This is a repository copy of *The evolution of the global selenium cycle: Secular trends in Se isotopes and abundances*.

White Rose Research Online URL for this paper:
http://eprints.whiterose.ac.uk/86400/

Version: Accepted Version

Article:

Stüeken, EE, Buick, R, Bekker, A et al. (7 more authors) (2015) The evolution of the global selenium cycle: Secular trends in Se isotopes and abundances. Geochimica et Cosmochimica Acta, 162. 109 - 125. ISSN 0016-7037

https://doi.org/10.1016/j.gca.2015.04.033

© 2015, Elsevier. Licensed under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International
http://creativecommons.org/licenses/by-nc-nd/4.0/

Reuse

Unless indicated otherwise, fulltext items are protected by copyright with all rights reserved. The copyright exception in section 29 of the Copyright, Designs and Patents Act 1988 allows the making of a single copy solely for the purpose of non-commercial research or private study within the limits of fair dealing. The publisher or other rights-holder may allow further reproduction and re-use of this version - refer to the White Rose Research Online record for this item. Where records identify the publisher as the copyright holder, users can verify any specific terms of use on the publisher's website.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

eprints@whiterose.ac.uk
https://eprints.whiterose.ac.uk/

The evolution of the global selenium cycle: secular trends in Se isotopes and abundances

E. E. Stüeken[1*], R. Buick[1], A. Bekker[2], D. Catling[1], J. Foriel[3], B. M. Guy[4], L. C. Kah[5], H. G. Machel[6], I. P. Montañez[7], S. W. Poulton[8]

1. Department of Earth & Space Sciences and Astrobiology Program, University of Washington, Seattle, WA 98195-1310, USA
2. Department of Earth Sciences, University of California, Riverside, CA 92521, USA
3. Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University in St. Louis, St. Louis, MI 63130, USA
4. Dept. of Geology, University of Johannesburg, Auckland Park 2006, South Africa; Present Address: Mineral Services, SGS South Africa, 58 Melville Street, Booysens, Johannesburg 2091, South Africa
5. Department of Earth & Planetary Sciences, University of Tennessee, Knoxville, TN 37996, USA
6. Department of Earth & Atmospheric Sciences, University of Alberta, Edmonton, Alberta T6G 2E3, Canada
7. Department of Earth and Planetary Sciences, University of California, Davis, CA 95616, USA
8. School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK

* corresponding author. evast@uw.edu

Abstract

The Earth's surface has undergone major transitions in its redox state over the past three billion years, which have affected the mobility and distribution of many elements. Here we use Se isotopic and abundance measurements of marine and non-marine mudrocks to reconstruct the evolution of the biogeochemical Se cycle from ~3.2 Gyr onwards. The six stable isotopes of Se are predominantly fractionated during redox reactions under suboxic conditions, which makes Se a potentially valuable new tool for identifying intermediate steps from an anoxic to a fully oxygenated world. $\delta^{82/78}$Se shows small fractionations of mostly less than 2‰ throughout Earth's history and all are mass-dependent within error. In the Archean, especially after 2.7 Gyr, we find an isotopic enrichment in marine (+0.37 ± 0.27‰) relative to non-marine samples (-0.28 ± 0.67‰), paired with increasing Se abundances. Student t-tests show that these trends are statistically significant. Although we cannot completely rule out the possibility of volcanic Se addition, these trends may indicate the onset of oxidative weathering on land, followed by non-quantitative reduction of Se oxyanions during fluvial transport. The Paleoproterozoic Great Oxidation Event (GOE) is not reflected in the marine $\delta^{82/78}$Se record. However, we find a major inflection in the secular $\delta^{82/78}$Se trend during the Neoproterozoic, from a Precambrian mean of +0.42 ± 0.45‰ to a Phanerozoic mean of -0.19 ± 0.59‰. This drop probably reflects the oxygenation of the deep ocean at this time, allowing Se oxyanions to be stable throughout the water column. Since then, reduction of Se oxyanions has likely been restricted to anoxic basins and diagenetic environments in sediments. In light of recent Cr isotope data, it is likely that oxidative weathering before the Neoproterozoic produced Se oxyanions in the intermediate redox state Se^{IV}, whereas the fully oxidized species Se^{VI} became more abundant after the Neoproterozoic rise of atmospheric oxygen.

1. Introduction

Se is an essential micronutrient for many organisms (e.g. Mayland, 1994; Gladyshev, 2012). In natural environments it can be found in four redox states, as Se^{VI} (SeO_4^{2-}), Se^{IV} (SeO_3^{2-} or $HSeO_3^-$), Se^0, and organic and inorganic Se^{-II}. In the modern ocean, the oxyanions Se^{VI} and Se^{IV} are most abundant and show typical nutrient abundance profiles with depletion in the photic zone, replenishment below the photic zone due to organic matter remineralization and constant concentration in the deep ocean (Cutter and Cutter, 2001). Organic Se^{-II} is common in surface waters but it is almost entirely re-oxidized at depth and thus insignificant below the photic zone. In anoxic water columns, remineralization of organic matter does not occur, such that organic Se^{-II} phases dominate below the chemocline and Se oxyanions remain low throughout the water column (Cutter, 1982; Cutter, 1992). Sediments that formed in anoxic environments therefore mostly contain reduced phases, including Se^0 and organic and pyrite-bound Se^{-II} (Kulp and Pratt, 2004; Fan et al., 2011).

The six stable isotopes of Se (masses 82, 80, 78, 77, 76 and 74) are most strongly fractionated during kinetic redox transformations, which favor the lighter masses. In laboratory experiments, abiotic reduction of Se oxyanions to Se^0 or Se^{-II} with HCl, NH_2OH, ascorbic acid, Fe^{2+} in green rust or sulfide can impart larger negative fractionations (ε = 10-25‰, where $\varepsilon = \delta^{82/78}Se_{reactant} - \delta^{82/78}Se_{product}$) than biotic reduction (ε = 6-14‰) (Krouse and Thode, 1962; Rees and Thode, 1966; Rashid and Krouse, 1985; Johnson et al., 1999; Herbel et al., 2000; Ellis et al., 2003; Johnson and Bullen, 2003; Mitchell et al., 2013). However, in natural systems, abiotic reduction is thought to be kinetically inhibited such that biological fractionation likely dominates (Johnson and Bullen, 2004). Large fractionations can also occur during equilibration of Se species with different redox states, where, as in kinetic isotope fractionation, the more oxidized forms become isotopically enriched by up to 33‰ (Li and Liu, 2011). Although it has so far not been demonstrated that equilibrium processes are insignificant in natural environments, the dominance of kinetic fractionation in other isotopic systems like S, as well as the co-occurrence of different Se redox species in thermodynamic disequilibrium in natural samples (e.g. Cutter and Bruland, 1984; Kulp and Pratt, 2004) suggests that kinetic processes are most important (reviewed by Johnson and Bullen, 2004). Moderate negative fractionations from <0.6‰ to 2.6‰ have been reported for Se^{VI} assimilation into biomass (Johnson et al., 1999; Hagiwara, 2000; Clark and Johnson, 2010), but those values greater than 0.6‰, which were measured by Hagiwara (2000), have been questioned due to possible fractionation during sample preparation (Johnson and Bullen, 2004). Hence isotopic fractionation associated with assimilation is probably on the order of 0.6‰ or less and thus minor. Similarly, Se^{IV} adsorption on Fe oxides results in small negative fractionations of up to 0.7‰ (average 0.1‰) (Johnson et al., 1999; Mitchell et al., 2013). Volatilization of organic Se^{-II} from incubated soils can impart moderate fractionations of up to 2.7‰ (Johnson et al., 1999; Schilling et al., 2011a), but Se gases have such a short atmospheric residence time of only a few hours (Wen and Carignan, 2007) that this pathway is insignificant over geologic timescales. Consequently, it appears that large Se isotope fractionations of greater than 1‰ in geological samples should be evidence of biological reduction of Se oxyanions. As noted by others (Ellis et al., 2003; Johnson, 2004; Johnson and Bullen, 2004), isotopic fractionations associated with oxyanion reduction may be smaller in natural ecosystems than under experimental conditions due to differences in physiology between cultured microorganisms and natural consortia. However, individual reports of fractionations up to 4‰ in some marine shales (Wen et al., 2014; Stüeken et al., submitted) suggest that Se oxyanion reduction can leave a detectable signature in old rocks if it occurred at the time of deposition. Smaller fractionations associated with oxyanion adsorption and assimilation into biomass may be significant in oxic environments where reduction does not occur. This raises the possibility of using Se isotopes as an independent tool for reconstructing environmental redox changes over Earth's history (Mitchell et al., 2012; Stüeken et al., 2015). Because of its relatively low abundance, multiple redox states and high redox potential (Johnson, 2004), Se may be more sensitive to redox and productivity changes than other proxies, such as S and perhaps Mo. We note that an impediment to this line of research is the current lack of data about Se isotopic fractionations associated with volcanic eruptions, which may have been important in the past, but we will discuss this issue as appropriate.

This study is composed of two parts with the aim of reconstructing the evolution of the Se cycle through Earth's history. First, we compile recent marine Se isotope data from the literature and create a working model for how Se isotopes behave on a global scale in the modern ocean under known redox conditions. This will provide a platform for interpreting Se isotope data in deep time. Second, we present new data from mudrocks through time with particular focus on the Precambrian, incorporating transects across environmental gradients in the late Archean and Mesoproterozoic. Combined with existing datasets (Johnson and Bullen, 2004; Rouxel et al., 2004; Mitchell et al., 2012; Layton-Matthews et al., 2013; Wen et al., 2014; Stüeken et al., 2015), this provides us with a record spanning the last 3.2 billion years, i.e. through the proposed Paleoproterozoic and Neoproterozoic oxidation events (reviewed by Lyons et al., 2014a). Both of these events could have affected the Se biogeochemical cycle, and hence the sedimentary Se record may provide independent evidence or additional information on them. More specifically, we test the following hypotheses: (1) Because the most mobile Se species Se^{IV} and in particular Se^{VI} are only stable under suboxic to oxic conditions, we would expect that the marine Se cycle changed profoundly with the oxygenation of the deep ocean in the Neoproterozoic (Canfield et al., 2007; Canfield et al., 2008; Shields-Zhou and Och, 2011; Sahoo et al., 2012). Se^{VI} and Se^{IV} should have become more stable ions in the water column, i.e. they should no longer have been subject to quantitative reduction, leading to larger net isotopic fractionations preserved in sediments. Hence, we expect to see a systematic difference in isotopic values before and after the Neoproterozoic oxidation event. (2) The high redox potential of Se oxyanions ($Se^{IV/VI}$) compared to sulfate (S^{VI}) (Johnson, 2004) may also have delayed the onset of the Se weathering flux from land into the ocean during the early stages of Earth surface oxygenation. Total S (TS) abundances in marine sediments increased in the late Archean, suggesting incipient oxidative weathering of sulfide minerals, enhanced by microbial activity (Stüeken et al., 2012). If conditions were not oxidizing enough for Se, then TS/TSe ratios in sediments should have been elevated for some time interval afterwards, perhaps until the Paleoproterozoic or Neoproterozoic oxidation events, when atmospheric oxygen levels rose globally. If, however, microbial activity led to locally high redox states sufficient for Se oxidation, then the Se^{IV} and/or Se^{VI} flux to the ocean may have increased concurrently with the S^{VI} flux and TS/TSe ratios should be constant through time. Hence marine TS/TSe ratios may serve as an indirect proxy for non-marine redox processes. We would further expect to see isotopic differences between non-marine, shallow marine and deeper marine sediments if $Se^{IV/VI}$ stability and abundance decreased from oxic terrestrial habitats to anoxic seawater.

2. Methods

2.1. Compilation of recent data

To better understand the modern Se cycle, we compiled data from the literature representing the last 500 kyr during which the ocean redox state is relatively well constrained. Included are data from the mid-Atlantic (Johnson and Bullen, 2004), the Bermuda Rise (Shore, 2010), the Cariaco Basin (Shore, 2010), the Arabian Sea (Mitchell et al., 2012) and the Black Sea (Johnson and Bullen, 2004; Mitchell et al., 2012). The data set was divided into two categories: open oxic ocean and restricted anoxic basins. Data from the mid-Atlantic, the Bermuda Rise, the Arabian Sea, and from the glacial oxygenated stages of the Cariaco Basin (Shore, 2010) were included in the oxic ocean category. Samples from the Arabian Sea include sediments that formed below an oxygen minimum zone (Mitchell et al., 2012), but because the Arabian Sea rapidly exchanges water masses with the open ocean by upwelling and therefore likely has a high supply of Se oxyanions, it is more similar to an oxic ocean. The restricted anoxic basin category includes data from the interglacial Cariaco Basin (Shore, 2010) and the Black Sea. Although some samples from the Black Sea have been described as oxic (Mitchell et al., 2012), euxinic conditions in the deeper water column probably result in low Se oxyanion concentrations and a short residence time throughout the basin (Cutter, 1992). Therefore, we assigned all Black Sea samples to the anoxic restricted basin category.

2.2. New analyses of ancient rocks

Our new analyses focused on whole-rock samples of kerogenous mudrocks (Table 1), because they are relatively abundant and Se-rich. This approach has the disadvantage that mudrocks can contain multiple isotopically distinct Se phases including elemental Se^0, Se^{-II} bound to organic matter or substituting for S^{-II} in sulfide minerals, and Se^{IV} adsorbed to mineral surfaces or kerogen (Kulp and Pratt, 2004; Fan et al., 2011; Schilling et al., 2014b; Stüeken et al., submitted). Combining these phases probably reduces the measured isotopic range and might make it more difficult to discern patterns. In some ways, this is analogous to measuring trends in C isotopes without separating organic C from carbonate. However, separation techniques for differing Se phases in rocks are only beginning to be developed (Kulp and Pratt, 2004; Fan et al., 2011; Schilling et al., 2014b; Stüeken et al., submitted), and it is uncertain if they are useful for ancient samples where isotopic ratios may have re-equilibrated. An alternative approach may be to analyze banded iron formations (BIF) that primarily contain just one phase, i.e. adsorbed Se^{IV} (Schilling et al., 2014b; Schirmer et al., 2014). However, the Se concentrations in such rocks are very low, presenting analytical difficulties, and BIF or equivalent deep-marine Fe oxides are not available from all time periods or from all environments. Mudrocks have formed throughout Earth's history in a diversity of environments including lakes, tidal flats and outer marine shelves, which allows us to compile data across both the Paleoproterozoic and the Neoproterozoic oxidation events (Lyons et al., 2014a) and to reconstruct environmental redox gradients.

One of our principal goals in this study was to determine if mass-independent fractionation of selenium isotopes (MIF-Se) occurred early in Earth's history, analogous to the Archean MIF anomaly seen in quadruple sulfur isotope studies. In order to assess this, we used a sample-standard bracketing analytical protocol rather than the more usual double-spike procedure. We measured all masses from 71 to 84 to allow post-analytical data correction for the full range of possible isobaric interferences without the assumption of strict mass-dependent fractionation (Stüeken et al., 2013). This procedure allows reproducible measurement of 5 selenium isotopes, the precise determination of 4 isotopic ratios to less than 0.2‰ for $\delta^{76/78}Se$, $\delta^{77/78}Se$ and $\delta^{82/78}Se$ and 0.5‰ for $\delta^{74/78}Se$, and thus accurate detection of mass-independent fractionation on three-isotope diagrams (Stüeken et al., 2013). Moreover, natural mass-independent fractionation in the sulfur and mercury isotopic systems is best expressed by the least abundant and odd-numbered masses (Farquhar et al., 2007; Gosh et al., 2008), which in the case of selenium are ^{74}Se and ^{77}Se, both isotopes that are often sacrificed in double-spike methodologies. Our technique has been successfully used to detect small but significant Se isotopic excursions at the Archean-Proterozoic boundary (Stüeken et al., 2013).

Our sample preparation methods, analytical protocols and interference corrections for Se isotopes are described in more detail in Stüeken et al. (2013). In brief, rock powders were digested with HF, HNO_3 and $HClO_4$; the Se was extracted by column filtration through thiol cotton fibers and further purified with aqua regia. Analyses were carried out with a hydride-generator (HGX-200) coupled to a multi-collector inductively-coupled plasma mass spectrometer (Nu Instruments). Instrumental mass bias was corrected by standard-sample bracketing. Isobaric interferences, most importantly by argon dimers, arsenic hydrides and germanium, were corrected post-analytically (Stüeken et al., 2013). Results are reported in standard delta notation relative to NIST SRM 3149. Unless noted otherwise, we used the ^{82}Se/^{78}Se ratio:

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

because with our method this particular isotope pair yields the most accurate and precise measurements. For conversion to $\delta^{82/76}$Se, which has been used by other laboratories, values can be multiplied by 1.54, because mass-independent fractionation is absent (see below). We analyzed a total of 202 samples and 127 of those in replicates. The average precision (1σ) was 0.10‰ for $\delta^{82/78}$Se and 1.6% (relative error) for Se concentrations. Our result for the international reference material SGR-1, processed with the same method, was +0.05 ± 0.18‰ (1σ, n = 9), which is in good agreement with recently published values (Schilling et al., 2011b;

Mitchell et al., 2012; Pogge von Strandmann et al., 2014). Data was statistically evaluated using Student's t-test and regression analysis.

Total organic C and total S were analyzed with established methods used routinely in the UW Isolab (Schoepfer et al., 2013; Stüeken, 2013) with precisions of 1% and 10%, respectively. For TOC, powders were decarbonated with 6N HCl. S was analyzed on untreated samples. Analyses were carried out by flash combustion with an elemental analyzer (Costech ECS 4010) coupled to a continuous-flow isotope-ratio mass spectrometer (Finnigan MAT 253).

Statistical comparisons between binned time intervals were carried out using Student's t-test. These methods have sufficient power to detect small but significant shifts in mean isotopic values through time and have been used to detect secular changes in other isotopic systems (e.g. Stüeken et al., 2012). Bins for statistical tests were chosen following previously noted transitions in sulfur (Stüeken et al., 2012) and selenium cycling (Large et al., 2014) in the late Archean and Neoproterozoic, respectively. We further tested for changes around the Paleoproterozoic Great Oxidation Event (Bekker et al., 2004; Anbar et al., 2007; Stüeken et al., 2015).

3. Results

3.1. Trends in the modern ocean

The compilation of published Se isotope data from marine sediments deposited over the last 500 kyr (Fig. 1) shows that sediments deposited from the open oxic ocean tend to have a slightly but statistically significantly lighter isotopic composition ($\delta^{82/78}Se_{avg} = -0.10 \pm 0.21$‰, range -0.90‰ to +0.41‰) than sediments formed under anoxic water in restricted basins (+0.07 ± 0.24‰, range -0.41‰ to +0.59‰; $p_{one\text{-}tailed} < 10^{-4}$). Sediments deposited in anoxic basins thus tend to be somewhat closer in composition to Se oxyanions ($Se^{IV/VI}$) dissolved in the open ocean

(≥ +0.3 ‰, Rouxel et al., 2004; Mitchell et al., 2012). The isotopic composition of Se^{VI} and Se^{IV} dissolved in seawater has not yet been measured directly, but as noted by Mitchell et al. (2012), measurements of Se^{IV} adsorbed onto Fe-Mn nodules (+0.32 ‰, n = 1, Rouxel et al., 2004) as well as the composition of phytoplankton (+0.27 ‰, n = 1, Mitchell et al., 2012) provide lower limits. If adsorption of Se^{IV} is associated with a fractionation of 0.1‰ on average (Mitchell et al., 2013), then dissolved Se^{IV} may have a composition of around +0.4‰. Although assimilation of $Se^{IV/VI}$ into biomass has a fractionation of 0.6‰ (Clark and Johnson, 2010), this fractionation may not be expressed if assimilation is quantitative in the photic zone, where Se oxyanion concentrations are depleted (Cutter and Bruland, 1984; Cutter and Cutter, 2001). Hence the composition of phytoplankton (+0.27‰, Mitchell et al., 2012) may approximate that of dissolved $Se^{IV/VI}$. But given the maximum observed fractionations during adsorption and assimilation, dissolved Se oxyanions may be as heavy as +1‰. Se^{IV} and Se^{VI} are probably isotopically homogenized, because Se^{IV} is mostly generated through remineralization of organic matter (Cutter and Bruland, 1984), which does not impart an isotopic fractionation (Johnson and Bullen, 2004).

Today, under a fully oxic atmosphere, the input of Se to the ocean from crustal weathering and volcanism probably has an average composition equivalent to that of the crust at +0.01 ± 0.49‰ (Rouxel et al., 2002), because oxidation as during weathering does not cause isotopic fractionations (Johnson et al., 1999) and normal Se-poor soils are unfractionated relative to crust (Schilling et al., 2011b). As meteorites show approximately the same value (+0.11 ± 0.34 ‰, Rouxel et al., 2002), it is unlikely that on a global scale the Se isotope composition of the upper crust has changed much throughout Earth’s history. If so, then our compilation suggests that sediments from the modern oxic ocean are systematically depleted relative to the crustal source whereas dissolved $Se^{IV/VI}$ is enriched. Sediments from anoxic basins are slightly heavier than the crust, but still somewhat lighter than the presumed composition of seawater.

3.2. New data from ancient sedimentary rocks

All our new Se isotope data (Table A1) plot within error along the theoretical mass-dependent fractionation line (Fig. 2), indicating that isobaric interferences occurring in the mass spectrometer have been properly corrected. Using our analytical protocol (Stüeken et al., 2013), $\delta^{82/76}Se$ is analytically the second most stable ratio after $\delta^{82/78}Se$ (Fig. 2a). $\delta^{82/77}Se$ (Fig. 2b) can be compromised by interferences with $^{77}(ArCl)$ and possibly $^{77}(AsH_2)$ that are difficult to monitor and to subtract (Stüeken et al., 2013; Stüeken et al., 2015), which probably explains the enhanced scatter in our measurements of this isotopic ratio. $\delta^{78/74}Se$ (Fig. 2c) suffers from interferences with ^{74}Ge, magnified by the low abundance of ^{74}Se. Occasional outliers in $\delta^{78/74}Se$ are thus likely due to improperly corrected residual ^{74}Ge. So overall we do not see any evidence of mass-independent fractionation (MIF) in Se at any time in the rock record, in stark contrast to the isotopic record of S (Farquhar et al., 2000). Photochemical reactions involving Se were either not conducive to MIF, or volatile Se compounds were insignificant in relative abundance. It is worth noting that eukaryotic algae, plants and fungi are significant contributors of the major Se gases today, i.e. methylated Se^{-II} (e.g. Chasteen and Bentley, 2003), and hence the flux of these gases may have been trivial in the earlier Precambrian prior to the oxygenation of the atmosphere and the radiation of eukaryotic life.

Combined with published Se isotope data from the late Archean Mt. McRae Shale (Stüeken et al., 2015) and several Phanerozoic basins (Johnson and Bullen, 2004; Shore, 2010; Mitchell et al., 2012; Wen et al., 2014), our results show that throughout Earth’s history (Fig. 3a) the range of mass-dependent Se isotope fractionation recorded in mudrocks (-3.1‰ to +2.9‰) is significantly smaller than the 6-25‰ measured in oxyanion reduction experiments in the laboratory (Johnson et al., 1999; Herbel et al., 2000; Ellis et al., 2003; Johnson and Bullen, 2003), but during most time intervals it exceeds the 0.7‰ maximum range expected for Fe-Mn-oxide adsorption and assimilation into biomass (Johnson et al., 1999; Clark and Johnson, 2010; Mitchell et al., 2013). As discussed above, the relatively small range in bulk sediments is probably in part due to mixing of multiple Se phases recording different isotopic fractionations, but it may also reflect a smaller magnitude in isotopic fractionation under natural, Se-poor conditions.

The mean of all new and published isotopic data is +0.09 ± 0.59‰ (n = 526) while the geometric mean of total Se (TSe) concentrations is 1.3 +4.8/-1.0 ppm (= $10^{0.12 \pm 0.67}$ ppm). We use the geometric mean here because of the wide TSe range over several orders of magnitude. In the normal marine record (Table 2), isotopic ratios decrease slightly but significantly from the mid-Archean (here 3.19-2.87 Gyr; +0.62 ± 0.27‰, n = 23, after removing one outlier of +1.43‰ and 2.23 ppm TSe) to the late Archean (2.71-2.50 Gyr; +0.35 ± 0.39‰, n = 110) ($p_{\text{one-tailed}} = 10^{-4}$) but show no major change from the late Archean to the Proterozoic (2.49-1.10 Gyr; +0.45 ± 0.55‰, n = 59; $p_{\text{one-tailed}} = 0.12$). The most significant change in Se isotopes occurs between the Proterozoic and the Phanerozoic (0.54 Gyr to modern; -0.19 ± 0.59‰, n = 240; $p_{\text{one-tailed}} = 10^{-25}$). Although we do not have any data for samples with ages between 1.10 Gyr and 0.55 Gyr, it is plausible that this isotopic transition coincides with the purported “second rise of oxygen” and the oxygenation of large parts of the deep ocean in the late Neoproterozoic (Canfield et al., 2007; Shields-Zhou and Och, 2011; Sahoo et al., 2012). This hypothesis is supported by recent evidence for a marked increase in pyrite-bound Se at around 600 Myr (Large et al., 2014), which also suggests a major reorganization in the marine Se cycle around this time.

In these compilation of normal marine Se isotopes and abundances, we excluded Phanerozoic basins known to be restricted: the modern Cariaco Basin and Black Sea, the 180 Myr Posidonia Shale, the 380 Myr New Albany Shale (total average $\delta^{82/78}$Se = +0.23 ± 0.40‰, n = 66) (Johnson and Bullen, 2004; Shore, 2010; Mitchell et al., 2012). These basins show distinctively higher TS/TSe ratios (1.82 +3.19/-1.16 = $10^{0.26 \pm 0.44}$ [%/ppm], n = 37) than most other Phanerozoic basins (0.27 +0.71/-0.20 = $10^{-0.57 \pm 0.56}$ [%/ppm], n = 130; $p_{\text{one-tailed}} = 10^{-14}$; Fig. 3c) due to higher TS concentrations. This is probably the result of locally distinct geochemical processes under restricted euxinic conditions, justifying our decision to exclude these basins from the normal marine record. In the Precambrian, the distinction between restricted and open marine basins is less certain. All Precambrian basins sampled for this study have been argued to openly exchange with the ocean, perhaps with the exception of the Belt Basin. But, as discussed in Section 4.5, Se likely had a short residence time in the Precambrian ocean, making the distinction between open and restricted basins unnecessary. We therefore treat all our Precambrian data as representative of normal marine conditions, but discuss environmental differences in more detail below.

A highly significant transition in average Se concentrations occurs between the mid-Archean (0.17 +0.11/-0.07 ppm = $10^{-0.76 \pm 0.21}$ ppm) and the late Archean (1.45 +2.75/-0.95 ppm = $10^{0.16 \pm 0.46}$ ppm; $p_{\text{one-tailed}} = 10^{-23}$). Concentrations then decrease slightly from the late Archean to the Proterozoic (0.74 +3.73/-0.62 ppm = $10^{-0.13 \pm 0.78}$ ppm; $p_{\text{one-tailed}} = 0.005$) and increase significantly again from the Proterozoic to the Phanerozoic (1.75 +7.42/-1.42 ppm = $10^{0.24 \pm 0.72}$ ppm; $p_{\text{one-tailed}} = 0.0006$).

Marine TS/TSe ratios [%/ppm] only show relatively subtle changes through time. They increase from 0.45 +0.58/-0.25 (= $10^{-0.35 \pm 0.36}$) before 2.71 Gyr to 0.78 +1.98/-0.56 (= $10^{-0.11 \pm 0.55}$) between 2.71 Gyr and 1.1 Gyr ($p_{\text{one-tailed}}$ = 0.04) with no significant change between the late Archean and the Proterozoic ($p_{\text{one-tailed}}$ = 0.42). They then decrease significantly to 0.17 +0.69/-0.13 (= $10^{-0.78\pm0.71}$) in the Phanerozoic ($p_{\text{one-tailed}} = 10^{-17}$).

A few sites further show environmental gradients in Se isotopes:

- In the mid-Archean Witwatersrand Supergroup (Fig. 4a) from South Africa (2.96-2.87 Gyr), all samples are isotopically positive, but fluvial samples are slightly lighter ($\delta^{82/78}$Se = +0.30 ± 0.19‰, n = 5) than proximal marine samples ($\delta^{82/78}$Se = +0.74 ± 0.28‰, n = 8) ($p_{\text{one-tailed}} < 0.01$). Distal marine samples are variable ($\delta^{82/78}$Se = +0.63 ± 0.51‰, n = 5). In general, marine shelf samples from the Witwatersrand Supergroup agree well with upper continental slope samples from the Soanesville Group in Western Australia (3.2 Gyr; $\delta^{82/78}$Se = +0.64 ± 0.18‰, n = 9).
- In the late Archean Fortescue Group (Fig. 4b) in Western Australia (2.75-2.65 Gyr), we find a significant contrast between marine environments ($\delta^{82/78}$Se = +0.37 ± 0.27‰, n = 28) and non-marine environments ($\delta^{82/78}$Se = -0.28 ± 0.67‰, n = 19) ($p_{\text{one-tailed}} < 0.001$). Shallow marine shales from the Carawine Dolomite ($\delta^{82/78}$Se = +0.32 ± 0.12‰, n = 7) are on average the same as deeper marine samples from the Jeerinah Formation ($\delta^{82/78}$Se = +0.38 ± 0.30‰, n = 21) but less variable. Both agree well with marine samples from the Ghaap Group in South Africa (2.56-2.52 Gyr; $\delta^{82/78}$Se = +0.41 ± 0.33‰, n = 15).
- Volcanogenic massive sulfides (VMS) from the late Archean Kidd Creek Basin (2.7 Gyr; $\delta^{82/78}$Se = +0.28 ± 0.24‰, n = 5) are statistically indistinguishable from associated marine black shales ($\delta^{82/78}$Se = +0.07 ± 0.22‰, n = 5) ($p_{\text{one-tailed}}$ = 0.10), but show a markedly smaller range and a large isotopic enrichment compared to modern hydrothermal sulfides from the Mid-

Atlantic Ridge ($\delta^{82/78}$Se = -0.98 ± 0.81‰, n = 51, Rouxel et al., 2004) and late Devonian VMS deposits from northwestern Canada ($\delta^{82/78}$Se = -1.88 ± 2.33‰, n = 23, Layton-Matthews et al., 2013).

- In the Mesoproterozoic Belt Supergroup (1.47 Gyr, Fig. 4c), isotopically light values ($\delta^{82/78}$Se = -0.07 ± 0.43‰, n = 7) mainly occur in offshore facies to the west, whereas onshore facies from the eastern basin margin tend to be relatively heavy ($\delta^{82/78}$Se = +0.73 ± 0.33‰, n = 8). Here, the offshore sites are located closer to the opening of the basin towards the ocean but also closer to the proposed major riverine inflow from the unsampled western basin margin (Ross and Villeneuce, 2003). Deep basinal facies from the roughly coeval Roper Basin (1.36 Gyr; $\delta^{82/78}$Se = +0.53 ± 0.20‰, n = 7) and samples of intermediate water depth from the Taoudeni Basin (1.1 Gyr; $\delta^{82/78}$Se = +0.45 ± 0.52‰, n = 5) are generally positive. If these sediments were deposited distal to the most significant riverine water inflow, then all three Mesoproterozoic basins may show relative isotopic enrichment with increasing distance from the major Se source.
- Our results for coastal Atlantic samples from the Cretaceous (120 Myr) Ocean Anoxic Event I (OAE I) are all negative ($\delta^{82/78}$Se = -0.41 ± 0.23‰, n = 8, Fig. 4f), whereas Mitchell et al. (2012) found primarily positive values ($\delta^{82/78}$Se = +0.19 ± 0.25 ‰, n = 27) in deep-marine Atlantic samples from OAE II (93 Myr). Hence, taken together, the Atlantic Ocean may have displayed a basinal gradient during anoxic stages.

When all normal marine data points are combined, $\delta^{82/78}$Se is not correlated with δ^{34}S ($r^2 = 0.005$), TS ($r^2 = 0.05$), TOC ($r^2 = 10^{-5}$) or TSe ($r^2 = 0.02$) and only weakly with $\delta^{13}C_{org}$ ($r^2 = 0.22$). TSe shows moderate correlations with TS and TOC in logarithmic space ($r^2 = 0.31$ and 0.50, respectively, Fig. 5), but much less so in linear space ($r^2 = 0.01$ and 0.22). We hypothesize that the logarithmic correlation is partly a result of lithology and sedimentation rate, i.e. finegrained black shales with low sedimentation rates tend to accumulate a larger quantity of reduced Se (Se^{-II} or Se^0), sulfide S and organic C than siltstones or more rapidly accumulating sediments, regardless of whether the three elements are biogeochemically related. Based on the relatively weak correlations in linear space, we therefore conclude that Se does not strictly follow either S or organic matter under all conditions. However, we do see moderately strong correlations between $\delta^{82/78}$Se and TOC in a few individual basins, in particular the Ghaap Group ($r^2 = 0.64$, $n = 15$, Fig. 4e) and the Belt Supergroup ($r^2 = 0.41$, $n = 15$, Fig. 4d). In both cases, $\delta^{82/78}$Se values decrease with increasing TOC, but TSe is not correlated with TOC or TS. TOC data are not available for the marine Fortescue Group. None of the other basins for which we have more than 10 data points show strong correlations.

4. Discussion

After first assessing the quality of samples analyzed in this study, we describe a conceptual model of the modern Se cycle based on our compilation of literature data. We then use this as a platform to reconstruct the evolution of the global Se cycle through time.

4.1. Sample quality

Diagenesis, metamorphism or weathering can potentially alter primary geochemical features in rock samples. As discussed in Section 4.2, diagenetic Se oxyanion reduction may occur in sediments deposited under oxic conditions where the Se supply is relatively high. Evidence for diagenetic oxyanion reduction in ancient rocks may thus be a diagnostic feature of oxygenated conditions and is therefore not an impediment to this study. Other diagenetic reactions between reduced Se phases, such as exchange of Se^{-II} between organic matter and pyrite, should not lead to isotopic fractionations, especially within bulk rocks.

Regarding metamorphism, Large et al. (2014) showed that sulfide-bound Se^{-II} is essentially immobile during metamorphic alteration, therefore isotopic alteration of this phase should be trivial. Organic Se^{-II}, Se^{0} or adsorbed Se^{IV} may be more sensitive to metamorphism, but associated isotopic fractionations are unknown. Most of our samples are of sub-greenschist metamorphic grade; only the Witwatersrand samples are greenschist grade. In the S isotope literature, metamorphic effects are commonly ignored in these metamorphic facies, and given the higher mass of Se relative to S, it is unlikely that Se is more mobile than S under metamorphic conditions. We therefore believe that our results are not significantly affected by metamorphism.

Weathering has been shown to cause large Se isotopic fractionations of several permil in a recent study of unusually Se-rich soils (5-26,000 ppm) from China (Zhu et al., 2014), where Se was apparently oxidized and then partially re-reduced during aqueous transport. However, in Se-poor soils (0.1-0.5 ppm) from Germany the range of fractionation was much smaller (<0.5‰, Schilling et al., 2011b), suggesting that the large fractionations observed by Zhu et al. (2014) may not necessarily be representative of typical weathering environments. Measurable isotopic effects may be restricted to Se-rich settings where the Se weathering flux is unusually high, such that partial reduction can add significantly to surrounding rocks. Se oxidation by itself does not impart a detectable isotopic fractionation (Johnson et al., 1999). Because most of our samples are from drill cores while any outcrop samples were relatively fresh and had their outer surfaces removed with a rock saw, weathering probably did not have significant effects on our results.

4.2. Proposed modern Se cycle

The relatively low $\delta^{82/78}$Se values preserved in sediments deposited in or near open oxic conditions ($\delta^{82/78}Se_{avg}$ = -0.10 ± 0.21‰, range -0.90‰ to +0.41‰) compared to the presumed composition of dissolved Se oxyanions in seawater ($\delta^{82/78}$Se ≥ +0.3, Section 3.1) are likely the result of non-quantitative Se^{VI} or Se^{IV} reduction to Se^{0} or inorganic Se^{-II} under suboxic conditions during diagenesis or in locally suboxic bottom water (Fig. 6) (Shore, 2010). The mechanism may have been either biological dissimilatory reduction or abiotic reduction. We emphasize that our ‘open oxic ocean’ category includes data from an oxygen minimum zone in the Arabian Sea (Mitchell et al., 2012) and therefore does not exclusively represent oxic conditions; however, all data points are from environments that are part of the open ocean and connected to the oxic water column, i.e. they are characterized by a high Se oxyanion supply, unlike restricted anoxic basins. Non-quantitative Se oxyanion reduction during diagenesis under an oxic water column or in locally suboxic bottom water may thus explain why residual Se^{VI} and Se^{IV} dissolved in modern oxic seawater are relatively enriched compared to average crust (~0‰, Rouxel et al., 2002). Addition of small amounts of isotopically heavy adsorbed Se^{IV} (~+0.3‰, Rouxel et al., 2002) or organic Se^{-II} (~+0.3‰, Mitchell et al., 2012) to isotopically light Se^{0} and inorganic Se^{-II} may explain why bulk $\delta^{82/78}$Se values in open marine sediments are not as negative as one might expect given the fairly large fractionations associated with reduction reactions observed in laboratory simulations (Johnson et al., 1999). Sequential extraction experiments indeed show that sediments and soils commonly contain multiple Se phases with distinct isotopic compositions (Kulp and Pratt, 2004; Schilling et al., 2014b). Sequential extractions have so far not been carried out on open marine sediments deposited under an oxic water column, but we would predict a mixture of isotopically light inorganic Se^{-II} and/or Se^{0} and small amounts of isotopically heavy Se^{IV} and/or organic Se^{-II}.

In the C and S cycle, the isotopically heavy reservoirs complementary to isotopically light reduced phases (organic matter and sulfide, respectively) are carbonate and sulfate minerals. In the case of Se, however, the most oxidized species Se^{VI} does not form major mineral deposits and incorporation into carbonate or sulfate minerals is probably minor (< 0.025 ppm total Se, Hagiwara, 2000). Adsorbed Se^{IV} on FeMn-oxides may be the most significant isotopically heavy reservoir today, complementary to the relatively light siliciclastic sediments from the open ocean; more data are needed to test this possibility. Based on our data compilation, we propose that sediments from restricted anoxic basins, which tend to be isotopically slightly heavier than sediments of open oxic basins, may represent another significant complementary positive repository to the isotopically lighter sediments from the global oxic ocean (Fig. 6). Under anoxic conditions, Se assimilated into biomass is not recycled by oxidation, leading to low concentrations of Se oxyanions in the anoxic water column (Cutter, 1982; Shore, 2010; Mitchell et al., 2012). Therefore, Se oxyanion reduction is likely more quantitative than under diagenetic conditions beneath an oxic water column where the concentrations of Se oxyanions are high. Following Rayleigh distillation, net isotopic fractionations during reduction relative to the crustal source may thus be smaller. Furthermore, compared to open oxic settings, organic Se may be more abundant. Biomass may also be isotopically heavier than in the open ocean, because with more quantitative oxyanion reduction, residual $Se^{IV/VI}$, i.e. the substrate for assimilation into biomass, may be heavier than +0.3‰. So although restricted anoxic settings do not appear to fully capture the isotopic composition of marine $Se^{IV/VI}$ (as is the case with Mo, Anbar, 2004), they at least approach it and are distinct from open marine oxic settings where the supply of Se oxyanions is higher. This means that the marine Se cycle should have evolved markedly through time as the global ocean evolved from an anoxic to an oxic state and the residence time of Se oxyanions presumably increased.

4.3. Mid-Archean

Throughout the Archean, the global ocean was generally anoxic (Poulton and Canfield, 2011; Lyons et al., 2014a), but oxygenic photosynthesis may have created local oxygen oases since at least 3.0 Gyr (Crowe et al., 2013; Planavsky et al., 2014a). Moreover, relatively high levels of TOC in the absence of Fe or S mineralization in the 3.2 Gyr Soanesville Group have been interpreted as potential indirect evidence of even older cyanobacterial oxygenic photosynthetic activity (Buick, 2008). However, the low concentrations of Se in mid-Archean sediments from the Soanesville Group and the Witwatersrand Supergroup suggest that there was no significant Se flux into the ocean. It is important to note that, unlike Mo for example, Se does not require H_2S in the water column or in pore waters to become enriched in anoxic sediments, because it can be immobilized by reduction to solid Se^0. Hence the absence of H_2S alone cannot explain low TSe concentrations in mid-Archean sediments. Instead it is more likely that atmospheric pO_2 was too low for a significant oxidative weathering flux of Se into the ocean (Reinhard et al., 2013a); any O_2 that was biologically produced at this time (Crowe et al., 2013; Planavsky et al., 2014a) was probably rapidly consumed by reductants with lower redox potentials. Mid-Archean marine sediments have TSe concentrations (0.20 ± 0.13 ppm, removing one outlier of 2.2 ppm from the Parktown Formation) only slightly above that of the upper crust (0.09 ppm, Rudnick and Gao, 2014), but they are isotopically heavier by 0.65 ± 0.58‰. Given that fluvial sediments from the Witwatersrand Supergroup are slightly lighter (+0.30 ± 0.19‰, Fig. 4a), it is possible that there was a small but non-trivial flux of $Se^{IV/VI}$ from O_2 oases on land into the anoxic ocean, and partial reduction or adsorption occurred during fluvial transport, rendering residual dissolved $Se^{IV/VI}$ isotopically enriched. S isotope data from the Witwatersrand Basin are also consistent with a small oxidative weathering source, because they point towards a crustal non-atmospheric sulfate contribution (Guy et al., 2012; Guy et al., 2014). However, we cannot rule out that the Se was instead of hydrothermal or volcanic origin and that isotopic fractionation occurred in the deep ocean or in volcanic eruptions.

4.4. Late Archean

The marked increase in average TSe concentrations in samples of the late Archean Fortescue Group and the Ghaap Group and in the Kidd Creek shales (Fig. 3b), concurrent with an increase in TS concentrations (Stüeken et al., 2012) (note relatively small change in TSe/TS, Fig. 3c), can be due to either unusually high volcanic or hydrothermal activity or the onset of oxidative Se weathering on land. A hydrothermal Se source can probably be ruled out because we also find relatively high Se concentrations in the lacustrine Tumbiana Fm (Table A1), which shows no evidence of hydrothermal activity (Buick, 1992). Moreover, the modern hydrothermal flux of Se into the ocean ($\sim 5 \cdot 10^5$ mol/yr, Rubin, 1997) is so low compared to other sources (see below) that it would have had to increase unrealistically.

While enhanced hydrothermal input in the late Archean cannot explain the TSe increase, we are unable to distinguish unambiguously between increasing volcanism and oxidative weathering as Se sources at that time. Today, volcanic eruptions generate $\sim 1 \cdot 10^7$ mol/yr of Se, including gaseous and particulate Se^0, SeO_2 and H_2Se (Suzuoki, 1965; Mosher and Duce, 1987; Wen and Carignan, 2007). On the modern Earth, this volcanic flux is much smaller than the riverine Se flux to the ocean ($\sim 6 \cdot 10^7$ mol/yr). The latter was calculated assuming a river flux of

$3.7 \cdot 10^{16}$ l/yr (Henderson and Henderson, 2009) with an average Se oxyanion load of 1.5 nM (Conde and Alaejos, 1997). However, this number includes uncertain anthropogenic contributions, whereas organic and particulate Se are not accounted for. It is thus probable that enhanced volcanism in the Precambrian dominated over the weathering flux as long as oxidative weathering was muted. Isotopic Se fractionations associated with volcanic processes are unknown, and so we cannot rule out that unprecedented volcanic activity caused both the rise in TSe ~2.7 Gyr and the significant isotopic contrast between non-marine and marine sediments in the Fortescue Group (Fig. 4b). For example, one could envision a scenario where volcanogenic SeO_2 dissolved in rivers proximal to the volcanic source, forming SeO_3^{2-} oxyanions, which were then isotopically fractionated by partial reduction during transport to the ocean. This would have produced isotopically depleted Se phases in fluvio-lacustrine sediments, as observed. The residual isotopically enriched Se would have been carried to the ocean and deposited in marine sediments following quantitative reduction or assimilation into marine biomass.

However, several lines of evidence support the alternative conclusion that Se oxyanions in river water were sourced from the onset of oxidative weathering rather than volcanism in the late Archean. First, the volcanic flux should also have been high in the mid-Archean and there is no independent evidence for a large increase in volcanic activity throughout the late Archean. Second, if volcanic eruptions were massive enough to increase marine Se concentrations by almost an order of magnitude, then large amounts of SeO_2 should have rained out directly into the ocean, so one would expect to see more negative fractionations in marine sediments. Hence the isotopic gradient from non-marine to marine facies is more readily explained if Se oxyanions were sourced locally in oxygen oases on land (e.g. Buick, 1992; Flannery and Walter, 2012; Lalonde and Konhauser, 2015). Third, Se concentrations peak during the ‘whiff of oxygen’ at 2.5

Gyr (Anbar et al., 2007; Stüeken et al., 2015), concurrently with Mo and Re, which cannot be explained by volcanism. Molybdenum concentrations and isotopic fractionations (Siebert et al., 2006; Wille et al., 2007; Kendall et al., 2010) as well as other geochemical proxies including sulfur (Stüeken et al., 2012), nitrogen (Garvin et al., 2009; Godfrey and Falkowski, 2009) and organic carbon isotopes (Eigenbrode and Freeman, 2006) all support mildly or locally oxidative conditions in surface environments since ~2.7 Gyr, making it plausible that also some Se was oxidized on land at that time.

Recent evidence suggests that oxidation of Cr^{III} to Cr^{VI} may have been subdued until the Neoproterozoic (Frei et al., 2009; Planavsky et al., 2014b), which may have also precluded abundant production of Se^{VI} in the earlier Precambrian because Se^{VI} and Cr^{VI} have similar redox potentials (Brookins, 1988). However, Se^{IV} has a much lower redox potential than Cr^{VI} and Se^{VI} (Brookins, 1988) and could thus have been a stable ion in lakes and rivers and the surface ocean long before the Neoproterozoic.

New data from the early Cambrian (Wen et al., 2014) show large Se isotopic fractionations under ferruginous conditions, indicative of partial oxyanion reduction in the open ocean, which suggests that although Fe^{II} is capable of reducing Se^{IV} (Zingaro et al., 1997), the reaction is evidently too slow to cause complete reduction. Thus Se^{IV} could have been produced in late Archean oxygen oases proximal to O_2-producing microbial mats (e.g. Buick, 1992; Flannery and Walter, 2012; Lalonde and Konhauser, 2015), and carried to the ocean in anoxic Fe^{II}-dominated (Rasmussen and Buick, 1999) river systems.

Regardless of the whether Se^{IV} was sourced from volcanic SeO_2 or oxidative weathering, and assuming that Se isotopic fractionations associated with volcanic gas phase reactions are insignificant, the wide range in $\delta^{82/78}Se$ values in the late Archean suggests that Se oxyanion reduction occurred at this time, because fractionations associated with adsorption or assimilation of Se (< 0.7 ‰, Johnson et al., 1999; Clark and Johnson, 2010; Mitchell et al., 2013) are too small to explain the data. Both processes may, however, contribute to the observed scatter.

4.5. Paleo- and Mesoproterozoic

Se isotopes and concentrations in marine mudrocks do not change markedly from the late Archean to the Paleo- and Mesoproterozoic. We found temporary $\delta^{82/78}$Se enrichments up to +2.01‰ in the 2.32 Gyr Pretoria Group immediately after one of the Paleoproterozoic glaciation events, which may be a result of the proposed Lomagundi atmospheric O_2 overshoot between 2.35 and 2.05 Gyr (Bekker et al., 2004; Bekker and Holland, 2012; Planavsky et al., 2012; Hardisty et al., 2014; Scott et al., 2014). Intuitively, more oxidizing conditions should lead to more negative values, as in the modern ocean (Section 4.2). However, it is conceivable that throughout the Precambrian a large fraction of Se dissolved in rivers was organically complexed, more so than today (Doblin et al., 2006), due to interaction with microbial life on land. In that case, moderately high atmospheric pO_2 during the O_2 overshoot could have increased the proportion of Se oxyanions in rivers relative to organically complexed Se. Consequently, a larger fraction of fluvial Se could have been subject to reduction, such that the residue would have been pushed to higher positive $\delta^{82/78}$Se values. Alternatively, positive values could be explained by the opposite effect, i.e. a smaller amount of Se oxyanions in rivers subject to a relatively larger degree of partial reduction and hence more positive values in the residual dissolved fraction that reached the ocean. However, in that case, large positive values up to 2‰ should be relatively common in the Precambrian and concentrations in marine sediments should drop, contrasting with the observed high concentrations in the Pretoria Group. Hence the Se oxyanion flux into the ocean was probably higher in the Paleoproterozoic than in the late Archean. The high $\delta^{82/78}$Se values at 2.32 Gyr may thus be an enhanced version of those recorded during the 'whiff of oxygen' around 2.5 Gyr (Anbar et al., 2007; Stüeken et al., 2015).

Cr isotope data suggest that in the Paleo- and Mesoproterozoic the atmosphere was still not oxidizing enough for the production of abundant Cr^{VI} (Frei et al., 2009; Planavsky et al., 2014b). If so, then Se oxyanions in rivers were probably still dominated by Se^{IV}. However, initial reports of Se isotopes in Se^{IV} adsorbed to BIF of Paleoproterozoic age show very negative values (Schilling et al., 2014a), consistent with non-quantitative reduction of Se^{VI} to Se^{IV} in seawater on the outer shelf and suggesting that the surface ocean was perhaps locally more oxic than non-marine environments, such that Se^{VI} was stable. But this situation still contrasts with the modern ocean where marine Se^{IV} is derived from organic-Se^{-II} oxidation rather than Se^{VI} reduction (Cutter and Bruland, 1984). Hence the BIF data may be further evidence for a strong chemocline within the Paleoproterozoic water column. Isotopically light Se^{IV} probably adsorbed to Fe-oxide particles in the photic zone and subsequently settled on the seafloor. Kerogenous shales, as analyzed in this study, could have preserved the composition of the residual heavy Se^{VI} by quantitative reduction below the chemocline.

Late Paleoproterozoic and Mesoproterozoic Se data from the Animikie Basin, the Pine Creek Inlier, the Roper Basin, the Belt Basin and the Taoudeni Basin do not show any enrichments above +1.1‰ (Fig. 3a) and are generally similar to the late Archean. However, data along a basinal profile in the Belt Basin, where we found more negative $\delta^{82/78}$Se closer to the major river inflow and positive values along the restricted basin margin (Fig. 4c), suggest that most $Se^{IV/VI}$ reduction may have occurred in the ocean rather than in rivers. As surface environments became more oxidizing from the late Archean to the Proterozoic (Lyons et al., 2014a), partial $Se^{IV/VI}$ reduction may thus have moved further towards the ocean. While oxidative weathering in the late Archean (if it occurred) was perhaps restricted to oxygen oases (Lalonde and Konhauser, 2015), it may have been more widespread in the Proterozoic, even if the redox potential at those weathering sites did not increase markedly (Planavsky et al., 2014b). However, Se oxyanions were probably not as well-mixed throughout the water column as they are today and were perhaps more rapidly consumed on a regional scale. As in the Archean, the total range of $\delta^{82/78}$Se values in the Proterozoic is too large to be explained by adsorption or assimilation alone, but these processes may contribute to the observed scatter in the data.

4.6. Phanerozoic

For large parts of the Phanerozoic, the marine Se cycle was probably similar to that of today (Section 4.2), as indicated by the more frequent occurrence of negative $\delta^{82/78}$Se values in marine sediments from various localities and an average difference of -0.64‰ compared to Proterozoic. We note that also Phanerozoic hydrothermal deposits (Rouxel et al., 2004; Layton-Matthews et al., 2013) are isotopically lighter than Archean counterparts from the Kidd Creek by more than 1‰, suggesting that the supply of Se oxyanions from oxic seawater to hydrothermal systems increased. Hence Se oxyanions were probably more abundant throughout the water column, except in restricted anoxic basins. The drop in TS/TSe ratios by a factor of 4.6 (Fig. 3c) in open marine sediments suggests an increase in the total Se flux into the ocean, possibly as a result of increasing redox potential at weathering sites (Planavsky et al., 2014b) leading to the production of Se^{VI} rather than Se^{IV} as in the earlier Precambrian (Sections 4.4, 4.5). Oxygenation of the deep ocean in the Neoproterozoic (Canfield et al., 2007; Johnston et al., 2012; Sahoo et al., 2012) would further have initiated seafloor weathering as an additional Se oxyanion source.

During anoxic events, such as in the Cretaceous, the Se cycle probably reverted to its Precambrian state, as shown by the gradient between negative $\delta^{82/78}$Se values from coastal samples during OAE-I and positive $\delta^{82/78}$Se values from deep marine samples during OAE-II (Mitchell et al., 2012), assuming Se sources were comparable during these events.

Large et al. (2014) recently reported a significant increase of Se concentration in sedimentary pyrite crystals across the Precambrian-Cambrian boundary, which is not as strongly reflected in our data from bulk sediments. It is conceivable that the difference between the two datasets is evidence for a change in Se speciation rather than total supply. In the Precambrian, most sedimentary Se was probably organic-bound, whereas in the Phanerozoic the greater abundance of Se oxyanions in an oxic water column may have allowed for more dissimilatory reduction and incorporation of inorganic Se^{-II} into sulfide minerals. If so, then the contrast between our whole-rock abundance data and that of the pyrite isolates presented by Large et al. (2014) is perhaps further evidence for widespread ocean oxygenation in the Neoproterozoic.

Conclusions

Our data support several conclusions about the evolution of the Earth's redox state and the global biogeochemical Se cycle:

1. Concurrently rising Archean TS and TSe between 2.8 Gyr and 2.7 Gyr and the significant isotopic contrast between marine and non-marine samples in the late Archean are consistent with an early onset of oxidative Se weathering in locally oxygenated terrestrial habitats long before the global rise of atmospheric pO_2 levels during the Paleoproterozoic GOE. However, we cannot disprove the possibility that both features were caused by volcanic Se production as long as isotopic fractionations and Se abundances associated

with volcanic eruptions are poorly known. In either case, Se^{IV} was probably more abundant than Se^{VI}, given the inferred low abundance of Cr^{VI} (Frei et al., 2009; Planavsky et al., 2014b), which has a similar redox potential as Se^{VI} (Brookins, 1988). Se oxyanions produced during weathering were partially reduced during fluvial transport to the ocean.

2. The GOE itself (~2.4-2.3 Gyr) (Bekker et al., 2004) did not leave a marked imprint on the Se isotopic or abundance record, except for perhaps a small enrichment in $\delta^{82/78}Se$ during the proposed O_2 overshoot between 2.35 Gyr and 2.05 Gyr (Bekker and Holland, 2012; Planavsky et al., 2012; Hardisty et al., 2014; Scott et al., 2014). This may be because organic complexation of Se during fluvial transport and in the ocean likely reduced the maximum observed fractionation in sediments.
3. A relatively greater abundance of Se oxyanions may have reached the ocean in the Proterozoic compared to the Archean, but reduction probably occurred along the chemocline, perhaps in the vicinity of river deltas. However, our lack of data from truly open marine settings, i.e. outside of epicontinental basins, makes it impossible to assess how Se behaved in the oligotrophic ocean. If significant portions of the deep ocean were oxic (Reinhard et al., 2013b; Ader et al., 2014), then partial $Se^{IV/VI}$ reduction and isotopic fractionation could also have occurred offshore, similar to today.
4. The most notable transition in the Se isotopic record occurred at some time between the Mesoproterozoic and the mid-Paleozoic, when $\delta^{82/78}Se$ values shifted from dominantly positive to frequently negative. The transition between the Proterozoic and modern Se cycle probably occurred during the oxygenation of the deep ocean in the Neoproterozoic (Canfield et al., 2007; Johnston et al., 2012; Sahoo et al., 2012). While Se^{IV} was perhaps

the dominant Se oxyanion in the earlier Precambrian, increasing atmospheric oxygen levels in the Neoproterozoic (Planavsky et al., 2014b) may have stabilized Se^{VI}.

5. In the modern ocean, sediments from localities that are well-connected to the open oxic ocean are on average isotopically depleted relative to the crustal source and dissolved marine $Se^{IV/VI}$. Sediments from restricted anoxic basins are also lighter than dissolved $Se^{IV/VI}$, but slightly heavier than the crust and also heavier than open marine sediments. Restricted anoxic basins may thus represent a complimentary Se isotopic reservoir to the open ocean, similar to the Mo cycle (Anbar, 2004) (Fig. 6).
6. At no time during Earth's history do any of the isotopes of Se show mass-independent fractionation, unlike the geochemically similar element S. Either photochemical reactions involving Se were not conducive to MIF, or volatile Se compounds were insignificant and/or too short-lived prior to the evolution of complex eukaryotic life.

In summary, bulk Se isotope ratios in mudrocks are consistent with the generally accepted view of Earth's redox evolution (Lyons et al., 2014b), but they have somewhat limited utility as a paleoredox proxy for two main reasons. First, whole rock analyses are likely to represent mixtures of heterogeneous Se phases, and in many siliciclastic samples, organic Se^{-II} is probably always one of the major phases. If organic Se^{-II} captures the composition of seawater (Section 4.2), then it will mask any negative fractionations carried by inorganic Se^{-II} or Se^{0}. Measured isotopic fractionations in whole-rocks are therefore relatively muted, in some cases making it more difficult to unambiguously distinguish between oxyanion reduction and adsorption or assimilation as the major fractionating mechanism. Second, Se isotopes appear to have been fractionated during transport to the ocean or along ocean margins for most of Earth's history, except perhaps in the Phanerozoic when the total average of marine $\delta^{82/78}$Se values is close to average crust, indicating quantitative transfer between reservoirs. Without spatial resolution it will thus be impossible to know the composition of Se entering a specific ocean basin. Hence, results from a single site cannot readily be extrapolated to the global ocean. However, detailed stratigraphic studies or large datasets, such as the one presented in this paper, have the potential to reveal trends. Indeed, the most notable trend in our Se isotopic data lends further support to the idea of deep ocean oxygenation in the Neoproterozoic.

Acknowledgments

All authors except DC contributed samples and background information, DC had the idea of looking for MIF-Se, EES prepared the samples, performed the analyses, interpreted the data and wrote the manuscript with advice and contributions from RB. The project was financially supported by a University of Washington Royalty Research grant to RB, the National Science Foundation grant EAR0921580 to RB, NASA Exobiology Program Grant NNX10AQ90G to DC, and the NAI Virtual Planetary Laboratory at the University of Washington. We thank the UW Isotope Geochemistry Lab and the UW Isolab for technical support. A. Knoll, B. Wing and N. Planavsky are thanked for additional samples.

Table 1: Major stratigraphic units analyzed in this study. Uncertainties are reported as 1σ.

Unit	Location	Age [Gyr]	Setting	n	$\delta^{82/78}$Se [‰]	log(TSe) [ppm]	log(S/Se) [%/ppm]
Soanesville Gp.	Australia	3.19	upper slope, open marine	9	+0.64 ± 0.18	-0.89 ± 0.10	-0.55 ± 0.14
Witwatersrand Spgp.	S. Africa	2.94-2.92	fluvial	5	+0.30 ± 0.19	-0.59 ± 0.22	+0.10 ± 0.37
		2.96-2.87	proximal marine, possibly restricted epeiric sea	8	+0.74 ± 0.28	-0.66 ± 0.26	-0.22 ± 0.45
		2.96-2.94	distal marine, epeiric sea, open to the ocean	5	+0.63 ± 0.51	-0.46 ± 0.49	-0.34 ± 0.45
Pongola Spgp.	S. Africa	2.90	epeiric sea connected to the ocean, possibly restricted	2	+0.41 ± 0.44	-0.76 ± 0.09	+0.05 ± 0.04
Kidd Creek deposit	Canada	2.71	open marine shelf	5	+0.07 ± 0.22	+0.55 ± 0.35	
			volcanogenic massive sulfide deposit (VMS)	5	+0.28 ± 0.24	+2.73 ± 0.78	
Fortescue Gp.	Australia	2.78-2.72	fluvio-lacustrine	19	-0.28 ± 0.67	+0.07 ± 0.58	-0.78 ± 0.67
		2.65	open marine shelf, onshore	7	+0.32 ± 0.12	-0.23 ± 0.21	
		2.65	open marine shelf, offshore	21	+0.38 ± 0.30	-0.02 ± 0.40	+0.27 ± 0.14
Ghaap Gp.	S. Africa	2.56-2.52	open marine shelf	15	+0.41 ± 0.33	+0.23 ± 0.51	-0.08 ± 0.63
Hamersley Gp.	Australia	2.49	open marine shelf	3	+0.46 ± 0.66	+0.16 ± 0.47	
Pretoria Gp.	S. Africa	2.32	epeiric sea, open to the ocean	8	+1.13 ± 0.56	+0.43 ± 0.78	-0.33 ± 0.51
Namoona Gp.	Australia	1.9	intracontinental rift basin, possibly restricted	8	-0.07 ± 0.13	+0.47 ± 0.68	-0.07 ± 0.13
Animikie Gp.	Canada	1.87-1.84	epeiric sea, open to the ocean	13	+0.40 ± 0.46	-0.28 ± 0.44	+0.23 ± 0.42
Belt Spgp.	USA	1.47	intracontinental rift basin, possibly restricted, onshore	8	+0.73 ± 0.33	-1.09 ± 0.34	-0.34 ± 0.49
			intracontinental rift basin, possibly restricted, offshore	7	-0.07 ± 0.43	-0.75 ± 0.39	-0.49 ± 0.62
Roper Gp.	Australia	1.36	epeiric sea, open to the ocean, offshore	7	+0.53 ± 0.20	-0.13 ± 0.71	-0.01 ± 0.14
El Mreiti Gp.	Mauritania	1.10	epeiric sea, open to the ocean, intermediate depth	5	+0.45 ± 0.52	+0.58 ± 0.69	-0.14 ± 0.70
Stephen Fm.	Canada	0.54	open marine shelf, submarine fan	1	+0.96	-1.11	+0.23
Woodbend Gp.	Canada	0.36	epeiric sea, open to the ocean	5	+0.04 ± 0.47	-0.27 ± 0.86	+0.21 ± 0.46
Wocklum Limestone	Germany	0.34	epeiric sea, open to the ocean	2	-0.72 ± 0.28	-1.46 ± 0.14	
Phosphoria Fm.	USA	0.26	epeiric sea, open to the ocean	3	+0.01 ± 0.74	-0.66 ± 0.23	
Peril/Sandilands Fm.	Canada	0.20	open marine shelf	12	+0.23 ± 0.34	+0.64 ± 0.45	-0.79 ± 0.48
Fidalgo Complex	USA	0.16	deep open basin, turbidite (preserved as ophiolite)	1	-0.29	-0.36	-0.50
Morrison Fm.	USA	0.15	interior seaway, possibly restricted	1	-1.20	-1.05	
North Atlantic	Portugal	0.12	open marine margin, submarine fan	8	-0.41 ± 0.23	+0.01 ± 0.26	-0.58 ± 0.30
Nanaimo Gp.	USA	0.08	open marine shelf, turbidite	1	+0.43	-0.31	-0.63
Mowry/Eagle/Cody Fm.	USA	0.10-0.07	interior seaway, possibly restricted	4	-0.44 ± 0.65	-0.53 ± 0.22	-1.20 ± 0.13
Hell Creek/Tullock Fm.	USA	0.065	fluvio-lacustrine	4	+0.25 ± 0.57	-0.06 ± 0.36	

Table 2: Long-term averages of individual data points from open marine basins.

	$\delta^{82/78}$Se [‰]	TSe [ppm]	S/Se [wt%/ppm]
mid-Archean (3.19-2.87Gyr)	+0.62 ± 0.27	$10^{-0.76 \pm 0.21}$	$10^{-0.31 \pm 0.36}$
late Archean (2.71-2.50Gyr)	+0.35 ±0.39	$10^{0.16 \pm 0.46}$	$10^{-0.12 \pm 0.59}$
Proterozoic (2.49-1.10Gyr)	+0.45 ±0.55	$10^{-0.13 \pm 0.78}$	$10^{-0.10 \pm 0.48}$
Phanerozoic (0.54Gyr to modern)	-0.19 ±0.59	$10^{0.24 \pm 0.72}$	$10^{-0.78 \pm 0.71}$

Figure captions

Figure 1: Se isotopes in open and restricted marine basins over the last 500 kyr. The compositions of the crust and the lower limit for the composition of seawater $Se^{IV/VI}$ are shown for reference (dashed black lines). Open marine sediments (n = 96) are systematically depleted where as restricted basins (n = 37) tend to preserve the composition of $Se^{IV/VI}$, probably due to more quantitative reduction. See text for references.

Figure 2: Mass-dependent fractionation in Se isotopes. a: $\delta^{82/76}Se$ versus $\delta^{82/78}Se$; b: $\delta^{82/77}Se$ versus $\delta^{82/78}Se$; c: $\delta^{78/74}Se$ versus $\delta^{82/78}Se$. One outlier with $\delta^{78/74}Se = -13.7‰$ is not shown. Residual interferences are the most likely explanation for outliers in panels b and c. We therefore conclude that all four isotope pairs display mass-dependent fractionation. Error bars are 1σ.

Figure 3: Whole-rock Se isotopes (a), abundances (b), and TS/TSe ratios (c) in mudrocks through time. Horizontal lines mark the total marine average (solid) ± 1σ (dashed) of new and published data.

Figure 4: Se in selected basins. a: Witwatersrand Supergroup; b: Fortescue Group; c and d: Belt Supergroup; e: Ghaap Group; f: Cretaceous Atlantic Ocean, where data from OAE-II are from Mitchell et al.(2012). Error bars are 1σ.

Figure 5: Total selenium (TSe) versus total sulfur (TS) and total organic carbon (TOC). Correlations are significant in logarithmic scale (panels a and b) but not in linear scale (panel c and d).

Figure 6: Proposed modern marine Se cycle. $\delta = \delta^{82/78}$Se. Sources to the ocean include continental and seafloor weathering, volcanic emissions and hydrothermal fluids with isotopic compositions probably similar to that of the crust. Se oxyanions (SeO_x^{2-}, where x = 3 for Se^{IV} or 4 for Se^{VI}) sourced from weathering may be reduced non-quantitatively to Se^0 or inorganic Se^{-II} (FeSe) during diagenesis, leading to negative $\delta^{82/78}$Se values in sediments under an oxic water column. These negative values may be diluted with isotopically positive organic Se^{-II} or Se^{IV} adsorbed to FeMn-oxides (FeMn-SeO_3). Reduction and/or assimilation into biomass are quantitative in restricted anoxic basins. Emissions of dimethyl selenide (DMSe) have apparently been negligible over geologic timescales. See text for references.

References

Ader, M., Sansjofre, P., Halverson, G.P., Busigny, V., Trindade, R.I., Kunzmann, M. and Nogueira, A.C., 2014. Ocean redox structure across the Late Neoproterozoic Oxygenation Event: A nitrogen isotope perspective. Earth and Planetary Science Letters, 396: 1-13.

Anbar, A.D., 2004. Molybdenum stable isotopes: observations, interpretations and directions. Reviews in Mineralogy and Geochemistry, 55: 429-454.

Anbar, A.D., Duan, Y., Lyons, T.W., Arnold, G.L., Kendall, B., Creaser, R.A., Kaufmann, A.J., Gordon, G.W., Scott, C., Garvin, J. and Buick, R., 2007. A whiff of oxygen before the Great Oxidation Event? Science, 317: 1903-1906.

Bekker, A. and Holland, H.D., 2012. Oxygen overshoot and recovery during the early Paleoproterozoic. Earth and Planetary Science Letters, 317: 295-304.

Bekker, A., Holland, H.D., Wang, P.L., Rumble III., D., Stein, H.J., Hannah, J.L., Coetzee, L.L. and Beukes, N.J., 2004. Dating the rise of atmospheric oxygen. Nature, 427: 117-120.

Brookins, D.G., 1988. Eh-pH Diagrams for Geochemistry. Springer-Verlag, New York.

Buick, R., 1992. The antiquity of oxygenic photosynthesis: evidence from stromatolites in sulphate-deficient Archaean lakes. Science, 255: 74-77.

Buick, R., 2008. When did oxygenic photosynthesis evolve? Philosophical Transactions of the Royal Society B: Biological Sciences, 363: 2731-2743.

Canfield, D.E., Poulton, S.W., Knoll, A.H., Narbonne, G.M., Ross, G., Goldberg, T. and Strauss, H., 2008. Ferruginous conditions dominated later Neoproterozoic deep-water chemistry. Science, 321: 949-952.

Canfield, D.E., Poulton, S.W. and Narbonne, G.M., 2007. Late-Neoproterozoic deep-ocean oxygenation and the rise of animal life. Science, 315: 92-95.

Chasteen, T.G. and Bentley, R., 2003. Biomethylation of selenium and tellurium: microorganisms and plants. Chemical Reviews, 103: 1-26.

Clark, S.K. and Johnson, T.M., 2010. Selenium stable isotope investigation into selenium biogeochemical cycling in a lacustrine environment: Sweitzer Lake, Colorado. Journal of Environmental Quality, 39: 2200-2210.

Conde, J.E. and Alaejos, M.S., 1997. Selenium concentrations in natural and environmental waters. Chemical Reviews, 97: 1979-2003.

Crowe, S.A., Døssing, L.N., Beukes, N.J., Bau, M., Kruger, S.J., Frei, R. and Canfield, D.E., 2013. Atmospheric oxygenation three billion years ago. Nature, 501: 535-538.

Cutter, G.A., 1982. Selenium in reducing waters. Science, 217: 829-831.

Cutter, G.A., 1992. Kinetic controls on metalloid speciation in seawater. Marine Chemistry, 40: 65-80.

Cutter, G.A. and Bruland, K.W., 1984. The marine biogeochemistry of selenium: a re-evaluation. Limnology and Oceanography, 29: 1179-1192.

Cutter, G.A. and Cutter, L.S., 2001. Sources and cycling of selenium in the western and equatorial Atlantic Ocean. Deep-Sea Research II, 48: 2917-2931.

Doblin, M.A., Baines, S.B., Cutter, L.S. and Cutter, G.A., 2006. Sources and biogeochemical cycling of particulate selenium in the San Francisco Bay estuary. Estuarine, Coastal and Shelf Science, 67: 681-694.

Eigenbrode, J.L. and Freeman, K.H., 2006. Late Archean rise of aerobic microbial ecosystems. Proceedings of the National Academy of Sciences, 103: 15759-15764.

Ellis, A.S., Johnson, T.M., Herbel, M.J. and Bullen, T., 2003. Stable isotope fractionation of selenium by natural microbial consortia. Chemical Geology, 195: 119-129.

Fan, H.F., Wen, H., Hu, M. and Zhao, H., 2011. Selenium speciation in Lower Cambrian Se-enriched strata in South China and its geological implications. Geochimica et Cosmochimica Acta, 75: 7725-7740.

Farquhar, J., Bao, H. and Thiemens, M., 2000. Atmospheric influence on Earth's earliest sulfur cycle. Science, 289: 756-758.

Farquhar, J., Peters, M., Johnston, D.T., Strauss, H., Masterson, A., Wiechert, U. and Kaufman, A.J., 2007. Isotopic evidence for Mesoarchaean anoxia and changing atmospheric sulphur chemistry. Nature, 449: 706-709.

Flannery, D.T. and Walter, M.R., 2012. Archean tufted microbial mats and the Great Oxidation Event: new insights into an ancient problem. Australian Journal of Earth Sciences, 59: 1-11.

Frei, R., Gaucher, C., Poulton, S.W. and Canfield, D.E., 2009. Fluctuations in Precambrian atmospheric oxygenation recorded by chromium isotopes. Nature, 461: 250-253.

Garvin, J., Buick, R., Anbar, A.D., Arnold, G.L. and Kaufman, A.J., 2009. Isotopic evidence for an aerobic nitrogen cycle in the latest Archean. Science, 323: 1045-1048.

Gladyshev, V.N., 2012. Selenoproteins and selenoproteomes. In: D.L. Hatfield, M.J. Berry and V.N. Gladyshev (Editors), Selenium: Its molecular biology and role in human health. Springer Science + Business Media, pp. 109-123.

Godfrey, L.V. and Falkowski, P.G., 2009. The cycling and redox state of nitrogen in the Archaean ocean. Nature Geoscience, 2: 725-729.

Gosh, S., Xu, Y., Humayun, M. and Odom, L., 2008. Mass-dependent fractionation of mercury isotopes in the environment. Geochemistry Geophysics Geosystems, 9: doi:10.1029/2007GC001827.

Guy, B.M., Ono, S., Gutzmer, J., Kaufman, A.J., Lin, Y., Fogel, M.L. and Beukes, N.J., 2012. A multiple sulfur and organic carbon isotope record from non-conglomeratic sedimentary rocks of the Mesoarchean Witwatersrand Supergroup, South Africa. Precambrian Research, 216: 208-231.

Guy, B.M., Ono, S., Gutzmer, J., Lin, Y. and Beukes, N.J., 2014. Sulfur sources of sedimentary "buckshot" pyrite in the Auriferous Conglomerates of the Mesoarchean Witwatersrand and Ventersdorp Supergroups, Kaapvaal Craton, South Africa. Mineralium Deposita, 49: 751-775.

Hagiwara, Y., 2000. Selenium isotope ratios in marine sediments and algae: A reconnaissance study. M.Sc. Thesis, University of Illinois at Urbana-Champaign, Urbana, IL, 62 pp.

Hardisty, D.S., Lu, Z., Planavsky, N.J., Bekker, A., Philippot, P., Zhou, X. and Lyons, T.W., 2014. An iodine record of Paleoproterozoic surface ocean oxygenation. Geology: doi:10.1130/G35439.1.

Henderson, P. and Henderson, G.M., 2009. The Cambridge Handbook of Earth Science Data. Cambridge University Press, New York.

Herbel, M.J., Johnson, T.M., Oremland, R.S. and Bullen, T., 2000. Fractionation of selenium isotopes during bacterial respiratory reduction of selenium oxyanions. Geochimica et Cosmochimica Acta, 64: 3701-3709.

Johnson, T.M., 2004. A review of mass-dependent fractionation of selenium isotopes and implications for other heavy stable isotopes. Chemical Geology, 204: 201-214.

Johnson, T.M. and Bullen, T., 2003. Selenium isotope fractionation during reduction by Fe(II)-Fe(III) hydroxide-sulfate (green rust). Geochimica et Cosmochimica Acta, 67: 413-419.

Johnson, T.M. and Bullen, T., 2004. Mass-dependent fractionation of selenium and chromium isotopes in low-temperature environments. Reviews in Mineralogy and Geochemistry, 55: 289-317.

Johnson, T.M., Herbel, M.J., Bullen, T.D. and Zawislanski, P.T., 1999. Selenium isotope ratios as indicators of selenium sources and oxyanion reduction. Geochimica et Cosmochimica Acta, 63: 2775-2783.

Johnston, D.T., Poulton, S.W., Goldberg, T., Sergeev, V.N., Podkovyrov, V., Vorob'eva, N.G., Bekker, A. and Knoll, A.H., 2012. Late Ediacaran redox stability and metazoan evolution. Earth and Planetary Science Letters, 335: 25-35.

Kendall, B., Reinhard, C.T., Lyons, T.W., Kaufman, A.J., Poulton, S.W. and Anbar, A.D., 2010. Pervasive oxygenation along late Archaean ocean margins. Nature Geoscience, 3: 647-652.

Krouse, H.R. and Thode, H.G., 1962. Thermodynamic properties and geochemistry of isotopic compounds of selenium. Canadian Journal of Chemistry, 40: 367-375.

Kulp, T.R. and Pratt, L.M., 2004. Speciation and weathering of selenium in Upper Cretaceous chalk and shale from South Dakota and Wyoming, USA. Geochimica et Cosmochimica Acta, 68: 3687-3701.

Lalonde, S.V. and Konhauser, K.O., 2015. Benthic perspective on Earth’s oldest evidence for oxygenic photosynthesis. Proceedings of the National Academy of Sciences: doi: 10.1073/pnas.1415718112.

Large, R.R., Halpin, J.A., Danyushevsky, L.V., Maslennikov, V.V., Bull, S.W., Long, J.A., Gregory, D.D., Lounejeva, E., Lyons, T.W., Sack, P.J., McGoldrick, P. and Calver, C.R., 2014. Trace element content of sedimentary pyrite as a new proxy for deep-time ocean-atmosphere evolution. Earth and Planetary Science Letters, 389: 209-220.

Layton-Matthews, D., Leybourne, M.I., Peter, J.M., Scott, S.D., Cousens, B. and Eglington, B., 2013. Multiple sources of selenium in ancient seafloor hydrothermal systems: compositional and Se, S and Pb isotopic evidence from volcanic-hosted and volcanic-sediment-hosted massive sulfide deposits of the Finlayson Lake District, Yukon, Canada. Geochimica et Cosmochimica Acta, 117: 313-331.

Li, X. and Liu, Y., 2011. Equilibrium Se isotope fractionation parameters: A first principle study. Earth and Planetary Science Letters, 304: 113-120.

Lyons, T.W., Reinhard, C.T. and Planavsky, N.J., 2014a. The rise of oxygen in Earth's early ocean and atmosphere. Nature, 506: 307-315.

Lyons, T.W., Reinhard, C.T. and Planavsky, N.J., 2014b. The rise of oxygen in Earth’s early ocean and atmosphere. Nature, 506: 307-315.

Mayland, H.F., 1994. Selenium in plant and animal nutrition. In: W.T. Frankenberger Jr. and S. Benson (Editors), Selenium in the environment. Marcel Dekker, Inc., New York.

Mitchell, K., Couture, R.M., Johnson, T.M., Mason, P.R. and Van Cappellen, P., 2013. Selenium sorption and isotope fractionation: Iron (III) oxides versus iron (II) sulfides. Chemical Geology, 342: 21-28.

Mitchell, K., Mason, P.R.D., Van Cappellen, P., Johnson, T.M., Gill, B.C., Owens, J.D., Ingall, E.D., Reichart, G.-J. and Lyons, T.W., 2012. Selenium as paleo-oceanographic proxy: A first assessment. Geochimica et Cosmochimica Acta, 89: 302-317.

Mosher, B.W. and Duce, R.A., 1987. A global atmospheric selenium budget. Journal of Geophysical Research, 92: 13289-13298.

Planavsky, N.J., Asael, D., Hofmann, A., Reinhard, C.T., Lalonde, S.V., Knudsen, A., Wang, X., Ossa Ossa, F., Pecoits, E., Smith, A.J.B., Beukes, N.J., Bekker, A., Johnson, T.M., Konhauser, K.O., Lyons, T.W. and Rouxel, O.J., 2014a. Evidence for oxygenic photosynthesis half a billion years before the Great Oxidation Event. Nature Geoscience, 7: 283-286.

Planavsky, N.J., Bekker, A., Hofmann, A., Owens, J.D. and Lyons, T.W., 2012. Sulfur record of rising and falling marine oxygen and sulfate levels during the Lomagundi event. Proceedings of the National Academy of Sciences, 109: 18300-18305.

Planavsky, N.J., Reinhard, C.T., Wang, X., Thomson, D., McGoldrick, P., Rainbird, R.H., Johnson, T., Fischer, W.W. and Lyons, T.W., 2014b. Low Mid-Proterozoic atmospheric oxygen levels and the delayed rise of animals. Science, 346: 635-638.

Pogge von Strandmann, P., Coath, C.D., Catling, D.C., Poulton, S. and Elliott, T., 2014. Analysis of mass dependent and mass independent selenium isotope variability in black shales. Journal of Analytical Atomic Spectrometry, 29: 1648-1659.

Poulton, S.W. and Canfield, D.E., 2011. Ferruginous conditions: a dominant feature of the ocean through Earth's history. Elements, 7: 107-112.

Rashid, K. and Krouse, H.R., 1985. Selenium isotopic fractionation during SeO_3 reduction to Se^0 and H_2Se. Canadian Journal of Chemistry, 63: 3195-3199.

Rasmussen, B. and Buick, R., 1999. Redox state of the Archean atmosphere: Evidence from detrital heavy minerals in ca. 3250-2750 Ma sandstones from the Pilbara Craton, Australia. Geology, 27: 115-118.

Rees, C.E. and Thode, H.G., 1966. Selenium isotope effects in the reduction of sodium selenite and of sodium selenate. Canadian Journal of Chemistry, 44: 419-427.

Reinhard, C.T., Lalonde, S.V. and Lyons, T.W., 2013a. Oxidative sulfide dissolution on the early Earth. Chemical Geology, 362: 44-55.

Reinhard, C.T., Planavsky, N.J., Robbins, L.J., Partin, C.A., Gill, B.C., Lalonde, S.V., Bekker, A., Konhauser, K.O. and Lyons, T.W., 2013b. Proterozoic ocean redox and biogeochemical stasis. Proceedings of the National Academy of Sciences, 110: 5357-5362.

Ross, G.M. and Villeneuce, M., 2003. Provenance of the Mesoproterozoic (1.45 Ga) Belt basin (western North America): another piece in the pre-Rodinia paleogeographic puzzle. Geological Society of America Bulletin, 115: 1191-1217.

Rouxel, O., Fouquet, Y. and Ludden, J.N., 2004. Subsurface processes at the Lucky Strike hydrothermal field, Mid-Atlantic Ridge: evidence from sulfur, selenium, and iron isotopes. Geochimica et Cosmochimica Acta, 68: 2295-2311.

Rouxel, O., Ludden, J., Carignan, J., Marin, L. and Fouquet, Y., 2002. Natural variations of Se isotopic composition determined by hydride generation multiple collector inductively coupled plasma mass spectrometry. Geochimica et Cosmochimica Acta, 66: 3191-3199.

Rubin, K., 1997. Degassing of metals and metalloids from erupting seamount and mid-ocean ridge volcanoes: observations and predictions. Geochimica et Cosmochimica Acta, 61: 3525-3542.

Rudnick, R.L. and Gao, S., 2014. Composition of the continental crust. Treatise on Geochemistry, 4: 1-51.

Sahoo, S.K., Planavsky, N.J., Kendall, B., Wang, X., Shi, X., Scott, C., Anbar, A.D., Lyons, T.W. and Jiang, G., 2012. Ocean oxygenation in the wake of the Marinoan glaciation. Nature, 489: 546-549.

Schilling, K., Basu, A., Johnson, T.M., Mason, P.R.D., Tsikos, H. and Mondal, S.K., 2014a. Se isotope signature of Paleoarchean and Paleoproterozoic banded iron formations, Goldschmidt Conference Abstract # 2207, Sacramento, CA, USA.

Schilling, K., Johnson, T.M. and Mason, P.R.D., 2014b. A sequential extraction technique for mass-balanced stable selenium isotope analysis of soil samples. Chemical Geology, 381: 125-130.

Schilling, K., Johnson, T.M. and Wilcke, W., 2011a. Isotope fractionation of selenium during fungal biomethylation by Alternaria alternate. Environmental Science and Technology, 45: 2670-2676.

Schilling, K., Johnson, T.M. and Wilcke, W., 2011b. Selenium partitioning and stable isotope ratios in urban topsoil. Soil Science Society of America Journal, 75: 1354-1364.

Schirmer, T., Koschinsky, A. and Bau, M., 2014. The ratio of tellurium and selenium in geological material as a possible paleo-redox prox. Chemical Geology, 376: 44-51.

Schoepfer, S.D., Henderson, C.M., Garrison, G.H., Foriel, J., Ward, P.D., Selby, D., Hower, J.C., Algeo, T.J. and Shen, Y., 2013. Termination of a continent-margin upwelling system at the Permian–Triassic boundary (Opal Creek, Alberta, Canada). Global and Planetary Change, 105: 21-35.

Scott, C., Wing, B.A., Bekker, A., Planavsky, N.J., Medvedev, P., Bates, S.M., Yun, M. and Lyons, T.W., 2014. Pyrite multiple-sulfur isotope evidence for rapid expansion and contraction of the early Paleoproterozoic seawater sulfate reservoir. Earth and Planetary Science Letters, 389: 95-104.

Shields-Zhou, G. and Och, L., 2011. The case for a Neoproterozoic Oxygenation Event: Geochemical evidence and biological consequences. GSA Today, 21: 4-11.

Shore, A.J.T., 2010. Selenium geochemistry and isotopic composition of sediments from the Cariaco Basin and the Bermuda Rise: a comparison between a restricted basin and the open ocean over the last 500 ka. Ph.D. Thesis, University of Leicester, Leicester, 307 pp.

Siebert, C., McManus, J., Bice, A., Poulson, R. and Berelson, W.M., 2006. Molybdenum isotope signatures in continental margin marine sediments. Earth and Planetary Science Letters, 241: 723-733.

Stüeken, E.E., 2013. A test of the nitrogen-limitation hypothesis for retarded eukaryote radiation: Nitrogen isotopes across a Mesoproterozoic basinal profile. Geochimica et Cosmochimica Acta, 120: 121-139.

Stüeken, E.E., Buick, R. and Anbar, A.D., 2015. Selenium isotopes support free O_2 in the latest Archean Geology, 43: 259-262.

Stüeken, E.E., Catling, D.C. and Buick, R., 2012. Contributions to late Archaean sulphur cycling by life on land. Nature Geoscience, 5: 722-725.

Stüeken, E.E., Foriel, J., Buick, R. and Schoepfer, S.D., submitted. Selenium isotope evidence for declining productivity under oxic conditions before the end-Permian mass extinction.

Stüeken, E.E., Foriel, J., Nelson, B.K., Buick, R. and Catling, D.C., 2013. Selenium isotope analysis of organic-rich shales: advances in sample preparation and isobaric interference correction. Journal of Analytical Atomic Spectrometry, 28: 1734-1749.

Suzuoki, T., 1965. A geochemical study of selenium in volcanic exhalation and sulfur deposits. II. On the behavior of selenium and sulfur in volcanic exhalation and sulfur deposits. Bulletin of the Chemical Society of Japan, **38**: 1940-1946.

Wen, H. and Carignan, J., 2007. Reviews on atmospheric selenium: Emissions, speciation and fate. Atmospheric Environment, 41: 7151-7165.

Wen, H., Carignan, J., Chu, X., Fan, H., Cloquet, C., Huang, J., Zhang, Y. and Chang, H., 2014. Selenium isotopes trace anoxic and ferruginous seawater conditions in the Early Cambrian. Chemical Geology, 390: 164-172.

Wille, M., Kramers, J.D., Nägler, T.F., Beukes, N.J., Schröder, S., Meisel, T., Lacassie, J.P. and Voegelin, A.R., 2007. Evidence for a gradual rise of oxygen between 2.6 and 2.5 Ga from Mo isotopes and Re-PGE signatures in shales. Geochimica et Cosmochimica Acta, 71: 2417-2435.

Zhu, J.M., Johnson, T.M., Clark, S.K., Zhu, X.K. and Wang, X.L., 2014. Selenium redox cycling during weathering of Se-rich shales: A selenium isotope study. Geochimica et Cosmochimica Acta, 126: 228-249.

Zingaro, R.A., Dufner, C.D., Murphy, A.P. and Moody, C.D., 1997. Reduction of oxoselenium anions by iron (II) hydroxide. Environment International, 23: 299-304.