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A Model for the Oceanic Mass Balance of Rhenium and Implications for the Extent of Proterozoic Ocean Anoxia

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Abstract

Emerging geochemical evidence suggests that the atmosphere-ocean system underwent a significant decrease in O_2 content following the Great Oxidation Event (GOE), leading to a mid-Proterozoic ocean (ca. 2.0–0.8 Ga) with oxygenated surface waters and predominantly anoxic deep waters. The extent of mid-Proterozoic seafloor anoxia has been recently estimated using mass-balance models based on molybdenum (Mo), uranium (U), and chromium (Cr) enrichments in organic-rich mudrocks (ORM). Here, we use a temporal compilation of concentrations for the redox-sensitive trace metal rhenium (Re) in ORM to provide an independent constraint on the global extent of mid-Proterozoic ocean anoxia and as a tool for more generally exploring how the marine geochemical cycle of Re has changed through time. The compilation reveals that mid-Proterozoic ORM are dominated by low Re concentrations that overall are only mildly higher than those of Archean ORM and significantly lower than many ORM deposited during the ca. 2.22–2.06 Ga Lomagundi Event and during the Phanerozoic Eon. These temporal trends are consistent with a decrease in the oceanic Re inventory in response to an expansion of anoxia after an interval of increased oxygenation during the Lomagundi event. Mass-balance modeling of the marine Re geochemical cycle indicates that the mid-Proterozoic ORM with low Re enrichments are consistent with extensive seafloor anoxia. Beyond this agreement, these new data bring added value because Re, like the other metals, responds generally to low oxygen conditions but has its own distinct sensitivity to the varying environmental controls. Thus, we can broaden our capacity to infer nuanced spatiotemporal patterns in ancient redox landscapes. For example, despite the still small number of data, some mid-Proterozoic ORM units have higher Re enrichments that may reflect a larger oceanic Re inventory during transient episodes of ocean oxygenation. An improved understanding of the modern oceanic Re cycle and a higher temporal resolution for the Re compilation will enable further tests of these hypotheses regarding changes in the surficial Re geochemical cycle in response to variations in atmosphere-ocean oxygenation. Nevertheless, the existing Re compilation and model results are in agreement with previous Cr, Mo, and U evidence for pervasively anoxic and ferruginous conditions in mid-Proterozoic oceans.

Keywords: rhenium; anoxia; Proterozoic; organic-rich mudrocks; ocean; oxygen

1. Introduction

The progressive oxygenation of the early Earth's surface had a profound impact on Earth’s biological and geochemical evolution (Lyons et al., 2014). A poorly oxygenated atmosphere-ocean system in the Archean is indicated by several lines of evidence in the sedimentary record (Farquhar et al., 2000; Bekker et al., 2010; Sverjensky and Lee, 2010; Lyons et al., 2014), such as abundant banded iron formations (BIF), common occurrence of redox-sensitive detrital minerals, and preservation of sulfur mass-independent fractionation (S-MIF). In addition, the low concentrations of some redox-sensitive elements (e.g., Mo, U) in sedimentary archives suggest low seawater concentrations of these elements because of their limited oxidative mobilization from the Archean continental crust (Scott et al., 2008; Partin et al., 2013). The Great Oxidation Event (GOE) is marked by a permanent increase of atmospheric O_2 content to >0.001% present atmospheric level (PAL), starting between 2.45 and 2.32 Ga (Pavlov and Kasting, 2002; Bekker et al., 2004; Bekker, 2014; Gumsley et al., 2017). This transition was accompanied by the appearance of new mineral species containing redox-sensitive elements in their highest oxidation states, reduction in BIF deposition, disappearance of S-MIF, and an increase in seawater Mo, U, and sulfate concentrations (Bekker et al., 2004, 2010, 2013; Schröder et al., 2008; Scott et al., 2008, 2014; Sverjensky and Lee, 2010; Hazen et al., 2011; Planavsky et al., 2012; Reuschel et al., 2012; Partin et al., 2013; Reinhard et al., 2013a). The latter part of the GOE was marked by a protracted episode of elevated organic carbon burial (Lomagundi Event) between ca. 2.22 and 2.06 Ga, which resulted in a long-lasting but transient increase in atmosphere-ocean O_2 contents to levels that may not have occurred again until the late Neoproterozoic (Karhu and Holland, 1996; Scott et al., 2008, 2014; Kump et al., 2011; Planavsky et al., 2011, 2012, 2014; Bekker and Holland, 2012; Partin et al., 2013).

Although dramatic swings in the extent of atmosphere-ocean oxygenation are recognized in the early and late Proterozoic, surficial redox dynamics during the intervening period are generally considered to be muted. Recent geochemical data (e.g., redox-sensitive trace metals and Fe speciation) suggest stratified ocean redox conditions for the middle portion of the Proterozoic (ca. 1.8–0.8 Ga; hereafter referred to as the mid-Proterozoic), wherein oxygenated surface waters were underlain by euxinic (anoxic and sulfidic) waters in highly productive marginal settings, and ferrous iron (Fe^{2+}) accumulated in suboxic to anoxic deep waters in offshore settings (ferruginous anoxia; Poulton et al., 2010; Planavsky et al., 2011; Reinhard et al., 2013a; Sperling et al., 2015). While Fe speciation data indicate ferruginous conditions at many times and localities in the mid-Proterozoic, the scarcity of preserved ancient seafloor, particularly of the deepest parts of the ocean, creates a challenge for postulating marine redox landscapes on a global scale.

Although low O_2 levels have been suggested for the mid-Proterozoic atmosphere and oceans (<0.1–1.0% PAL; Planavsky et al., 2014; Liu et al., 2016; Reinhard et al., 2016; Tang et al., 2016; Hardisty et al., 2017), such conditions imply poorly buffered surface O_2 inventories and the potential for significant spatiotemporal variability (Planavsky et al., 2014; Cole et al., 2016; Reinhard et al., 2016; Daines et al., 2017). Indeed, there has been much recent interest in the possibility of dynamic spatiotemporal variations in atmosphere-ocean redox conditions during this time (e.g., Sperling et al., 2014; Gilleaudeau and Kah, 2015; Gilleaudeau et al., 2016; Mukherjee and Large, 2016; Planavsky et al., 2016; Reinhard et al., 2016; Zhang et al., 2016) against a background of lower atmospheric pO_2 compared with today (e.g., Cole et al., 2016). Hence, additional data and proxies sensitive to global redox conditions are needed to better understand the spatiotemporal evolution and the dominant redox state of the mid-Proterozoic oceans. Such information is critical to a full understanding of the relationship between Earth's surface oxygenation and the evolution of both eukaryotic organisms and complex metazoan life, and integrated use of diverse metals spanning a broad range of redox sensitivity (e.g., Reinhard et al., 2013a), detrital backgrounds, uptake pathways, and crustal sources will strengthen our conclusions.

The concentrations of some redox-sensitive trace metals in marine organic-rich mudrocks (ORM) can provide insight into global ocean redox conditions. Behaving largely conservatively in oxygenated seawater, trace metals such as Mo, Cr, Re, and U are removed to anoxic sediments at higher rates compared with oxygenated sediments, with removal rates dependent on the specific chemistry of the water column and underlying sediment pore fluids (e.g., Morford and Emerson, 1999; Tribovillard et al., 2006). Chromium, U, and Re become authigenically enriched in sediments overlain by anoxic water columns (at both high and low levels of dissolved H_2S) and, to a lesser extent, in anoxic sediments overlain by mildly oxygenated bottom waters (Crusius et al., 1996; Morford and Emerson, 1999; Morford et al., 2005; Partin et al., 2013; Reinhard et al., 2013a). By contrast, high authigenic Mo enrichments in sediments require the accumulation of dissolved H_2S in the water column. Anoxic sediments beneath mildly oxygenated bottom waters display mild Mo enrichments if dissolved H_2S is present in sediment pore fluids at shallow depths below the sediment-water interface (Crusius et al., 1996; Morford and Emerson, 1999; Morford et al., 2005).

Because these trace metals have long seawater residence times relative to the average ocean turnover time (~1–2 kyr), their enrichment record in open-marine anoxic sediments reflects, in principle, the global marine redox state. Once an environment becomes authigenically active for a particular redox-sensitive trace metal, the degree of authigenic enrichment of that metal in sediments will be broadly proportional to its dissolved seawater inventory (Algeo and Lyons, 2006; Scott et al., 2008; Reinhard et al., 2013a), which on a global scale will be controlled mainly by the collective state of marine redox conditions—once pervasive oxidative continental weathering and the associated riverine flux of dissolved anionic metal complexes are established (Scott et al., 2008; Partin et al., 2013; Reinhard et al., 2013a). In an ancient ocean that was more anoxic than today, a globally higher rate of metal burial in seafloor sediments should occur, leading to a decrease in seawater metal concentrations and thus lower metal enrichments in coeval ORM (Scott et al., 2008; Sahoo et al., 2012; Partin et al., 2013; Reinhard et al., 2013a).

Building from the approach of Scott et al. (2008), new constraints on the extent of ocean anoxia were recently presented for the mid-Proterozoic ocean using trace element records. Through a mass-balance model combined with Mo and Cr enrichments in ORM, Reinhard et al. (2013a) estimated the extent of mid-Proterozoic anoxia to be at least 30–40% of the modern seafloor area, with euxinic conditions covering less than ~1–10% of the modern seafloor. However, the Cr enrichment record is also consistent with virtually complete seafloor anoxia. A disadvantage of Cr is its high detrital contribution to ORM (Reinhard et al., 2013a), which makes it an intrinsically less precise tracer for benthic redox landscapes under conditions of pervasive marine anoxia. Based on the U record, Partin et al. (2013) postulated that anoxic conditions covered over 50% of the modern seafloor area. However, this estimate assumes that the U burial flux in anoxic basins on continental margins applies to the global seafloor. Hence, the mass-balance model of Partin et al. (2013) is over-sensitive to anoxic conditions and consequently may underestimate the true extent of ocean anoxia.

Rhenium (Re) behaves conservatively in oxygenated seawater and, unlike Mo, can be efficiently removed to anoxic sediments at low dissolved H_2S levels when the bottom waters are weakly oxygenated or anoxic, thus making it a more effective proxy for tracking general ocean anoxia (i.e., combined euxinic and ferruginous anoxia) (Colodner et al., 1993; Crusius et al., 1996;

Morford and Emerson, 1999; Morford et al., 2005, 2012). Although Cr and U behave similarly in this regard (Partin et al., 2013; Reinhard et al., 2013a), the magnitude of authigenic Re enrichment in anoxic marine sediments is significantly higher than the detrital background compared with Cr and U, as reflected by higher Re enrichment factors in organic-rich sediments relative to upper crust (Table 1). These higher Re enrichments indicate that Re is more sensitive to O_2-deficient conditions than Cr and U and can potentially provide more quantitatively precise information on deep-sea redox state. Because of these distinct geochemical properties, the enrichment record of Re in anoxic marine ORM may provide a novel and complementary perspective on global ocean redox conditions.

To yield new insights into the evolution of marine redox conditions during the mid-Proterozoic as well as to infer first-order variations in the seawater concentration of Re through geologic time, we compiled Re concentration data for ORM from the literature and report new Re concentration data from several Precambrian intervals. We quantify the sources and sinks of the Re marine cycle based on modern observations and integrate these observations with the mass-balance approach developed by Reinhard et al. (2013a). Using this mass-balance model, we discuss the sensitivity of the marine Re cycle with respect to the expansion and contraction of ocean anoxia during this interval of Earth's history and its implications for the extent and variability of mid-Proterozoic ocean anoxia.

2. The modern marine Re cycle

2.1 Marine sources

Rhenium exists in seawater primarily as the soluble perrhenate oxyanion ReO_4^-, with a concentration of 40 pmol kg^{-1} (Anbar et al., 1992; Colodner et al., 1993). In the modern ocean, most of this dissolved reservoir is derived from oxidative weathering of sulfide minerals and ORM in the upper continental crust, based on the good correlation observed globally between Re and sulfate concentrations in rivers (Colodner et al., 1993; Miller et al., 2011; Dubin and Peucker-Ehrenbrink, 2015). Excluding anthropogenic inputs, the average Re concentration of rivers has been calculated to be 11.2 pmol kg^{-1} based on data from 38 rivers on five continents (~37% of total water discharge; 25% of continental exorheic drainage area). This estimate yields a riverine flux of 4.29×10^5 mol yr^{-1}, which corresponds to a seawater residence time of 1.3×10^5 yr (Miller et al., 2011).

Seafloor hydrothermal vents have been considered as an additional component of the marine Re cycle (Morford and Emerson, 1999). It is postulated that Cl^- complexation in high-temperature hydrothermal fluids may yield high Re concentrations (Xiong and Wood, 1999; 2002). However, Re may be removed from such fluids by precipitation of sulfides under fluid-sulfide equilibrium (Miller et al., 2011). Miller et al. (2011) presented the first published Re measurements in high-temperature hydrothermal fluids in the Manus Basin, from which an estimated flux of 1.2×10^3 mol yr^{-1} was derived. If globally representative, this flux constitutes 0.1% of the pre-anthropogenic riverine Re input flux and thus has a negligible influence on the modern oceanic Re mass balance.

Low-temperature hydrothermal fluids are a possible minor source of Re to the modern ocean (like Mo; Morford and Emerson, 1999), but no data exist to quantify this flux. Reinhard et al. (2013a) calculated that the modern low- and high-temperature hydrothermal fluxes of Mo and Cr are unlikely to be above ~10% and ~1% of their riverine fluxes, respectively. Given the similar geochemical behaviour of Re and Mo, it is reasonable to assume that the modern hydrothermal flux of Re to the oceans is also small.

2.2 Marine Sinks

2.2.1 Overview

Sink fluxes of Re from modern seawater comprise sediment burial in three redox settings: oxic, suboxic (defined below), and anoxic. Because of the solubility of ReO_4^-, Re accumulation is typically very slow in well-oxygenated marine settings where O_2 penetrates more than 1 cm below the sediment-water interface. By contrast, Re accumulation is significantly more efficient in anoxic marine settings. Rhenium removal from an anoxic water column is likely dominated by abiotic redox reactions rather than biological uptake. In anoxic conditions, Re is reduced from the soluble heptavalent (VII) to the insoluble tetravalent (IV) state (Colodner et al., 1993; Crusius et al., 1996; Morford and Emerson, 1999; Morford et al., 2005). Scavenging of Re^{4+} by organic matter is suggested by the direct association of Re with organic matter in fine-grained sediments and their lithified equivalents (ORM) (Selby and Creaser, 2003; Georgiev et al., 2012). In some ORM, a good positive correlation is observed between Re concentration and total organic carbon (TOC) content (e.g., Rooney et al., 2010) as has been observed for Mo (Algeo and Lyons, 2006), but this is not observed in all ORM (e.g., Cohen et al., 1999). Decoupling of Re and TOC contents in ORM may reflect temporal (i.e., stratigraphic) variations in local bottom water Re concentrations at the site of deposition. Co-precipitation of Re^{7+} with a Fe–Mo–S phase has also been proposed for removal of Re from sulfide-bearing waters (Helz and Dolor, 2012), which might be responsible for a scatter of Re concentration vs. TOC content in ORM.

Rhenium burial rates characteristic of each of the three settings are calculated based on observations in modern marine environments (Table 2; supplementary tables S1, S2). Below, we describe how representative burial rates were calculated for each sink.

2.2.2 Oxic sink

Oxic settings are characterized by permanent burial of Mn oxides in sediments where O_2 penetration depths below the sediment-water interface are large. To be consistent with previous trace metal studies, we define oxic settings as those with an O_2 penetration depth >1 cm, at which point Mn redox cycling begins (Morford and Emerson, 1999). Rhenium adsorption onto Fe–Mn oxides is minimal relative to other redox-sensitive trace metals such as Mo (Koide et al., 1986; Colodner et al., 1993). As discussed in Reinhard et al. (2013), the extent of modern seafloor covered by oxic sediments with an O_2 penetration depth >1 cm is ~84%.

The modern oxic Re flux is dominated by continental margin sediments, where the sediment mass accumulation rate is high. It was assumed in previous Re budget reconstructions that pelagic sediments, which form the majority of modern-day oxic seafloor, are a negligible sink. This is supported by an average $[\mathrm{Re}]_{\mathrm{sed}}$ of 0.05 ppb in pelagic sediments of the North Atlantic (Colodner, 1991), which translates into a burial flux of 1.2×10^{-5} ng cm^{-2} yr^{-1} (assuming an average linear sedimentation rate). The pelagic burial rate, designated to represent Re burial in abyssal regions of the seafloor, is combined with an average burial rate of 7.4×10^{-3} ng cm^{-2} yr^{-1} for Re in shelf sediments deposited from well-oxygenated waters on continental margins (Sea of Japan, Central Arctic Ocean, Northwestern US margin, and African margin; Table 2) to yield an area-weighted average oxic Re burial rate of 1.6×10^{-3} ng cm^{-2} yr^{-1} (continental margin and deep-sea abyssal regions cover an area of 7.4×10^{17} cm^2 and 2.7×10^{18} cm^2, respectively; Sverdrup et al., 1942; Wollast, 2003). Again, the oxic burial rate is dominated by continental margin sediments and is unlikely to vary significantly with new estimates for pelagic sediments.

2.2.3 Suboxic sink

Similar to Mo, Cr, and U, a significant difference exists in Re accumulation rates under anoxic water columns and those under weakly oxygenated bottom waters (Colodner et al., 1993; Crusius et al., 1996; Morford and Emerson, 1999; Morford et al., 2005). To be consistent with previous studies on trace element redox modeling, we define the suboxic setting as areas where the O_2 penetration depth below the sediment-water interface is <1 cm (Partin et al., 2013; Reinhard et al., 2013a). This condition accounts for areas of the seafloor where dissolved O_2 is present in bottom waters but typically at levels low enough (<10–100 μM; higher values are possible in shallow coastal locations; Morford and Emerson, 1999; Morford et al., 2005, 2007, 2012) so that Fe–Mn oxides are not permanently buried and reduction of Re occurs in the anoxic sediment pore waters, resulting in appreciable authigenic accumulation of Re in sediments. In modern suboxic continental margin environments, authigenic Re accumulation occurs in anoxic sediments without significant Mo accumulation if dissolved H_2S in shallow pore waters is low, thus demonstrating that Re removal rate is not scaled to H_2S availability (Morford and Emerson, 1999; Morford et al., 2005).

Depending on the organic carbon flux and oxygen penetration depth, modern suboxic Re burial rates range from 0.2–0.3 ng cm^{-2} yr^{-1} at the Northwestern US margin to ~1.5 ng cm^{-2} yr^{-1} in the Gulf of California. Our estimate of the suboxic Re burial rate combines these values with those observed in oxygen-minimum zones and high productivity regions in the Californian Borderlands, African margin, Laurentian Trough, Buzzards Bay, Hingham Bay, and the Arabian Sea (Table 2). Weighting by relative areal extent yields a suboxic Re burial rate of 0.41 ng cm^{-2} yr^{-1}. The total area of modern suboxic seafloor is not precisely known and is solved using other sink parameters in the mass-balance model, following Reinhard et al. (2013). The modern suboxic seafloor is calculated to make up ~4.7% of the global seafloor.

2.2.4 Anoxic sink

Rhenium is most effectively removed to sediments deposited from anoxic bottom waters. In the modern ocean, such environments are restricted to marginal basins (e.g., Cariaco Basin), seafloors beneath areas of intense upwelling (e.g., Peru margin, Namibian shelf), and highly restricted basins (e.g., the Black Sea). In the modern ocean, anoxic seafloors are dominated by euxinia due to the excess of sulfide relative to Fe (i.e., above a ratio of 1Fe:2S, the stoichiometric proportions of pyrite). During the Proterozoic Eon, however, ferruginous anoxia is believed to have been more widespread (Poulton et al., 2010; Planavsky et al., 2011). Extrapolating from modern observations of significant authigenic Re accumulation without Mo accumulation in anoxic sediments when dissolved H_2S in pore waters is low, we infer that Re burial in sediments below anoxic waters does not depend on H_2S availability in the water column. This independence allows us to merge both types of anoxia into one sink in this study.

We adopt the latest estimate of ~0.11% for the modern anoxic seafloor area published by Reinhard et al. (2013a), which combines results from anoxic basin studies. A portion of modern anoxic sediments are found in highly restricted basins where Re is significantly depleted in deep waters due to slow renewal rates (as demonstrated for the Black Sea; Colodner et al., 1995). As such, Re burial rates in restricted anoxic settings are lower compared with more open-water anoxic settings. For example, the estimated burial rate of Re in the Black Sea (<0.5 ng $cm^{-2}yr^{-1}$; Ravizza et al., 1991) is lower than those estimated for the less restricted Cariaco Basin (1.3–1.6 ng cm^{-2} yr^{-1}; Calvert et al, 2015; this study) and Saanich Inlet (1–1.5 ng cm^{-2} yr^{-1}; Poirier, 2006). For the purpose of establishing a model for the well-mixed open ocean, such highly restricted basins (e.g., the Black Sea) are excluded from our Re mass-balance.

Published measurements of anoxic Re burial rates exist for a few small basins such as Walvis Bay and Saanich Inlet (2.1 and 1–1.5 ng cm^{-2} yr^{-1}, respectively; Colodner et al., 1993; Poirier, 2006). Measurements from anoxic sediments in a few continental margins (characterized by intense upwelling) display much higher variation (Table 2). For our study, we select the large and well-characterized Cariaco Basin from which new [Re]$_{sed}$ data yield an anoxic burial rate of 1.34 ng cm^{-2} yr^{-1}, consistent with published values (Calvert et al., 2015; SI). The Cariaco Basin is the largest and best understood modern anoxic basin that has a relatively unrestricted connection to the open ocean, as well as a fairly constant [Re]$_{sed}$ record and a linear sedimentation rate (Peterson et al., 2000). Hence, we believe that this value is more representative of anoxic conditions in the modern ocean than assuming arithmetic or area-weighted averages of anoxic burial rates. In any case, the Re burial rate in the Cariaco Basin is roughly in the middle of the range of Re burial rates observed in other anoxic basins and upwelling continental margin systems.

Our estimated anoxic burial rate of ~1.34 ng cm^{-2} yr^{-1} is three times greater than the suboxic burial rate, averaged at 0.42 ng cm^{-2} yr^{-1}. The oxic burial rate, 1.6×10^{-3} ng cm^{-2} yr^{-1}, is extremely low by comparison. These averages are combined with the areal extent of each setting to determine the magnitude of the sink fluxes (Table 3). In summary, Re removal from modern seawater is dominated by the suboxic sink, which equates to 88% of the riverine flux. The oxic and anoxic sinks are much smaller, both at ~6% of the riverine flux. This relationship is comparable with the modern Cr budget estimated by Reinhard et al. (2013a), where the oxic, suboxic, and anoxic sinks constitute 10%, 84%, and 6% of the riverine Cr flux, respectively. Again, anoxic sinks are relatively small because this redox condition is minor in the modern ocean. The oxic, suboxic, and anoxic seafloor areas in our mass balance totals ~89% (Table 3), implying that ~11% of the seafloor is authigenically neutral with respect to Re.

Based on a redox-sensitive behavior of Re that is generally comparable to other redox-sensitive elements (e.g., Mo, Zn, U), it is postulated that Re burial flux associated with the anoxic sink is controlled by the size of the dissolved Re reservoir; this is an important assumption in our study and remains to be confirmed and ideally quantified by experimental work or measurements of bottom water Re concentrations from modern anoxic basins (i.e., other than the Black Sea). A significant implication of this assumption is that the size of the dissolved reservoir can be locally influenced by the degree of basin restriction from the open ocean. In the highly restricted Black Sea, for example, slow deep-water renewal rates have caused depletion of Re in the bottom waters (Colodner et al., 1995), which should cause lower Re enrichments and burial fluxes in organic-rich sediments (when normalized to TOC) relative to less restricted anoxic settings. Indeed, the Re concentration and burial flux of Unit I sediments in the Black Sea is generally lower than those of the Cariaco Basin and other relatively open-ocean anoxic settings (Table 2; keeping in mind that sedimentation rate and organic carbon flux also locally influence Re concentrations in organic-rich sediments). A similar relationship between metal concentrations in bottom waters and organic-rich sediments in anoxic basins has been noted for other redox-sensitive elements (e.g., Mo, U, and Zn; Algeo and Lyons, 2006; Scott et al., 2008, 2013; Partin et al., 2013).

Extrapolating from this observation, the Re concentration of anoxic sediments deposited in relatively open-marine settings (i.e., negligible to mild basin restriction) should show a first-order relationship with the size of the global seawater Re reservoir, which in turn depends on the riverine flux and the temporally varying extent of oxic, suboxic, and anoxic conditions on the seafloor. The riverine flux of Re is assumed to have become largely independent of atmospheric O_2 levels at the early stage of the GOE, when atmospheric O_2 levels rose above the threshold (as low as <0.001% PAL) required to support subaerial oxidative dissolution of crustal sulfide minerals and delivery of the related products to the oceans (Reinhard et al., 2013b; Greber et al., 2015). Details of these assumptions await further study, particularly weathering relationships. However, changes in the size of the seawater Re inventory during the Proterozoic and Phanerozoic were likely controlled primarily by global marine redox distribution. The first-order temporal and spatial extent of anoxic conditions in the mid-Proterozoic ocean can thus be inferred by examining the magnitude of Re enrichment in ORM.

3. Analytical methods

The pronounced enrichment of authigenic Re in anoxic ORM make this lithology the ideal archive for tracking changes in the oceanic Re reservoir through geological time. Hence, we compiled a database of Re concentrations and associated TOC contents in marine ORM through a literature survey, supplemented with new analyses of Precambrian ORM (see Supplementary data files). New Re concentration data were obtained via HF–HNO_3–HCl dissolution of ashed sample powders followed by analysis on a Thermo Scientific X Series quadrupole inductively-coupled plasma mass-spectrometer (Q–ICP–MS) at the W. M. Keck Foundation Laboratory for Environmental Biogeochemistry, Arizona State University, following the specific methods described in Anbar et al. (2007) and Kendall et al. (2010). Some new Re data were also obtained via Carius tube dissolution of sample powders in a Cr^{VI}–H_2SO_4 medium, chemical separation of Re, and analysis by isotope dilution–negative thermal ionization mass-spectrometry (ID–NTIMS; Thermo TRITON) at the Canadian Centre for Isotopic Microanalysis, University of Alberta (e.g., Kendall et al., 2015a). The accuracy of Re measurements by Q–ICP–MS was verified by analysis of ORM for which the Re concentrations were also determined by the more precise ID–NTIMS method (Kendall et al., 2010). Data reported in the literature were predominantly derived by ID–NTIMS and ICP–MS. Uncertainties for Re concentrations are usually <10% for Q–ICP–MS, and typically <1% for isotope dilution analysis using NTIMS or MC–ICP–MS. All TOC contents in the compilation were reported in previous studies. For samples with pre-existing TOC data, the Re concentrations were measured on the same sample powders used for TOC determinations.

All datasets compiled from previous studies (supplementary tables S3, S4) were filtered first for marine, fine-grained siliciclastic sediments based on petrographic examination. ORM are defined by having a total organic carbon content of >0.4 wt% (Lyons and Severmann, 2006; Partin et al., 2013; Reinhard et al., 2013a), so to avoid spuriously high Re/TOC ratios. We further applied the geochemical filter of $Fe_T/Al > 0.5$ which delineates sediments deposited under anoxic conditions (e.g., Lyons and Severmann, 2006; Poulton et al., 2010; Planavsky et al., 2011). Where the above information is not available, efforts were made to determine local redox conditions using other geochemical proxies (e.g., Mo enrichments). We define Re concentrations equal or greater than 5.0 ppb (i.e., >10 times the crustal average of ~0.2–0.4 ppb; Esser and Turekian, 1993; Peucker-Ehrenbrink and Jahn, 2001; Dubin and Peucker-Ehrenbrink, 2015) as being diagnostic for deposition from sediment anoxia. This approach enables an internally consistent compilation that includes samples deposited from mildly/weakly oxygenated waters (with sediment anoxia) and from fully anoxic waters. We assume that levels of authigenic Re enrichment generally scale to first-order with water column Re concentrations (i.e., following Scott and Lyons, 2012 for Mo), thus allowing us to track broad first-order changes in the Re concentration of ORM via comparison of time-bin averages. Although Re concentrations of less than 5.0 ppb may occur in some Archean ORM deposited beneath a fully anoxic atmosphere, only a minority of Archean samples had sufficiently low Re concentrations to be excluded from the compilation. We also note that Re concentrations in Unit I and II sediments of the restricted Black Sea are significantly above this threshold (~20–76 ppb; Ravizza et al., 1991; Crusius et al., 1996; Piper and Calvert, 2011); the filter therefore does not exclude Black Sea-type restricted basins from the compilation. As Re burial is independent of sulfide (H_2S) availability, no filter for euxinia is required as in the case for Mo. Temporal averages were binned at 5 Myr intervals ("time-point means") to compensate for age uncertainties; for example, the time-point mean $[Re]_{sed}$ for 660 Ma is the arithmetic mean of all $[Re]_{sed}$ data from the ca. 657 Ma Aralka Formation (Schaefer and Burgess, 2003; Kendall et al., 2006) and the ca. 659 Ma Tashir Formation (Rooney et al., 2015).

Basin connectivity was inferred from sedimentology and paleogeographic reconstructions, where available. Because we model Re burial in unrestricted marine basins, we excluded units deposited in settings with obvious extreme basin restriction/isolation (i.e., terrestrial settings), where Re accumulation rates in sediments are typically lower compared with open-marine settings.

Published Re–Os depositional ages are listed in supplementary data tables to demonstrate minimal post-depositional disturbance of Re (Anbar et al., 2007). Oxidative weathering is known to cause scattered Re–Os isotope systematics (e.g., Georgiev et al., 2012), therefore it is reasonable to expect that deep penetration of O_2 below the sediment-water interface would similarly disturb Re–Os systematics in the sediment (Crusius and Thomson, 2003). ORM affected by post-depositional hydrothermal alteration, which is known to remobilize both elements, are excluded from the compilation (Kendall et al., 2009; Rooney et al., 2011). We included samples that have experienced anhydrous greenschist facies metamorphism because the Re–Os isotope systematics in ORM is not usually disturbed under such conditions (e.g., Rooney et al., 2011).

Radioactive decay of ^{187}Re, which makes up ~63% of naturally occurring Re, causes the present-day Re concentration of ORM to be lower than that at the time of deposition. However, the slow rate of ^{187}Re decay (half-life = 41.6 Ga) has a minimal effect on observed Re concentrations (maximum correction factor of ~3% for Archean ORM), and hence no correction was made for this effect.

4. Results

Our filtered compilation of $[\mathrm{Re}]_{\mathrm{sed}}$ (76 binned time points) and $[\mathrm{Re}]_{\mathrm{sed}}$/TOC (52 binned time points) through geologic time is presented in figures 1 and 2, with statistical parameters summarized in Table 4. The full compilation database is available as supplementary spreadsheet files. A salient observation of the compilation is that both $[\mathrm{Re}]_{\mathrm{sed}}$ and $[\mathrm{Re}]_{\mathrm{sed}}$/TOC display broad fluctuations through geologic time and that four distinct stages are discerned. For comparison, we calculated mean $[\mathrm{Re}]_{\mathrm{sed}}$ and $[\mathrm{Re}]_{\mathrm{sed}}$/TOC for the four stages by taking the arithmetic mean of the binned time-point means in each stage. Using the binned time-point means serves to minimize skewing of the stage mean values by individual ORM units with larger datasets.

Mean $[\mathrm{Re}]_{\mathrm{sed}}$ for the four stages, calculated from time-point mean $[\mathrm{Re}]_{\mathrm{sed}}$ values (Table S4 in the supplementary database), are 13.0 ± 4.4 ppb (Stage 1; 1SD; 9 binned time points), 102.2 ± 15.1 ppb (Stage 2; 1SD; 2 binned time points), 20.8 ± 19.8 ppb (Stage 3; 1SD; 21 binned time points), and 154.9 ± 207.9 ppb (Stage 4; 1SD; 44 binned time points) (Table 4). Mean $[\mathrm{Re}]_{\mathrm{sed}}$/TOC for the four stages are 4.7 ± 2.7 ppb/wt.% (Stage 1; 1SD; 5 binned times points), 14.8 ± 6.2 ppb/wt.% (Stage 2; 1SD; 2 binned time points), 8.1 ± 3.5 ppb/wt.% (Stage 3; 1SD; 10 binned time points), and 31.3 ± 39.2 ppb/wt.% (Stage 4; 1SD; 35 binned time points). The time-point mean $[\mathrm{Re}]_{\mathrm{sed}}$ and $[\mathrm{Re}]_{\mathrm{sed}}$/TOC values at 1105 Ma (82.6 ppb, 16.0 ppb/wt.%) are significantly higher than the other stage 3 values, which range between 5.7 and 52.2 ppb and between 4.3 and 10.4 ppb/wt.%. If the 1105 Ma time-point mean is excluded, stage 3 has a mean $[Re]_{sed}$ of 17.7 ± 14.5 ppb (1SD; 20 binned time points) and a mean $[Re]_{sed}$/TOC of 7.3 ± 2.4 ppb/wt.% (1SD; 9 binned time points) (Table 4).

As the time-binned mean $[Re]_{sed}$ in each stage do not follow a normal or log-normal distribution, bootstrap analysis was carried out to estimate the confidence interval of each of the four sets of binned time-point mean $[Re]_{sed}$ (SI). The means of 10,000 $[Re]_{sed}$ bootstrap time-point means (and associated 95% confidence intervals) for stages 1, 3, and 4 are 13 ppb (10, 17), 25 ppb (14, 37), and 151 ppb (95, 220), respectively (Table 4). The means of 10,000 $[Re]_{sed}$/TOC bootstrap time-point means (and associated 95% confidence intervals) for the same three stages are 5 ppb/wt.% (2, 7), 7 ppb/wt.% (5, 9), and 28 ppb/wt.% (18, 40), respectively (Table 4). A direct comparison of bootstrap statistics between stages 1, 3, and 4 shows that the bootstrap mean $[Re]_{sed}$ of stage 4 is distinct from the other two stages, with 95% confidence intervals taken into account; however, the bootstrap 95% confidence intervals for stages 1 and 3 overlap. The bootstrap analysis demonstrates that while high Re enrichment in stage 4 is statistically significant, the low $[Re]_{sed}$ in stages 1 and 3 are statistically similar to each other.

Our plot of $[Re]_{sed}$ through time (Fig. 1) best shows the trend in maximum $[Re]_{sed}$ values, which to first-order reflects the maximum size of the Re seawater reservoir in each stage. The significance of the pattern displayed by the maximum $[Re]_{sed}$ trend is supported by mean $[Re]_{sed}$ values derived via bootstrap analysis (Table 4). Our compilation suggests two separate stages of elevated $[Re]_{sed}$ during the latter part of the GOE (stage 2) and the Phanerozoic (stage 4), with the latter characterized by much higher maximum enrichments. Maximum $[Re]_{sed}$ in stages 1 and 3 (except the Touirist Formation) are lower by comparison, with stage 3 containing mildly higher values than stage 1. We further tested for possible bias of $[Re]_{sed}$ distribution by sample size. Median $[Re]_{sed}$ binned at 100 Myr intervals show only a very weak correlation with sample size ($R^2 = 0.02, n = 19, \rho = 0.57$; Fig. 3). We therefore consider it unlikely that the distribution of $[Re]_{sed}$ data is biased by sample size.

5. Discussion

5.1 Temporal trends in Re concentrations

Our temporal compilation of Re concentrations ($[Re]_{sed}$) in anoxic marine ORM (Fig. 1) displays four distinct stages that correspond to the evolution of atmospheric and oceanic O_2 content (Table 4). The choice of divisions is supported by statistical tests which confirm that the difference in average $[Re]_{sed}$ between stages is statistically significant (see section 4.1). We note that these first-order trends are still observed for a less rigorously filtered compilation. A similar trend is observed when Re concentrations are normalized to TOC contents (Fig. 2), demonstrating that the first-order secular variations in $[Re]_{sed}$, as represented by the four stages, likely result from first-order changes in the global seawater Re reservoir rather than changes in local organic carbon fluxes to the seafloor. Although variations in riverine Re fluxes might be linked to changes in crustal exhumation rates (e.g., during supercontinent assembly vs. dispersal) and a hypothesized transition from relatively more mafic to felsic continental crust by ~2.5 Ga (Dhuime et al., 2015; Tang et al., 2016), a simple sensitivity test of our mass-balance model demonstrates that such input flux variations should impart minimal influence on the $[Re]_{sed}$ record (SI). In general, our interpretation of atmosphere-ocean O_2 levels based on the Re record conforms well to that derived from the higher-resolution Cr and U records (Partin et al., 2013; Reinhard et al., 2013a).

Stage 1 covers the Archean and the earliest Proterozoic prior to the GOE. Consistently low $[Re]_{sed}$ during this interval indicates a small oceanic Re inventory, which in turn points to extensive seafloor anoxia and a small pre-GOE riverine Re flux because of an O_2-poor atmosphere. Some Late Archean units near the end of this stage have higher Re concentrations that are consistent with other geochemical evidence for transient increases in atmosphere-ocean O_2 levels that enabled oxidative dissolution of crustal sulfide minerals (Siebert et al., 2005; Anbar et al., 2007; Wille et al., 2007; Reinhard et al., 2009; Kendall et al., 2010, 2015a).

Stage 2 spans the time interval between 2.50 and 2.05 Ga and corresponds to an increase in global atmosphere-ocean O_2 content associated with the GOE (Bekker et al., 2004; Bekker and Holland, 2012; Planavsky et al., 2012; Partin et al., 2013). During the second half of the GOE, the ca. 2.22–2.06 Ga Lomagundi Event was likely marked by elevated organic matter burial with sedimentary rocks as inferred from high $\delta^{13}C$ values in coeval carbonates. The high rates of primary productivity may have been driven by enhanced phosphorus fluxes to the oceans caused by the initial oxidative weathering of sulfide minerals in exposed Archean continental crust (Bekker and Holland, 2012). This organic matter burial event was likely accompanied by significant release of O_2 to the atmosphere (Karhu and Holland, 1996), consistent with geochemical and geological evidence for a shift to higher seawater concentrations of Mo, U, Cr, V, and SO_4^{2-} in response to this hypothesized increase in atmosphere-ocean oxygenation (Schröder et al., 2008; Scott et al., 2008, 2014; Bekker and Holland, 2012; Planavsky et al., 2012; Reuschel et al., 2012; Sahoo et al., 2012; Partin et al., 2013; Reinhard et al., 2013a). As for other redox-sensitive metals, the increase in oxidative terrestrial weathering accompanying the GOE would have permanently established a continuous riverine flux of dissolved Re to the oceans that, along with contraction of seafloor anoxia, enabled buildup of a larger dissolved Re reservoir in oxygenated seawater. Such a scenario is supported by high average $[Re]_{sed}$ values for the Sengoma Argillite and Zaonezhskaya formations (117.4 and 87.1 ppb, respectively), which are well above the maximum average $[Re]_{sed}$ observed for any ORM in stage 1 (19.9 ppb).

After the GOE, $[Re]_{sed}$ drops significantly during stage 3 (2.05–0.61 Ga), approaching near-Archean values in many ORM. This decrease in authigenic Re enrichment mirrors a similar drop in the U, V, and Cr concentrations in ORM deposited over the one billion years after the Lomagundi Event (Sahoo et al., 2012; Partin et al., 2013; Reinhard et al., 2013a). Molybdenum abundances in stage 2 and 3 ORM, which are far more sensitive to the extent of ocean euxinia than general anoxia compared with other redox-sensitive metals, are intermediate between those seen in Archean and Phanerozoic ORM (Scott et al., 2008; Sahoo et al., 2012; Reinhard et al., 2013a). The lack of S-MIF in stage 3 sedimentary rocks indicates that atmospheric O_2 levels were high enough to support persistent oxidative mobilization of Re from crustal sulfide minerals and organic matter (Reinhard et al., 2013b; Planavsky et al., 2014; Greber et al., 2015; Cole et al., 2016). Hence, the drop in authigenic Re enrichments during stage 3 likely reflects an expansion of global ocean anoxia rather than a decline in the riverine Re flux. The $[Re]_{sed}$ in most stage 3 ORM are similar to stage 1 ORM, indicating that the extent of oxygenation generally remained far below that of the Lomagundi Event (stage 2) and the Phanerozoic (stage 4).

The ca. 1.1 Ga Touirist Formation, deposited in an epeiric sea during global sea-level high-stand conditions (e.g., Gilleaudeau and Kah, 2015), has an average $[Re]_{sed}$ (82.6 ppb) that is significantly higher than the overall average of other stage 3 ORM (25.2 ppb) and is similar to stage 2 levels, suggesting that atmosphere-ocean oxygenation at ca. 1.1 Ga may have been higher than at other times during stage 3 after the Lomagundi Event. Some samples of the Touirist Formation have undergone contact metamorphism. However, the Re–Os isotope systematics of these thermally overmature samples are not significantly perturbed by flash pyrolysis as indicated by a Re-Os age of 1105 ± 37 Ma (MSWD = 8.8) that, although exhibiting evidence for minor open-system behavior (MSWD > 1), is not statistically different from a Re–Os age of 1107 ± 12 Ma (MSWD = 1.1) derived for a separate stratigraphic interval of thermally immature samples in the Touirist Formation (Rooney et al., 2010). Two samples with high Re concentrations of > 85 ppb come from the interval yielding a Re–Os isochron with MSWD ~ 1, suggesting that the high Re levels in the Touirist Formation represent a primary sedimentary enrichment. As a similar spike in sedimentary enrichment is absent from the correlative stage 3 records of U (Partin et al., 2013), a higher-resolution record of Re concentration for stage 3 is needed to robustly evaluate if the Touirist Formation truly represents an episode of higher oxygenated conditions at ca. 1.1 Ga.

Stage 4 (<0.61 Ga) covers the latest Neoproterozoic and the Phanerozoic Eon. Along with high Mo, U, V, and Cr concentrations, the overall higher Re concentrations in ORM from this stage point to the build-up of dissolved, redox-sensitive trace metals in more oxygenated oceans, (Scott et al., 2008; Sahoo et al., 2012; Partin et al., 2013; Reinhard et al., 2013a). Given the growing geochemical evidence for dynamic fluctuations in Neoproterozoic ocean redox conditions extending back to ca. 800 Ma (e.g., Sahoo et al., 2012, 2016; Planavsky et al., 2014; Kendall et al., 2015; Sperling et al., 2015; Thomson et al., 2015; Cole et al., 2016; Kuznetsov et al., in press), the boundary between stages 3 and 4 may potentially shift back in time with new Re data. We also note the general absence of high Re enrichments (like those observed in the Late Ediacaran, Early Cambrian (>535 Ma), and Late Phanerozoic ORM) during the early Paleozoic (ORM deposited between 535 and 375 Ma). Although the temporal resolution of the Re dataset is low for this time interval, the lower Re enrichments are consistent with less oxygenated conditions during the early Paleozoic compared with other Phanerozoic intervals. This inference is also consistent with generally lower U concentrations, lighter Mo isotope compositions, and Fe speciation evidence for widespread anoxic deposition of the Early Paleozoic ORM (Dahl et al., 2010; Partin et al., 2013; Sperling et al., 2015).

Following permanent establishment of widespread ocean oxygenation and contraction of anoxia to mostly marginal marine settings (i.e., oxygen-minimum zones and restricted basins), expansions of anoxia occurred as transient and sporadic oceanic anoxic events (OAEs), typically associated with mantle plume events, emplacement of Large Igneous Provinces (LIPs), submarine ocean plateau, greenhouse conditions, extreme rates of continental weathering, and high pCO_2. During the Toarcian OAE, the Re and Mo enrichments of ORM are muted, indicating drawdown of the oceanic Re and Mo reservoirs in response to expanded anoxia (Pearce et al., 2008; Owens et al., 2016). Conversely, during the Cretaceous OAEs 1a and 2, which were associated with LIP emplacement, Re concentrations of ORM are often not muted and are mildly correlated with excursions to higher Os concentrations and unradiogenic $^{187}Os/^{188}Os$—suggesting delivery of magmatic Re (and Os) to seawater in sufficient quantities to offset the increased burial of Re (and Os) into anoxic sediments (Turgeon and Creaser, 2008; Bottini et al., 2012; du Vivier et al., 2014; Kendall, 2014).

5.2 Constraints on the extent of mid-Proterozoic ocean anoxia

To arrive at a quantitative estimate for the extent of mid-Proterozoic ocean anoxia, we constructed a model relating seafloor redox distribution, Re burial rates under different redox regimes, and authigenic Re enrichment in anoxic sediments within a mass-balance framework built on observations from modern environments. Our model is adopted from that developed by Reinhard et al. (2013a) for the Cr and Mo records.

We begin by defining the global Re marine reservoir in a conventional steady-state mass-balance, where the difference between mass entering (M_{in}) and exiting the system (M_{out}) equals change in storage:

$$M_{in} - M_{out} = \int_0^V [\mathrm{Re}]\, dV, \qquad \text{Eq. 1}$$

Where dissolved Re concentration, [Re], is integrated over a global ocean volume, V. By taking the derivative with respect to time, t, the mass terms are replaced with source (F_{in}) and sink (F_{out}) fluxes:

$$F_{in} - F_{out} = \frac{d}{dt}\int_0^V [\mathrm{Re}]\, dV. \qquad \text{Eq. 2}$$

As we are interested in long-term temporal shifts (>10^6 years) in ocean redox distribution, we assume steady-state conditions in the system ($\frac{d}{dt}\int_0^V [\mathrm{Re}] dV = 0$, and therefore $F_{in} = F_{out}$).

As outlined above, riverine delivery dominates the Re input flux to the oceans and is assumed to be constant for a post-GOE atmosphere-ocean system. Hydrothermal fluids, which are assumed to constitute a minor flux relative to riverine input in a post-GOE world (i.e., excluding transient magmatic-hydrothermal events), are excluded from consideration. Sink fluxes consist of removal to sediments under oxic, suboxic, and anoxic settings. Hence:

$$F_{in} = F_{oxic} + F_{suboxic} + F_{anoxic}. \qquad \text{Eq. 3}$$

The sink terms are each expressed as:

$$F_i = \kappa A_i b_i, \qquad \text{Eq. 4}$$

where A_i is the seafloor area covered by the specific redox setting (dimensions cm^2), and b_i is the characteristic metal burial rate for that setting as observed in the modern ocean (dimensions ng cm^{-2} y^{-1}). The non-dimensional coefficient κ relates Re burial flux to seawater concentration:

$$\kappa = \left(\frac{[\mathrm{Re}]'}{[\mathrm{Re}]_{\mathrm{M}}}\right)^{\alpha}, \qquad \text{Eq. 5}$$

where $[\mathrm{Re}]'$ represents the seawater Re concentration under steady state in the investigated time interval, and $[\mathrm{Re}]_{\mathrm{M}}$ represents the modern seawater Re concentration. For a first-order mass-balance approach, α is set to unity to reflect the principle that, within a particular sink setting, the burial rate of a metal scales linearly with the size of its seawater reservoir (cf., Algeo and Lyons, 2006; Scott et al., 2008; Partin et al., 2013). Substitution and rearrangement of equations 3–5 yields a generalized expression for Re concentration under new steady-state conditions following a perturbation to the global Re oceanic mass balance (e.g., Reinhard et al., 2013a):

$$[\mathrm{Re}]' = [\mathrm{Re}]_{\mathrm{M}}\left(\frac{F_{in}}{\sum A_i b_i}\right). \qquad \text{Eq. 6}$$

A pitfall with previous attempts at modeling marine trace metal reservoirs is the assumption of a constant metal burial rate within a given sink—especially the anoxic sink—across the global seafloor. Essentially, a characteristic burial rate observed in anoxic basins is applied to the global seafloor, which is dominated by abyssal plains where overall sediment mass accumulation rates are low. Given that the fluxes of both detrital material and organic carbon decrease across the gradient from high-productivity margins to the open, deep-ocean floor, such an assumption results in unrealistically high sink fluxes for most deep sea anoxic sediments. This exaggeration leads to a model that is oversensitive to reducing conditions and thus underestimates the true extent of anoxia associated with a given inventory as recorded in the authigenic metal enrichment of anoxic ORM (e.g., Scott et al., 2008; Sahoo et al., 2012; Partin et al., 2013). Although this spatial dependence of metal burial rate is difficult to specify precisely in simple models and represents an important area of future work, we follow the approach of Reinhard et al. (2013a) by coupling a function that relates organic carbon flux to water depth with global bathymetric data (SI). A tuneable burial rate ratio is then imposed to reproduce the characteristic modern Re anoxic burial rate (based on the Cariaco Basin data; see below and SI). As a significant improvement on the polynomial approximation used by Reinhard et al. (2013a) for relating carbon flux with water depth and bathymetry, we use bathymetric data from the eTOPO database (Amante and Eakins, 2009) and treat the bathymetric profile as a differentiable function to more accurately account for Re burial in shallow waters (SI).

Authigenic Re enrichment in anoxic sediments under new steady-state conditions (i.e., after a perturbation to global ocean redox conditions) is governed by the general relationship:

$$b_a{}' = b_a \left(\frac{[\mathrm{Re}]'}{[\mathrm{Re}]_{\mathrm{M}}} \right), \qquad \text{Eq. 7}$$

where $b_a{}'$ is the anoxic burial rate under the new steady state, and b_a is the modern average anoxic burial rate. The anoxic burial rate at a specific point in time is a function of the magnitude of the marine reservoir, which in turn is controlled by the spatial distribution of the oxic, suboxic, and anoxic sinks. To explore the marine Re cycle in ancient oceans, we apply a perturbation in the form of progressive anoxic expansion, with predicted authigenic Re enrichment in open-ocean anoxic sediments, $[\mathrm{Re}]_{\mathrm{pred}}$, as the output.

We adopted values from the well-characterized Cariaco Basin for our starting anoxic burial rate and bulk mass accumulation rate (BMAR; SI). As the largest, relatively open-marine anoxic basin in the modern ocean, the Cariaco Basin best approximates the open-ocean conditions our model simulates (e.g., Reinhard et al., 2013a). Anoxic Re burial rates in highly restricted basins (e.g., the Black Sea) are not appropriate because Re is strongly depleted from the water column by burial in anoxic sediments deposited under conditions of slow deep-water recharge (Colodner et al., 1995). Because the Cariaco Basin has relatively high sedimentation and organic carbon burial rates compared with other modern anoxic basins and continental margin settings, we use the lowest BMAR of 0.01 g cm^{-2} yr^{-1} (with a factor of 1.5 above and below this value) from the range of published values for the Cariaco Basin (0.01–0.08 g cm^{-2} yr^{-1}; Calvert et al., 2015) to avoid overestimating Re burial fluxes for the anoxic sink (cf. Reinhard et al., 2013a). An ocean with BMAR values higher than the maximum value used for our model would be unrealistically efficient at removing Re to sediments and would yield anomalously small extents of seafloor anoxia required to achieve the observed $[Re]_{sed}$.

The results of our mass-balance model are presented in Fig. 4. Overall, our model reveals that the marine Re reservoir is highly sensitive to the expansion of seafloor anoxia. The most drawdown in Re occurs with an expansion of anoxia from ~1% to ~10% of the modern seafloor area (Fig. 4), dominated by authigenic scavenging in the shallowest and most productive marginal settings where organic carbon export to sediments is highest. At greater than 10% seafloor anoxia, the $[Re]_{pred}$ becomes significantly less sensitive to the extent of anoxia and decreases only slightly (by <10 ppb) between 10% and 100% of seafloor anoxia. Under conditions of complete seafloor anoxia, $[Re]_{pred}$ is 16–35 ppb for open-ocean ORM for the assumed range of BMAR. A model with a Re burial rate decoupled from spatial variations in organic carbon flux results in a steeper decrease of $[Re]_{pred}$ with increasing seafloor anoxia. In this case, significant underestimation of $[Re]_{pred}$ occurs past ~5% seafloor anoxia, at which point anoxia expands beyond the ocean margins into the open ocean where rates of primary productivity and organic carbon burial are lower than at the margins.

The uncertainty of mid-Proterozoic bathymetry is a challenge for our model. In particular, epeiric seas are virtually absent today but were more prevalent during at least some time intervals in the Precambrian and Phanerozoic (Eriksson et al., 1998). To evaluate the effect of epeiric seas, we repeated our model exercise and simulated epeiric sea expansion by applying prescribed sea-level rise to modern ocean bathymetry (Fig. 5; SI). In this scenario, Re drawdown is enhanced by elevated burial with organic-rich sediments underlying more extensive and productive shallow waters. The net effect of epeiric sea expansion is a reduction in the predicted extent of seafloor anoxia required to achieve the same value of $[\mathrm{Re}]_{\mathrm{pred}}$ when modeled with only limited extent of epeiric seas.

To allow robust comparison of the model's $[\mathrm{Re}]_{\mathrm{pred}}$ for anoxic ORM with the mid-Proterozoic record, we determined the mean $[\mathrm{Re}]_{\mathrm{sed}}$ values for those stage 3 ORM that have independent Fe speciation evidence for deposition from anoxic bottom waters—specifically ratios of biogeochemically highly reactive Fe to total Fe ($\mathrm{Fe}_{\mathrm{HR}}/\mathrm{Fe}_{\mathrm{T}}$) greater than 0.38 or degree-of-pyritization (DOP) values greater than 0.45 (supplementary table S5; Raiswell and Canfield, 1998; Poulton and Raiswell, 2002; Lyons and Severmann, 2006). These filters should largely exclude any ORM deposited under suboxic bottom waters. Based on the observed Re enrichments in independently constrained mid-Proterozoic anoxic ORM, we can infer the extent of seafloor anoxia using the model. For comparison, we performed the same exercise for the anoxic ORM from stages 1 and 2.

Based on comparison with the model, the five ORM units from stage 3 with Fe data reveal a range of ocean redox states based on Re enrichments (Table 5). The ca. 1417 Ma Lower Velkerri Formation and ca. 1050 Ma Bylot Supergroup are characterized by low average $[\mathrm{Re}]_{\mathrm{sed}}$ values that imply near-total seafloor anoxia for the entire range of assumed BMAR (except for an oxygenated surface layer in contact with the mildly oxygenated post-GOE atmosphere). However, the average $[\mathrm{Re}]_{\mathrm{sed}}$ values for these units are lower than those predicted by the model for total seafloor anoxia (Fig. 4), suggesting partial basin restriction, a greater extent of epeiric seas during their deposition relative to today, and/or an unusually low local BMAR. The Re data from the ca. 1825 Ma Rove Formation are also consistent with a significant extent of ocean anoxia except at the lowermost end of the modeled range of BMAR. Similarly, Re data for Archean ORM predominantly require extensive ocean anoxia for most of the assumed range of BMAR.

Despite the complications posed by partial basin restriction and development of epeiric seas on the magnitude of Re enrichment in some ORM, the stage 3 ORM in our full compilation have Re enrichments that are generally similar or only mildly higher than those of the stage 1 ORM from the predominantly anoxic Archean. This observation, independent of the model constraints, points to generally low O_2 concentrations in the post-GOE ocean. Whereas muted Re enrichment in stage 1 reflects a low riverine input due to low atmospheric O_2 levels, muted Re enrichment in stage 3 is a product of substantial drawdown fluxes despite a greater input flux. A similar line of reasoning was invoked to explain the nearly similar U concentrations in Archean and mid-Proterozoic ORM (Partin et al., 2013); both records are consistent with interpretations based on the Cr enrichment (Reinhard et al., 2013a) and isotope (Planavsky et al., 2014; Cole et al., 2016) records. However, as stressed by Partin et al. (2013) and Cole et al. (2016), such an interpretation is only meant to represent the first-order marine redox landscape and does not preclude the possibility of spatiotemporal variations in atmosphere-ocean redox during mid-Proterozoic time.

Indeed, the higher average $[Re]_{sed}$ values from the ca. 1361 Ma Upper Velkerri Formation and ca. 641 Ma Black River Dolomite yield estimates of only 2–13% and 1–4% seafloor anoxia, respectively, suggesting that a larger oceanic Re reservoir and thus a greater extent of ocean oxygenation may have existed during these intervals, albeit not all comparable to Phanerozoic levels. Consistent with this interpretation, U isotope data from the same samples of the Upper Velkerri Formation suggest that <25% of the seafloor was covered by anoxic waters (Yang et al., in press). Our interpretation is also consistent with Mo concentration and isotope data for these ORM (Kendall et al., 2009, 2015b), which only constrained the extent of ocean euxinia rather than general ocean anoxia. The model does not preclude the possibility that a significant portion of the low-productivity regions of the deep oceans may have been covered by weakly oxygenated waters (Slack et al., 2007, 2009) and oxygenated surface waters in highly productive regions (Reinhard et al., 2016). In contrast, comparison of our model with stage 2 $[Re]_{sed}$ suggests that a smaller extent (<3%) of the seafloor was covered by anoxic waters during the GOE.

Rhenium enrichments in the Black River Dolomite are consistent with increased ocean oxygenation in the wake of the Sturtian glaciation, as suggested by Planavsky et al. (2010). While Re data from the upper Velkerri and Touirist formations may potentially reflect transiently oxygenated marine conditions, the extent to which these data represent spatiotemporal variations in the mid-Proterozoic atmosphere-ocean redox remains to be tested with higher-resolution Re data for stage 3. Given recent trace element evidence for fluctuating redox conditions in the Neoproterozoic (e.g., Sahoo et al., 2012, 2016; Planavsky et al., 2014; Kendall et al., 2015; Sperling et al., 2015; Thomson et al., 2015; Cole et al., 2016; Kuznetsov et al., in press), transient episodes of broader ocean oxygenation in the Mesoproterozoic may be part of a dynamic, longer-term trend of protracted oxygenation—one characterized by significant temporal oscillations in atmosphere-ocean O_2 levels likely around still low baselines and which extended into the Neoproterozoic and early Paleozoic.

6. Conclusions

The redox-sensitive behavior of Re can be used to characterize the evolution of ancient marine redox conditions by examining the sedimentary enrichment of Re in ORM through geologic time. A salient feature of our $[Re]_{sed}$ compilation is significantly lower Re concentrations in mid-Proterozoic ORM compared to many ORM deposited during the ca. 2.22–2.06 Ga Lomagundi

Event and during the Phanerozoic Eon; at the same time $[Re]_{sed}$ in these mid-Proterozoic ORM are overall only mildly higher than those of Archean ORM. Given that efficient oxidative mobilization of Re from sulfide minerals and organic matter in the exposed upper continental crust has been established since the GOE, the muted Re enrichments in mid-Proterozoic ORM are consistent with an expansion of global marine anoxia after ca. 2.05 Ga that led to significant drawdown of the ocean Re inventory. This is further supported by mass-balance modeling of the marine Re geochemical cycle, which indicates that low Re enrichments in some mid-Proterozoic ORM are consistent with extensive seafloor anoxia. In this respect, the Re compilation agrees with previous Cr, Mo, and U evidence for pervasively anoxic and ferruginous conditions in mid-Proterozoic oceans. The distinctive sensitivity of Re to varying environmental controls allows additional capacity to resolve spatiotemporal patterns in ancient redox landscapes. This is evidenced in a subset of the mid-Proterozoic ORM which displays higher Re enrichments that may reflect transient episodes of ocean oxygenation. The extent to which these data represent spatiotemporal variations in the mid-Proterozoic atmosphere-ocean redox state, the duration of these variations, and the degree to which they are unique remains to be tested with an improved understanding of the modern oceanic Re cycle and a higher temporal resolution for the Re compilation.

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