaran deep-sea anoxia. The data of this study suggest that the anoxic pelagic deep-sea condition had survived until the end of the Ediacaran at the latest. In the Neoproterozoic deep-ocean, redox condition may have been fluctuated, which contrasts with the traditional view of unidirectional oxidation. Further study of the deep-sea sedimentary rocks in Lleyn and Anglesey is warranted to document diagnostic deep-sea signals in the OPS of this subduction-accretion complex.

7. Conclusions

Our stratigraphic-structural reconstruction of the imbricated OPS demonstrates that the 5 m-thick black mudstones at Porth Felen are the first direct or specific evidence for an Ediacaran pelagic deep-sea anoxia. The $^{57}$Fe Mössbauer spectroscopy defined the iron species in the black mudstones and red claystones, and confirmed that deep-sea anoxic conditions existed in the late Ediacaran. Previous studies have suggested that a gradual change from an anoxic to an oxic ocean condition occurred after the Gaskiers glaciation but based only on epicontinental marginal basin sedimentary rocks. In this study, we propose that the Neoproterozoic deep-ocean turned from anoxic to oxic in the period 564–542 Ma based on pelagic deep-sea sedimentary rocks. The Ediacaran deep-sea anoxia likely existed after the Gaskiers glaciation.

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Table 1
Mössbauer parameters (I.S.; isomer shift, Q.S.; quadrupole splitting, and Hi; inner magnetic field) of black mudstones (LLY489, 494, 500) from Porth Felen and red claystones (LLY326, 359) from Braich in the Lleyn Peninsula, Wales. Rock type of each sample is described with a color index.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Locality</th>
<th>Rock type (color)</th>
<th>Species</th>
<th>Area (%)</th>
<th>I.S. (mm/s)</th>
<th>Q.S. (mm/s)</th>
<th>Hi (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLY500</td>
<td>Porth Felen</td>
<td>dark gray mudstone</td>
<td>pyrite</td>
<td>15.0 ± 0.1</td>
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<td>0.60 ± 0.01</td>
<td>2.64 ± 0.00</td>
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<td>LLY494</td>
<td>Porth Felen</td>
<td>dark gray mudstone (N3)</td>
<td>Fe2+ (h.s., outer)</td>
<td>85.0 ± 0.1</td>
<td>1.13 ± 0.00</td>
<td>2.64 ± 0.00</td>
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</tr>
<tr>
<td>LLY489</td>
<td>Porth Felen</td>
<td>gray mudstone (SPB 5/2)</td>
<td>pyrite</td>
<td>28.3 ± 0.4</td>
<td>0.32 ± 0.00</td>
<td>0.64 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>LLY539</td>
<td>Braich</td>
<td>red siliceous mudstone (5R 4/6)</td>
<td>hematite</td>
<td>86.2 ± 0.3</td>
<td>0.37 ± 0.00</td>
<td>−0.21 ± 0.00</td>
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</tr>
<tr>
<td>LLY326</td>
<td>Braich</td>
<td>red siliceous mudstone (5R 4/6)</td>
<td>hematite</td>
<td>81.4 ± 0.4</td>
<td>0.37 ± 0.00</td>
<td>−0.21 ± 0.00</td>
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</tbody>
</table>

Fig. 8. Reconstructed OPS in Lleyn (Porth Felen and Braich) and Anglesey (Llanddwyn), with estimated ocean-water redox conditions through the Cryogenian to the early Cambrian in pelagic deep-sea compared with epicontinental surface/deep oceans (modified from Canfield et al., 2008; Lyons et al., 2014; Lenton et al., 2014). The age data in each OPS are from Asanuma et al. (2015). Newly obtained redox data from Lleyn show that the eventual change from a Precambrian reducing deep ocean to a Phanerozoic oxidizing deep ocean likely occurred during the late Ediacaran (between 564–542 Ma).

References