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

Eva E. Stüeken^{1*}, Julien Foriel^{1,‡}, Roger Buick¹, Shane D. Schoepfer¹

1. Department of Earth & Space Sciences and Astrobiology Program, University of Washington, Seattle, WA 98195-1310, USA

‡ present address: Tokyo Institute of Technology, Earth-Life Science Institute (ELSI), 2-12-1 IE-13 Ookayama, Meguro-ku, Tokyo, 152-8550, Japan

* corresponding author. evast@uw.edu

Abstract

The causes of the greatest known 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 commonly cited hypotheses about 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 was 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 thus 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.

1. Introduction

The latest Permian featured the largest known mass extinction in Earth's history (251.0 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.* Kajiwarara *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.*, 2014). So, despite paleontological evidence of a > 90% mass extinction among macro-organisms, 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) 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 levels below (Cutter and Cutter, 2001). This behavior reflects Se uptake into biomass in the photic zone, forming organic $\text{Se}^{-\text{II}}$, and subsequent re-oxidation of organic $\text{Se}^{-\text{II}}$ at depth (Cutter and Bruland, 1984). In sediments, especially under anoxic conditions, organic $\text{Se}^{-\text{II}}$ is usually a major component of the total Se content, in addition to Se^0 , inorganic $\text{Se}^{-\text{II}}$ and adsorbed Se^{IV} (Fan et al., 2011; Kulp and Pratt, 2004). In anoxic basins, the organic $\text{Se}^{-\text{II}}$

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 Se^0 or inorganic $\text{Se}^{-\text{II}}$ 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 ($0.0 \pm 0.5\text{‰}$, 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 Se^0 and/or $\text{Se}^{-\text{II}}$. Data from bulk sediments of the oxygen minimum zone in the Arabian Sea ($-0.07 \pm 0.08 \text{ ‰}$, 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 ($+0.3 \text{ ‰}$, 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 $\text{S}^{-\text{II}}$ at depth (*i.e.* euxinic), are indeed isotopically heavy ($+0.22 \pm 0.14 \text{ ‰}$, 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 ($+0.29 \pm 0.07 \text{ ‰}$, 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 ($+0.3 \text{ ‰}$ 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 ($+0.3 \pm 0.3 \text{ ‰}$) in variety of Phanerozoic rocks with high total organic carbon contents ($\text{TOC } 10.6 \pm 6.9 \text{ ‰}$), 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 ($0.0 \pm 0.5\text{‰}$, Rouxel *et al.*, 2002) and potential fractionations by adsorption or assimilation ($\leq 0.6\text{‰}$, 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 Fe^{2+} -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 (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 Tribovillard, 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 (Schoepfer et al., 2013; Schoepfer et al., 2012). This nutrient influx probably led to moderately high primary productivity and a water column oxygen-minimum zone (Georgiev et al., 2015; Schoepfer et al., 2013; Schoepfer et al., 2012). Productivity likely peaked in the late Permian, resulting in a brief episode of euxinia. Productivity is then thought to have declined as the ocean warmed under a CO₂-enriched atmosphere and circulation slowed down (Schoepfer et al., 2013; Schoepfer et al., 2012).

The samples we analyzed span the time interval from when productivity was highly active in the Middle and Late Permian, until well after the principal extinction horizon but before the paleontologically defined recovery period. The extinction event itself is marked by the abrupt disappearance of sponge spicules and bioturbation ~40 cm above the Ranger Canyon-Sulphur Mountain unconformity (Schoepfer *et al.*, 2012) (labeled ‘EXT’ in Fig. 1) whereas the biostratigraphic Permian-Triassic boundary occurs ~1.1 m above the extinction horizon. Assuming an average sedimentation rate of 2 cm kyr⁻¹ for this section (Farley *et al.*, 2005), the time span between the unconformity and the extinction horizon is approximately 20 kyr, which is the close to the residence time of selenium in the modern ocean (26 kyr, Henderson and Henderson, 2009). The unconformity between the Ranger Canyon and Sulphur Mountain Formations represents a time gap of 5-7 Myr, representing the entire Wuchiapingian stage and part of the Changhsingian stage.

Though bedding is tilted to near vertical, the rocks have experienced only moderate burial temperatures (< 150 °C) as constrained by the Conodont Alteration Index (Schoepfer *et al.*, 2012). Chemical weathering is limited to a thin surface layer (see also Georgiev *et al.*, 2015), which can be removed with a rock saw. We are therefore confident that our measured isotope ratios are not affected by alteration (cf. Zhu *et al.*, 2014). Lithologies are predominantly

spiculitic chert and silicified siltstones in the Ranger Canyon Fm., and organic-rich and variably sulfidic shales to siltstones in the overlying Sulphur Mountain Fm. (Fig. 1).

3. Methods

3.1. Bulk sample preparation

A detailed description of our sample preparation and analytical protocol is given in Stüeken *et al.* (2013). We used two slightly different preparation procedures (methods D and E in Stüeken *et al.*, 2013, and in Table 1) for this sample set, because method development was still in progress during the initial stages of this study. All samples were digested with HF, HClO₄, and HNO₃ and Se was separated from the matrix by filtration through a column of thiol cotton fibers (TCF). The Se was then desorbed with HNO₃, partially evaporated and redissolved in HCl for analysis. The two preparation procedures differ in that some samples were treated with aqua regia after column filtration to further minimize Ge concentrations (method E), whereas most samples were not (method D). But as shown in Table 1, we do not observe any systematic differences between the two methods.

3.2. Sequential extraction of selenium phases

One sample (position -40 cm) was subjected to a sequential extraction procedure to separate three different selenium phases (Fig. 2) (*e.g.* Schilling *et al.*, 2014): first adsorbed Se^{IV}, second inorganic Se^{-II} bound to pyrite and possibly Se⁰, and third refractory organic Se^{-II} and residual Se⁰. Traces of Se⁰ may be contained in both fractions two and three because we could not extract it separately. The stratigraphic level of -40 cm was chosen because that part of the section is below any isotopic excursions and so represents background conditions. The protocol

was adapted from Kulp & Pratt (2004) and carried out on four sample aliquots. Errors reported in the results are equal to the standard deviation between those four separate aliquots. Initial tests showed that acetic-acid-soluble, phosphate-exchangeable and water-soluble Se (e.g. Kulp and Pratt, 2004; Martens and Suarez, 1997; Wright et al., 2003) were below detection limit (<0.1ppb) and thus were ignored in the final protocol.

*** NaOH-soluble selenium:** Se^{IV} strongly adsorbed to oxides and clay minerals as well as labile organic Se^{II} compounds are soluble in NaOH (Kulp and Pratt, 2004; Martens and Suarez, 1997). For extraction of this phase, 5g of rock powder were weighed into 50 ml polypropylene centrifuge tubes and mixed with 50ml of 0.1M NaOH for 2 h in a 90°C water bath. The powder was kept in suspension with a magnetic stir bar. After cooling to room temperature, the solution containing the desorbed Se was separated by centrifugation for 20 minutes. The residual powder was washed with 20ml DI- H_2O , which was added to the NaOH solution. This solution was then filtered twice through a 0.2 μm pore-size filter to remove colloidal particles, acidified with 8.86 ml of 6N HCl, and then passed through a TCF column. All subsequent steps followed the bulk sample protocol (using the method without aqua regia). Because the sample was not subject to oxidation during or after NaOH leaching, any labile organic Se^{II} extracted by NaOH should not have been captured by the TCF, which is optimized for Se^{IV} (Yu *et al.*, 2002). However, we cannot exclude the possibility that O_2 dissolved in the NaOH or HCl oxidized some of the labile organic Se^{II} or inorganic reduced Se phases. This fraction will therefore be referred to simply as the NaOH extract. The residual sample powder was dried in a 60°C oven over night.

*** Cr-reducible selenium:** Chromium reduction is commonly used to extract inorganic sulfides from bulk rocks (Canfield *et al.*, 1986) and thus would extract inorganic Se^{II} contained in sulfide minerals. This step may also mobilize Se^0 as it does S^0 (e.g. Gröger *et al.*, 2009). We used a

diffusion process adapted from Burton *et al.* (2008), Ulrich et al (1997) and Hsieh & Shieh (1997). Two grams of rock powder were weighed into a 200ml serum bottle and wetted with a few drops of DI-H₂O. Three 5ml pyrex test tubes were added to the bottle and filled by a syringe with 4ml of N₂-purged Zn-acetate solution (10% by weight) under a constant stream of N₂ gas. The bottle was then capped with a vacuum-tight rubber septum and evacuated and purged with N₂ three times through a needle. Then 15ml of 12N HCl and 15ml of 2M CrCl₂ were added sequentially through the needle with a syringe. Both solutions were previously purged with N₂ gas for two hours. The CrCl₂-solution was prepared from CrCl₃ by reduction with mossy zinc in 0.5M HCl (Hsieh and Shieh, 1997; Hsieh and Yang, 1989). After addition of all reagents, the serum bottles were sonicated for 20 minutes and placed on an orbital shaker for two days. Sonication was repeated on the second day. Zinc sulfide and ZnSe that precipitated in the Zn acetate traps were transferred together with residual Zn acetate into a 90ml Teflon beaker and mixed with 10ml HClO₄ and 10ml concentrated HNO₃. The beaker was capped tightly and left at 130°C overnight. Subsequent extraction of selenium with TCF followed the bulk sample protocol. Residual rock powder was transferred from the serum bottle into a centrifuge tube, washed three times with DI-H₂O, and dried at 60°C overnight.

*** Total residual selenium:** The residual powder contained refractory organic Se^{-II} and residual Se⁰. All rock powder remaining from the Cr-reduction was transferred into a 90ml Teflon beaker and digested following the same protocol as for bulk samples.

Selenium abundances in each phase were calculated relative to the initial bulk sample, assuming that the total mass loss associated with NaOH desorption was negligible. This assumption is not required for Cr-reduction, because here the remaining rock powder is transferred quantitatively to the subsequent step.

3.3. Isotopic analyses

Analyses were carried out by multi-collector inductively-coupled plasma mass-spectrometry (Nu Instruments), where Se was introduced as H₂Se through a cold-vapor hydride generator (Cetac HGX-200). Analytical parameters are described in more detail in Stüeken *et al.* (2013). Instrumental mass bias was corrected by standard-sample bracketing. Interferences with ^{74,76,78}(ArAr), ⁷⁶(AsH) and ^{74,76}Ge were corrected post-analytically (Stüeken *et al.*, 2013). Unless otherwise noted, all results are reported in terms of ⁸²Se/⁷⁸Se relative to NIST SRM 3149:

$$\delta^{82/78}\text{Se} [\text{‰}] = ((^{82}\text{Se}/^{78}\text{Se})_{\text{sample}} / (^{82}\text{Se}/^{78}\text{Se})_{\text{SRM3149}} - 1) \cdot 1000 \quad (\text{Eq. 1}),$$

because this is the most precise ratio using our protocol. It avoids isobaric interferences with ⁷⁶Ge and ⁷⁶(AsH) and only suffers from comparatively minor interferences with ⁷⁸(ArAr) and ⁸²Kr, which makes it more reliable than $\delta^{82/76}\text{Se}$ for complex geochemical matrices. Three-isotope diagrams (Fig. 3) show that within error our data plot along the predicted mass-dependent fractionation line, indicating that all major interferences have been corrected and that mass-independent fractionation is absent. Thus $\delta^{82/78}\text{Se}$ values can be multiplied by 1.54 to convert them to the more commonly used $\delta^{82/76}\text{Se}$ ratio. Our average precision for $\delta^{82/78}\text{Se}$, here defined as the average standard deviation of replicate analyses, was 0.16‰, and the average relative error for total Se concentrations was 7%. Analyses of the USGS rock standard SGR-1 gave a value of $-0.38 \pm 0.44\text{‰}$ (2σ , $n = 9$) when treated with method D and a value of $+0.05 \pm 0.38\text{‰}$ (2σ , $n = 9$) when treated with method E (Stüeken *et al.*, 2013). The difference between the two methods is consistently smaller in other types of samples, which, as discussed by Stüeken *et al.* (2013), may be due to the relatively low thermally maturity of the SGR-1 oil shale. Published values for SGR-1 range from $-0.13 \pm 0.06\text{‰}$ (2σ , $n = 11$, Mitchell *et al.*, 2012) to

+0.40 ± 0.42‰ (2σ, n = 3, Layton-Matthews et al., 2006), converted to $\delta^{82/78}\text{Se}$ and the NIST SRM 3149 scale after Carignan & Wen (2007). Part of this spread may also reflect sample heterogeneity. In the following discussion all literature values were converted to $\delta^{82/78}\text{Se}$ for better comparison, assuming strictly mass-dependent behavior. Literature values reported as $\delta^{80/76}\text{Se}$ were not converted, because they only differ from $\delta^{82/78}\text{Se}$ by a factor of 1.05, which is negligible within error.

3.4. Carbon and sulfur isotope analyses

Data of organic C and total S abundances and isotopes are mostly taken from Schoepfer *et al.* (2013). We added a few additional analyses (at -40, -21, +3, +4, +5, +6 and +8 cm) to increase stratigraphic resolution. Sample preparation and analyses were carried out with the same protocol and facilities as described by Stüeken (2013) and Schoepfer *et al.* (2013). For TOC, the average relative error (RE) was 15%, and the average standard deviation for $\delta^{13}\text{C}_{\text{org}}$ (values relative to VPDB) was 0.3‰. For total sulfur, the average RE was 7%, and the average standard deviation for $\delta^{34}\text{S}$ (values relative to VCDT) was 0.5‰.

3.5. Fractionation model description

We used a standard mass balance model of isotope fractionation to provide a framework for a quantitative evaluation of the isotope data. The isotopic composition of complementary oxidized ($\delta^{82/78}\text{Se}^{\text{VI/IV}}$) and reduced ($\delta^{82/78}\text{Se}^{\text{red}}$) selenium phases is a function of the fraction (*f*) of oxidized Se remaining in the system and the fractionation factor (α) of the reduction reaction (cf. Canfield, 2001). The fractionation factor is related to the maximum fractionation ($\epsilon \approx \delta^{82/78}\text{Se}^{\text{VI/IV}} - \delta^{82/78}\text{Se}^{\text{red}}$) via the following approximation which is accurate for delta values of a few permil:

299 $\epsilon \approx 1000 \cdot (\alpha - 1)$ (Eq. 2)

300 In an open, steady-state system with progressive reduction, the composition of residual Se^{VI}
 301 ($\delta^{82/78}\text{Se}^{\text{VI}}_{\text{res}}$) evolves from its initial value ($\delta^{82/78}\text{Se}^{\text{VI}}_{\text{in}}$) as follows:

302
$$\delta^{82/78}\text{Se}^{\text{VI/IV}}_{\text{res}} = ((\delta^{82/78}\text{Se}^{\text{VI}}_{\text{in}} / (1-f)) + ((\alpha-1) / \alpha) \cdot 10^3) / ((1/\alpha) + f / (1-f))$$
 (Eq. 3)

303 In a closed system, where the Se demand exceeds the supply, isotopic fractionation is described
 304 by Rayleigh fractionation:

305
$$\delta^{82/78}\text{Se}^{\text{VI/IV}}_{\text{res}} = (\delta^{82/78}\text{Se}^{\text{VI}}_{\text{in}} + 1000) \cdot f^{(1-\alpha)} - 1000$$
 (Eq. 4)

306 In both systems, the composition of cumulative reduced Se ($\delta^{82/78}\text{Se}^{\text{red}}$) can be obtained by mass
 307 balance:

308
$$\delta^{82/78}\text{Se}^{\text{red}} = (\delta^{82/78}\text{Se}^{\text{VI}}_{\text{in}} - \delta^{82/78}\text{Se}^{\text{VI/IV}}_{\text{res}} \cdot f) / (1-f)$$
 (Eq. 5)

309 The initial composition of $\text{Se}^{\text{VI/IV}}$ entering the ocean ($\delta^{82/78}\text{Se}^{\text{VI/IV}}_{\text{in}}$) is assumed to be 0‰, *i.e.*
 310 equal to that of bulk Earth (Rouxel *et al.* 2002, converted to NIST scale after Carignan and Wen,
 311 2007). The maximum observed fractionation associated with biotic reduction of Se oxyanions to
 312 Se^0 is 14‰ (Johnson and Bullen, 2004, excluding abiotic fractionation, which can be up to
 313 25‰), but because most unaltered sediments display $\delta^{82/78}\text{Se}$ values within a small range of -2‰
 314 to +2‰ (Johnson and Bullen, 2004; Mitchell *et al.*, 2012, this study; Shore, 2010; Stüeken *et al.*,
 315 2015a; Stüeken *et al.*, 2015b), it is unknown if fractionations of this magnitude occur under
 316 natural marine conditions with low Se supply. We therefore use 2‰ and 14‰ as the two end-
 317 members to calculate typical and extreme values for f (Fig. 4). Because of this relatively small
 318 range in $\delta^{82/78}\text{Se}$ values in natural samples compared to laboratory experiments, it is not possible
 319 to distinguish between Se^{VI} and Se^{IV} reduction to Se^0 . However, it is likely that these two
 320 oxidized species are isotopically similar in the modern ocean, because they are generated by

oxidation of organic matter (Cutter and Bruland, 1984), a process which does not induce isotopic fractionation (Johnson *et al.*, 1999).

4. Results

4.1. Bulk selenium isotope data

Our results show a brief positive isotopic excursion in $\delta^{82/78}\text{Se}$ followed by a large negative excursion leading up to the main extinction horizon (Fig. 1, Table 2). We divided our dataset into four stages, capturing the time before the positive excursion (-40 cm to +3.5cm, stage I), the positive excursion itself (+4 cm to +9 cm, stage II), the negative excursion (+10.5 cm to +46cm, stage III) and the return to stability (+49.9 cm to 1684 cm, stage IV). In stage I, $\delta^{82/78}\text{Se}$ averages $+0.05 \pm 0.62\text{‰}$ (2σ , $n = 6$). We note that after exclusion of the data point at +1.5 cm (because it lies outside the 2σ uncertainty range of the other five data points and may be an outlier) stage I has a slightly negative average of $-0.07 \pm 0.12\text{‰}$ (2σ), in good agreement with values from an upwelling zone in the modern Arabian Sea ($-0.07 \pm 0.16\text{‰}$, 2σ , Mitchell *et al.*, 2012). Apart from this outlier, the $\delta^{82/78}\text{Se}$ record in stage I does not show a pronounced discontinuity across the unconformity. In stage II, $\delta^{82/78}\text{Se}$ increases to $+0.55 \pm 0.42\text{‰}$ (2σ , $n = 5$). This small but statistically significant ($p_{\text{one-tailed}} = 0.01$) positive excursion coincides with a pyrite-rich bed and a positive excursion in organic carbon isotopes (Schoepfer *et al.*, 2013). Above the pyrite bed and extending up to the main extinction horizon (stage III), $\delta^{82/78}\text{Se}$ decreases to a minimum of $-1.8 \pm 0.6\text{‰}$ (2σ) followed by a steady recovery back to $\sim -0.5\text{‰}$ by the time of peak metazoan extinction. This large negative excursion coincides with declines in $\delta^{34}\text{S}$, $\delta^{13}\text{C}_{\text{org}}$ and total organic carbon (TOC) during this stage (Schoepfer *et al.*, 2013; Schoepfer *et al.*, 2012). In stage IV, $\delta^{82/78}\text{Se}$ gradually increases to around $+0.3\text{‰}$ at the Permian-Triassic

boundary (100 cm), which is similar to the proposed minimum composition of modern seawater Se^{IV} and Se^{VI} (Mitchell et al., 2012; Rouxel et al., 2004). Both $\delta^{34}\text{S}$ and $\delta^{13}\text{C}_{\text{org}}$ remain low, and TOC reaches values of up to 2 %. The transition from stage III to stage IV is gradual and apparently not controlled by facies changes.

4.2. Sequential extraction experiment

The three Se extracts from one sample (-40 cm; Table 3) show distinct isotopic compositions and abundances (Fig. 5). The residual fraction, *i.e.* refractory organic $\text{Se}^{-\text{II}}$ ($\pm \text{Se}^0$) represents the major component, similar to samples analyzed in other studies (Fan et al., 2011; Kulp and Pratt, 2004). Compared to the bulk sample, this fraction is isotopically slightly enriched by +0.20‰ in $\delta^{82/78}\text{Se}$. The next most abundant species is the Cr-reducible Se, *i.e.* inorganic $\text{Se}^{-\text{II}}$ ($\pm \text{Se}^0$), followed by NaOH-soluble Se (adsorbed Se^{IV} , possibly oxidized phases). Their relative abundances are comparable to those reported from Cretaceous (Kulp and Pratt, 2004) and Cambrian samples (Fan *et al.*, 2011). Both fractions are isotopically depleted relative to the bulk sample ($\delta^{82/78}\text{Se} = -0.17\text{‰}$) by -0.74‰ and -0.76‰, respectively.

Overall, nearly 92% of the total selenium was recovered by the sequential extraction protocol. The weighted mean of the three fractions has an isotopic composition of -0.16 ± 0.24 ‰ (2σ), *i.e.* only 0.01‰ heavier than the bulk sample. This very close agreement suggests that the lost 8% belongs to the organic selenide $\pm \text{Se}^0$ fraction, which is so large that an additional 8% would have very little effect on the calculated weighted mean. If so, loss of organic selenides likely occurred during the treatment with NaOH, which has been shown to mobilize organic selenides from black shales and cherts of Cambrian age (Fan *et al.*, 2011). As mentioned above,

most of this labile organic Se^{-II} fraction would have been lost during TCF filtration of the NaOH extract, unless it reacted with O₂ dissolved in the NaOH.

5. Discussion

The negative isotopic excursion in selenium isotopes associated with the latest Permian extinction reaches values that are noticeably lighter than most previously reported measurements from the sedimentary marine record (Johnson and Bullen, 2004; Mitchell et al., 2012; Rouxel et al., 2002; Shore, 2010; Stüeken et al., 2015a; Stüeken et al., 2015b). Comparable values were recently reported from very Se-rich samples (up to 116 ppm) of early Cambrian age that were originally deposited under a ferruginous water column (Wen *et al.*, 2014). As discussed in Section 1, negative $\delta^{82/78}\text{Se}$ values are likely the result of non-quantitative Se oxyanion reduction under locally suboxic conditions, *i.e.* in an environment that was connected to a large Se oxyanion supply such as the oxygenated ocean. The short residence time of Se in seawater does not allow us to extrapolate confidently from our sampling locality to the global ocean. However, our data suggest that at least the Ishbel Trough experienced a brief interval around the latest Permian extinction event during which (a) the supply of Se oxyanions exceeded the rate of reduction, and (b) organic Se^{-II} production was relatively minor compared to oxyanion Se reduction to inorganic phases. For at least this particular basin, this finding supports the hypothesis that euxinia was not sufficiently widespread to draw down dissolved Se to low levels throughout the extinction interval, and that biological productivity was only temporarily depressed relative to Se supply. We interpret our data as a sequence of events represented by stages I to IV as follows.

5.1. Stage I: high-productivity upwelling zone

Stage I (Fig. 1), spanning the unconformity, is thought to have coincided with a period during which regional coastal upwelling caused moderately high productivity and the development of an oxygen minimum zone along the eastern margin of the Panthalassic ocean (Georgiev et al., 2015; Henderson, 1997; Schoepfer et al., 2013; Schoepfer et al., 2012). Bulk $\delta^{34}\text{S}$ is relatively high in stage I, indicative of minor diagenetic sulfate reduction within the sediment as a closed system rather than in the open water column (Georgiev et al., 2015; Schoepfer et al., 2013). However, enrichment in trace elements (including Mo, U, V) suggests that the redox state of the water column was too reducing for efficient remineralization of organic matter and thus probably suboxic (Schoepfer *et al.*, 2013). Se in sediments should thus include both organic Se^{II} as well as inorganic reduced phases produced from a continuous supply of upwelled Se oxyanions. The organic fraction should be isotopically heavy, perhaps similar to modern marine biomass (+0.3‰, Mitchell *et al.*, 2012), while the inorganic phases should be significantly lighter, especially if upwelling continuously replenished Se oxyanions and reduction was non-quantitative. Our results (averaging $-0.07 \pm 0.12\text{‰}$, as described in Section 4.1) are indeed consistent with a mixture of several Se phases with distinct isotopic compositions, and they agree well with samples from the upwelling zone of the modern Arabian Sea ($-0.07 \pm 0.16\text{‰}$, Mitchell *et al.*, 2012). A high local supply of Se oxyanions is further indicated by Se/TOC ratios that are more than one order of magnitude greater than those in modern phytoplankton (Fig. 6a). Se concentrations are also high relative to S (Fig. 6b), suggesting that reduction of Se oxyanions was independent from sulfate reduction and proceeded under suboxic conditions, perhaps concurrently with denitrification (Oremland, 1990), for which there is evidence in these samples in the form of enriched nitrogen isotope ratios (Schoepfer *et*

al., 2012). Our data are thus further evidence that Se does not behave as the geochemical twin of S in the marine environment (Mitchell *et al.*, 2012).

The sequential extraction experiment, which was conducted at the -40cm level from this part of the section, confirms our interpretation of isotopic partitioning between inorganic and organic reduced Se, and it also rules out the possibility that the Se in sediments of stage I is purely detrital (cf. Georgiev *et al.*, 2015). The Cr-reducible fraction (inorganic $\text{Se}^{-\text{II}} \pm \text{Se}^0$; $-0.90 \pm 0.46\text{‰}$) is significantly lighter than the residual fraction (refractory organics $\pm \text{Se}^0$; $+0.03 \pm 0.14\text{‰}$). If we had been able to extract Se^0 separately, the residual organic fraction would probably be slightly heavier and capture more accurately the composition of marine biomass. Inorganic reduced Se is evidently significantly depleted relative to organic $\text{Se}^{-\text{II}}$ and probably relative to dissolved $\text{Se}^{\text{IV}/\text{VI}}$, consistent with partial reduction of Se oxyanions.

The isotopically light NaOH-soluble fraction (adsorbed Se^{IV} or oxidized reduced phases; $-0.93 \pm 0.46\text{‰}$) is probably not derived from Se^{IV} dissolved in seawater; dissolved Se^{IV} is produced from organic matter remineralization (Cutter and Bruland, 1984), which does not fractionate isotopes (Johnson *et al.*, 1999). It should therefore be isotopically heavy. Instead, if it is adsorbed Se^{IV} , then it is likely derived from Se^{VI} reduction in sediments. In that case, the close agreement between Se^{IV} and inorganic $\text{Se}^{-\text{II}}$ and/or Se^0 would suggest that Se^{VI} -to- Se^{IV} reduction was not quantitative, perhaps because it occurred close to the sediment-water interface, but further reduction to Se^0 or inorganic $\text{Se}^{-\text{II}}$, perhaps deeper in the sediments, was quantitative (with the exception of the Se^{IV} that was preserved by adsorption). Alternatively, the close match between the NaOH-extract and the Cr-reducible fraction may indicate that the NaOH extraction partially oxidized some inorganic reduced phases such as Se^0 or $\text{Se}^{-\text{II}}$. Oxidation does not impart significant isotopic fractionation ($<0.5\text{‰}$, Johnson *et al.*, 1999).

5.2. Stage II: euxinia

The positive carbon isotope excursion during stage II (Fig. 1) likely marks a pulse in productivity, perhaps due to increased nutrient input by volcanism or enhanced terrestrial weathering (Georgiev et al., 2015; Schoepfer et al., 2013). It coincides with a massive pyrite bed, which has been interpreted as mainly consisting of either diagenetic or hydrothermal overgrowths on pre-existing pyrite framboids and organic particles (Schoepfer *et al.*, 2013). Our new analyses show that the pyrite bed is slightly depleted in $\delta^{34}\text{S}$ compared to stage I, which would be consistent with a relatively higher contribution of syngenetic pyrite formed by microbial sulfate reduction in the water column or at the sediment-water interface (Schoepfer *et al.*, 2013). The $\delta^{34}\text{S}$ values in the pyrite bed are however dissimilar to typical hydrothermal pyrites (Seal, 2006). It is thus likely that stage II marks a brief interval during which increasing biological productivity resulted in local bottom water euxinia and rapid precipitation of sulfide minerals due to enhanced microbial sulfate reduction, both in the water column and under diagenetic conditions (Georgiev *et al.*, 2015). Widespread water-column euxinia may have developed along continental margins shortly before the mass extinction event (Brennecka *et al.*, 2011), and the short interval of intense pyrite formation in this section is plausibly a local manifestation of this phenomenon.

The positive excursion in $\delta^{82/78}\text{Se}$ to around +0.5‰ during stage II is consistent with locally anoxic conditions in which incoming Se oxyanions (either from weathering or upwelling) were nearly quantitatively consumed by assimilation in the photic zone and/or by reduction below, similar to modern anoxic basins (Cutter, 1982; Cutter, 1992). We speculate that a large fraction of total Se in these samples is in the form of inorganic Se^{II} because of the high

concentrations of both Se and S (Fig. 6b). Bulk sedimentary $\delta^{82/78}\text{Se}$ values may thus approach the composition of seawater $\text{Se}^{\text{VI/IV}}$ in the Ishbel Trough at this time. By mass balance the small positive excursion in $\delta^{82/78}\text{Se}$ at this locality implies an isotopically light selenium sink elsewhere. If euxinia was localized to oxygen minimum zones along continental margins (Algeo *et al.*, 2010; Brennecka *et al.*, 2011; Proemse *et al.*, 2013), then the isotopically light sink may have been partial diagenetic reduction in deeper marine sediments further offshore in the Ishbel Trough or even elsewhere in the ocean. To achieve an isotopic enrichment in residual dissolved $\text{Se}^{\text{VI/IV}}$ of +0.5‰ by partial reduction, according to our fractionation model (Section 3.5) only 3.5% to 26% of the total $\text{Se}^{\text{VI/IV}}$ reservoir needs to be reduced (which is $1-f$, expressed as a percentage in the calculations, see Fig. 4). This relatively small fraction supports the hypothesis that most of the deep ocean was oxic during this interval and that euxinia and the positive excursion in $\delta^{82/78}\text{Se}$ were not global features (Algeo *et al.*, 2010; Brennecka *et al.*, 2011; Proemse *et al.*, 2013; Winguth and Maier-Reimer, 2005). The high Se/TOC ratios (Fig. 6a) also support the conclusion that Se deposition was enhanced by local processes, because if euxinia and Se drawdown had been an ocean-wide phenomenon, then the total marine Se reservoir should have become so small that total concentrations at individual localities should have been minimal. Our isotope and abundance data from stage II thus support the view that euxinia prior to the mass extinction was not widespread or long-lived (Brennecka *et al.*, 2011).

5.3. Stage III: extinction

Above the highly pyritic interval, $\delta^{13}\text{C}$ decreases and $\delta^{15}\text{N}$ drops sharply from +9‰ to values around +2‰ (Fig. 1), which has been interpreted as indicating the cessation of coastal upwelling and a decline in productivity (Schoepfer *et al.*, 2012). High TOC/S ratios, Fe

speciation and the lack of trace metal enrichment are consistent with suboxic conditions in the water column, *i.e.* somewhat more oxidized than in the preceding euxinic interval (Georgiev et al., 2015; Schoepfer et al., 2013). The decline in $\delta^{34}\text{S}$ and the occurrence of framboidal pyrite with diagenetic sulfide overgrowths and interstitial carbonate indicates that microbial sulfate reduction occurred close to the sediment-water interface at a slower rate of sulfate consumption than during stage II (Schoepfer *et al.*, 2013). Hence sediments were probably suboxic to anoxic, a process possibly accentuated by an increased sedimentation rate (Algeo and Twitchett, 2010). Negative excursions in carbon and sulfur isotopes are observed globally at this time (Erwin et al., 2002; Fenton et al., 2007; Korte and Kozur, 2010; Korte et al., 2004; Newton et al., 2004; White, 2002), suggesting that this interval marks a worldwide perturbation in major biogeochemical cycles.

Sedimentary $\delta^{82/78}\text{Se}$ at Opal Creek decreases to a minimum of -1.8‰, which is lighter than most marine sediments (Mitchell et al., 2012; Stüeken et al., 2015a; Stüeken et al., 2015b; Wen et al., 2014). It is unlikely that this excursion reflects volcanic input of Se from the Siberian Traps (Campbell *et al.*, 1992) or enhanced weathering due to vegetation loss on land (Georgiev et al., 2015; Ward et al., 2000) because both of those sources would have had a Se isotopic composition near the crustal average of 0‰. Although one study of unusually Se-rich rocks (up to 26,000ppm) showed large fractionations of several permil during weathering (Zhu *et al.*, 2014), fractionations were minimal ($\pm 0.25\%$) in a Se-poor soil (up to 0.5 ppm, Schilling *et al.*, 2011) which is more representative of average crust (0.09 ppm, Rudnick and Gao, 2014). Hence a pulse of continental weathering probably did not cause the large negative excursion observed in stage III. The only other type of geological samples known to be isotopically depleted by 2‰ or more relative to the crust are hydrothermal precipitates and supergene alteration products

(Layton-Matthews et al., 2013; Rouxel et al., 2004; Wen and Carignan, 2011; Zhu et al., 2014). However, it is unlikely that enhanced hydrothermal fluid input or erosion of hydrothermal deposits caused this excursion because other elements such as Cu, with short ocean residence times and commonly associated with hydrothermal activity, are close to crustal background levels during stage III and into stage IV (Schoepfer *et al.*, 2013). Post-depositional supergene alteration (Wen and Carignan, 2011; Zhu *et al.*, 2014) can be ruled out because the selenium isotope excursion correlates well with global excursions in $\delta^{34}\text{S}$ and $\delta^{13}\text{C}$, and because below a weathering rind, which was removed during sample preparation, pyrite is well preserved without any sign of oxidation (see also Georgiev *et al.*, 2015). Se input from weathering of altered rocks elsewhere (cf. Zhu *et al.*, 2014) is improbable because then similarly light values should be common throughout Earth's history (cf. Mitchell et al., 2012; Stüeken et al., 2015b) and should not correlate with seawater redox conditions (cf. Wen *et al.*, 2014). The most plausible explanation for a negative excursion of this magnitude in marine sediments is thus partial reduction of Se oxyanions to Se^0 and/or inorganic $\text{Se}^{-\text{II}}$ at the site of deposition.

Preservation of $\delta^{82/78}\text{Se}$ values significantly below the crustal average can only occur if dissolved Se oxyanions are not quantitatively consumed, *i.e.* if there was a stable Se oxyanion reservoir in the water column. Given the uncertainty in natural fractionation factors, the amount of reduction required to explain a value of -1.8‰ may be anywhere between 9% and 96% of the oceanic $\text{Se}^{\text{VI/IV}}$ reservoir according to our fractionation model (Fig. 4). But if the fractionation factor was small (Fig. 4a,c), *i.e.* close to the range of $\delta^{82/78}\text{Se}$ values observed in marine sediments, a smaller percentage is more likely. If so, then this implies that the water column must have been sufficiently oxygenated for residual dissolved $\text{Se}^{\text{VI/IV}}$ concentrations to exceed biological demand, which may also explain the relatively high Se/TOC ratios during the

excursion interval (Fig. 6a). Anoxia or suboxia probably only existed locally in bottom waters (Georgiev *et al.*, 2015), such that partial $\text{Se}^{\text{IV/VI}}$ reduction and preservation of Se^0 and/or $\text{Se}^{-\text{II}}$ were thermodynamically favored. This interpretation is consistent with other geochemical evidence indicating widespread (sub-)oxic conditions in the open ocean across the extinction event (Algeo *et al.*, 2010; Brennecke *et al.*, 2011; Proemse *et al.*, 2013). Although our data represent only one basin, it is thus possible that Se oxyanions were stable throughout most the ocean at this time and were not removed by euxinia. Sulfur concentrations are not particularly high during this interval (Fig. 6b), so Se oxyanion reduction probably occurred independently from sulfate reduction, as in stage I, perhaps at the oxic-suboxic interface in sediments or in bottom waters.

By comparison, a smaller negative isotope excursion down to -0.63‰ has been reported for the late Cretaceous Ocean Anoxic Event 2 when volcanic activity may have increased the supply of nutrients, including selenium (Mitchell *et al.*, 2012). That report (Mitchell *et al.*, 2012) argued that high nutrient input stimulated productivity, but that Se oxyanions were supplied in amounts beyond the capacity for complete biological reduction. In the Opal Creek section, however, productivity evidently declined during stage III (Schoepfer *et al.*, 2013; Schoepfer *et al.*, 2012), trace metals are not enriched with respect to crustal compositions (Schoepfer *et al.*, 2013) and TOC concentrations are 1-2 orders of magnitude lower than in the late Cretaceous excursion (Mitchell *et al.*, 2012). It is thus more likely that at Opal Creek dissolved $\text{Se}^{\text{VI/IV}}$ excess resulted not from a high Se supply but instead from a relatively low demand.

Because biological assimilation and reduction are the major sinks of Se from the ocean, this decrease in the consumption rate could indicate a decline in organic Se export from the surface ocean to the sediments. Thus, Se isotopes were possibly sensitive, at least locally, to the

collapse in productivity by macroscopic organisms associated with the latest Permian mass extinction. Assuming a small isotopic fractionation factor between 2 and 2.5‰, the isotopic composition of residual dissolved Se^{VI} during the peak of the negative $\delta^{82/78}\text{Se}$ excursion would have been between +0.2‰ and +1.6‰, depending on whether partial reduction occurred under open- or closed-system conditions (Section 3.5). The complementary sink of this isotopically enriched dissolved Se may have been in restricted basins or in localized euxinic parts of the ocean (Algeo *et al.*, 2010; Brennecka *et al.*, 2011).

The slight offset between the minimum in $\delta^{82/78}\text{Se}$ and the major paleontological extinction horizon defined by conodont turnover and the disappearance of sponge spicules and bioturbation (Schoepfer *et al.*, 2012) is perhaps due to weakened upwelling that led to a local decrease in the dissolved Se oxyanion supply. Consequently, Se reduction or assimilation may have become more quantitative, resulting in less negative $\delta^{82/78}\text{Se}$ values even when biological productivity was very low. If so, then the extinction at this site was perhaps influenced by a limiting supply of nutrients, including Se. Alternatively, it is possible that total macroscopic productivity was indeed at its minimum prior to the extinction peak due to reasons other than nutrient supply, but microbial productivity resumed quickly (e.g. Algeo *et al.*, 2011; Georgiev *et al.*, 2015; Shen *et al.*, 2014) and already dominated Se consumption and export by the time major groups of metazoans died out. However, Se/TOC ratios decline steadily throughout stage III (Table 2), supporting the first scenario of dwindling Se input. In either case, our data suggest that locally, and perhaps over a wider area, total biological productivity collapsed over the course of ~1kyr (from ~10cm to 12cm, assuming the sedimentation rate of 0.5kyr cm⁻¹ (Farley *et al.*, 2005)) under relatively oxygenated conditions.

5.4. Stage IV: recovery

During stage IV (Fig. 1), sulfur and carbon isotopes in the Ishbel Trough change little compared to the end of stage III, indicating that the ocean probably continued to be oxic to suboxic and productivity remained low (Georgiev et al., 2015; Schoepfer et al., 2012). Bottom-water suboxia and rapid burial likely limited organic matter re-oxidation, leading to the high TOC content of these samples.

$\delta^{82/78}\text{Se}$ is the only tracer that returns to values similar to stage I (average $-0.05 \pm 0.42 \text{ ‰}$, $n = 14$, Fig. 1), probably because Se is a much rarer element than C and S with a shorter residence time in the ocean and so is perhaps more sensitive to environmental changes and ocean circulation. The return to slightly heavier values could have resulted from two processes: (i) consumption of a relatively higher proportion of Se oxyanions by partial reduction than during stage III, leading to a smaller net fractionation in the reduced phase compared to the starting composition (as modeled in Fig. 4 for large values of f), or (ii) isotopically heavy organic Se^{II} becoming the major component in marine sediments, leading to dilution of isotopically light Se^0 and/or inorganic Se^{II} produced from oxyanion reduction. Both processes would have been facilitated by a lower supply of Se oxyanions to the shelf, *i.e.* through continued suppression of coastal upwelling, but also by local recovery of biological activity. The first possibility is supported by Se/TOC ratios, which are distinctly lower in stage IV than in other parts of the section (Fig. 6a). Hence low nutrient supply under oxic to suboxic conditions perhaps continued to delay biological recovery into the early Triassic.

Combined with data from stage III, we observe an inverse relationship between $\delta^{82/78}\text{Se}$ values and the logarithm of Se/TOC ratios ($R^2 = 0.57$). Low Se/TOC ratios paired with high $\delta^{82/78}\text{Se}$ values may reflect a situation in which the supply of Se was locally limited and only

organic Se^{-II} was preserved; high Se/TOC ratios paired with low $\delta^{82/78}\text{Se}$ values likely indicate increased availability of Se oxyanions, which were then subject to partial reduction. If the sample with highest $\delta^{82/78}\text{Se}$ and lowest Se/TOC (Fig. 6a, circle A) represents nearly pure biomass with no addition of Se⁰ and/or inorganic Se^{-II} to the sediment, then it may capture the composition of seawater Se^{VI} in the early Triassic.

During stage IV, the $\delta^{82/78}\text{Se}$ record returns to values typical of Stage I, diverging markedly from the $\delta^{34}\text{S}$ record which shows a comparatively small recovery (Fig. 1). The sulfur system is only sensitive to profound redox changes, which, as discussed above and elsewhere (Algeo et al., 2010; Proemse et al., 2013; Schoepfer et al., 2012), did not occur between the onset of the extinction (stage III) and the subsequent recovery. Even though the dissolved sulfate reservoir may have contracted (Luo *et al.*, 2010), sulfate was likely a conservative ion before, during and after the latest Permian extinction event. Se, however, being a trace element in the ocean, is more sensitive to subtle and local redox and productivity changes. In this case, our Se data indicate more clearly than the S record alone that ocean circulation was sluggish, though not absent, across the Permian-Triassic boundary.

6. Conclusion

At Opal Creek, Se isotopes display a large negative excursion in marine sediments, slightly before the largest mass extinction of the Phanerozoic eon. We proposed that these low $\delta^{82/78}\text{Se}$ values in bulk sediments resulted from a unique decline of macro-biological activity and organic Se export, leading to excess Se oxyanion concentrations in the water column, which were then subject to partial reduction in suboxic bottom waters or at the sediment-water interface. The event is preceded by a small positive excursion, which was likely caused by

locally euxinic conditions due to a temporary increase in productivity, and hence quantitative consumption of isotopically heavy Se in the water column. However, euxinia was likely limited to continental margins, consistent with recent evidence from Mo and U isotopes and metal abundances (Algeo *et al.*, 2010; Algeo *et al.*, 2011; Brennecka *et al.*, 2011; Proemse *et al.*, 2013), and thus probably not responsible for the mass extinction. Instead, our data suggest that at least this basin was oxic at the onset of the productivity decline, because otherwise Se oxyanions would not have been stable in the water column. Although we can only confidently speak for this one locality, our data support models of oxic conditions in the open Panthalassic ocean at the time of the mass extinction (e.g. Winguth and Maier-Reimer, 2005). Productivity during the extinction appears to have collapsed quickly over ~1kyr. During the peak extinction in the latest Permian and continuing into the early Triassic, an increasingly stratified ocean (Song *et al.*, 2013) decreased the supply of nutrients to the surface, leading to more quantitative Se consumption even under oxic to suboxic conditions. Hence nutrient limitation probably did not cause the initial collapse of the marine biosphere but it may have inhibited its recovery.

Lastly, this study shows that Se isotopes can be a valuable proxy for geobiological changes in deep time. As demonstrated with one sample, the sequential extraction and isotopic analysis of different Se phases may help disentangle some of the complexity of this new isotopic system and should be pursued in future studies.

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Table 1: Method comparison. Selenium isotope results, given in ‰, for four samples processed with two different protocols (D) and (E). M = number of replicate analyses. Differences between protocols are not systematic.

[cm]	Method D							Method E						
	M	$\delta^{82/78}\text{Se}$	2 σ	$\delta^{76/78}\text{Se}$	2 σ	$\delta^{77/78}\text{Se}$	2 σ	M	$\delta^{82/78}\text{Se}$	2 σ	$\delta^{76/78}\text{Se}$	2 σ	$\delta^{77/78}\text{Se}$	2 σ
-4	5	-0.05	0.58	-0.04	0.32	0.05	0.24	4	-0.01	0.26	-0.01	0.22	0.01	0.08
22	8	-1.95	0.58	0.93	0.34	0.55	0.26	4	-1.58	0.10	0.84	0.48	0.43	0.02
49.5	2	-0.32	0.28	0.39	0.08	0.37	0.42	4	-0.60	0.14	0.37	0.34	0.18	0.04
159.5	3	-0.06	0.30	-0.77	1.20	-0.12	0.32	4	-0.08	0.20	0.04	0.08	0.09	0.08

652 **Table 2: Data set.** M(Se) = number of replicate Se measurements, using method D in Stüeken *et al.* (2013) unless noted otherwise in
653 column 1; RE = relative error; blank = not determined; dashed lines = stages boundaries discussed in the text. While $\delta^{82/78}\text{Se}$, $\delta^{77/78}\text{Se}$
654 and $\delta^{76/78}\text{Se}$ were directly measured, $\delta^{82/76}\text{Se}$ was calculated from $\delta^{82/78}\text{Se}$ by multiplication with a factor of 1.54 to facilitate
655 comparison of our data with other recent studies. C and S data are from Schoepfer *et al.* (2013; 2012) unless listed in Section 3.4.

depth	M	Se	RE	$\delta^{82/78}\text{Se}$	2 σ	$\delta^{82/76}\text{Se}$	2 σ	$\delta^{76/78}\text{Se}$	2 σ	$\delta^{77/78}\text{Se}$	2 σ	S	$\delta^{34}\text{S}$	TOC	$\delta^{13}\text{C}$	log(Se/S)	log(Se/TOC)
[cm]	(Se)	[ppm]	[%]	[‰]	[‰]	[‰]	[‰]	[‰]	[‰]	[‰]	[‰]	[%]	[‰]	[%]	[‰]	[mol/mol]	[mol/mol]
-40	9	9.61	2.91	-0.17	0.22	-0.26	0.33	0.06	0.13	0.07	0.20	0.65	-2.90	0.52	-29.77	-3.22	-3.55
-21	7	25.08	17.39	-0.09	0.51	-0.14	0.78	0.02	0.22	0.00	0.13	0.86	-1.27	0.95	-29.66	-2.93	-3.40
-4 (a)	9	8.49	4.63	-0.03	0.45	-0.05	0.69	-0.03	0.27	0.03	0.18	0.86	0.63	0.36	-28.90	-3.39	-3.45
1.5 (b)	3	9.40	1.35	0.68	0.26	1.04	0.40	-0.35	0.22	-0.15	0.07	1.74	-2.73	1.29	-29.68	-3.66	-3.95
3	2	8.52	4.07	0.00	0.02	-0.01	0.03	-0.09	0.03	0.11	0.32	4.37	-11.06	0.08	-27.00	-4.10	-2.80
3.5 (b)	3	12.50	1.79	-0.06	0.19	-0.09	0.29	0.05	0.11	0.02	0.04	3.47	-7.47	1.24	-29.75	-3.84	-3.82
4	2	24.42	5.90	0.60	0.03	0.92	0.05	-0.24	0.02	-0.11	0.13	29.87	-8.99	0.13	-27.05	-4.48	-2.53
5	2	25.56	31.64	0.59	0.31	0.91	0.48	-0.33	0.13	-0.24	0.52	28.71	-7.73	0.12	-27.44	-4.44	-2.48
6	2	18.56	52.70	0.70	0.46	1.08	0.71	-0.31	0.07	-0.01	0.60	9.32	-8.48	0.32	-29.65	-4.09	-3.05
8	2	22.88	6.28	0.67	0.06	1.03	0.09	-0.35	0.07	-0.17	0.15	27.86	-8.38	0.12	-26.38	-4.48	-2.53
9	2	18.49	2.54	0.19	0.30	0.29	0.45	-0.16	0.14	0.01	0.09	26.35	-7.34	0.21	-25.68	-4.55	-2.87
10.5	7	8.31	3.96	-0.41	0.65	-0.63	1.00	0.16	0.28	0.10	0.25	5.77	-11.85	0.10	-25.77	-4.23	-2.88
15	4	4.35	7.61	-1.08	0.53	-1.66	0.82	0.52	0.32	0.26	0.26	1.76	-7.30	0.07	-26.69	-4.00	-3.02
17.5 (b)	2	3.94	0.22	-1.54	0.12	-2.37	0.19	0.82	0.06	0.39	0.03	2.58	-17.73	0.08	-27.16	-4.21	-3.11
22 (a)	12	2.31	10.98	-1.83	0.59	-2.81	0.91	0.90	0.39	0.51	0.24	2.96	-19.52	0.10	-27.06	-4.50	-3.46
24.25 (b)	2	2.30	0.47	-1.74	0.05	-2.68	0.07	0.95	0.02	0.48	0.02	2.67	-21.50	0.00		-4.46	
29	5	2.06	5.61	-1.53	0.71	-2.36	1.10	1.10	0.32	0.38	0.25	5.36	-30.90	0.29	-29.59	-4.81	-3.97
30.75	8	2.46	13.10	-1.22	0.35	-1.88	0.54	0.84	0.22	0.40	0.18	3.74	-23.99	0.46	-30.76	-4.57	-4.09
36.5 (b)	2	2.48	0.19	-1.08	0.05	-1.67	0.08	0.58	0.07	0.32	0.00	2.57	-23.34	0.62	-29.73	-4.41	-4.21
37.5 (b)	2	2.39	8.06	-1.06	0.12	-1.63	0.18	0.59	0.01	0.37	0.07	3.93	-19.00	0.39	-30.37	-4.61	-4.03
40 (b)	2	2.82	0.57	-0.79	0.25	-1.22	0.38	0.43	0.13	0.26	0.09		-22.59	0.48	-30.96		-4.04
43	2	5.14	6.67	-0.52	0.25	-0.81	0.39	0.39	0.03	0.21	0.24	3.55	-23.58	0.66	-30.55	-4.23	-3.93
46 (b)	2	3.19	0.48	-1.28	0.12	-1.98	0.19	0.71	0.00	0.40	0.02			0.89	-30.92		-4.27
49.5 (a)	6	2.53	4.22	-0.51	0.33	-0.78	0.51	0.38	0.26	0.25	0.27	2.60	-25.96	0.40	-31.34	-4.40	-4.01
72	2	2.26	1.18	-0.54	0.26	-0.84	0.40	0.38	0.14	0.31	0.21	3.31	-19.43	0.70	-31.04	-4.56	-4.31
90.15	5	1.64	5.47	-0.51	0.46	-0.78	0.71	0.56	0.14	0.26	0.23	3.54	-19.99	0.75	-31.16	-4.73	-4.48
106.25	5	1.35	4.08	-0.57	0.50	-0.88	0.77	0.31	0.25	0.29	0.19	2.80	-19.52	1.01	-30.70	-4.71	-4.69
116.75	4	1.16	8.45	-0.35	0.87	-0.53	1.34	0.29	0.40	0.18	0.28	3.35	-16.77	1.45	-30.49	-4.85	-4.91
133.5	5	1.72	2.23	-0.19	0.39	-0.29	0.60	0.13	0.18	0.11	0.25	2.65	-20.59	1.97	-31.64	-4.58	-4.88
159.5 (a)	6	0.58	7.08	-0.17	0.35	-0.27	0.54	0.10	0.19	0.10	0.07	3.63	-9.79	0.62	-31.97	-5.19	-4.85
310.5	3	0.58	4.02	-0.02	0.44	-0.04	0.68		0.00	0.17	0.34	1.89	-20.41	1.57	-31.62	-4.90	-5.25
386	5	0.90	4.36	0.59	0.56	0.90	0.87	-0.26	0.61	0.00	0.26	1.88	-20.42	1.66	-32.06	-4.71	-5.08
494.2	3	1.17	2.09	0.35	0.27	0.55	0.42	-0.21	0.12	-0.10	0.12	3.09	-13.70	2.01	-31.92	-4.81	-5.05
563	3	0.92	5.65	0.49	0.18	0.76	0.28	-0.32	0.86	0.17	0.45	1.62	-20.03	2.30	-31.90	-4.64	-5.22
850.5	4	1.35	6.53	0.35	0.39	0.54	0.59	-0.41	0.28	0.02	0.17	1.96	-10.89	2.26	-31.57	-4.55	-5.04
1237	2	0.96	1.82	-0.11	0.18	-0.16	0.28	-0.35	0.05	0.09	0.04	1.47	-14.30	2.14	-30.97	-4.58	-5.16
1684	2	0.58	7.80	0.35	0.34	0.54	0.52	-0.63	0.67	0.18	0.22	1.25	-18.25	1.62	-30.57	-4.72	-5.26

656 (a) Prepared with both protocols D and E in Stüeken *et al.* (2013). See Table 1 for method comparison.

657 (b) Only prepared with protocol E in Stüeken *et al.* (2013).

658 **Table 3: Selenium species in sample from -40 cm.** Isotopic values are given in ‰, selenium concentrations in ppm. % tot. = fraction
659 of bulk rock. Each fraction was prepared and analyzed in four replicates. SeX = uncertain contributions of reduced Se phases that were
660 oxidized by O₂ dissolved in NaOH. Reported errors for the three extracts are the standard deviations of the four replicates for each
661 extraction step. Errors for the weighted average are propagated. As in Table 2, values for $\delta^{82/76}\text{Se}$ were calculated from $\delta^{82/78}\text{Se}$
662 whereas all others were measured directly.
663

reagent	Se species	[Se]	2 σ	% tot.	2 σ	$\delta^{82/78}\text{Se}$	2 σ	$\delta^{82/76}\text{Se}$	2 σ	$\delta^{76/78}\text{Se}$	2 σ	$\delta^{77/78}\text{Se}$	2 σ
NaOH	Se ^{IV} _{ads} $\pm$ SeX	0.62	0.04	6.4%	0.4%	-0.93	0.46	-1.44	0.36	0.47	0.24	0.29	0.48
CrCl ₂ + HCl	Se ^{II} _{pyr} $\pm$ Se ⁰	1.26	0.34	13.2%	3.4%	-0.90	0.46	-1.39	0.36	0.47	0.28	0.20	0.30
HF+HClO ₄ +HNO ₃	Se ^{II} _{org} $\pm$ Se ⁰	6.93	1.26	72.2%	13.0%	0.03	0.14	0.04	0.11	-0.08	0.12	0.05	0.38
weighted average		8.82	1.84	91.7%	9.4%	-0.16	0.12	-0.24	0.16	0.04	0.10	0.08	0.28
missing				8.3%	9.4%								
BULK		9.61	0.28			-0.17	0.22	-0.26	0.17	0.06	0.14	0.07	0.20

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Figure captions

Figure 1: Stratigraphic section across the PT extinction event in the Western Canada Basin at Opal Creek. Sulfur data are from Schoepfer *et al.* (2013); carbon and nitrogen data and lithostratigraphy are from Schoepfer *et al.* (2012). Triangles = chert, broken lines = siltstone, solid lines = shale, dotted black line = unconformity, PYR and yellow bar = pyrite-rich bed (based on TS concentrations in Table 1; its usage here does not correspond exactly with its usage by Schoepfer *et al.* (2013; 2012), because our sampling density is higher during this interval), EXT and dashed red line = main extinction horizon, PTB and solid green line = Permian-Triassic boundary. $\delta^{82/78}\text{Se}$ data show 2-sigma error bars. Roman numerals refer to stages described in the text. **A:** complete section. **B:** detail of the section between -0.5 and +1.0 m.

Figure 2: Sequential extraction protocol. Solid arrows mark transfer of rock powder; dashed arrows mark separation and removal of selenium species from rock powder. See Section 3.2 for detailed descriptions of each step.

Figure 3: Mass-dependent fractionation and interference correction. Empty diamonds are individual measurements, filled diamonds are averages $\pm 2\sigma$ (Table 2). **a:** $\delta^{77/78}\text{Se}$ versus $\delta^{82/78}\text{Se}$. **b:** $\delta^{76/78}\text{Se}$ versus $\delta^{82/78}\text{Se}$. Line marks the theoretical relationship of mass-dependent fractionation. Within 2σ , almost all samples fall along the mass-dependent fractionation line, indicating that natural mass-independent mass fractionation is absent and that major isobaric interferences have been adequately corrected.

Figure 4: Possible solutions for Se isotope mass balance. a, b: Open system fractionation with a maximum fractionation of $\varepsilon = 2\text{‰}$ (a) or 14‰ (b). **c, d:** Closed system Rayleigh fractionation with a maximum fractionation of $\varepsilon = 2\text{‰}$ (c) or 14‰ (d). Dashed arrows point to values of f needed to obtain $\delta^{82/78}\text{Se}^{\text{VI/IV}} = +0.5\text{‰}$, dotted arrows point to values of f needed to obtain $\delta^{82/78}\text{Se}^{\text{red}} = -1.8\text{‰}$. Model calculations are explained in Section 3.5.

Figure 5: Sequential extraction of Se phases in sample -40 cm. a: isotopic compositions. Blue diamond = adsorbed Se^{IV} with potential traces of reduced Se phases (SeX) oxidized by O_2 dissolved in NaOH; yellow square = inorganic $\text{Se}^{\text{-II}} \pm \text{Se}^0$; brown triangle = refractory organic $\text{Se}^{\text{-II}} \pm \text{Se}^0$; black circle = bulk sample; red x = weighted average of extracted fractions; solid line = theoretical mass-dependent fractionation line. b: Relative proportions of Se phases in bulk sample, using the same color scheme as in panel a. nd = not determined (missing fraction). All errors are 2σ and listed in Table 3.

Figure 6: $\delta^{82/78}\text{Se}$ versus Se/TOC (a) and total Se versus total S (b). In panel a, green bar marks Se/TOC ratio of modern phytoplankton ($1.7 \cdot 10^{-6}$ to $5.7 \cdot 10^{-6}$, Mitchell *et al.*, 2012). A: a circle that represents the range for a putative biomass end-member that may capture the isotopic composition of early Triassic seawater. B: Effects of Se addition to sediments by reductive scavenging in oxygen-minimum zone (stage I) or local euxinia (stage II). C: Effects of Se addition by partial (diagenetic) reduction in suboxic bottom water or sediment (stages III and IV).

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Figure 2

Figure 3

OPEN SYSTEM

CLOSED SYSTEM

Figure 5

Figure 6