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Oceanic molybdenum drawdown by epeiric sea expansion in the Mesoproterozoic

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ABSTRACT

Molybdenum is a bioessential micronutrient whose abundance in the global oceans may have played a primary role in evolution of the Earth's nitrogen cycle and, ultimately, in the timing of the ecologic expansion of early eukaryotes. Because molybdenum (Mo) is delivered to the ocean under conditions of oxic weathering and is removed in suboxic and euxinic environments, the concentration of Mo in the oceans reflects a complex function of global redox and the hydrologic conditions that influence the areal extent of euxinic sedimentation. Recent compilations of Mo within euxinic shales (Scott et al., 2008; Och and Shields-Zhou, 2012; Sahoo et al., 2012) indicate that the oceanic reservoir of Mo did not rise substantially above crustal values until the Great Oxidation Event (~2.3 Ga), and a modern Mo cycle did not develop until the contraction of ocean euxinia in the latest Proterozoic.

At present, a paucity of data from euxinic shales of the late Mesoproterozoic (1.3 to 1.0 Ga) limits our ability to relate marine redox evolution to biological innovation during a critical interval of eukaryotic development. Here we present data from marine shales of the 1.1 Ga Atar and El Mreiti groups, Mauritania, which were deposited during sea level highstand when shallow, epeiric seas covered much of the West African craton. Epicratonic strata of the El Mreiti Group were deposited under fluctuating redox conditions near a shallow chemocline (as evidenced by iron speciation), and record generally low Mo concentrations (<15 ppm) and Mo/TOC ratios (<2 ppm/wt.%), along with a weak covariance between Mo and TOC. By contrast, craton margin strata of the coeval Atar Group were deposited under relatively persistent euxinic conditions, yet record Mo concentrations largely <1 ppm and show no covariance between Mo and TOC. Combined, data suggest that Mo sourced from terrestrial weathering was preferentially sequestered in proximal regions of the epeiric sea, and that onshore sequestration led directly to critically low Mo concentrations in offshore waters. We suggest that a Mesoproterozoic expansion of nearshore euxinia (at least in pore waters) within epeiric seas led directly to a critical depletion of the global oceanic Mo reservoir. This hypothesis is supported by a series of first-order sensitivity tests that estimate the extent to which expansion of epeiric seas would have drawn down oceanic Mo concentrations. Ultimately, this study suggests that substantial lateral redox heterogeneity may have limited the availability of bioessential trace metals in the Mesoproterozoic oceans, despite evidence for increased biospheric oxygenation. Extreme Mo limitation in open oceans environments would have had profound effects on the global nitrogen cycle and may help explain observed onshore–offshore patterns in early eukaryotes.

1. Introduction

Molybdenum (Mo) is the most abundant transition metal in modern seawater with a concentration of 105 nM, and a residence time of ~0.8 Ma (Collier, 1985; Emerson and Huested, 1991). It is liberated from continental crust during oxidative weathering and is delivered to the oceans as the stable and conservative molybdate anion (MoO_4^{2-}) via riverine influx (Emerson and Huested, 1991; Lyons et al., 2009). Once reaching the ocean, the three main pathways for Mo removal to marine sediments are largely dictated by redox conditions. Under oxygenated conditions, Mo is enriched in sediments in association with Mn-oxyhydroxides at a near constant Mo/Mn ratio of 0.002 (Shimmield and Price, 1986; Crusius et al., 1996; Tribovillard et al., 2006). Despite the dominance of oxic environments in the modern ocean, only 35–50% of Mo removal is associated with the Mn-oxide pathway (Scott et al., 2008; Poulson Brucker et al., 2009). In the presence of hydrogen sulfide, even at concentrations as low as 10 μm, MoO_4^{2-} is converted to the thiomolybdate species ($MoS_{4-x}O_x^{2-}$), and is rapidly sequestered by organic matter and authigenic sulfide minerals (Helz et al., 1996; Erickson and Helz, 2000; Tribovillard et al., 2004; Lyons et al., 2009; Helz et al., 2011). This more efficient process accounts for ~15% of Mo removal, even though water column sulfidic conditions overlie only a small fraction of the modern seafloor (<0.1%).

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The remainder of oceanic Mo removal occurs in suboxic environments, where sulfidic conditions are confined to within sediment pore fluids, and a combination of the oxic and sulfidic Mo removal pathways can operate along substrate redox gradients (Scott and Lyons, 2012). Mo can also be removed from the water column by adsorption to iron oxyhydroxides (Goldberg et al., 2009). The effect of this removal mechanism on the global oceanic Mo reservoir is negligible today, but may have had greater importance in the Proterozoic when the deep oceans were anoxic and potentially iron-rich (cf. Planavsky et al., 2011).

Because sediments deposited under sulfidic conditions can effectively sequester Mo from the water column, the Mo content of ancient euxinic shales has been used as a proxy for both past seawater Mo concentrations and the global extent of oceanic euxinia (Scott et al., 2008; Wille et al., 2008; Dahl et al., 2011; Kendall et al., 2011; Sahoo et al., 2012). Mo concentration data—along with Mo/TOC ratios—have previously been compiled from Precambrian marine black shales (Scott et al., 2008; Och and Shields-Zhou, 2012; Sahoo et al., 2012), and in Fig. 1 we present a more recent compilation that is restricted to shales deposited under euxinic conditions as constrained by previously reported iron speciation data (Section 3.2.2).

Our compilation (Fig. 1) reveals a broad, three-part division in Mo concentration through the Archean and Proterozoic—similar to that reported by Scott et al. (2008). In the Archean, oceanic Mo was exceedingly low (similar to average crustal values of 1–2 ppm; Lyons et al., 2009), which is commonly attributed to reduced Mo supply to the oceans in the absence of oxidative weathering on land (Anbar and Knoll, 2002; Buick, 2007; Scott et al., 2008, 2011). Oxygen levels in the Archean atmosphere are constrained to less than 10^{-5} times present atmospheric levels (Pavlov and Kasting, 2002; Bekker et al., 2004), and may have been appreciably less (Hazen et al., 2008), although a 'whiff of oxygen' at ~2.5 Ga may have induced a short-lived spike in oceanic Mo delivery (Anbar et al., 2007; Duan et al., 2010; Kendall et al., 2010; Scott et al., 2011). The Great Oxidation Event (GOE) at ~2.3 Ga (*see* Holland, 2006) marks the onset of widespread oxidative weathering on land, and thus the sustained transfer of transition metals from the continental crust to seawater. This is reflected by a jump in the Mo concentration of euxinic shales to >50 ppm in some cases (Scott et al., 2008). It has been suggested that enhanced Mo delivery to the oceans was sustained in the Paleoproterozoic by the addition of a large volume of new crust associated with supercontinent formation at ~1.9 Ga (Parnell et al., 2012). Despite a sustained increase in oxidative weathering and delivery of Mo to the oceans, a strongly stratified water column and widespread development of oceanic euxinia (Canfield, 1998; Poulton et al., 2004; Pufahl et al., 2010) may have stripped large quantities of Mo from marine environments, resulting in generally low oceanic Mo through much of the Proterozoic (Scott et al., 2008).

These Mo-limited conditions may have had substantial biospheric implications, as Mo is a bioessential micronutrient that serves as a critical structural component in a variety of enzymes used within the nitrogen cycle (*see* Mendel and Bittner, 2006; Schwarz et al., 2009). In particular, nitrate assimilation by eukaryotes is a Mo-demanding process and under Mo-limiting conditions, prokaryotes can readily outcompete eukaryotes for bioavailable nitrogen (Glass et al., 2009), leading to the hypothesis that Mo-limitation in Proterozoic oceans may have played a primary role in the delayed evolution of eukaryotes (Anbar and Knoll, 2002; Saito et al., 2003; Zerkle et al., 2006; Buick, 2007). Reduced oceanic Mo concentrations persisted until the contraction of euxinic environments following late Neoproterozoic (~630 Ma, Sahoo et al., 2012) glaciation and deep-ocean ventilation—allowing the oceanic Mo reservoir to expand to modern levels for the first time in Earth history, and possibly facilitating the marked transition in marine primary producers from cyanobacteria to eukaryotic algae through this interval (Falkowski et al., 2004; Knoll, 2007).

The initial expansion of eukaryotic alga, however, appears to have occurred in the mid-Mesoproterozoic, with diversification of both unicellular and multicellular algal clades (Butterfield, 2000; Javaux et al., 2004; Knoll et al., 2006). During this same interval, a stepwise increase in C-isotope values of dissolved inorganic carbon (DIC) in the oceans (Kah et al., 1999; Kah and Bartley, 2011), expansion of the marine sulfate reservoir (Kah et al., 2001, 2004), and widespread deposition of marine gypsum (Whelan et al., 1990; Kah et al., 2001; Kah et al., 2012) all suggest an increase in biospheric oxygen and the potential delivery of terrestrial weathering products to the marine system (e.g. Kah and Bartley, 2011). Clearly, in order to examine the linkage between Mo availability and the early evolution of eukaryotes, data are needed from sedimentary successions from within this critical, late Mesoproterozoic interval.

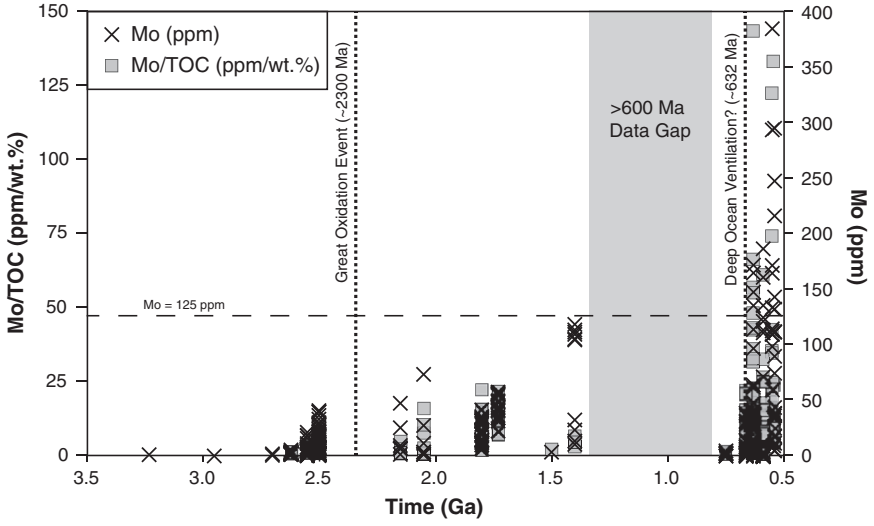

Fig. 1. Compilation of Mo concentrations and Mo/TOC ratios of Precambrian to early Cambrian shales. Points represent data accompanied by independent constraint of deposition under euxinic conditions (from iron speciation or degree of pyritization), and evidence for deposition under open ocean conditions. In cases where full iron speciation data were not available, pyrite concentrations exceeding 1 wt.% were considered euxinic. After the Great Oxidation Event (GOE), Mo concentrations of <125 ppm suggest modest increase in the oxidative delivery of Mo to oceanic systems. Increased biospheric oxygenation in the late Mesoproterozoic (Kah and Bartley, 2011) might be expected to increase oxidative delivery of Mo to the oceans yet, at present, no Mo concentration data have been reported from euxinic basins for this critical interval. Data presented here are from: Anbar et al. (2007), Arnold et al. (2004), Dahl et al. (2011), Feng et al. (2010), Guo et al. (2007), Kendall et al. (2009, 2010, 2011), Li et al. (2010, 2012), Lyons et al. (2000), Poulton et al. (2004), Sahoo et al. (2012), Scott et al. (2008, 2011), Shen et al. (2002, 2003), and Siebert et al. (2005).