Empirical links between trace metal cycling and marine microbial ecology during a large perturbation to Earth's carbon cycle

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ABSTRACT

Understanding the global redox state of the oceans and its cause-and-effect relationship with periods of widespread organic-carbon deposition is vital to interpretations of Earth's climatic and biotic feedbacks during periods of expanded oceanic oxygen deficiency. Here, we present a compilation of new and published data from an organic-rich locality within the proto-North Atlantic Ocean during the Cenomanian–Turonian boundary event that shows a dramatic drawdown of redox-sensitive trace elements. Iron geochemistry independently suggests euxinic deposition (i.e., anoxic and sulfidic bottom waters) for the entire section, thus confirming its potential as an archive of global marine metal inventories. In particular, depleted molybdenum (Mo) and vanadium (V) concentrations effectively record the global expansion of euxinic and oxygen-deficient but non-sulfidic waters, respectively. The V drawdown precedes the OAE, fingerprinting an expansion of oxygen deficiency prior to an expansion of euxinia. Molybdenum drawdown, in contrast, is delayed with respect to V and coincides with the onset of OAE2. Parallel lipid biomarker analyses provide evidence for significant and progressive reorganization of marine microbial ecology during the OAE in this region of the proto-North Atlantic, with the smallest relative eukaryotic contributions to total primary production occurring during metal-depleted intervals. This relationship may be related to decreasing supplies of enzymatically important trace elements. Similarly, box modeling suggests that oceanic drawdown of Mo may have approached levels capable of affecting marine nitrogen fixation. Predictions of possible nitrogen stress on eukaryotic production, locally and globally, are consistent with the low observed levels of Mo and a rise in 2-methylhopane index values during the peak of the OAE. At the same time, the environmental challenge presented by low dissolved oxygen and euxinia coincides with increased turnover rates of radiolarian clades, calcareous nanofossils, and foraminifera, suggesting that the temporal patterns of anoxia/euxinia and associated nutrient limitation may have contributed to the fabric of OAE2-related turnover.

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1. Introduction

The oceanic anoxic event at the Cenomanian–Turonian boundary (OAE2, 93.9 Ma) is one of the best documented episodes of widespread carbon burial in Earth history and is characterized by a large coeval positive carbon isotope excursion (as reviewed in Jenkyns, 2010). Despite the presence of a well-oxygenated atmosphere (Berner et al., 2003), multiple geochemical proxies record anoxic and/or euxinic (anoxic and sulfidic water column) conditions during OAE2 (Hetzel et al., 2011; Jenkyns, 2010, and references therein; Lu et al., 2010; Owens et al., 2012; Turgeon and Brumsack, 2006). During this short-lived event [∼0.5 million yrs, Myr, Voigt et al., 2008, and references therein] dissolved hydrogen sulfide appears, on occasion, to have penetrated the photic zone (as reviewed in Jenkyns, 2010). However, despite the apparent extremes in oxygen deficiency, accompanied by widespread deposition of organic-rich shales, direct geochemical evidence for local bottom-water anoxia/euxinia has mostly been restricted to the Atlantic and Tethys Oceans, while redox conditions in the Pacific, Indian and Arctic Oceans remain less well constrained due to minimal geochemical analysis. Despite recent model estimates of ∼40–50% ocean anoxia by volume (Monteiro et al., 2012), and

sulfur isotope systematics suggesting that ~5% of the seafloor was overlain by euxinic waters (Owens et al., 2013), further geochemical constraints are needed that more specifically delineate the redox structure of the wider ocean and its potential role in regulating nutrient availability. OAE2 marks a biotic turnover in the Mesozoic (Bambach, 2006, and references therein), which has been causally linked to an expansion of anoxia and/or euxinia (Leckie et al., 2002).

Increased organic carbon burial during an OAE can, in principle, be attributed to enhanced productivity and/or increased preservation (as reviewed in Jenkyns, 2010). However, maintenance of enhanced productivity and export at a global scale would require exceptional availability of major nutrients and bio-essential trace metals within the ocean. Mechanisms of enhanced nutrient delivery and/or recycling include increased hydrothermal activity (as reviewed in Jenkyns, 2010), continental weathering (Pogge von Strandmann et al., 2013, and references therein) and recycling of phosphorus from sediments due to more pervasive anoxia (Kraal et al., 2010); however, the relative contribution of each remains poorly constrained. Additionally, trace metals are important micronutrients for a range of catalytic metabolisms such as nitrogen fixation (Bellenger et al., 2011; Glass et al., 2010, and references therein), and it has been shown that growth status and nitrogen fixation rates undergo sharp changes at Mo concentrations below ~10 nM (Glass et al., 2010; Zerkle et al., 2006). In this light, we combine new and existing trace element data (Hetzel et al., 2009; Owens et al., 2012), geochemical modeling and lipid biomarkers to explore the spatiotemporal distribution of bioessential trace metals during and proximal to OAE2, with the specific goal of providing novel insight into the extent and timing of ocean redox changes and their possible impact on marine ecosystems.

2. Background

2.1. Trace metal geochemistry

The relationship between sedimentary metal enrichment, local redox and dissolved seawater concentrations is well known for modern euxinic basins (Lyons et al., 2009). For example, concentrations of Mo, V and Zn are significantly greater than those observed in oxic environments, and their relative stratigraphic variability can be explained by differences in their redox behavior. Molybdenum is the most abundant transition metal in the well-oxygenated modern ocean due to its high solubility as MoO_4^{2-} [~104 nM, Miller et al., 2011, and references therein] and is characterized by a relatively long residence time [~450 kyr Miller et al., 2011, and references therein]. Scavenging of Mo by Mn-oxide phases is an important removal pathway in the ocean; however, Mo is most efficiently buried in the presence of free sulfide, both in the sediments and the water column, with the latter being substantially more effective (Scott and Lyons, 2012). We distinguish between sulfidic sediments and a sulfidic water column and define *reducing environments* as those in which sulfide accumulation is restricted to pore fluids. These conditions often occur beneath low-oxygen bottom-waters similar to modern oxygen minimum zone environments (Little et al., 2015). In the modern oxic ocean, V is characterized by a shorter residence time [~50 to 100 kyr, Algeo, 2004; Morford and Emerson, 1999] and a smaller dissolved marine reservoir [35 to 45 nM, Morford and Emerson, 1999, and references therein], regulated primarily through its removal as vanadate oxyanions (HVO_4^{2-} and HVO_4^-) associated with Mn- and Fe-oxides and by efficient burial in low oxygen settings (as reviewed by Tribovillard et al., 2006).

Efficient sequestration of sedimentary V starts in low oxygen environments and continues through euxinic conditions (Algeo, 2004; Morford and Emerson, 1999). Therefore, in contrast to Mo,

reductive enrichment of V in marine sediments can be independent of sulfide. We can therefore use V as an indicator of low oxygen and anoxic conditions—an important contrast to the sulfide-dependent enrichment of Mo. The residence time of Zn is also relatively short, ~11 ka (Little et al., 2014), with a small dissolved marine concentration of ~5.4 nM. Importantly, sequestration of sedimentary Zn, like V, begins in low oxygen environments and continues through euxinic conditions (Algeo, 2004). Under low oxygen conditions both V and Zn are likely associated with organic matter, humic and fulvic acids and are buried as vanadyl ion and sphalerite minerals, respectively (Algeo, 2004; Tribovillard et al., 2006).

2.2. Organic geochemistry

In thermally immature, sulfur-rich sedimentary rocks, a high proportion of the total biomarker pool is often bound covalently in geomacromolecules due to early diagenetic vulcanization processes that take place in euxinic water columns and shallow sediments (Sinninghe Damsté and de Leeuw, 1990). Selective preservation of lipids in these environments may lead to signal bias in biomarker records (Kohnen et al., 1992; Sinninghe Damsté and de Leeuw, 1990) if only the extractable (free) hydrocarbons are analyzed. Catalytic hydropyrolysis (HyPy) is a well-established analytical technique for generating high yields of hydrocarbon products from kerogen and immature sediment while retaining important structural and stereochemical features (Love et al., 1995). HyPy has been useful in previous studies of OAE samples (Blumenberg and Wiese, 2012).

Hopanoids and steroids are polycyclic lipids that are synthesized by diverse groups of bacteria and eukaryotes, respectively, with similarly high preservation potential in the geological record. The Phanerozoic marine average for the hopane/sterane ratio for organic-rich rocks and oils typically lies in the range of 0.5–2.0 (Cao et al., 2009). Additionally, abundance patterns for the steroid carbon number in the C_{27}–C_{30} range broadly reflect the algal community composition (e.g., Kodner et al., 2008; Schwark and Empt, 2006; Volkman, 2003). C_{29} steroids are the precursors to the 24-ethylcholestanes found in ancient rocks and oils and are particularly abundant in green algal clades, whereas C_{27} sterane (cholestane) precursor lipids are more abundant in red algae (rhodophytes and dinoflagellates) (Kodner et al., 2008). C_{28} steroids (preserved as 24-methylcholestanes) are important in higher order endosymbiotic red algal lineages that were not dominant or diverse until late Mesozoic time and younger (Grantham and Wakefield, 1988), including haptophytes and diatoms, but also in some prasinophytes from the green lineage (Kodner et al., 2008; Volkman, 2003). The C_{30} steranes, 24-n-propylcholestanes are mainly derived from sterol precursors produced by the exclusively marine algal class Pelagophyceae, although these have also been reported as minor constituents of foraminifera (Giner et al., 2009; Grabenstatter et al., 2013).

3. Materials and methods

3.1. Samples

We present a compiled organic and inorganic dataset from a high-resolution spliced section from Demerara Rise, Ocean Drilling Program (ODP) Site 1258, holes 1258A, 1258B and 1258C (Fig. 1). Site 1258 was the deepest of the holes drilled during Leg 207, estimated to have been at paleodepths >1000 m. The Demerara Rise transect of Leg 207 was along the continental slope, approximately hundreds of kilometers from the coastline of Suriname (Erbacher et al., 2004). Importantly, past researchers have argued that connections between this region and the open proto-North Atlantic