



Cadmium-isotopic evidence for increasing primary productivity during the Late Permian anoxic event



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ABSTRACT

Earth's most extreme extinction event near the end of the Late Permian decimated more than 90% of all extant marine species. Widespread and intensive oceanic anoxia almost certainly contributed to the catastrophe, though the driving mechanisms that sustained such conditions are still debated. Of particular interest is whether water column anoxia was a consequence of a 'stagnant ocean', or if it was controlled by increases in nutrient supply, primary productivity, and subsequent heterotrophic respiration. Testing these competing hypotheses requires deconvolving sedimentary/bottom water redox conditions from changes in surface water productivity in marine sediments. We address this issue by studying marine shales from East Greenland and the mid-Norwegian shelf and combining sedimentary redox proxies with cadmium-isotopic analyses. Sedimentary nitrogen-isotopic data, pyrite framboid analyses, and organic and inorganic shale geochemistry reveal sulfidic conditions with vigorous upwelling, and increasingly anoxic conditions with a strengthening upwelling in the Greenland and Norwegian sections, respectively. Detailed analysis of sedimentary metal budgets illustrates that Cd is primarily associated with organic carbon and records primary geochemical signatures, thus enabling reconstruction of surface water nutrient utilization. Cadmium-isotopic analyses of the authigenic shale fraction released by *inverse aqua regia* digestion yield an average $\delta^{114/110}\text{Cd}$ of $+0.15 \pm 0.01\%$ (2 SE, $n = 12$; rel. NIST SRM 3108), indicative of incomplete surface water nutrient utilization up-section. The constant degree of nutrient utilization combined with strong upwelling requires increasing primary productivity – and not oceanic stagnation – to balance the larger nutrient fluxes to both study sites during the development of the Late Permian water column anoxia. Overall, our data illustrate that if bottom water redox and upwelling can be adequately constrained, Cd-isotopic analyses of organic-rich sediments can be used to provide valuable information on nutrient utilization and therefore past productivity.

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1. Introduction

Exceptionally widespread oceanic anoxia is widely considered one of the main contributing factors to the Late Permian marine biotic extinction (e.g., Isozaki, 1997; Wignall and Twitchett, 2002a; Bond and Wignall, 2010). Oxygen deficiency was already widespread in the pre-extinction Late Permian oceans, with possible sulfidic conditions developing in mid-water column depths that

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reached some surface waters (e.g., Algeo et al., 2010; Brennecke et al., 2011). Further expansion and development of peak anoxic conditions coincided with the main biotic extinction (Brennecke et al., 2011), which decimated most marine taxa ~251.9 Ma ago (Burgess et al., 2014).

The mechanisms that formed, expanded and sustained the Late Permian anoxia are still debated, but are generally thought to be related to either a more sluggish oceanic circulation, or an increase in marine primary productivity (and associated heterotrophy) in response to greater oceanic upwelling. A general slowdown in oceanic circulation is consistent with the decreased latitudinal temperature gradients of the Late Permian greenhouse world (e.g., Isozaki, 1997). Such conditions were likely triggered/sustained by

the injection of substantial greenhouse gas emissions associated with the eruption of the Siberian Trap basalts (e.g., Wignall and Twitchett, 2002a). Alternatively, increased upwelling and biological mechanisms have been hypothesized to contribute to the anoxia (e.g., Algeo et al., 2010; Meyer et al., 2011). A particular focus has been on the oxygen consuming feedback associated with increased upwelling, primary productivity, and subsequent heterotrophy (e.g., Wyrski, 1962). However, distinguishing between the stagnation and upwelling hypotheses requires proxies that can discriminate nutrient supply from nutrient utilization (i.e. the amount of nutrient available and the fraction of nutrients that are consumed, respectively). The marine geochemistry of Cd (cadmium) offers a potential solution to this problem.

Cadmium is a post-transition metal that is actively cycled by marine microbes in the water column (e.g., Sunda, 2012). Dissolved cadmium in seawater has a nutrient-like distribution that follows – albeit with some scatter – that of dissolved inorganic PO_4^{3-} (phosphate; e.g., Boyle et al., 1976; Cullen, 2006; Hendry et al., 2008). Microbial Cd uptake efficiently removes most dissolved Cd from surface waters, where it is exported to the deep ocean and seafloor in the form of particulate organic matter (OM). As this OM is remineralized, most of the fixed Cd (and PO_4^{3-}) is released back to seawater, leading to marine Cd distributions that resemble those of the major algal nutrients (e.g., Bruland, 1980). The physiological mechanisms underpinning the similarities between dissolved Cd and PO_4^{3-} concentrations are controversial, however. Several possible explanations have been put forward, ranging from true biochemical utilization of Cd by diatoms in a cambialistic Cd/Zn carbonic anhydrase (Lane et al., 2005), to mistaken uptake followed by internal storage and detoxification (Horner et al., 2013). Nonetheless, the remarkable similarity of Cd distributions to the other marine macronutrients has proven particularly valuable in Quaternary paleoceanography, and has enabled the successful reconstruction of water mass PO_4^{3-} concentrations from the Cd/Ca ratios of foraminiferal tests (e.g., Boyle, 1988; Marchitto and Broecker, 2006), and of paleoproductivity from the Cd concentration of clastic sediments (e.g., Brumsack, 2006; Wagner et al., 2013).

More recently, improvements in seawater sampling techniques and isotopic analytical capabilities have revealed large and systematic variations in the Cd-isotopic composition of seawater. These variations are thought to reflect the preferential uptake of isotopically light Cd by phytoplankton (Lacan et al., 2006; John and Conway, 2014), which renders residual Cd-depleted surface waters isotopically heavy by up to several permil (e.g., Ripperger et al., 2007; Abouchami et al., 2011, 2014; Xue et al., 2012, 2013; Conway et al., 2013). Studies of Cd-isotopic fractionation in seawater demonstrate that dissolved Cd-isotopic compositions are strongly related to the extent of Cd (and by association, PO_4^{3-}) utilization in surface waters, modulated by ocean circulation (e.g., Abouchami et al., 2011; Xue et al., 2013). As such, the Cd-isotopic composition of surface seawater and corresponding exported organic products offer an independent measure of macronutrient use efficiency in the upper ocean. The release of Cd by degraded sinking phytoplankton in deeper waters, and the long residence time of Cd in the oceans (~50 kyr; Morford and Emerson, 1999), means that water masses below ~200–500 m exhibit largely homogeneous Cd-isotopic compositions that are significantly lighter than the overlying surface waters (e.g., Ripperger et al., 2007). Because of this, the upwelling source of Cd to the surface ocean – the dominant source of Cd to surface-dwelling marine phytoplankton (e.g., Martin and Thomas, 1994) – is largely isotopically homogeneous throughout much of the oceans. These investigations of Cd-isotopic fractionation in the modern ocean thus enable the application of Cd-isotopic measurements to geological samples as tracers of macronutrient utilization efficiency in past surface ocean environments.

Organic-rich shales are a particularly good candidate for reconstructing the efficiency of nutrient utilization from Cd-isotopic measurements. Although Cd has only a single oxidation state of +2, sedimentary Cd enrichments are primarily controlled by the redox state of oceanic bottom waters and sedimentary porewaters via two mechanisms. Firstly, the preservation of sinking OM, and the Cd contained therein, is greatly improved in anoxic waters/sediments compared to oxic settings. Secondly, anoxic conditions favor the co-precipitation of labile Cd with sulfides that form in the sediment (e.g., Framson and Leckie, 1978), and possibly even the water column itself (Janssen et al., 2014); Cd adsorption to OM may also be facilitated. Consequently, sedimentary Cd enrichments patterns in shales from modern continental margins closely follow those of redox-sensitive elements with multiple oxidation states (e.g., Mo, U and Re; Morford and Emerson, 1999; Nameroff et al., 2002). Although potential Cd-isotopic fractionation related to Cd precipitation in shales and/or sulfides is not well understood, indirect evidence suggests that CdS may be isotopically lighter than ambient seawater (e.g., Schmitt et al., 2009; Janssen et al., 2014). Despite this uncertainty, our data suggest that the Cd-isotopic composition of organic-rich sediments ultimately reflects the Cd-isotopic signature of OM in surface waters. This may come about either directly from organically-bound Cd within the sediment, or indirectly from remineralized OM-bound Cd that coprecipitates into sulfides in bottom/pore waters. Regardless, sedimentary Cd-isotopic compositions ultimately depend on the Cd-isotopic composition of the sinking particulate OM that is exported from the surface to the sediment.

Here, we apply Cd-isotopic measurements to reconstruct macronutrient utilization efficiency in a past marine environment, using modern ocean Cd-isotopic systematics as our interpretive framework. We focus on a series of organic-rich shales from Greenland and offshore Norway that were deposited during the onset of ocean anoxia prior to the latest Permian mass extinction. Sedimentary N-isotopic compositions (nitrogen) and trace metal geochemistry are used to reconstruct the quantity of upwelled nutrients (supply), and Cd-isotopic compositions are used to interpret the degree of macronutrient utilization (demand). Thus, these data enable the reconstruction of past nutrient supply and demand (hence productivity), allowing us to single out the major cause – stagnation or upwelling – for the Late Permian anoxia in the Greenland–Norway basin.

2. Geological setting and sample selection

2.1. Geological context

Our study focuses on Upper Permian laminated shales of the Ravnefjeld Formation in East Greenland (GRL) (Surlyk et al., 1986; Piasecki and Stemmerik, 1991) and correlative intervals from the Lower Turbidite Unit in the mid-Norwegian shelf (MNS) (Bugge et al., 2002). These samples were deposited on the facing sides of a major extensional basin that developed between Greenland and Norway from the Middle Permian onwards (Surlyk et al., 1986; Bugge et al., 2002; Torsvik et al., 2002) at paleolatitudes of ~30°N. This basin was part of an elongated seaway that may have connected the Panthalassa Ocean with the Tethys Ocean, providing a pathway for interhemispheric water exchange (Sengör and Atayman, 2009).

The organic-rich intervals in GRL and MNS were deposited in anoxic bottom waters with interlayered bioturbated siltstones and sandstones likely representing periods of more oxic bottom water conditions. The two shelf sections (GRL and MNS) were deposited in fairly shallow water (Bugge et al., 2002). Detailed estimates for water depths during deposition of the Ravnefjeld Formation vary from 25 m up to 125 m in the different parts of the GRL Permian

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