



Selenium isotope ratios, redox changes and biological productivity across the end-Permian mass extinction



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ABSTRACT

The causes of the greatest mass extinction in Earth's history, in the latest Permian, remain actively debated. Here we use Se isotopes and abundances in marine sediments from an outer-shelf environment to test one of the most common hypotheses for the collapse of the biosphere, *i.e.* widespread euxinia in the open ocean. Our data show a small positive excursion in $\delta^{82/78}\text{Se}$ prior to the extinction, consistent with local euxinia. However, this is followed by a significant negative excursion with a minimum of -1.8‰ (relative to NIST SRM 3149), immediately preceding the principal extinction horizon. A net fractionation of this magnitude likely resulted from partial reduction of Se oxyanions dissolved in the water column. Due to their low abundance, Se oxyanions are rapidly scavenged in anoxic basins or regions of high biological productivity with little net isotopic fractionation. We therefore interpret the uniquely negative fractionations in this section as an indicator for relatively oxygenated conditions in this marine basin at the time when biological productivity declined. The offset between the peak excursion and the major extinction horizon possibly reflects a slow-down in ocean circulation leading to nutrient limitation, which may thus have prohibited a rapid recovery of the local biosphere in the early Triassic. Although we are unable to extrapolate to the global ocean due to the short residence time of Se in seawater, our data are consistent with the newly emerging view that euxinia developed along ocean margins and in oxygen minimum zones before the extinction, but was probably replaced by (sub-)oxic conditions during the ~ 1 kyr peak productivity decline and was thus not solely responsible for the extinction event.

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1. Introduction

The latest Permian featured the largest known mass extinction in Earth's history at 251.9 Myr (Burgess et al., 2014), yet the causes and consequences are still not well understood (e.g. Erwin et al., 2002; White, 2002). While ocean euxinia (a state of anoxia with abundant dissolved S^{2-} in the water column) is widely considered to be a factor contributing to the extinction (e.g. Grice et al., 2005; Kump et al., 2005; Wignall and Twitchett, 1996), the geographic extent and duration of euxinic conditions in different ocean environments remain uncertain. Perturbations in sulfur isotopes (e.g. Kajiwarra et al., 1994; Luo et al., 2010) and widespread occurrences of pyritic black shale (e.g. Wignall and Twitchett, 2002) have been interpreted as evidence for euxinia, but new data from transition element abundances and isotopes suggest that euxinia was localized along continental margins and in mid-water oxygen minimum zones, while large parts of the continental shelves remained oxic during the extinction event (Algeo et al., 2010; Algeo et al., 2011; Brennecke et al., 2011; Proemse et al., 2013). It is therefore uncertain if euxinia was

indeed the primary kill mechanism resulting in a catastrophic loss of marine diversity (*cf.* Grice et al., 2005; Kump et al., 2005; Wignall and Twitchett, 1996). Furthermore, it is also not well known if biological productivity actually declined during the extinction event. There is no independent evidence for a decline in net biological productivity and organic-matter export at this time, other than theoretical models of total carbon fluxes (Algeo et al., 2013; Shen et al., in press). So, despite paleontological evidence of a $>90\%$ mass extinction among macroorganisms, it is conceivable that algal and microbial organisms maintained a high flux of organic matter to the sediments even though bulk productivity shifted from eukaryotic to prokaryotic plankton during the extinction event (Cao et al., 2009; Luo et al., 2013; Xie et al., 2005). Selenium isotopic ratios represent a newly emerging biogeochemical proxy (e.g. Mitchell et al., 2012; Wen et al., 2014; Stüeken et al., 2015b) that may help constrain our understanding of changes in ocean redox state and productivity associated with the latest-Permian mass extinction. The processes that control the partitioning of Se isotopes in marine environments are not yet fully understood, but existing information reviewed below and elsewhere (Stüeken et al., 2015b) allows us to construct hypotheses that we seek to test in this study.

In the modern oxic ocean, Se is mainly present as oxyanions (both Se^{IV} and Se^{VI}), and it shows a nutrient-type profile in the water column, with lowest concentrations in the surface layer and nearly constant

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levels below (Cutter and Cutter, 2001). This behavior reflects Se uptake into biomass in the photic zone, forming organic Se^{-II}, and subsequent re-oxidation of organic Se^{-II} at depth (Cutter and Bruland, 1984). In sediments, especially under anoxic conditions, organic Se^{-II} is usually a major component of the total Se content, in addition to Se⁰, inorganic Se^{-II} and adsorbed Se^{IV} (Fan et al., 2011; Kulp and Pratt, 2004). In anoxic basins, the organic Se^{-II} component is likely enhanced because remineralization of organic matter is suppressed (Cutter, 1982; Cutter, 1992).

Se isotopes (here reported as $\delta^{82/78}\text{Se}$ relative to NIST SRM 3149) are fractionated by up to 25‰ during Se^{VI} and Se^{IV} reduction to Se⁰ or inorganic Se^{-II} where the residual oxyanions become isotopically enriched (Ellis et al., 2003; Herbel et al., 2000; Johnson and Bullen, 2003; Johnson et al., 1999). Fractionations are generally smaller when these reduction reactions are biologically catalyzed (max. 14‰ in microbial cultures) and perhaps significantly smaller in natural environments where the supply of Se oxyanions and reductants (organic or inorganic) may be lower (Johnson and Bullen, 2004). However, individual reports of fractionations over a range of several permil in marine sediments (e.g. Stüeken et al., 2015b; Wen et al., 2014, this study) suggest that Se oxyanion reduction can leave a detectable signature in the rock record. Fractionations associated with assimilation into biomass and Se^{IV} adsorption are minor, up to 0.6‰ in favor of the lighter isotopes (Clark and Johnson, 2010; Johnson et al., 1999; Mitchell et al., 2013). Biomass forming in the photic zone (+0.3‰, Mitchell et al., 2012), where Se is quantitatively consumed, may thus record the composition of Se^{IV} and Se^{VI} in seawater, or at least provide a minimum constraint; assuming fractionation of 0.6‰ during assimilation into biomass (Clark and Johnson, 2010), seawater Se oxyanions may be as heavy as +0.9‰. It is plausible that this small isotopic enrichment of dissolved Se oxyanions relative to the Earth's crust ($0.0 \pm 0.5\%$, Rouxel et al., 2002) results from non-quantitative Se oxyanion reduction in suboxic environments, such as in local oxygen minimum zones or in sedimentary pore waters, i.e. in environments that are directly connected to the relatively large Se oxyanion supply from the open ocean. Reduction likely occurs concurrently with denitrification, i.e. at higher Eh than sulfate reduction (e.g. Oremland, 1990). We would therefore predict that sediments from suboxic settings contain some proportion of isotopically light reduced Se phases, including Se⁰ and/or Se^{-II}. Data from bulk sediments of the oxygen minimum zone in the Arabian Sea ($-0.07 \pm 0.08\%$, Mitchell et al., 2012) and from the Bermuda rise in the open Atlantic ocean (-0.10 ± 0.16 , Mitchell et al., 2012) may indeed reflect the presence of an isotopically negative reduced Se phase that may have formed during Se oxyanion reduction in the water column or during diagenesis. Sequential extraction would be necessary to test this conclusion. In contrast, sediments that are dominated by organic Se (+0.3‰, Mitchell et al., 2012) due to high biological productivity or where Se oxyanion reduction is relatively more quantitative than in the open ocean, should on average be isotopically heavy. Values from the oceanographically restricted Black Sea, which is largely anoxic and dominated by S^{-II} at depth (i.e. euxinic), are indeed isotopically heavy ($+0.22 \pm 0.14\%$, Mitchell et al., 2012) compared to the sediments from the open ocean quoted above. We note that this includes data from oxic parts of the Black Sea ($+0.29 \pm 0.07\%$, Mitchell et al., 2012), but the overall scarcity of Se oxyanions in this restricted basin (Cutter, 1982; Cutter, 1992) makes it unlikely that those sediments contain a significant proportion of reduced Se phases that were formed by non-quantitative Se oxyanion reduction.

These observations suggest that Se isotopes in ancient marine sediments can be used to draw inferences about productivity and redox state of the overlying water column. Positive values in bulk sediments should be indicative of high biological productivity and/or anoxic conditions. The former would result in an overabundance of isotopically heavy biomass (+0.3‰ in today's open ocean, Mitchell et al., 2012) over other Se phases, whereas the latter results in nearly quantitative Se oxyanion reduction and further enhances organic matter preservation.

For example, Mitchell et al. (2012) found predominantly positive values ($+0.3 \pm 0.3\%$) in variety of Phanerozoic rocks with high total organic carbon contents (TOC $10.6 \pm 6.9\%$), irrespective of redox state. High biological productivity and hence organic Se may have dominated in those sediments. Negative isotopic composition of less than -1% , i.e. lighter than the crust ($0.0 \pm 0.5\%$, Rouxel et al., 2002) and potential fractionations by adsorption or assimilation ($\leq 0.6\%$, Clark and Johnson, 2010; Johnson et al., 1999; Mitchell et al., 2013), should in turn be indicative of oxic to suboxic conditions and low biological productivity, because then organic Se is less abundant and Se oxyanions can be reduced non-quantitatively in pore waters or in oxygen minima in the water column. In other words, negative values should reflect a high Se oxyanion supply relative to the demand. Wen et al. (2014) recently observed negative $\delta^{82/78}\text{Se}$ values down to -3.3% in very Se-rich Cambrian sediments (up to 121 ppm Se) that were deposited under an Fe²⁺-dominated water column. Such ferruginous conditions can be classified as suboxic if sulfate was stable in the water column (which is unknown) and may thus not have been conducive for rapid quantitative Se reduction, especially if Se input was high. Importantly, both Wen et al. (2014) and Mitchell et al. (2012) found relatively more negative $\delta^{82/78}\text{Se}$ values in sediments with molar Se/TOC ratios greater than $\sim 10^{-5}$, i.e. when the Se/TOC ratio exceeded that of marine biomass ($2 \cdot 10^{-6}$ to $6 \cdot 10^{-6}$, Mitchell et al., 2012). Hence light sedimentary $\delta^{82/78}\text{Se}$ values (-1% or less) likely reflect the presence of a significant Se oxyanion reservoir in seawater and by extension, absence of euxinia and relatively low productivity. Se isotopes therefore have the potential to test the validity of the newly emerging picture of the latest Permian mass extinction, i.e. the collapse of biological productivity under non-euxinic conditions in the open ocean.

In this study, we present whole-rock Se isotope and abundance data from a marine stratigraphic section across the latest Permian extinction horizon. In addition, as a proof of concept, we sequentially extracted different Se phases from one sample and show that they are isotopically distinct, consistent with our interpretation of the bulk data. Sequential extraction analyses thus have the potential to provide additional information (see also Fan et al., 2011; Schilling et al., 2014) and should be revisited in future studies, but we emphasize that the focus of this study is on bulk rocks. We conclude that bulk Se isotopes can be a valuable new biogeochemical proxy in deep time, where in our case a large negative excursion reveals a decline of macro-biological productivity in oxic to suboxic ocean waters in the late Permian. The short residence time of Se in seawater (~ 26 kyr today, Henderson and Henderson, 2009) may imply that our results are only representative of this local basin and cannot be extrapolated to the global ocean, but we hope that this will be tested in future studies.

2. Geologic setting

Our samples are from outcrops of the Ranger Canyon and the unconformably overlying Sulphur Mountain Formations in the Western Canada Sedimentary Basin at Opal Creek, Kananaskis Valley, southwest Alberta (50.675171°N , 115.080011°W , e. g. Farley et al., 2005; Henderson, 1997; Schoepfer et al., 2012). As evidenced by the abundance of cold-water sponge spicules and phosphatic material and the absence of shallow-water sedimentary features (Henderson, 1997), these marine sediments were probably deposited in an outer shelf setting, named the Ishbel Trough (Henderson et al., 1994), along the eastern margin of the Panthalassic Ocean (Henderson, 1997; Henderson et al., 1994). Although it is possible that the Ishbel Trough was located inboard of a volcanic arc, molar Mo/U ratios of 0.3 ± 0.2 times that of seawater (Schoepfer et al., 2013) indicate open exchange with the global ocean (Algeo and Tribouillard, 2009). Furthermore, high nitrogen isotope ratios of up to $+10\%$ and trace metal concentrations significantly above detrital background suggest that during the mid-Permian this site was located in an area with a significant influx of nutrients from the sea, possibly due to upwelling of deep water along the continental margin

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