Coupled molybdenum, iron and uranium stable isotopes as oceanic paleoredox proxies during the Paleoproterozoic Shunga Event

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A B S T R A C T

The Paleoproterozoic Era was a time of remarkable importance in the redox evolution of Earth’s atmosphere and oceans. Here, we present a multi-proxy study of Mo, U and Fe isotopes together with Fe speciation of black shales and siltstones from the upper Zaonega Formation of the Onega Basin in Karelia. We attempt to better understand oceanic redox conditions during the 2.05 Ga Shunga Event as the next step following the Great Oxidation Event (GOE) and the Lomagundi carbon isotopic excursion Event. A cautious examination of the Fe speciation data shows that the studied section was deposited under dominantly euxinic conditions (anoxic and sulfidic) and that the lower part of the section experienced metamorphism through which pyrite was altered to pyrrhotite. During this episode, the system was closed with respect to Fe but not sulfur. The Mo and U isotopic compositions (corrected for detrital input) were not affected by the metamorphism and loss of S and are fairly uniform throughout the entire section. The Fe isotopic compositions are exceptionally heavy in the lower part of the section (up to δ56FeIRMM-14 = 0.83‰) and become lighter towards the upper intervals, which also show significant [Mo] and [U] enrichments. We suggest that this pattern reflects changes in the position of the deposition site relative to the redox structure of the water column. The upper part was deposited within a locally euxinic portion of the basin where H2S availability was highest, removal of Mo and U was more efficient and precipitated pyrite captured relatively non-fractionated dissolved Fe. In other words, quantitative uptake of Fe was favored. In contrast, the lower interval was deposited on the lower margin of a euxinic wedge where H2S availability was lower, and removal of Mo and U was less efficient. Pyrite precipitation in this part of the water column reflected a more fractionated dissolved Fe reservoir due to more protracted, non-quantitative Fe uptake because of less efficient pyrite formation under lower sulfide conditions and greater access to the large oceanic pool of Fe. The U isotopic signal was corrected for detrital contribution giving compositions similar to the riverine input and suggesting that co-precipitation into carbonates was the main process of U removal at this time. We estimate the Mo isotope composition of the contemporaneous ocean to be $^{108}$Mo $\Delta$O = 0.85 ± 0.21‰. This is the lowest value yet reported for the Proterozoic ocean, suggesting that the oceanic Mo cycle was dominated by euxinic and anoxic sinks with negligible Mo removal into oxic environments. Recent studies have proposed a sharp increase in ocean–atmosphere oxygen levels during the Lomagundi Event followed by a dramatic crash. Our results from black shales of the 2.05 Ga Shunga Event are consistent with a post-Lomagundi decrease in biogenic oxygen levels.

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1. Introduction

The “Great Oxidation Event” (GOE) in the Paleoproterozoic was one of the most significant events in Earth history (Holland, 2006). At that time, atmospheric oxygen levels rose from Archean values of ca. $10^{-5}$ times the present atmospheric level (PAL) to mid-late Proterozoic values of ca. $10^{-2}$ to $10^{-1}$ PAL (Pavlov and Kasting, 2002). This event had a remarkable effect on Earth surface biogeochemical cycles through the initiation of oxidative weathering, shifts in ocean chemistry and a boosting of redox gradients and thus microbial metabolism on a global scale. The recognition that substantial Mass Independent Fractionation (MIF) of sulfur isotopes is restricted to the time interval before ~2.3 Ga argues for an anoxic atmosphere at that time (Farquhar, 2000; Pavlov...
and Kasting, 2002; Mojzsis et al., 2003; Ono et al., 2003; Bekker et al., 2004; Farquhar et al., 2007). “False-starts” in biospheric oxygenation, referred to as “whiffs” of atmospheric oxygen (Anbar et al., 2007) may have occurred one or more times during the latest Archean, although evidences are currently disputed (Kirschvink et al., 2012). These presumably transient increases in oxygen are reflected in enrichments in the redox-sensitive elements molybdenum and rhenium in marine shales and a reduction in the extent of MIF precisely coincident with the peak in Mo and FeS2 enrichment (Anbar et al., 2007; Kaufman et al., 2007; Reinhard et al., 2009; Kendall et al., 2010). The interval between 2.45 Ga and 2.0 Ga (the early Paleoproterozoic) was a period of transition and dramatic environmental change, with evidence for widespread glaciation (Evans et al., 1997; Kirschvink et al., 2000), the first appearance of red beds, giant Mn deposits (e.g., the Hotazel Formation) and the disappearance of detrital grains of pyrite and uraninite consistent with the onset of an oxidative weathering environment (Holland, 1994; Farquhar and Johnston, 2008). Banded iron formations, which were frequent and voluminous in the Archean, largely disappeared during the early Paleoproterozoic (2.3–2.0 Ga), despite later reappearance at ~1.9 Ga due to enhanced global volcanism (Condie, 2001; Rasmussen et al., 2012). A significant increase in mass-dependent Si isotopic fractionation and decrease in Fe isotopic fractionation in sedimentary pyrite after ~2.32 Ga (Bekker et al., 2004; Canfield, 2005; Rouxel et al., 2005), and the first appearance of sedimentary sulfate evaporates (Reuschel et al., 2012) likely reflect an increase of seawater sulfate concentrations by that time. The ocean redox state in the aftermath of the rise of atmospheric oxygen remains poorly constrained and various models ranging fromoxic (Holland, 1984), to euxinic (Canfield, 1998), and to suboxic (Slack et al., 2007) have been proposed, and recent work hypothesizes a redox structure characterized by pervasive anoxia within the deep sea and dynamic regions of euxinia along productive ocean margins (e.g., Poulton et al., 2010; Planavsky et al., 2011; Reinhard et al., 2013a). However, the temporal dynamics and cause-and-effect relationships among the various transitions in the surface environment in the wake of the GOE and the Logamundi Event remain poorly known.

The Logamundi–Jatuli Event—the largest carbon isotope excursion in Earth’s history (2.3–2.1 Ga)—is associated with global burial of organic matter and release of oxygen to the atmosphere (Melezhik et al., 1999a,b). Bekker et al. (2008) showed that in contrast to the Late Neoproterozoic and Phanerzoic, mechanisms of carbon fractionation were different in the Paleoproterozoic redox-stratified ocean, and the signal of primary productivity below the redoxcline was overprinted. This relationship complicates the reconstruction of spatial patterns and secular trends in the δ13C values of dissolved inorganic carbon in Paleoproterozoic seawater.

We have studied the Shunga Event sequence from the Onega Basin, which directly follows the Logamundi–Jatuli Event and, somewhat paradoxically in the face of decreasing δ13C values, shows remarkable organic carbon accumulation and the first sedimentary phosphorite accumulation (Melezhik et al., 2005). The Shunga Event is part of the stratigraphic section of the Onega Basin which was deposited in regional platformal sequence, where similar sediments are found also in the Franciscan Group in Gabon (Melezhik et al., 2004; and references within). Together, these observations suggest that the studied section of the Shunga Event can provide insight into the open Paleoproterozoic ocean and associated global phenomena. The Shunga Event, well-known for its huge volume of Paleoproterozoic Corg-rich sediments (up to 99% C), represents a giant petrifed oil field, including petroleum source rock, joint-trapped metamorphosed oil, veins of migrated petroleum, redeposited subaerial oil spills and organo-silicicous substances forming diapirs (Melezhik et al., 2004). The Zaonega Formation from the Onega Basin is composed mainly of organic-rich shale, organo-silicicous rocks and mafic lavas and gabbro sills, and it also contains a petrifed oil reservoir. Kump et al. (2011) observed a negative δ13C excursion during the Shunga Event, which was considered to represent intense oxidative weathering of rocks as the result of the initial establishment of an oxygen-rich atmosphere. The studies of Ovchinnikova et al. (2007) and Puchtel et al. (1998, 1999) constrained the age of the Zaonega Formation to be ca. 2.06 Ga.

Here, we aim to document the sequence of environmental changes associated with the Shunga Event by analysis of drill core from Fennoscandia, so that we may evaluate the following hypotheses:

1. The evolution of the oceanic sulfur cycle through the Paleoproterozoic was such that by the time of the Shunga event (ca. 2000 Ma) it could support exceptionally widespread euxinic conditions in the marine realm.

2. Oxidative continental weathering was important in setting up the sulfate and metal oxynion inventories of seawater (e.g., U and Mo) in the aftermath of the GOE and during the Logamundi Event.

We present here Fe speciation; Mo abundance; and Fe, U and Mo isotopes data recorded in Paleoproterozoic sulfidic shales from the Fennoscandian Shield and now available in the FAR-DEEP drillcores. The FAR-DEEP project (Fennoscandian Arctic Russia—Drilling Early Earth Project) was initiated in the frame of the International Continental Drilling Program (ICDP) (Melezhik et al., 2013). About 3650 m of drill core were recovered and logged from the early Paleoproterozoic of Arctic Russia during the summer and fall of 2007 and represent a critical window into the tempo and mode of early Earth oxygenation.

2. The Fe, Mo and U proxies

2.1. Molybdenum in the ocean—sources, sinks and fluxes

The Mo isotopic system has drawn considerable attention in the past decade as a way to better understand the ocean redox structure of modern and ancient oceans (McManus et al., 2002; Arnold et al., 2004; Nägler et al., 2005; Siebert et al., 2005; Poulsen et al., 2006; Siebert et al., 2006; Wille et al., 2007; Archer and Vance, 2008; Dahl et al., 2008; Neubert et al., 2008; Pearce et al., 2008; Kendall et al., 2009; Dahl et al., 2012; Duan et al., 2010a,b; Kendall et al., 2011; Nägler et al., 2011; Wen et al., 2011). Many of the above studies have focused on the authigenic record of Mo isotopes in black shales, trying to establish linkages between the evolution of oxygen in the atmosphere and the sources and sinks of Mo in the ocean. These studies are based on (1) the principle that the Mo isotopic composition of sea water is a function of the balance between the different Mo sedimentary sinks in the ocean, and (2) that the Mo isotope composition of contemporaneous ocean can be reconstructed directly from euxinic sediments, as there is often no net fractionation during Mo removal to such sediments (e.g., Anbar and Rouxel, 2007; Gordon et al., 2009). Therefore, in order to make a reliable use of Mo as a paleoredox proxy, it is first essential to show that the removal of Mo was quantitative. We may achieve that by demonstrating euxinia in the site of depositions using other geochemical tools (e.g., Fe speciation and Mo concentrations). Nonetheless, we must keep in mind that even under strongly euxinic conditions Mo removal may not be quantitative (e.g., Helz et al., 2011), resulting in significant Mo isotope fractionation. Therefore, the inferred Mo isotope composition of seawater should be used cautiously when reconstructing the oceanic Mo budget, which in turn can reflect the global oceanic redox state (i.e., Mo sinks) and atmospheric oxygen levels (Anbar, 2004; Gordon et al., 2009; Lyons et al., 2009).

The oceanic Mo cycle is dominated by two sources—rivers and hydrothermal fluids—and three sinks defined by the redox conditions at the site of deposition in the ocean: euxinic, oxic and suboxic (Berner, 1981). For the Mo isotope system, suboxic and anoxic conditions are lumped together (see Table 1). The common theme for both is that sulfide is limited to the pore fluids, and only euxinic sites, by definition, have free sulfide in the water column. Riverine Mo input constitutes at least 90% of the total modern Mo input to the oceans, with a small flux possibly tied to hydrothermal fluids (McManus et al., 2002). Archer
and Vance (2008) analyzed various modern rivers and showed a range of δ⁹⁸⁄⁹⁵Mo values between 0.2 and 2.3‰ and an average of δ⁹⁸Mo = 0.7‰, which is similar to the values reported by Pearce et al. (2010) and Neubert et al. (2011). However, on long time scales we expect rivers to represent the average crustal value, which is probably lower and in the range of ca. −0.1 to 0.4‰ (Barling et al., 2001; Siebert et al., 2003). The hydrothermal input may constitute as much as 10% of the total Mo input to the ocean, and its isotope composition is currently poorly constrained. McManus et al. (2002) measured a value of δ⁹⁸Mo = 0.8‰ for low-temperature ridge flank springs, though these authors acknowledged that much of this Mo may be coming from suboxic diagenesis in sediments along the fluid flow path. Pearce et al. (2010) measured a value of δ⁹⁸Mo = −3.4‰ for terrestrial hydrothermal spring waters. In any case, as a first approximation, it can be considered that the total oceanic Mo input, including riverine and hydrothermal fluids together, is about δ⁹⁸Moinput = 0.5 ± 0.2‰, although this issue may need to be revisited as the Mo isotope systematic in rivers and hydrothermal systems and their relative Mo contributions to seawater become better understood. In the modern ocean Mo is found primarily as the non-reactive molybdate ion (MoO₄²⁻) with the average seawater concentration of 100 nM and an oceanic residence time of ca. 700,000 yr. Under euxinic conditions, where [H₂S] ≥ 11 µM and [O₂] ≈ 0 µM, the molybdate ion is converted through adsorption to Fe-oxide minerals in the following general reaction (Erickson and Helz, 2000; Siebert et al., 2003):

\[
4H₂S + MoO₄²⁻ \leftrightarrow Me(MoO₄²⁻)(H₂O)ₙ⁻ + H₂O
\]

Where Me stands for the metal-oxide surface. Mo isotope fractionation in these environments will vary with different phases and conditions, and Δ²⁶⁹Mo(Seawater-Sediment) ranges from approximately 0.8 to 2.2‰ (Goldberg et al., 2009) with typical values of ca. 1‰. Goldberg et al. (2009) also argued that during early diagenesis processes of Mo release due to reduction of Fe-(oxyhydr)oxides, augmentation by drawdown of seawater, and finally sequestration, may affect the isotopic composition of the sediment.

### 2.2. Uranium in the oceans—sources, sinks and fluxes

In the modern oceanic uranium, uranium occurs mainly in the highly soluble U⁴⁺ oxidation state, dominantly in the form of the uranyl carbonate ion UO₂⁻(CO₃)₂⁻⁻ (Djogic et al., 1986). Uranium is conservative, meaning its concentration varies linearly with salinity (Ku et al., 1977; Robinson et al., 2004). In seawater with an average salinity of 3.5 g/L, the U concentration is 13.8 ± 0.3 nmoL/L. This concentration should be homogeneous for a salinity-normalized ocean since the U mean residence time (~400 kyr) is much larger than the global ocean mixing time, determined as 1–2 kyr by ¹⁴C reservoir ages (Ku et al., 1977; Chen et al., 1986). The latest estimates of the U budget in the modern ocean (Morford and Emerson, 1999; Dunk et al., 2002; Henderson, 2003) agree within uncertainties and describe three main sinks, which represent roughly similar total removal rates of U: biogenic carbonates, anoxic sediments and suboxic sediments. It should be noted that hydrothermally altered oceanic crust represents a fourth sink of secondary importance, whose contribution to the oceanic budget is not well constrained.

Modern seawater has a U isotope composition of δ²³⁴U ≈ −0.38 ± 0.03‰ (relative to CRM112a) (Stirling et al., 2007; Weyer et al., 2008; Tissot and Dauphas, 2011). The modern riverine input has a δ²³⁴U value of about −0.22 ± 0.05‰ (Stirling et al., 2007), while continental crust (i.e., granites and basalts) has a δ²³⁴U of about −0.28 ± 0.03‰ (Telus et al., 2012; Tissot and Dauphas, 2012). Isotopic fractionation associated with U incorporation in the three main U sinks described above is detailed in Table 1. From the limited available data (Noordmann et al., 2009, 2012) it seems that the processes of U weathering from continental crust, transport to the oceans, and re-deposition as well as removal into hydrothermally altered oceanic crust, are accompanied by relatively small isotopic fractionation.

The process of U removal from the seawater occurs in three steps: (1) transport of U to the sediment/water interface; (2) diffusion to porewater and reduction of U in the porewater column; and (3) sorption or precipitation (Anderson et al., 1989). The main source of U to the sediment/water interface is dissolved U⁴⁺ but U can also be taken up in plankton, sorbed to organic matter, concentrated in calcareous and siliceous tests, or adsorbed and/or co-precipitated with Fe/Mn oxides and transported to the sediment/water interface (Langmuir, 1978; Cochran, 1992; Barnes and Cochran, 1993). At the sediment/water interface, U delivered from the water column can be released via reduction of...
Fe–Mn oxides (Barnes and Cochran, 1993), or from the decomposition of organic matter (20% or less of the flux in porewater (Klinkhammer and Palmer, 1991)), U then diffuses into the porewater, where reduction and removal of U, which is mainly coupled to oxidation of Fe, occurs at about the depth of Fe remineralization or below (Cochran, 1992; Morford and Emerson, 1999). The initial reduction is thought to occur as amorphous UO₂(OH), which later transform to uraninite UO₂(s) (Langmuir, 1978).

Depending on the redox environment, reduction of soluble U⁴⁺ into insoluble U⁰ is accompanied by different fractionation factors and can occur through a variety of reactions. These reactions include abiotic reduction, coupled or not to adsorption onoxic hydroxide and microbially mediated reduction (see Appendix 1).

Sediments deposited under anoxic ( euxinic/ferruginous) conditions show heavier isotopic compositions than seawater by 0.44 to 0.80‰, with an average Δ²³⁸/²³⁵U (Suboxic) ≈ −0.5‰. Sediments deposited in suboxic condition show δ²³⁸U of −0.29 ± 0.08‰ equivalent to Δ²³⁸/²³⁵U (Suboxic) ≈ −1.3‰ (Weyer et al., 2008). In oxic environments U can be removed from the water column through adsorption onto Mn-nodules or during precipitation of banded Iron Formations (BIFs) in the ancient ocean. Adsorption experiments as well as measurements of ²³⁸U/²³⁵U ratios in Mn-oxhydroxides point to an associated fractionation factor of Δ²³⁸/²³⁵U (Adsorption) ≈ 0.2‰ (Stirling et al., 2007; Weyer et al., 2008; Brennecka et al., 2011), while the fractionation associated with BIF deposition is poorly constrained due to the limited and highly scattered data available (Weyer et al., 2008). The Mn-nodule and BIF sinks are negligible in the modern ocean. However, in anoxic ancient oceans, deposition of BIFs occurred on short timescales in localized, oxygen-rich waters. The process of BIF deposition is still a matter of debate, and their role in the U budget in the ancient ocean remains unknown. At present, BIFs have not been studied enough to reveal their role in the U geochemical cycle, and so it is important to keep in mind that BIFs represent a source of uncertainty in the U mass balance.

The last main fate for U in the modern ocean is co-precipitation into carbonates. In oxic environments, soluble U⁴⁺ is preferentially incorporated and sequestered in aragonite over calcite with [U]aragonite ≈ 10 × [U]calcite (Qafoku and Icenhower, 2008; Weyer et al., 2008). Incorporation and long-term sequestration of U⁴⁺ into calcite was at one time a matter of debate but has recently been documented in natural settings (Kelly et al., 2003, 2006, 2007), thus validating U-related dating of calcite formed in oxic environments. However, sequestration of U in carbonates is not restricted to oxic environments, and the substitution of insoluble tetravalent uranium (U⁴⁺) for divalent calcium (Ca²⁺) in calcite deposited under anoxic conditions explains the otherwise anomalously high concentration of U in these deposits (Israelson et al., 1996; Sturchio, 1998). Other mechanisms of U sequestration into carbonates have been proposed (e.g., sorption, adsorption) but are somewhat reversible and probably do not play an important role in the long-term oceanic budget for U (see Qafoku and Icenhower (2008) and reference therein for more information). The overall U burial rate in carbonates in the modern ocean is estimated to be 334 mg/cm²·kyr. The co-precipitation/substitution of U in carbonates is not accompanied by significant U isotope fractionation as δ²³⁸U/Carbonate ≈ −0.44 ± 0.06‰ (Stirling et al., 2007; Weyer et al., 2008; Brennecka et al., 2011).

Theory and experiments explain U isotope variations during U reduction as a result of mass-independent, volume-dependent fractionation mechanism called Nuclear Field Shift, which states that differences in nuclear charge radius associated with the number of neutrons shifts the atomic energy levels of the isotopes (Fujii et al., 1989; Bigeleisen, 1996; Schauble, 2007; Abe et al., 2008). This translates into a preferential incorporation of ²³⁸U into the reduced species U⁰. A second mechanism, fractionating U towards lighter δ²³⁸U, has been shown to take place during adsorption of U onto Mn-oxhydroxide (Brennecka et al., 2011). In this case, fractionation is thought to be due to a difference in the U–O coordination shell between dissolved and adsorbed U.

The potential of the ²³⁵U/²³⁸U system as a paleoredox tracer has been explored in three recent studies (Kendall et al., 2013–in this issue; Montoya-Pino et al., 2010; Brennecka et al., 2011). Kendall et al. (2013–in this issue) found a co-occurrence heavy δ²³⁸U values and authigenic enrichments of Re and Mo but not U in late Archean shales. Such elemental enrichment pattern suggests atmospheric oxygen levels sufficient for oxidative weathering of Re and Mo but too low to mobilize U, a conclusion consistent with a model of local pulses in the production of O₂ by photosynthesis (Sverjensky and Lee, 2010). However, the preservation of a heavy δ²³⁸U signature in the sediments implies the presence of small amount of dissolved U in the deep waters. Kendall et al. (2013–in this issue) proposed local submarine oxidative weathering within anoxic oasis as the source of dissolved U. Montoya-Pino et al. (2010) investigated the extent of marine anoxia by looking at black shales deposited during and after the mid-Cretaceous Cenomanian–Turonian Oceanic Anoxic Event (OAE). They speculated that the ocean prior to the OAE was slightly less oxic compared to today’s ocean and that the Cenomanian–Turonian OAE corresponds to a threefold increase of oceanic anoxia relative to the present day. A similar method was applied to Late Permian and Early Triassic carbonate rocks by Brennecka et al. (2011), who interpreted a global shift to lower ²³⁵U/²³⁸U ratios in the rock record as a consequence of increased anoxia in the ocean just before the end-Permian mass extinction.

2.3. Fe speciation and isotopes

The distribution and systematics of Fe within ancient sedimentary rocks can provide crucial information about the local redox of a depositional environment (reviewed in Lyons and Severmann, 2006; Raiswell and Canfield, 2012; and Reinhard et al., 2013b). Although such information is useful in its own right, an understanding of depositional redox chemistry is essential if we wish to use Mo isotopes as an oceanic paleoredox proxy and specifically to address extents of euxinia on ocean scales (Arnold et al., 2004; Gordon et al., 2009). In this approach, different Fe mineral phases are separated by means of a well-calibrated sequential extraction scheme described briefly in the methodology and in detail elsewhere (Raiswell et al., 1994; Raiswell and Canfield, 1998; Poulton et al., 2004; Poulton and Canfield, 2005; Reinhard et al., 2009).

We focus here on highly reactive iron (FeHR), a pool of Fe that is biogeochemically labile and reactive to dissolved S²⁻ species on depositional and early diagenetic (burial) timescales (e.g., Raiswell and Canfield, 1998). In addition to the Fe sulfide pool (Fe₄s), Fe₄s also includes a number of ferrous carbonates (e.g., siderite, FeO(OH), ankerite, Ca₆(Fe,Mg,Mn)(CO₃)₂), crystalline ferric oxides (hematite, Fe₂O₃; goethite, FeOOH) and the mixed valence Fe oxides magnetite (Fe₃O₄). By the conventional interpretation, a ratio of Fe₄s to total Fe (Fe₄ TOTAL) that is well in excess of detrital background levels represents authigenic enrichment in a system that was anoxic and reducing with respect to Fe (Canfield et al., 1996; Lyons, 1997; Raiswell and Canfield, 1998; Wijisman et al., 2001). Values for Fe₄s/Fe₄ TOTAL in anoxic environments are commonly greater than 0.38, well above values for oxic siliciclastic marine sediments from modern (Fe₄s/Fe₄ TOTAL = 0.26 ± 0.08) and Phanerozoic (Fe₄s/Fe₄ TOTAL = 0.14 ± 0.08) systems (Raiswell and Canfield, 1998; Poulton, 2002; Raiswell et al., 2008).

We can further distinguish anoxic environments buffered by dissolved Fe³⁺ (termed “ferruginous”) from anoxic environments buffered by dissolved S²⁻ species (termed “euxinic”) by examining the extent to which biogeochemically labile Fe has been converted to sulfide minerals, a consequence of the very low solubility of Fe–S phases. Fe₄s-enriched systems in which the majority of reactive Fe has been converted to pyrite Fe (Fe₄py) are operationally defined by values of Fe₄py/Fe₄ TOTAL in excess of 0.7–0.8 (e.g., Poulton and Canfield, 2011) and are diagnostic of euxinic water columns. Importantly, it is these sulfidic systems in particular that can serve as a repository for the Mo isotope composition of contemporaneous seawater.
Stimulated by the potential to use Fe isotopes as a biosignature and as a tracer of the redox state of ancient oceans, studies of the Fe isotope composition of laminated organic-rich sediments and sedimentary sulfide shales attracted great interest in recent years (Matthews et al., 2004; Rouxel et al., 2005; Yamaguchi et al., 2005; Archer and Vance, 2006; Jenkyns et al., 2007; Duan et al., 2010a,b; Fehr et al., 2010; Guilbaud et al., 2011). Microbiological experiments have shown that significant Fe isotope fractionations occur during dissimilatory Fe(III) reduction (e.g., Beard et al., 2003a,b; Icopini et al., 2004; Johnson and Beard, 2005; Crosby et al., 2007) but also during anaerobic photosynthetic Fe(II) oxidation (Croal et al., 2004). Fe isotopes can be also fractionated by abiotic Fe(II) oxidation and precipitation of ferric hydroxides (Bullen et al., 2001; Balci et al., 2006) and by sorption of aqueous Fe(II) onto ferric hydroxides. The largest equilibrium isotope fractionation (−3‰) is observed and theoretically calculated between coexisting Fe(III) and Fe(II) aqueous species (Johnson et al., 2002; Welch et al., 2003). It should be noted that significant kinetic Fe isotope fractionations are involved in non-redox processes such as inorganic mineral precipitation of Fe-oxides (Skulan et al., 2002) and sulfides (Butler et al., 2005; Guilbaud et al., 2011). The difficulty of clearly identifying biotic versus abiotic processes of Fe isotope fractionation has been the subject of intense debate in recent years (e.g., Beard, 1999; Anbar et al., 2000; Bullen et al., 2001; Rouxel et al., 2005; Guilbaud et al., 2011).

Lithogenic sources of Fe on the modern oxygenated Earth have similar Fe isotope compositions to that of bulk silicate Earth (Beard et al., 2003a,b). In contrast, marked variations in Fe isotope composition have been reported in organic-rich sediments, especially in Precambrian black shales and sedimentary pyrites ~2.3 Ga old. Although several interpretations of the Fe isotope record in black shales have been proposed (Rouxel et al., 2005; Archer and Vance, 2006; Rouxel, 2006; Severmann et al., 2008; Guilbaud et al., 2011), there is a general consensus that the shift from high δ56Fe variability in >2.3 Ga black shales to little variability ~1.8 Ga reflects redox-related changes in the global oceanic Fe cycle. Subsequent studies have all confirmed that the iron cycle before 1.8 to 2.3 billion years ago was different from that of today and reflected the rise of atmospheric oxygen and the subsequent moderate atmospheric oxygen levels in the Paleoproterozoic (Bekker and Kaufman, 2007; Planavsky et al., 2012b). Regarding the processes leading to Fe isotope variations in sedimentary pyrite, it appears that Fe isotopes are particularly sensitive to the concentrations of dissolved Fe(II) and H2S (i.e., the sizes of the seawater Fe and sulfate reservoirs) and can be used to constrain the sources and sinks of the Fe(II) reservoir in past oceans.

In cases where oxidation and/or precipitation of aqueous iron is quantitative the isotopic composition of the sediment will directly reflect that of the source solution (e.g., sea water). If the process is not complete, the mass balance between the phases and the precipitation model should be considered (i.e., Rayleigh vs. equilibrium fractionation). This difference is particularly relevant in sediments that record the redox evolution of the oceans and atmosphere and to specific redox events such as the GOE. Rouxel et al. (2005) showed that the Fe isotope composition of marine sediments over geological time divides Earth’s history into three stages that are strikingly similar to the stages defined by the Δ34S and Δ33S records. Highly variable and negative δ56Fe values in pyrites before ~2.32 Ga were interpreted to reflect reservoir effects in dissolved oceanic Fe across an iron chemocline resulting from the removal of isotopically heavy Fe during oxidative precipitation. Similarly, the positive δ56Fe values of pyrites between 1.8 and 2.3 Ga are attributed to the development of a discrete redoxcline and diminishing reservoir effects. After 1.8 Ga, the near-complete scavenging of dissolved Fe by the reaction with dissolved oxygen or biogenic H2S to form Fe oxide and sulfide minerals, respectively, has limited the extent of Fe isotope variability in sediments (Rouxel et al., 2005; Anbar and Rouxel, 2007; Planavsky et al., 2012b).

2.4. Samples

Our samples were collected from Hole 13A of the Fennoscandia Arctic Russia—Drilling Early Earth Project (FAR-DEEP) with support of the International Continental Scientific Drilling Program (ICDP). This project includes a total of 3650 m of core from fifteen holes drilled through sedimentary and volcanic formations in Fennoscandia, recording several global environmental changes spanning the time interval 2.5–2.0 Ga, including the Great Oxidation Event (GOE).

Hole 13A intersects the upper part of the Zaonega Formation, which, together with the overlying Suissari Formation, records the Shunga Event in the Onega Basin in Karelia (Fig. 1), Russia (Eastern Fennoscandian Shield). The Shunga Event is defined by the oldest known significant accumulation of organic-carbon-rich sediments (termed “shungite” in the Onega Basin) and petroleum generation (Medvedev et al., 2009). Sedimentary rocks of the Onega Basin were deposited in a marine basin within a rifted active continental margin (e.g., Melezhik et al., 1999a,b; Kump et al., 2011). Samples of fine-grained laminated and massive siliciclastic rocks, with occasional turbidite intervals, were selected for this study. Sporadic macroscopic and obviously secondary textures and features were avoided, with the aim of providing insight into the depositional redox characteristics of the Onega Basin during typical background sedimentation.

Fig. 1. Composite (~5000-m-thick) and simplified section of the Onega Basin linked to major paleoenvironmental events, modified from Melezhik et al. (2010). Radiometric dates from bottom to top are taken from Pukhtel et al. (1992) and Ovchinnikova et al. (2007). Vertical red line shows the position of drill hole 13A studied in this work.
Table 2
Summary of XRD data giving semi-quantitative mineral abundances. Symbols represent the following abundances: 0 < * < 5 wt.%; 6 < ** < 10 wt.%; 11 < √ < 20 wt.%; √√ > 20 wt.%

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3. Methodology

3.1. Sample preparation and chemical and mineralogical characterization

Quarter-core samples were chipped in a ceramic jaw crusher, and the rock chips were subsequently powdered in a SPEX rock crusher with an aluminium dish. Due to the high content of organic matter, all samples were ashed in quartz beakers at 600 °C for at least 24 h and loss of weight during ignition (LOI) was determined. All later chemical procedures were undertaken in clean labs using distilled acids (HNO₃; HCl) or trace metal-grade HF. About 200 mg of ashed sample were dissolved with concentrated HNO₃ (7 mL) + HF (1.5 mL) and evaporated on a hot plate at 60 °C. Dry residues were further dissolved with concentrated HNO₃ + HCl, taken to dryness and finally dissolved with 7 mol/L HCl. Molybdenum and U concentrations were measured using a Thermal Scientific X-series 2 Quad ICP-MS and for Fe and Al using an ICP-AES. Calibration of the instruments was done by running a multi-elemental solution at different concentrations and blank solutions, while standardization was done via routine tests of reference materials (BHVO-1, BHVO-2, SDO-1, Nod A-1 and Nod P-1).

X-ray diffraction (XRD) analyses were conducted with a BRUKER AXS D8 Advance machine at the Laboratoire de Géochimie et Métallogénie at IFREMER institute, Brest, France. The results are presented in Table 2. Abundances were obtained on samples for which we had a sufficient amount of powder using the Rietveld method, which yields semi-quantitative results.

3.2. Molybdenum isotope analysis

A portion of each sample solution, using an amount determined from the measured Mo concentration, was doped with a double spike to keep a constant spike/sample ratio and taken through chromatographic separation described in Table 3. Molybdenum purification was done using a two-stage column procedure: a first stage of anion resin for separating Mo and most Fe from the matrix and a second stage of cation exchange separating Mo from remaining Fe. Molybdenum and Fe isotope composition measurements were done using a Thermo Neptune MC-ICP-MS at the Pole Spectrometry Ocean, Brest at IFREMER, France.

We used δ⁹⁸⁵⁶Fe = 10⁰⁰⁵⁴Fe double spike solution prepared gravimetrically from Oak Ridge Laboratory metal powders. Optimization of the double spike isotope composition relative to the SPEX standard gave 9⁵Mo/⁹⁵Mo, 9⁷Mo/⁹⁷Mo and 1⁰⁰⁰Mo/¹⁰⁰⁰Mo isotope ratios of 0.278, 16.663 and 15.704, respectively. Data reduction was done according to Siebert et al. (2001), where iterations were repeated until the difference in the δ⁹⁸⁵⁶Mo value between two consecutive iterations was smaller than 0.001‰. The typical number of iterations was ≤ 4. Molybdenum concentrations during isotope measurements varied from 100 to 500 ppb, depending on the Mo content of the sample powders. Within a given session, standards and samples were measured at a constant concentration. However, the external precision of the measurement was not affected within this range—yielding 2SD = ± 0.06‰, where the typical standard error of a single measurement (2SE) was 0.05‰. Molybdenum concentrations were derived from the spike/sample ratio determined as part of the double spike data reduction scheme.

The MC-ICP-MS machine was operated at low resolution with an ESI Apex Q introduction system measuring all Mo isotopes masses together with ⁹²Zr and ⁹⁹Ru in order to monitor isobaric interferences.

During each session of Mo isotope analysis, we performed frequent measurements of our in-house laboratory Mo standard (Mo SPEX lot 11-177Mo), the NIST-3137 standard and the Johnson Matthey Specpure® Mo plasma standard (Lot #802309E; RochMo2) used in previous studies (Farling and Anbar, 2004; and others). We have also preformed frequent measurements of georeference materials including SDO-1, Nod A-1 and Nod P-1. The results of these measurements are presented in Table 4. Mo isotope compositions are reported using the δ notation, where 9⁵Mo/⁹⁵Mo = 1000[(9⁸⁵Mo/9⁵Mo)sample/(9⁸⁵Mo/9⁵Mo)standard − 1] calculated relative to our in-lab Mo SPEX standard (Lot 11-177Mo). A Calibration of the SPEX standard relative to NIST-3137 (lot 891307) and Rochester (Lot 802309E) gave:

\[ \delta^{98/95} \text{Mo}_{\text{SPEX}} = \delta^{98/95} \text{Mo}_{\text{NIST3137}} - 0.35 \pm 0.12\% \]
\[ \delta^{98/95} \text{Mo}_{\text{SPEX}} = \delta^{98/95} \text{Mo}_{\text{Roch}} - 0.05 \pm 0.06\% \]

We choose to report our results relative to the SPEX standard since it is, within error (2SD), identical to the Rochester standard which is the most common standard in the recent Mo isotope literature.

3.3. Iron isotope analysis

For the determination of Fe isotope ratios we followed the methods of Rouxel et al. (2005, 2008a, 2008b), providing us with high precision measurements without argon interferences on the Neptunite instrument. We operated the MC-ICP-MS in either medium or high-resolution mode, and we used Ni as an internal standard for mass bias correction. We also used the “sample-standard bracketing” technique to correct for instrumental mass discrimination by normalizing the isotope ratios to the average measured composition of the standard that was run before and after the sample. Fe isotope values are reported relative to the standard IRMM-14 using the following conventional delta notations:

\[ \delta^{56/54} \text{Fe} = 1000 \left( \frac{^{56}_{25} \text{Fe}}{^{54}_{25} \text{Fe}} \right)_{\text{sample}} \left/ \frac{^{56}_{25} \text{Fe}}{^{54}_{25} \text{Fe}} \right. \text{IRMM-14} - 1 \]

Table 4

<table>
<thead>
<tr>
<th>NIST3137</th>
<th>Roch</th>
<th>Nod P-1</th>
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<th>SDO-1</th>
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<tr>
<td>δ⁵⁶Mo</td>
<td>0.36</td>
<td>0.05</td>
<td>−0.48</td>
<td>−0.22</td>
</tr>
<tr>
<td>2SD</td>
<td>0.06</td>
<td>0.06</td>
<td>0.10</td>
<td>0.04</td>
</tr>
<tr>
<td>n</td>
<td>29</td>
<td>29</td>
<td>12</td>
<td>5</td>
</tr>
</tbody>
</table>
Based on a complete duplicated procedure (i.e., powder ashing, acid attack, chemical purification and isotope analysis), the long-term external reproducibility is 0.07% for $\delta^{56}$Fe values (2 standard deviations). We also measured the following georeference materials: BHVO-2 ($\delta^{56}$Fe = 0.09 ± 0.07‰) and Nod-P1 ($\delta^{56}$Fe = −0.49 ± 0.08‰).

### Table 5

<table>
<thead>
<tr>
<th>Step</th>
<th>Acid</th>
<th>Volume [mL]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wash</td>
<td>0.05 N HCl</td>
<td>20</td>
</tr>
<tr>
<td>Conditioning</td>
<td>3 N HNO$_3$</td>
<td>6</td>
</tr>
<tr>
<td>Sample loading</td>
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<td>10</td>
</tr>
<tr>
<td>Matrix rinse</td>
<td>3 N HNO$_3$</td>
<td>40</td>
</tr>
<tr>
<td>Conversion to HCl</td>
<td>11 N HCl</td>
<td>6</td>
</tr>
<tr>
<td>Th</td>
<td>5 N HCl + 0.1 N oxalic acid rinse</td>
<td>20</td>
</tr>
<tr>
<td>Oxalic acid rinse</td>
<td>5 N HCl</td>
<td>10</td>
</tr>
<tr>
<td>U</td>
<td>0.05 N HCl</td>
<td>25</td>
</tr>
</tbody>
</table>

3.4. Iron speciation

For the Fe speciation procedure ca. 100 mg of sample powder was first treated with a buffered sodium acetate solution for 48 h to mobilize ferrous carbonate phases. A split of the extract was removed for analysis, the sample was then spun down, and the remaining supernatant was discarded. The sample was then treated with a sodium dithionite solution for 2 h to dissolve crystalline ferric oxides (Fe$_{O*X}$) and processed as before. Finally, the sample was treated with an ammonium oxalate solution to mobilize magnetite (Fe$_{Mag}$). All extractions were performed at room temperature in 15 mL centrifuge tubes under constant agitation. The sequential extracts were analyzed on an Agilent 7500ce ICP-MS after 100-fold dilution in trace-metal grade HNO$_3$ (2%). Pyrite iron (Fe$_{Pyr}$) was calculated separately based on weight percent pyrite sulfur extracted during a 2-hour, hot chromic chloride distillation followed by iodometric titration (Canfield et al., 1986), assuming a stoichiometry of FeS$_2$.

We have modified our procedure to include a wet chemical extraction for pyrrhotite (Fe$_1$–$_x$S, where $x$ is usually −0.02). Crystalline pyrrhotite was isolated from pyrite through a boiling 6 N HCl distillation.
with SnCl₂ serving as a reductant (in case Fe(III) is simultaneously liberated). This method (specifically the boiling rather than cold extraction) mobilizes some pyrite in modern sediments and is thus too aggressive for complete separation of pyrrhotite from pyrite in these systems (Chanton and Martens, 1985; Cornwell and Morse, 1987). However, some previous work suggests that this method provides accurate separation in more crystalline sedimentary rocks (e.g., Rice et al., 1993), and our internal tests with crystalline pyrrhotite and pyrite standards showed relative yields of pyrrhotite and pyrite of >97% and <4%, respectively, when treated with hot 6 mol/LHCl and SnCl₂. A cold HCl approach will badly underestimate the amount of crystalline pyrrhotite present. In contrast, it is well known that the conventional chromium reduction procedure (Canfield et al., 1986) will effectively mobilize all sulfide phases in sediments and sedimentary rocks. Pyrite sulfur can thus be quantified by the difference between chromium-reducible sulfur and that sulfur which is extracted with a hot 6 mol/LHCl leach as described above. Separate measurement of pyrrhotite and pyrite allows one to quantify the total amount of ‘sulfidized’ Fe (Fe₅) as follows:

$$Fe₅ = \frac{Feₐ + Fe₇₀}{Fe₄₀}$$

where in addition to the terms described above Fe₇₀ denotes Fe present as pyrrhotite. This essentially amounts to a stoichiometric correction of the sulfur-bound Fe pool and is important when appreciable pyrrhotite is present.

For measurement of total iron (Fe₄), sample powders are ashed overnight at 450 °C (in order to remove organic matter but preserve volatile metals, such as rhenium) and digested using sequential HNO₃–HF–HCl acid treatments (see, for example, Kendall et al., 2009). After digestion, samples are reconstituted in trace-metal grade HNO₃ (2%), diluted and analyzed by ICP-MS.

**3.5. Uranium isotope analysis**

Sample preparation for U analyses was adapted from Tissot and Dauphas (2011). Depending on U concentration in the samples, digested mass varied from ~20 mg to ~650 mg. Samples were first placed in individual aluminum foil envelopes and ashed at ~500 °C overnight in a 47900 Barnstead Thermolyne furnace, to burn off the organic matter. All samples were double-spiked after ashing but before digestion using the ²³⁵U/²³⁶U IRMM-3636 spike (containing ~49.51% of ²³⁶U and ~50.46% of ²³⁵U). The amount of spike added was determined to achieve au/ₚspike/u/ₚsample of ~3%. Samples were then dissolved on hot plates by at least two 24 h acid attacks in HF/HNO₃(2:1) followed by at least two 24 h acid attacks in HCl/HNO₃(2:1). Samples were then dried down before being reconstituted in concentrated HNO₃ and put back on the hot plate for an additional 24 h, followed by dilution to 3 mol/L HNO₃. To check that the ashing step was not affecting the results, replicates of five core samples with U concentrations ranging from 0.45 ppm to 6.45 ppm were prepared following an identical procedure but with no ashing step. Comparison of ashed and non-ashed samples showed no difference in U isotopic composition.

The U fraction was extracted from matrix elements and purified using U/Teva resin® (Eichrom). The elution procedure is the same as described in Telus et al. (2012) and is shown in Table 5. Uranium measurements were performed at the Origins Lab of the University of Chicago on a Thermo Neptune MC-ICP-MS, upgraded with an OnTool Booster 150 jet pump (Pfeiffer), using a combination of an Aridus-II desolvating nebulizer and a spray chamber for improved stability of the signal. The signal intensity was typically ~20 V for a 20 ppb solution with a flow rate of ~100 μl/min. Use of a ²³⁵U/²³⁶U double spike allowed us to correct for mass fractionation during sample preparation and spectrometry. A further correction was applied via sample-standard bracketing, along with a tailing correction of ²³⁸U onto ²³⁶U, which was estimated to be 0.6 ± 0.1 ppm, in good agreement with the value of 0.5 ppm reported by Weyer et al. (2008). The procedural blank was estimated to be...
0.07 ng U. A blank correction was applied despite having little effect on the result. All values are reported in $\delta^{238}\text{U} = \left( \frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{sample}} / \left( \frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{CRM-112a}} - 1 \right) \times 10^3$.

4. Results

4.1. Mineralogy, lithostratigraphy and chemostratigraphy

Lithological and mineralogical characterization of the samples based on XRD diffraction and the original drilling log is found in Table 6. In general, the studied section is predominantly composed of organic-rich silty black shale with varying sand and carbonate contributions. The chemostratigraphy data together with the Mo, Fe and U isotopic data are presented in Table 6 and in Fig. 2. Based on the down-hole profiles for $[\text{Mo}]$, $[\text{U}]$, $\delta^{238}\text{U}$ and TOC, the section can be divided into three units: Unit A (166 to 176 m), which shows relatively high $[\text{Mo}]$, $[\text{U}]$ and TOC; Unit B (145 to 165 m) marked by lower $[\text{Mo}]$, $[\text{U}]$ and TOC; and Unit C (129 to 144 m), which is defined by the highest $[\text{Mo}]$, $[\text{U}]$ and TOC. The Fe speciation data show only a minor difference between units A and B, where $\text{Fe}_{HR}/\text{Fe}_{T}$ ratios in Unit B is only slightly lower than those in unit A. On the other hand, the transition from unit B to unit C is marked by a sharp change, where $\text{Fe}_{HR}/\text{Fe}_{T}$ and $\text{Fe}_{PY}/\text{Fe}_{HR}$ become significantly higher and $\text{Fe}_{PO}/\text{Fe}_{HR}$ ratios decrease dramatically. In fact, $\text{Fe}_{PY}$ and $\text{Fe}_{PO}$ show clear negative covariation throughout the section. Similarly, total S in unit C is higher than in units A and B.

4.2. Molybdenum, iron and uranium isotopic compositions

The $\delta^{98}\text{Mo}$ values of the entire section range from $-0.25\%\text{oo}$ to $1.41\%\text{oo}$ and average $0.77 \pm 0.26\%\text{oo}$ ($n = 45$; Table 6). Seven samples, all from unit C, identified to be precipitated under euxinic conditions (i.e., $\text{Fe}_{HR}/\text{Fe}_{T} > 0.38$ and $\text{Fe}_{PO}/\text{Fe}_{HR} > 0.8$) yield an average $\delta^{98}\text{Mo}$ of $0.85 \pm 0.21\%\text{oo}$ ($n = 10$). The data also show one negative outlier of $\delta^{98}\text{Mo}$ at $-0.25\%\text{oo}$, and three positive outliers lying between 1.24 and 1.41%oo. For the identification of euxinic conditions we use $\text{Fe}_{S} = \text{Fe}_{PY} + \text{Fe}_{PO}$. Here, we consider that $\text{Fe}_{PO}$ is typically a product of $\text{Fe}_{PY}$ metamorphism, and therefore $\text{Fe}_{S}$ is a better estimation of the original $\text{Fe}_{PY}$ content. This issue is examined in detail below. The $\delta^{98}\text{Mo}$ data show no clear correlation with Mo/Al ratios (Fig. 3a). Also, molybdenum concentration versus TOC shows no clear correlation, where most samples have $[\text{Mo}]/\text{TOC}$ ratios lower than those found in the modern euxinic sediments of the Black Sea. The euxinic samples, however, are generally closer to the Black Sea trend of $[\text{Mo}]$ vs. TOC (Fig. 3b).

The $\delta^{56}\text{Fe}$ values of the entire section range from $-0.22\%\text{oo}$ to $0.83\%\text{oo}$ and average $0.09 \pm 0.22\%\text{oo}$ ($n = 45$) (Fig. 2 and Table 6). The $\delta^{56}\text{Fe}$ values show no clear correlation with Fe/Al ratios (Fig. 4a). Square, diamond and circle symbols stand for the samples from units A, B and C, respectively. Light shaded area shows mixing field of the detrital endmember with negative $\delta^{56}\text{Fe}$ authigenic pyrite and dark shaded area shows mixing field of the detrital endmember with positive $\delta^{56}\text{Fe}$ authigenic pyrite (see text). Shown in (b) are $\delta^{56}\text{Fe}$ values vs. $\text{Fe}_{S}/\text{Fe}_{HR}$ ratios, showing how high $\text{Fe}_{S}/\text{Fe}_{HR}$ values correlate with low $\delta^{56}\text{Fe}$ values. $\delta^{56}\text{Fe}$ error bars are plotted where greater than symbol size.
values vary among the different units and are mostly negative in unit C ($\delta^{56}\text{Fe} = -0.07 \pm 0.08\%$), becoming positive down-hole in units B ($\delta^{56}\text{Fe} = 0.24 \pm 0.24\%$) and A ($\delta^{56}\text{Fe} = 0.42 \pm 0.20\%$). No correlation is observed between $\delta^{56}\text{Fe}$ and Fe/Al ratios (Fig. 4a), where low $\delta^{56}\text{Fe}$ values correlate with high FeS/FeHR values (Fig. 4b).

The $\delta^{238}\text{U}$ values of the entire section range from $-0.33\%$ to $0.39\%$ and average $0.07 \pm 0.18\%$ (n = 45) (Fig. 2 and Table 6). A good correlation is observed between $\delta^{238}\text{U}$ and AI/U ratios (Fig. 5a; $R^2 = 0.48$), whose origins and implications are discussed further in the next section. The average $\delta^{238}\text{U}$ values in the three units are: $\delta^{238}\text{U} = 0.14 \pm 0.16\%$ in unit C, $\delta^{238}\text{U} = -0.05 \pm 0.19\%$ in unit B, and $\delta^{238}\text{U} = 0.07 \pm 0.13\%$ in unit A.

5. Discussion

5.1. Iron speciation and isotopic composition

Our primary observation with respect to Fe speciation chemistry is a striking up-section shift in the proportion of sulfur-bound Fe that is present as pyrite relative to pyrrhotite. Specifically, in the lower units (A and B), S-bound Fe is predominantly present as pyrite, while in the upper unit (C) S-associated Fe is mostly pyrrhotite. It has been suggested that some pyrrhotite can accumulate in low temperature systems as either a detrital phase or through authigenic formation in a sulfur-limited system (Roberts and Turner, 1993; Horng and Roberts, 2006; Larrasoña et al., 2007). If this is the case, the reactive Fe system can be relatively straightforwardly interpreted by using the FeS/FeHR values as an index of iron-limited sulfide formation, as discussed above (e.g., Reinhard et al., 2013b).

However, there are good reasons to suspect that the low-temperature formation of pyrrhotite as an authigenic or diagenetic phase should be rare (e.g., Schoonen and Barnes, 1991a,b; Lennie, 1995; Rickard and Luther, 2007). We thus consider it far more likely that the pyrrhotite component of our samples is a result of metamorphic pyrite alteration, which can sometimes occur at relatively low metamorphic grades (sub-greenschist facies), particularly in the presence of appreciable organic matter (Ferry, 1981; Poulton, 2002). The likelihood of pyrite conversion to pyrrhotite is also supported by the observed anti-theptic relationship between the concentrations of the two phases.

The process of post-depositional pyrrhotite formation typically occurs through one of following three mechanisms (Ferry, 1981; Oliver et al., 1992; Alonso-Azcarate et al., 1999), which have different ramifications for the ultimate Fe–S stoichiometry:

(a) Partial oxidation of the host rock balances the conversion of pyrite to pyrrhotite: $2\text{FeS}_2 + 2\text{FeO} + C_{\text{red}} \rightarrow 4\text{FeS} + \text{CO}_2$, where the “FeO” component can come from oxide or silicate phases in the host rock, and reduced carbon serves as the redox partner. In this case, the net result is no stoichiometric change in the total Fe and S contents of the rock, but there is a change in the distribution of reactive Fe in that S-bound Fe forms at the expense of an oxide phase, leaving the overall FeS budget unchanged but potentially yielding a spurious euxinic signal. Alternatively, silicate phases can be involved, thus introducing unreactive Fe from the host rock into the FeHR pool.

(b) Introduction of Fe-bearing fluid during metamorphism, which then reacts with pyrite to yield pyrrhotite and an acidic fluid: $2\text{FeS}_2 + 2\text{FeCl}_3 + 2\text{H}_2\text{O} + C_{\text{red}} \rightarrow 4\text{FeS} + 4\text{HCl} + \text{CO}_2$, where “FeCl$_3$” represents mobile Fe within the alteration fluid. In this case, although there is no stoichiometric change in the total S content of the rock, there can be an increase in total Fe if the iron is delivered from external sources external to the immediately surrounding host rock. This pathway would have the effect of artificially increasing Fe$_{\text{HR}}$, Fe$_{\text{T}}$ and Fe$_{\text{S}}$, but because these would all be increased in a commensurate fashion there would be no change in the normalized ratios (Fe$_{\text{HR}}$/Fe$_{\text{T}}$ and Fe$_{\text{S}}$/Fe$_{\text{HR}}$) provided that the stoichiometry of sulfur-bound Fe is accurately assessed.

(c) Pyrrhotite formation through thermal decomposition of pyrite, generating an H$_2$S-bearing fluid: $4\text{FeS} + 4\text{HCl} + \text{CO}_2 \rightarrow 2\text{FeS}_2 + 2\text{H}_2\text{S} + \text{CO}_2$. Here, there is no net stoichiometric change in the total Fe content of the host rock, but S is lost from the rock to a reducing fluid during thermal decomposition of pyrite.

We can evaluate the likelihood of each of these processes by comparing the bulk and reactive Fe–S stoichiometry with an index of metamorphic alteration, defined as (Ferry, 1981):

$$F_{\text{py}} = \frac{S_{\text{py}}}{S_{\text{py}} + S_{\text{po}}},$$

where $S_{\text{py}}$ denotes pyrite sulfur and $S_{\text{po}}$ denotes pyrrhotite sulfur. Domination of the S pool by pyrite ($F_{\text{py}} \rightarrow 1$) implies that the Fe–S chemistry is relatively unaltered. In contrast, as $F_{\text{py}} \rightarrow 0$ pyrrhotite becomes the dominant host for S-bearing Fe, more extensive alteration of original Fe–S chemistry is indicated.

The behavior of bulk Fe chemistry (Fe$_{\text{T}}$ and Fe$_{\text{HR}}$) and bulk S chemistry as a function of $F_{\text{py}}$ is shown in Fig. 6. The core can be easily divided with respect to Fe–S chemistry into a lower interval dominated by pyrrhotite (units A and B) and an upper interval dominated by pyrite (unit C, Fig. 2). We find no apparent trends in the behavior of bulk Fe chemistry between these two zones, either in terms of Fe$_{\text{T}}$ or Fe$_{\text{HR}}$ (Fig. 6a).
However, there is a striking systematic trend toward lower S/FeHR ratios with decreasing F_PY values (Fig. 6b), a trend that can also be seen in bulk rock S content. This strongly suggests that the mechanism of pyrrhotite formation in these units was the thermal breakdown of pyrite and subsequent loss of S from the rock. Importantly, this relationship also suggests that the system was effectively closed on a bulk-rock scale with respect to FeT and FeHR (discussed below).

The trend between F_PY and S/FeHR in Fig. 6b can be reproduced fairly well by a simple model that makes the following assumptions: (1) the molar S/FeHR ratio of the Fe–S system in the unmetamorphosed host rock is 2.0 (corresponding to a stoichiometry of FeS₂), (2) the molar S/FeHR ratio of the Fe–S system at complete breakdown of pyrite to pyrrhotite is 1.0 (corresponding to a stoichiometry of FeS), (3) there is an initial amount of residual FeHR present in the unaltered parent rock that behaves conservatively, and (4) the system is completely closed with respect to reactive Fe. The third assumption effectively accounts for the fact that the wet chemical extractions are operational in nature. For example, euxinic settings should, in theory, always have Fe_PY/FeHR = 1.0, but this is often not the case in practice because some unreactive Fe is extracted during our characterization of reactive Fe. The correspondence between the data and our simple model provides additional support for the notion that reactive Fe is behaving conservatively in this system during metamorphism and that the alteration patterns observed are straightforwardly interpreted to reflect sulfur loss during pyrite decomposition.

Many of the samples analyzed here are clearly anoxic, particularly within Unit C, as expressed in the elevated FeHR/FeT ratios (Fig. 2). When we examine the reactive Fe systematics in more detail, it becomes apparent that this unit also shows clear characteristics of a euxinic setting (Fig. 7b)—that is, a strong correlation between FeHR and Fe_PY (the latter of which is dominated by Fe_PY; R² = 0.98) and high FeS/FeHR ratios that fall within the euxinic field, both of which are consistent with the Fe-limited conditions that typify euxinia. The reactive Fe systematics of the lower units (Unit A and Unit B) are more complex (Fig. 7a). Here we observe strong correlation between FeHR and Fe_PY with linear least-squares regression yielding an R² value of ~0.97, suggesting euxinic Fe limitation but with Fe_PY dominated by FeO. However, reactive Fe phases other than pyrite and pyrrhotite in units A
and B make up a non-trivial fraction of the reactive Fe system, with the result that $\text{Fe}_d/\text{Fe}_\text{tot}$ falls out of the euxinic field (Fig. 7a).

If interpreted at face value purely in terms of $\text{Fe}_{\text{HR}}/\text{Fe}_d$ and $\text{Fe}_{\text{S}}/\text{Fe}_{\text{HR}}$ these patterns would suggest units A and B were deposited under ferruginous conditions. However, we consider this unlikely. The striking correspondence between $\text{Fe}_d$ and $\text{Fe}_{\text{HR}}$ and the relative dominance of sulfur-bound Fe phases within the overall reactive Fe pool are difficult to explain in the context of a strongly $\text{Fe}^{2+}$-buffered anoxic system. Indeed, if we were to apply a recently proposed lower threshold for euxinic deposition of $\text{Fe}_{\text{HR}}/\text{Fe}_d - 0.7$ (März et al., 2008; Poulton and Canfield, 2011), many of the unit A and B samples would fail very close to the lower end of the euxinic field. Moreover, both the lower and upper portions of the core show authigenic Mo enrichment suggestive of sulfidic conditions (Fig. 2), with little to no systematic difference in $\delta^{56}\text{Mo}$ values between the clearly euxinic Unit C and the more ambiguous units A and B. Taken together, these observations suggest that most of the core was deposited under euxinic conditions, with Fe chemistry that has been obscured by metamorphic overprinting within units A and B.

We therefore conclude that Unit C provides a faithful repository of contemporaneous seawater $\delta^{56}\text{Mo}$. The limited systematic variability in $\delta^{56}\text{Mo}$ between the lower and upper portions of the core indicates that the same can be said also for the metamorphically overprinted units A and B. We stress, most importantly, that these units provide an object lesson in the difficulties inherent, and the attendant level of required care, in any application of reactive Fe speciation to heavily altered rocks. In addition, it is instructive to consider that were the Fe speciation data to be interpreted at face value, the lower portion of the core would be interpreted to reflect ferruginous deposition, a signal that we consider likely to be spurious in this case.

The Fe isotope compositions are unexpectedly heavy for black shales (up to 0.8‰), especially in the lower part of the section (Units A and B). Our $\delta^{56}\text{Fe}$ values do not correlate with Fe/Al ratios, eliminating the possibility of a simple two endmember mixing relationship between an Al-rich detrital endmember with crustal $\delta^{56}\text{Fe}$ values, and a Fe-rich authigenic endmember with generally negative values (Severmann et al., 2008; Duan et al., 2010a,b). Similar positive $\delta^{56}\text{Fe}$ values from this time period have only been reported so far for separated pyrite (Rouxel et al., 2005). Such values may result from one of the following processes: (1) a preferential loss of isotopically light Fe, which will also result in lower Fe/Al ratios. This was demonstrated at low temperature in soil environments and during microbial leaching of silicates (Brantley et al., 2001, 2004) and also during alteration of seafloor basalts (Rouxel et al., 2003); (2) an addition/deposition of isotopically heavy Fe, which may be either in the form of authigenic Fe-sulfides (Rouxel et al., 2005) or Fe-oxides, for example produced through partial Fe(II) oxidation within the water column (Planavsky et al., 2012b), thereby increasing the Fe/Al ratio; or (3) precipitation of isotopically heavy pyrite from seawater enriched in heavy Fe as a result of Rayleigh effects linked to prior pyrite precipitation and possibly as a result of weak shelf-to-basin Fe transfer (i.e., relatively weak Fe shuttle) and attendant Rayleigh distillation during Fe transport through the basin.

Although the average of Fe/Al ratio of 0.46 ± 0.26 compares well with the average continental crust values (0.05) (Taylor and McLennan, 1995), Fe/Al values as low as 0.1 to 0.3 were encountered at certain depths (e.g., samples: 3109562, 3109566, 3109608, 3109732, 3109736). On the one hand, such low values may point to mobility of Fe after deposition. On the other hand, they may also result from low Fe content in the protolith/detrital Fe source and a strong local control on sediment sourcing. An examination of the XRD data reveals high content of Al-rich detrital minerals (mainly feldspars and biotite; Table 2) in our samples, suggesting that low Fe/Al ratios were a primary feature of the detrital sediment load. Thus, authigenic input of Fe-minerals, dominated by pyrite precipitation in our case, was the main factor to determine the Fe isotope compositions of the bulk sediment. The Fe isotope composition of the precipitated pyrite is in turn a function of the seawater composition and mass balance between the dissolved and precipitated Fe. A post-depositional event was responsible for the pyrrhotite formation in units A and B. In any case it seems that this alteration was not involved in a significant gain or loss of Fe, and therefore the authigenic isotopic signature of the bulk rock has most likely been preserved.

The low $\delta^{56}\text{Fe}$ values, mainly observed in unit C, can be explained by mixing of detrital Fe with authigenic pyrite. A mixing relationship between such two endmembers—a detrital endmember with low Al content (Fe/Al ≥ 0.05) and $\delta^{56}\text{Fe}$ ≈ 0.09‰ (Beard et al., 2003a,b), and an authigenic pyritic endmember with $\delta^{56}\text{Fe}$ ranging from −0.4 to 0‰ (light shaded area in Fig. 4a)—can account for all samples with $\delta^{56}\text{Fe}$ values of ≤ 0‰. Samples with high $\delta^{56}\text{Fe}$ values and high Fe/Al ratios may testify to relatively weak shelf-to-basin Fe transfer of light Fe, and considerable Rayleigh effects that would enrich the seawater in heavy Fe and give rise to precipitation of pyrites with positive $\delta^{56}\text{Fe}$. This process can happen at the lower region of or slightly below the core of a locally euxinic portion of the basin, which itself provides a sink of light Fe (i.e., the same part of the basin recorded in Unit C). A mixing relationship between a detrital endmember and a heavy Fe endmember such as mentioned above (dark shaded area in Fig. 4a) can account for most of the samples with $\delta^{56}\text{Fe}$ values of ≥ 0‰. In this context we can say that the transition observed in the $\delta^{56}\text{Fe}$ values from units A and B to unit C represents a shift in the relative location in the water column from the bottom margins of an euxinic wedge into its core or a region more proximal to the shallower shelf. It could be noted that benthic Fe flux with positive $\delta^{56}\text{Fe}$ values has been already reported in modern oceanic setting as a result of Fe-sulfide precipitation at or near the seawater/porewater interface (Roy et al., 2012) and may also occur at largest scale in the water column. Unit C also shows higher $[\text{Mo}]$ and $[\text{U}]$, which are typical of strongly sulfidic conditions. There are few samples with high $\delta^{56}\text{Fe}$ and low Fe/Al values, which clearly fall outside the above considerations. In such cases, the only plausible explanation is loss of light Fe during metamorphic processes, which increased the $\delta^{56}\text{Fe}$ values and decreased the Fe/Al ratios or simply reflect an unusual detrital source composition.

5.2. Molybdenum concentration and isotopic composition

The elevated Mo/Al ratios (average of 2.2 for the entire section and 4.6 for unit C, compared to 0.19 for upper continental crust) together with the fact that the Mo isotope compositions show no correlation to $[\text{Mo}]$ or $[\text{Mo}]/[\text{TOC}]$ (Fig. 3a), indicate that the Mo in these rocks is predominately authigenic and that detrital contributions are negligible.

When taken at face value, the $\text{Fe}_{\text{HR}}/\text{Fe}_d$ and $\text{Fe}_{\text{PY}}/\text{Fe}_{\text{HR}}$ ratios suggest that euxinic conditions were found only in unit C. However, more careful evaluation of the Fe data shows they are consistent with euxinia over all three units. This is further suggested by the observation that the Mo isotope compositions are relatively uniform at 0.77 ± 0.26‰ throughout the entire section, while we would expect to see larger Mo isotopic variations in case of changes in the redox conditions. Moreover, the $\delta^{56}\text{Mo}$ values do not respond to changes in the $[\text{Mo}]/[\text{TOC}]$ ratios or Fe speciation (Fig. 2), and $[\text{Mo}]/[\text{TOC}]$ ratios along the entire section are relatively low ($[\text{Mo}]/[\text{TOC}] = 1.9 ± 1.4$; compared with ~4.5 for Black Sea euxinic sediments and ~14 for SDO-1 (Devonian black shale)). Such low $[\text{Mo}]/[\text{TOC}]$ values may represent Mo reservoir limitation due to widespread euxinia. These findings support our interpretation of the Fe speciation data that the section was deposited under predominantly euxinic conditions. Based on geological considerations showing that the studied section is part of a regional platformal sequence, we eliminate the possibility the low Mo/TOC values are a result of deposition in a very restricted basin which was not connected to the global ocean.

Unit C yields the highest $\text{Fe}_{\text{HR}}/\text{Fe}_d$ and $\text{Fe}_{\text{PY}}/\text{Fe}_{\text{HR}}$ with lowest $\text{Fe}_{\text{PO}}/\text{Fe}_{\text{HR}}$ (Fig. 2) and is thus the only part of our section that did not undergo an obvious significant metamorphic/post-depositional overprint, and euxinic conditions can be comfortably identified using Fe speciation data. Therefore, we suggest that the best evaluation of the contemporaneous Mo
isotope composition of the seawater may be derived from this unit, giving $\delta^{98}_{\text{SMOW}}$ value of 0.85 ± 0.21‰. A simple calculation by Kendall et al. (2011) shows that the oceanic residence time of Mo during the late Archean and Proterozoic would likely have been one or two orders of magnitude longer than timescales of ocean mixing, suggesting that during this time interval the oceans were probably homogenous with respect to Mo.

If we argue that the isotopic composition of seawater ($\delta^{98}_{\text{SMOW}}$) was 0.85 ± 0.21‰ during deposition of the entire studied section, the one low $\delta^{98}_{\text{Mo}}$ outlier value of −0.25‰ (sample 3109566) is best explained through non-quantitative removal of the Mo to the sediment. This low value also correlates with low Fe$_{\text{FeR}}$ and TOC values, supporting a temporary local change to non-euxinic conditions where significant negative fractionation took place during Mo removal. The section also contains three positive outliers with $\delta^{98}_{\text{Mo}}$ values ranging from 1.24 to 1.41‰, which are among the highest values yet measured for Paleoproterozoic black shales (Kendall et al., 2009, 2011; Duan et al., 2010a,b) and are close to some Phanerozoic samples (Lehmann et al., 2007). Since net fractionation during Mo removal can only be negative or zero (in case of complete removal), the $\delta^{98}_{\text{Mo}}$ value of the original seawater can only be higher or equal to that of the sediment. Therefore, the high $\delta^{98}_{\text{Mo}}$ values (higher than the contemporaneous $\delta^{98}_{\text{SMOW}}$ estimates in samples 3109562 at 129.91 m, 3109622 at 142.65 m and 3109778 at 175.3 m) are less straightforward to explain. We suggest a water column mechanism whereby enhanced Mo removal to non-euxinic sinks led to a concomitant enrichment of local seawater. We propose a water column mechanism whereby enhanced Mo removal to non-euxinic sinks led to a concomitant enrichment of local seawater. This mechanism is consistent with the lack of negative fractionation during Mo removal and the presence of high $\delta^{98}_{\text{Mo}}$ values in the sediment.

5.3. Uranium concentrations and isotopic compositions

The U isotope compositions correlate with Al/U ratios (Fig. 5a). Unit C shows the highest U concentrations and $\delta^{238}_{\text{U}}$ values, with unit B mostly notably showing lower U concentrations and $\delta^{238}_{\text{U}}$ values. Similar patterns are also observed in Fe speciation and Mo concentrations, all pointing to changes in the deposition conditions along the section. In addition, the XRD data (Table 2) show a high detrital content in all samples. These observations indicate that the bulk rock U isotope compositions are mainly a result of mixing relationship between a low $\delta^{238}_{\text{U}}$ detrital endmember and a high $\delta^{238}_{\text{U}}$ authigenic endmember. Therefore, before interpreting the data in terms of global ocean redox conditions, we need to constrain the detrital signature. Carbonates should directly record the isotopic composition of the seawater they are precipitating from (Brennecka et al., 2011). However, samples from our section with high carbonate content show high variations in their $\delta^{238}_{\text{U}}$ values, which in part are close to the detrital endmember, suggesting detrital contribution. Therefore, a direct estimation of the contemporaneous $\delta^{238}_{\text{U}}$ seawater value based on carbonates is not possible.

A correction for the detrital component in the samples was thus made by extrapolating the isotopic composition at Al/U = 0 (i.e., no detrital influence) using the following equation:

$$\delta^{238}_{\text{U}} = \delta^{238}_{\text{U}} - \left(\frac{A_i}{U} \right) \times \left( \frac{\delta^{238}_{\text{U}} \text{det} - \delta^{238}_{\text{U}}}{\delta^{238}_{\text{U}} \text{det} - \delta^{238}_{\text{U}}} \right)$$

where the det stands for detrital. The detrital endmember was obtained by averaging basalt and granite geostandards measured at the Origins Lab (Tissot and Dauphas, 2012) and led to $\delta^{238}_{\text{U}} \text{det} = -0.267‰$ and $(\text{Al}/\text{U})_{\text{det}} = 3.19$ (geometric mean of the basalts and granites Al/U ratios). Similarly, the error in the $\delta^{238}_{\text{U}}$ value was calculated using the following equation (which propagates any error in the $\delta^{238}_{\text{U}}$ value of the sample but not the error in Al/U ratio of the sample or the errors in the detrital endmember):

$$\sigma_{\delta^{238}_{\text{U}}} = \sqrt{\left(1 + \frac{\sigma_{\delta^{238}_{\text{U}}} (\text{Al}/\text{U})}{\sigma_{\delta^{238}_{\text{U}}} (\text{Al}/\text{U}) \text{det} - \sigma_{\delta^{238}_{\text{U}}} (\text{Al}/\text{U})} \right)^2 \times \sigma_{\delta^{238}_{\text{U}}}}^2$$

A cut-off in the Al/U ratios of the samples was placed at 3, to avoid meaningless interpolations—i.e., the measured data are too close to the detrital component and there is no leverage to properly extrapolate, and error becomes too large. The corrected isotopic compositions are heavier, showing an average $\delta^{238}_{\text{U}}$ value of 0.35 ± 0.22‰, where before correction the average $\delta^{238}_{\text{U}}$ was 0.07 ± 0.18‰ (Figs. 2 and 5). The euxinic samples show similar average $\delta^{238}_{\text{U}}$ value of 0.32 ± 0.15‰, which we use to infer the U isotope composition of the contemporaneous seawater. It is important to note that the corrected $\delta^{238}_{\text{U}}$ values show no clear difference between the three units of the section or correlation to other proxies such as [Mo] and Fe speciation. This observation also supports our conclusion that the entire section was deposited under euxinic conditions. Using the seawater-anoxic/euxinic sink fractionation factor of $\Delta^{238}_{\text{U}/235}_{\text{U}} = -0.5‰$ (Weyer et al., 2008; Brennecka et al., 2011), the authigenic composition recorded corresponds to seawater with a $\delta^{238}_{\text{U}}$ value of −0.18 ± 0.15‰, which is identical within to the modern riverine input value (−0.2‰, Stirling et al., 2007). This result can only be explained if the U removal process did not involve significant fractionation and suggests that either (1) the oceanic U budget was dominated by co-precipitation into carbonates or U removal during alteration of the oceanic crust (as none of these processes seem to fractionate U isotopes) or (2) the oceanic U budget involved different reservoirs incorporating preferentially the heavy (e.g., anoxic, suboxic sediments) and the light isotopes of U (adsorption onto oxides: Mn-nodules, BIFs) in order for the $\delta^{238}_{\text{U}}_{\text{Seawater}}$ to remain constant. Though we cannot rule out any of these two hypotheses, the second one would make sense in the frame proposed by Kendall et al. (2013–in this issue) where U is not mobilized by oxidative weathering in land but is instead oxidatively mobilized in subaerial settings (perhaps in oxygen oasis). Such oases would also be the place where oxidation and precipitation of Fe and Mn oxides would preferentially occur, possibly allowing removal of dissolved U through adsorption. Given the low amount of available dissolved U, iron and manganese oxides could then represent a sink of U large enough to balance the fractionation imparted by U incorporation into anoxic/euclidean/suboxic sediments, and thus keep the $\delta^{238}_{\text{U}}_{\text{Seawater}}$ close to the value of detrital/riverine input.

6. Conclusions

We have presented a multi-proxy geochemical study of the 2.05 Ga Shunga Event black shale from the Onega Basin in Karelia. Using a cautious examination of the Fe speciation data we showed that the lower part of the studied section underwent a post-depositional event in which pyrite was altered to pyrrhotite, with concomitant sulfur escape from the sediment. However, this post-depositional event did not appear to affect the bulk rock Mo, U and Fe isotope compositions and consequently made it possible to use the Mo, Fe and U isotope systems as reliable paleoredox proxies. The authigenic U isotope composition corresponds to a seawater $\delta^{238}_{\text{U}}$ of −0.18 ± 0.15‰ and suggests that co-precipitation into carbonates was the main process of U removal at this time.

We conclude that the studied section was deposited under euxinic conditions, where the global contemporaneous oceans had a $\delta^{98}_{\text{Mo-SW}}$ value of 0.85 ± 0.21‰. The relatively uniform Mo and U isotope compositions across the studied section also point to stable redox conditions during deposition. The high Mo and U concentrations in unit C, with respect to units A and B, may represent the following: (1) a shift in the relative location in the water column of the deposition site from
the bottom margins of an euxinic wedge into its core or a region more proximal to the shallower shelf; and/or (2) an episode of enhanced oxidative weathering on the continents and therefore greater delivery of Mo and U to the sediment. This scenario is also in accord with the observed Fe isotope variations, where in units A and B, precipitation of pyrite from an already fractionated seawater reservoir resulted in isotopically heavy bulk rock Fe isotope composition; and in unit C, pyrite formation under more sulfidic conditions led to lower δ63Fe values, similar to those observed in modern anoxic basins such as Black Sea or in Phanerozoic shales (Sévermann et al., 2008; Duan et al., 2010a,b).

Our estimation for the contemporaneous δ34S of 0.85 ± 0.21‰ is the lowest value yet reported for the Proterozoic (cf., 1.19 ± 0.28‰ at 1.84 Ga—(Kendall et al., 2011); 1.03 ± 0.14‰ at 1.36 Ga—(Kendall et al., 2009); 0.99 ± 0.13‰ at 0.75 Ga—(Dahl et al., 2011); 1.06 ± 0.11‰ at 0.54 Ga—(Lehmann et al., 2007)). The implication is that at this time, after the GOE and the massive burial of organic matter associated with the Logamundi Event, the global oceans were exceptionally anoxic with relatively widespread euxinia. Recent studies have proposed a rise and fall of oxygen levels over the span of the GOE at ca. 2.3Ga and the Logamundi Event between 2.3 and 2.1 Ga (Kump et al., 2011; Bekker and Holland, 2012; Planavsky et al., 2012a). The Shunga Event is situated in the aftermath of these events and testifies to the possibility of a severe decrease in oceanic oxygenation at this time.

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Appendix 1. Uranium reduction under anoxic, euxinic and suboxic conditions

In anoxic, euxinic and suboxic environments reduction of soluble UVI to insoluble UIV and concentration in the sediment can be the results of various mechanisms. First, as a result of abiotic reduction. In this case the uranyl carbonate ion is reduced to uraninite in the following total reaction:

\[ 4\text{UO}_2^2+ (CO_3)^{3–} + HS^- + 15H^+ = 4\text{UO}_2 (c) + 3\text{CO}_2 (g) + 8H_2O \]

(from Langmuir (1978)) or, if the reduction is mediated by iron instead of sulfur:

\[ \text{UO}_2 (\text{CO}_3)^{4–} + 2\text{Fe}^{3+} + 2\text{H}_2\text{O} = \text{UO}_2 (c) + 2\text{Fe(OH)}_3 + 3\text{CO}_2 (g) \]

(from Langmuir (1978))

In porewater, we expect U reduction to be mainly coupled to oxidation of Fe (Reaction 2) as this reaction is thermodynamically favored at pH = 8 and 25 °C (from Langmuir, 1978; Zheng et al., 2002). Similar reactions can occur through oxidation of pyrite, methane or H2. The first reaction, under sulfidic conditions, requires production of HS– through microbially mediated reduction of sulfate (Klinkhammer and Palmer, 1991; Barnes and Cochrans, 1993). There is no evidence that inorganic U reduction occurs at in-situ concentrations of U and H2S, or only extremely slowly (Anderson et al., 1989; Lovley et al., 1991; Barnes and Cochran, 1993; Tribovillard et al., 2006).

Second, as a result of microbial reduction. Direct microbial reduction mechanisms of U are thought to occur, such as during oxidation of organic matter:

\[ \text{CH}_3\text{O} + 2\text{UO}_2 (\text{CO}_3)^{4–} + \text{H}_2\text{O} + 2\text{H}^+ = 2\text{UO}_2 (c) + 6\text{HCO}_3^- + \text{CO}_2 \]

(Cochran et al., 1986; Barnes and Cochrans, 1993)

Third, as a result of adsorption to ferric hydroxide. A last mean of removing U from porewater is through adsorption to ferric hydroxide, which is thought to happen in two ways. Either by adsorption of U as the uranyl ion, UO22+: If pH < 5: FeOH + UO22+ = [FeO – UO2]2+ + H+ (Langmuir, 1985)

If 5 < pH < 6: FeOH + UO22+ + H2O = [FeO – UO2(OH)]2+ + 2H+ (Langmuir, 1985)

Or by adsorption of U as the uranyl carbonate species:

FeOH + UO22+ + 3 CO22– = [FeOH2– – UO2 (CO3)32–] Langmuir (1985)

Fe(OH)2 + UO22+ + CO22– = [Fe2O – UO2CO32–]2– + 2H+ (Waite et al., 1994).

The main removal process of U has been reported to be abiotic reduction in the sediment porewater (Cochran, 1992; Morford and Emerson, 1999), but one should keep in mind that all of the above mechanisms can to some extent remove U from the water column and concentrate it in the sediment under anoxic, euxinic and/or suboxic conditions.

References


