Selenium isotopes record extensive marine suboxia during the Great Oxidation Event

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The accumulation of molecular oxygen in Earth’s atmosphere and ocean fundamentally restructured biogeochemical pathways, and ultimately allowed the evolution of aerobically respiring eukaryotic life. Determining the tempo of the rise of oxygen to modern levels has thus been the focus of decades of research (1, 2). The beginning of the Paleoproterozoic Era (2.5–1.6 Ga) is of particular interest, because it was the first time in Earth’s history when oxygen-rich conditions prevailed in surface environments for a prolonged interval (3).

The first permanent step in the oxygenation of Earth’s surface, the Great Oxidation Event (GOE), was originally identified by the disappearance of redox-sensitive detrital minerals (4, 5) and the appearance of red beds (6) around the Archean–Proterozoic boundary. More recently, the record of mass-independent fractionation of sulfur isotopes (MIF-S) in sedimentary sulfates and boundary. More recently, the record of mass-independent fractionation of sulfur isotopes (MIF-S) in sedimentary sulfates and sulfur isotope anomaly. These redox fluctuations could have profoundly influenced the course of eukaryotic evolution, as eukaryotes have several metabolic processes that are obligately aerobic. Here we investigate the magnitude of these proposed oxygen perturbations using selenium (Se) geochemistry, which is sensitive to redox transitions across suboxic conditions. We find that δ^{82/78}Se values in offshore shales show a positive excursion from 2.32 Ga until 2.1 Ga (mean ± 1.03 ± 0.67‰). Selenium abundances and Se/TOC (total organic carbon) ratios similarly show a peak during this interval. Together these data suggest that during the GOE there was pervasive suboxia in near-shore environments, allowing nonquantitative Se reduction to drive the residual Se oxyanions isotopically heavy. This implies O_2 levels of >0.4 μM in these settings. Unlike in the late Neoproterozoic and Phanerozoic, when negative δ^{82/78}Se values are observed in offshore environments, only a single formation, evidently the shallowest, shows evidence of negative δ^{82/78}Se. This suggests that there was no upwelling of Se oxyanions from an oxic deep-ocean reservoir, which is consistent with previous estimates that the deep ocean remained anoxic throughout the GOE. The abrupt decline in δ^{82/78}Se and Se/TOC values during the subsequent Shunga–Franceville anoxia indicates a widespread decrease in surface oxygenation.

Paleoproterozoic | trace metals | oxygen | eukaryote evolution

Significance

Oxygen is essential for eukaryotic life. The geologic record of early Earth contains abundant evidence of low oxygen levels, and accordingly, a lack of eukaryote fossils. The rise of oxygen to near-modern levels at the end of the Proterozoic Era is thus often cited as the trigger for the evolutionary radiation of complex life forms at this same time. Here we present selenium geochemical data that indicate an expansion of suboxic (≥0.4 μM O_2) habitats in the shallow oceans between 2.32 and 2.1 Ga—more than one billion years before eukaryotes become abundant in the fossil record. These environments could have harbored the earliest stages of eukaryotic evolution, but may have been too transient for substantial diversification to occur.
basinal redox gradients that could be critical for eukaryote ecology. Conversely, Fe speciation is a well-developed local redox indicator, and has been used to identify euxinia in offshore environments during the GOE (16, 21). But, because this signal records local conditions, with spatially limited data it lacks the ability to distinguish an oxygen-minimum zone in an otherwise globally oxic ocean from a globally anoxic deep ocean.

Selenium (Se) is well-suited for bridging the gaps between the aforementioned proxies, as its relatively short oceanic residence time (∼10^3 y) makes Se sensitive to basin-scale redox dynamics. Selenium is predominantly delivered to the oceans via oxidative weathering, making the marine Se reservoir scale with continental oxidative weathering rates. Additionally, Se isotopes can be fractionated by several permil during oxygenation (SeO_2^4-, SeO_3^3-, HSeO_4^-) reduction to elemental Se and selenide in suboxic environments, such as modern oxygen-minimum zones and suboxic pore waters. In these settings, if Se oxyanions are continuously supplied from oxygenated waters, reduction is nonquantitative and the resulting isotopic values of reduced Se compounds are typically negative (22, 23). Negative Se isotope ratios in sedimentary rocks can therefore be an indication that the sediments were deposited in an environment that was linked to a large oxic reservoir. Selenium isotopes have been used in this way to track the oxygenation of the deep ocean in the late Neoproterozoic, where fractionations down to ~1.5‰ have been recorded in offshore shales that received upwelling Se oxyanions from oxic deep oceans (24). In modern anoxic basins where Se oxyanions are not continuously resupplied, Se is largely consumed by uptake into biomass without net fractionation and the reduction of Se oxyanions is quantitatively (25). Isotopic values in these settings are therefore typically heavy, approaching or exceeding the composition of seawater, which is ~4±0.3‰ today (23).

We measured Se abundance and isotope ratios in organic-rich shales from seven stratigraphic units deposited in offshore environments during and after the GOE. These lithologies capture the offshore Se reservoir, which records basin-scale redox structure. Viewed together, these snapshots of individual basins at different stages of the GOE offer a glimpse of secular changes in the redox structure of the global ocean. Our results thus provide a proxy record that can test the predictions made by other redox-sensitive indicators and help resolve the spatial and temporal distribution of oxic, suboxic, and anoxic marine environments during the GOE.

Specifically, these data allow us to test whether the Neoproterozoic oxygen overshoot was at any time comparable in magnitude to the Neoproterozoic oxygenation event, and to assess the implications for the early evolution of eukaryotic life.

**Materials**

We analyzed 75 samples from 7 shale units deposited between 2.2 and 1.85 Ga. These data were compared with 567 published Se measurements from samples with ages spanning 3.25 Ga to the present. Samples corresponding to the early stage of the GOE come from the Rooihoogete and Timeball Hill formations of the Pretoria Group (2.32 Ga), which were analyzed by Stueken et al. (23), and are the oldest open-marine shales deposited without an MIF-S signature. In addition, we sampled the Weewee Slate (~2.2–2.1 Ga) and Sengoma Argillite Formation (~2.2–2.1 Ga), which were deposited in the middle of the GOE, and the Lomagundi carbon isotope excursion. Samples straddling the end of the GOE and Lomagundi carbon isotope excursion come from the Hautes Chutes Formation of the Labrador Trough (~2.1 Ga), the Francavillian Series of Gabon (~2.083 Ga), the Zaonega Formation of Karelia, Russia (~2.11–2.06 Ga), and the Union Island Group of the Slave craton (~2.1–2.0 Ga). In addition, organic-rich shales of the Menihk Formation from the Labrador Trough (1.85 Ga), postdating the LE, were also analyzed. These samples span the latest stages of the GOE and the 200 My interval after its termination, and include the formations in which the Shunga–Francavillian negative carbon isotope anomaly was originally discovered (11).

**Results**

Shales deposited in offshore environments show a broad trend in Se concentrations across the GOE, with abundances increasing in the late Archean and subsequently falling through the Paleoproterozoic, with a peak between 2.32 and 2.1 Ga (max. 27.97 ppm; Fig. 1). Mean Se abundance of shales deposited between 2.32 and 2.1 Ga (6.79 ppm) is significantly higher than the mean Se abundance for shales older than 2.45 Ga (2.04 ppm; p one-tailed = 10^-8) and with ages between 2.1 and 1.1 Ga (2.02 ppm; p one-tailed = 10^-8). Se/TOC (total organic carbon) ratios similarly show a peak (max. 26.84 ppm/wt %) in the early stage of the GOE, but rapidly decline between 2.1 and 2.0 Ga to <1 ppm/wt % (Figs. 1 and 2).

δ^{34}S values are consistently positive from 2.32 Ga until 2.1 Ga, and higher than in any other time in the geologic record (avg. +1.03 ± 0.67‰; Figs. 2 and 3). The mean δ^{34}S value for samples older than 2.45 Ga is statistically indistinguishable from that for samples dating between 2.1 and 1.1 Ga (p two-tailed = 0.11), whereas samples with 2.32–2.1 Ga ages have significantly higher δ^{34}S values than both groups (p one-tailed = 10^-10, 10^-10). Negative δ^{32/34}Se values do not become prevalent until the late Neoproterozoic (24), and persist throughout the Phanerozoic (23) (Fig. 3).

**Oxidative Weathering and the Marine Se Reservoir.** In light of mounting evidence for elevated atmospheric oxygen levels between 2.32 and 2.06 Ga (3, 15–19), it is unsurprising that shales show an increase in Se abundance at this time (Fig. 1). Whereas Se can also be sourced to the marine environment by volcanism and hydrothermal activity, oxidative weathering is by far the dominant source on the modern Earth (~90% of flux to oceans; volcanism ~10%, hydrothermal input ~1%; ref. 26). Furthermore, the parallel enrichment of U (19), Mo (18), and Se in samples from the Rooihoogete and Lower Timeball Hill formations and the Sengoma Argillite Formation is most parsimoniously explained by enhanced oxidative weathering. Unlike Se, U is exclusively delivered to the oceans via oxidative mobilization, and not by volcanic or hydrothermal inputs. Additionally, Mo is not volatile and thus cannot derive from volcanic sources. Although it is not possible to definitively rule out a volcanic contribution to the sedimentary Se enrichment seen during the GOE, the vast majority of Se was likely delivered by oxidative continental weathering.

The trend in Se abundance does not correspond exactly with the inferred beginning and end of the GOE (Fig. 1). Se concentrations begin to increase in the late Archean (~2.7 Ga), perhaps due to increasing rates of oxidative weathering in locally oxic environments on land (27). In the wake of the GOE, Se abundances remain higher than mid-Archean values until at least 1.9 Ga, and
greater than 10 ppm/wt % are not observed again for ~1 Gy after the termination of the GOE.

Ocean Redox Structure during the GOE. Shales deposited between 2.32 and 2.1 Ga show the largest and longest-lived positive Se isotope excursion seen in the geologic record (Fig. 2). Several processes other than oxygenion reduction are known to fractionate Se isotopes, but their fractionation factors are too small to explain the shift of $\delta^{82/78}$Se values to $>+1\sigma$ (max. $+2.25\sigma$) during the GOE. Oxidative weathering alone is unlikely to generate this magnitude of fractionation relative to crustal values because oxidation generally imparts a small ($<0.5\sigma$) fractionation (28). Large fractionations associated with weathering have only been observed in unusually Se-rich soils (up to 2% Se content, ref. 29), whereas Se-lean soils ($<0.5$ ppm)—more representative of average crust ($<0.1$ ppm)—show no significant fractionation ($<0.25\sigma$, ref. 30). The absence of a significant fractionation during weathering is further supported by isotopic mass balance of marine sediments (26). Assimilation into biomass also causes only small fractionation ($<+0.6\sigma$, ref. 31), so changes in biological utilization of Se cannot account for the large excursion. A shift in Se crustal sources cannot explain the heavy isotopic values seen between 2.32 and 2.1 Ga because there is little variability in the Se isotopic composition of different terrestrial reservoirs (crustal source rocks range from $-0.3\sigma$ to $+0.6\sigma$, ref. 32).

Fig. 2. Trends in Se/TOC, $\delta^{82/78}$Se, and $\delta^{13}$C_carb (triangles, this study; circles, published data). Gray bands mark range of phytoplankton Se/TOC (Top) and crustal $\delta^{82/78}$Se (Middle). $\delta^{13}$C_carb curve adapted from Lyons et al. (2). Solid data points are average per formation, error bars are 1σ; shadowed data points are individual samples. Note log scale in top plot.

then return to low levels in the mid-Proterozoic. This trend could suggest that atmospheric oxygen levels (and thus oxidative weathering rates) did not experience a sharp fall at the end of the GOE. However, weathering of Se-rich sediments that were deposited during the GOE and subsequently uplifted on tectonic timescales of $\sim$100 My could have potentially contributed to the Se enrichment seen in shales deposited after $\sim$2.06 Ga, leaving open the possibility that atmospheric oxygen levels did indeed decline abruptly, but the Se flux decayed slowly. In either case, it would seem that the marine Se reservoir grew larger during the GOE than at any other time before the late Neoproterozoic.

Se/TOC ratios may be a more robust indicator of Se reservoir size than Se abundance, because they account for differences in primary productivity across depositional environments. Biological incorporation of Se and subsequent settling of organic material may be the dominant mechanism of Se transport to anoxic sediments; normalizing data to organic carbon contents can thus gauge “Se excess” in the system. Like Se abundance, Se/TOC ratios steadily increase through the late Archean, and peak during the GOE at 2.32 Ga (max. 26.63 ppm/wt %). However, in contrast to the trend seen in Se abundance, Se/TOC ratios decline rapidly at the end of the GOE (Figs. 1 and 2). This decline coincides with the falling limb of the Lomagundi carbon isotope excursion, which has been argued to record a time of rapid oxygenation (15, 16). The decreasing Se/TOC ratios therefore may suggest that the marine Se reservoir was in fact rapidly shrinking at the end of the GOE with the expansion of marine anoxia. Maximum enrichments

Fig. 3. Histogram of all published shale $\delta^{82/78}$Se values in different stages of geologic time. Dotted lines indicate crustal $\delta^{82/78}$Se range. The interval from $-2.32-2.1$ Ga marks the only time when offshore shales record persistently positive $\delta^{82/78}$Se values. Archean and mid-Proterozoic Se isotope ratios are near crustal values, whereas Neoproterozoic and Phanerozoic values are often negative.
This leaves partial reduction of Se oxyanions as the most likely process to generate large (>1‰) fractionations that can be preserved in sedimentary rocks. In laboratory settings, both biotic and abiotic partial reduction generate isotopic fractionations of several permil, with lighter Se isotopes being preferentially enriched in reduced compounds (33). In bulk samples from natural settings, observed fractionations tend to be smaller (range from −2 to +2‰), perhaps because the isotopic signature of reduced Se gets diluted by codeposition of biologically assimilated Se in sediments (34). Still, dissimilatory reduction can alter the Se isotopic composition of residual oxyanions dissolved in seawater, and this has been documented in the Phanerozoic (35), Neoproterozoic (24), and Archean (36). In the 2.5 Ga Mt. McRae Shale, Se isotopes show a positive excursion parallel with a positive excursion in nitrogen isotopes and enrichments in redox-sensitive trace metals that have been interpreted as evidence for a transient pulse of oxygen that occurred before the onset of the GOE (36-38). Stüeken et al. (36) argued that this Se isotope excursion was generated in a redox-stratified water column where Se was partially reduced in shallow-marine, suboxic waters, driving the residual Se reservoir to more positive δ\(^{34}\)S/δ\(^{32}\)S values, which were then recorded in offshore shales. The positive δ\(^{34}\)S/δ\(^{32}\)S values seen during the GOE seem to indicate a similar scenario, although in this instance persisting in multiple basins on separate continents over a timescale of hundreds of millions of years.

The fact that most sedimentary Se isotope ratios in Archean and mid-Proterozoic shales do not significantly deviate from crustal values (Fig. 3) suggests that either Se influx was generally low or that Se oxyanions in the oceans during these intervals were quantitatively reduced and assimilated (Fig. 4A), allowing sediments to roughly record the isotopic composition of crustal source rocks. The observation of significantly positive δ\(^{34}\)S/δ\(^{32}\)S values in all analyzed offshore sediments dating within the GOE thus suggests an extreme isotopic distillation of an expanded marine Se reservoir at this time. To generate such a large isotopic excursion, there were likely extensive near-shore suboxic environments where Se oxyanions were constantly resupplied, allowing substantial nonquantitative reduction to occur in the water column. This would sequester isotopically light Se in near-shore sediments that were not sampled in this study, perhaps with the exception of the Wewe Slate (see below) (Fig. 4B). The residual Se reservoir would thus have been driven diagenetically. These heavy values could then have been recorded in the offshore environments sampled in this study either by quantitative or nonquantitative reduction and/or biological assimilation, depending on the extent of suboxia on the outer shelf.

This stands in contrast to the modern ocean, which receives a large flux of Se oxyanions but generates only small isotopic fractionations (Fig. 4C). Suboxic waters are scarce in the fully oxygenated modern oceans (<10% of ocean area; ref. 39) and diagenetic Se reduction in sediments seems to produce relatively small fractionations, perhaps because the supply of Se oxyanions is diffusion-limited in pore waters. Thus, the magnitude of the positive δ\(^{34}\)S/δ\(^{32}\)S excursion seen in shales deposited during the GOE suggests that suboxia was a widespread and persistent feature along continental margins during this interval.

The lack of negative δ\(^{34}\)S/δ\(^{32}\)S values in offshore sediments deposited during the GOE also suggests that—unlike in the late Neoproterozoic and Phanerozoic—there was not any resupply of Se oxyanions from an oxic deep-ocean reservoir. This is consistent with previous work that has suggested the deep ocean remained anoxic throughout the GOE (40). So, whereas the Se data alone remain somewhat ambiguous as to the precise redox state of the sampled offshore depositional environments, they can be used to confidently infer the persistence of widespread near-shore suboxia, and predominantly anoxic conditions in the deep ocean.

An isotopic record of Se in near-shore sediments that preserve the complementary negative δ\(^{34}\)S/δ\(^{32}\)S values and were deposited coevally with the shales bearing the positive δ\(^{34}\)S/δ\(^{32}\)S excursion would provide a test of this hypothesis. However, given current sensitivity limits for Se isotope analysis, this remains a challenging prospect. Se concentrations in carbonates, sandstones, and low-TOC shales associated with near-shore depositional environments are orders of magnitude less than in offshore organic-rich shales, requiring unfeasibly large sample sizes to obtain accurate measurements. Further methodological refinement may eventually enable analysis of such materials.

Still, there is some evidence for a complementary light Se reservoir in shallow-water environments during the GOE. The Wewe Slate (~2.2–2.1 Ga) displays by far the largest range of δ\(^{34}\)S/δ\(^{32}\)S Se values of units analyzed in this study (~1.34 to +2.25‰; Dataset S1). We suspect that this is because this unit is capturing the seawater Se composition near the environmental gradient for Se reduction. The Wewe Slate is underlain by mature quartz sandstones andstromatolitic dolostones (41) and has relatively low TSe and TOC contents (Fig. 1, SI Appendix), all consistent with a near-shore depositional environment, in contrast to the TSe-
TOC-rich shales from other units included in this dataset. Because there is no noticeable stratigraphic trend in Se isotopes or abundance through the Wewe Slate (SI Appendix), it is unlikely that the range of values reflects secular change in the depositional environment. We cannot rule out the possibility that the Wewe Slate is capturing transient deep-ocean oxygenation in the midst of the GOE, but the sedimentologic context is consistent with deposition of the Wewe Slate in a setting that straddled a chemocline with fluctuating depth, thus sampling both the shallow and deep Se reservoirs.

At the end of the GOE (2.1–2.0 Ga), $\delta^{82/78}\text{Se}$ values sharply return to crustal values (Fig. 2), consistent with rapid deoxygenation of the ocean (16). The occurrence of some negative $\delta^{82/78}\text{Se}$ values in the Zoenaga and Franconville formations may result from the weathering of isotopically light Se that was deposited in shallow settings during the GOE, and subsequently uplifted and eroded on tectonic timescales of $\sim$100 My. However, we cannot definitively rule out the possibility that these data represent a pulse of oxygenation at the culmination of the GOE (11). In either case, the longer-term trend reveals an ultimate return to widespread anoxia. Even if Se influx to the ocean decayed gradually as Se-rich sediments deposited during the GOE were weathered, a contraction of suboxic water masses and takeover by anoxic and strongly euxinic conditions could have rapidly pushed the system toward quantitative reduction of Se oxyanions, thus ending the Se isotopic excursion preserved in the GOE. Contraction of the marine Se reservoir during deoxygenation would further accelerate the loss of isotopic fractionation, because a smaller Se reservoir could be quantitatively reduced more easily.

**How Oxic Were Near-Shore Environments During the GOE?** These data can be used to provide an approximate lower limit on shallow-marine oxygen levels across the GOE. Specifically, when used in conjunction with the iodine record, the Se data point to the presence of conditions that were at least suboxic. In the modern ocean, quantitative reduction of iodate ($\text{IO}_3^-$) to iodide ($\text{I}^-$) has been observed at dissolved $\text{O}_2$ concentrations less than $\sim$5 $\mu$M (42). In the same study, Se oxynion reduction was nonquantitative at oxygen concentrations down to $\sim$1 $\mu$M $\text{O}_2$. Another investigation of Se speciation in the anoxic Saanich Inlet found that Se oxynions became depleted to below the detection limit at $0.4 \mu$M $\text{O}_2$ (25). Within this framework, the occurrence of positive $\delta^{82/78}\text{Se}$ values across the GOE implies a conservative lower limit for shallow-water oxygen concentrations of >0.4 $\mu$M $\text{O}_2$. In reality, it is likely that $\text{O}_2$ concentrations were higher in these settings, because reduction of Se oxynions in near-shore environments was evidently far from being quantitative. High $\text{I}/(\text{Ca + Mg})$ ratios in LE-aged carbonates (17) may push the lower limit for surface ocean oxygen up to $\sim$5 $\mu$M $\text{O}_2$, for the later stage of the GOE. This would still only be a small fraction of the modern surface ocean oxygen concentration of $\sim$325 $\mu$M $\text{O}_2$, but it could have had important evolutionary implications.

**Implications for Biological Evolution.** Whether or not oxygen availability was the primary control on the evolution of deeply rooted eukaryotes remains a highly contentious issue. Recent evidence for extremely low mid-Proterozoic oxygen levels (43) has hinted that the oceans, thus ending the Se isotopic excursion seen during the GOE. Contraction of the marine Se reservoir during deoxygenation would further accelerate the loss of isotopic fractionation, because a smaller Se reservoir could be quantitatively reduced more easily.

**Conclusions**

An increase in the abundance of Se in organic-rich shales deposited during the GOE is consistent with enhanced oxidative continental weathering at this time, and corroborates evidence from other redox-sensitive proxies (S, Mo, and U). A shift to the most positive offshore $\delta^{82/78}\text{Se}$ values in geologic history suggests that extensive partial reduction of Se oxyanions in shallow, suboxic seawater drove the isotopic composition of residual oceanic Se heavier. Shallow-marine sediments thus acted as a sink for isotopically light Se, perhaps recorded by the negative $\delta^{82/78}\text{Se}$ ratios found in the Wewe Slate. This state of enhanced oxidative continental weathering and extensive shallow-ocean suboxia appears to have prevailed until near the end of the GOE, when plummets Se/TOC ratios and $\delta^{82/78}\text{Se}$ values suggest that the marine Se reservoir rapidly diminished and suboxic water masses contracted at the expense of anoxic and, possibly, strongly euxinic waters. Thus, the period from $\sim$2.32–2.1 Ga was the first interval in Earth’s history when conditions that were at least suboxic persisted on continental margins on geological timescales, perhaps supporting the early evolution of aerobically respiring life forms. The contraction of oxic and suboxic environments after the GOE may have limited the available habitats for the evolutionary radiation of eukaryotic life until the second rise of oxygen in the late Neoproterozoic.

**Methods**

Samples were prepared and analyzed following the methods of Stüeken et al. (57). Rock powders were dissolved using HF, HNO$_3$, and HClO$_4$, and Se was isolated using thiol-cotton fiber columns. All analyses were conducted on a hydride-generator multicollector inductively coupled plasma mass spectrometer (Nu Instruments). Measurements were normalized using standard-sample bracketing. We note that both $\delta^{79/75}\text{Se}$ and $\delta^{78/76}\text{Se}$ notations are used in the literature; our data are expressed as $\delta^{78/76}\text{Se}$ relative to National Institutes of Standards and Technology reference SRM 3149 because, using our isotopic measurement method, mass 78 is much less affected by isobaric interferences than mass 76 (57). Average precision (1σ) for samples was 0.067% for $\delta^{78/76}\text{Se}$ values and 0.022 ppm for Se concentrations. $\delta^{78/76}\text{Se}$ values for international reference material SGR-1 and in-house standard
The Geological Survey of Botswana for access to samples critical to this work. We thank the University of Washington Isotope Geochemistry Lab for technical support. Funding for this work was provided by National Science Foundation (NSF) Grant EAR-0921580, NSF Frontiers in Earth System Dynamics Grant 1338810, and NSF Grant NX16A537G to R.B., as well as NSF Grant EAR-05-45484, NASA Astrobiology Institute Award NNA04CC09A, and an Natural Sciences and Engineering Research Council of Canada Discovery and Accelerator Grant (to A.B.). M.A.K. acknowledges support from an NASA Graduate Research Fellowship. E.E.S. is supported by a NASA Postdoctoral Fellowship. Additional support was provided by the NASA Astrobiology Institute Virtual Planetary Laboratory team Grant NNA13AA33A.

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**Geologic Context**

*Menihek Formation, Upper Labrador Trough (ca. 1.85 Ga)*

The Menihek Formation of the Labrador Trough in eastern Canada is the youngest division of the Knob Lake Group and overlies the ca. 1.88 Ga Sokoman Iron Formation (1, 2). It was deposited in a deep-water setting along the eastern margin of the Superior craton. Hoffman (3) regarded this unit as foreland basin fill; however, correlative units along the southern margin of the Superior craton in the Animikie basin are considered to have been deposited in a back-arc basin (e.g., ref. 4). Regardless of the exact tectonic setting, this formation was deposited in a deep-water, open-marine environment. The Menihek Formation consists of organic-rich, sulfidic, thinly laminated, fissile shales, slates and siltstones more than 300 m in thickness (5–7). The contact with the underlying granular iron formation is sharp with locally developed conglomerates. The sampled drill-core, 12-HR-1322D, is from the Howse River area. The age of ca. 1.85 Ga places deposition of the Menihek Formation >200 Myrs after the end of the Lomagundi carbon isotope excursion (8).

*Union Island Group, Canada (ca. 2.1-2.0 Ga)*

The Union Island Group in the southwestern region of the East Arm basin in the Great Slave Lake area is now considered to be the lowermost unit of the Paleoproterozoic cover succession deposited on the margin of the Slave craton (9), in contrast to previous interpretations (10–13). The age of the group is poorly constrained, but is younger than the 2217 ± 4 Ma Simpson Islands dikes that intrude the Archean basement but not the Union Island Group (11, 14, 15), and older than the unconformably overlying ca. 1.86 Ga Sosan Group (11, 13). The group has been subdivided (refs. 12, 14, 16) into the following from the base to the top: 1) a lower massive dolostone, locally underlain by quartzite and/or quartz pebble conglomerate, which rests on Archean granitic basement and a well-developed regolith; 2) organic-rich and sulfidic mudstone with decimeter-thick carbonate beds; 3) alkaline to sub-alkaline, asthenosphere-derived and crustally uncontaminated basalts with flows, flow breccia, pillows, and pillow breccia; 4) well-bedded and laminated upper dolostone with thin red mudstone beds at the top and locally developed, sub-alkaline pillow basalts; and 5) red and green laminated mudstone with soft-sediment deformation structures. Deposition was below the wave- and storm-base and possibly the photic zone for the most of the succession with the exception of the upper part of the unit 4 and unit 5. Carbonates of the first and second units have highly positive carbon isotope values, comparable to carbonates deposited during the Lomagundi carbon isotope excursion, whereas carbonates of the fourth unit have carbon isotope values close to 0‰ V-PDB. We therefore consider that the black shales analyzed in this study – collected from the second unit – were deposited in the aftermath of the Lomagundi carbon isotope excursion, after ca. 2.11-2.06 Ga (17). Samples were collected from outcrops on Union Island.
The Zaonega Formation of Karelia, Russia comprises a 1500 m thick sequence of basaltic tuffs, siltstones, mudstones, and cherts. The Upper Zaonega sub-formation contains the majority of the organic-rich shales in the Zaonega Formation (18). It is from these horizons that samples were selected for Se analysis.

The minimum age of the Zaonega Formation is constrained by dolerite sills that are thought to be co-magmatic with volcanics of the overlying Suisar Formation, and yield U-Pb ages of 1983 ± 6.5 and 1984 ± 8 Ma (19). In the Onega Basin, the Zaonega Formation lies disconformably above the Tulomozero Formation, which contains isotopically heavy carbonates (>+10‰ δ¹³C) – consistent with deposition during the Lomagundi carbon isotope excursion (8). A carbonate Pb-Pb age of 2090 ± 70 Ma for the Tulomozero Formation (20) suggests that the Zaonega Formation was deposited during the latest stages of the GOE/LE (ca. 2.11-2.06 Ga, ref. 17). This is further supported by smaller carbon isotope enrichments seen in carbonates of the Lower Zaonega sub-formation than in the Tulomozero Formation (up to +7.9‰ δ¹³C; refs. 4, 5).

Samples analyzed in this study come from three drill cores: 13A, 5190 and 175. Core 13A was drilled in the Onega Basin as part of the Fennoscandia Arctic Russia-Drilling Early Earth Program (FAR-DEEP). These cores have been studied for C, N, Mo and U isotopes as well as Fe speciation (23, 24). The C isotope trends were used to identify the Shunga-Francevillian anomaly (23), and were argued to reflect a widespread decrease in environmental oxygen levels in the wake of the GOE. While post-depositional alteration rendered the Fe speciation data difficult to interpret, Mo isotopes corroborated the story of deoxygenation (24), suggesting deposition in a euxinic environment connected to a largely anoxic global ocean.

Cores 5190 and 175 have been studied for C, S and Mo isotopes, as well as Fe speciation. Multiple S isotope systematics have been interpreted as reflecting a smaller marine sulfate reservoir during deposition of the Zaonega Formation than during the Lomagundi excursion (25). Fe speciation data suggest that these units were deposited in an environment that was transiently euxinic (25).

**FC Member, Francevillian Series, Gabon (ca. 2.1 Ga)**

The unmetamorphosed Paleoproterozoic Francevillian Basin developed on the Archean Chaillu Block (Congo craton). Its tectonic setting is still debated with interpretations ranging from intracratonic basin (26) to foreland basin (27). Regardless of the tectonic setting, the basin was open to the global ocean. The Francevillian Series hosts carbonates recording the Lomagundi carbon isotope excursion and organic-rich shales with highly negative carbon isotope values linked to the Shunga-Francevillian anomaly (28, 29). The age of the Francevillian Series is best constrained by a U-Pb SHRIMP age for the welded tuff at the top of the FD member of 2083 ± 6 Ma (30, 31). Black shales suggest deposition under anoxic and even euxinic conditions based on Fe speciation and Mo concentrations and isotope ratios (32–34); whereas sulfur and iron isotope values of diagenetic pyrites indicate access to large sulfate and dissolved Fe reservoirs (33, 35). The sampled interval in the drillcore LST-12 collared in the Lastoursville sub-basin belongs to the FC Member and straddles the end of the
Lomagundi carbon isotope excursion. The FC Member in this drillcore contains organic-rich and sulfidic shales, grey massive carbonates, and cherts. Deposition was likely below wave-base and the photic zone. Sediments passed through the oil and gas windows and migrated, solidified pyrobitumen is present in the drillcore.

*Hautes Chutes Formation, Lower Labrador Trough (ca. 2.1 Ga)*

The Hautes Chutes Formation is the lowermost unit of the Swampy Bay Subgroup, and immediately overlies carbonates of the Pistolet Subgroup (Uve and Alder formations) that have highly positive carbon isotope values recording the Lomagundi carbon isotope excursion (36). The age of this unit is between 2169 ± 2 Ma, an age of the granophyre dike that intrudes the underlying Seward Subgroup but not the Swampy Bay Subgroup (37), and ca. 1.88 Ga, the age of the overlying Sokoman Iron Formation (1, 2). It was deposited on the passive margin along the eastern boundary of the Superior craton and consists of up to 100 m of graphitic, pyritiferous, thinly laminated slate (38). The samples were collected from the drillcore 12-LR-1036D that was collared in 2012 in the Lake Raeitch area.

*Sengoma Argillite Formation, Bushveld Basin, S.E. Botswana (ca. 2.2-2.1 Ga)*

The Sengoma Argillite Formation (SAF) was deposited in an offshore, open-marine environment on the Kaapvaal craton (39). Deposition evidently occurred during the Lomagundi carbon isotope excursion (8), as evidenced by highly $^{13}$C-enriched carbonates occurring above and below the SAF (40, 41). While there are no direct geochronologic constraints on the timing of SAF deposition, the 2.05-2.06 Ga age of the unconformably overlying Rooiberg Group and intruding Bushveld Complex confirm the inference that deposition occurred before the termination of the LE (42, 43). Thus, a depositional age of 2.2-2.1 Ga has previously been inferred for the SAF (25, 41). Studies of organic carbon isotopes in the SAF have shown a large offset between $\delta^{13}$C$_{\text{carb}}$ and $\delta^{13}$C$_{\text{org}}$, implying a redox-stratified ocean that supported vigorous secondary production below the chemocline (41). Fe speciation data suggest that the SAF was deposited under mostly euxinic conditions (25), but S isotope systematics indicate that the marine sulfate reservoir had expanded considerably (25), consistent with studies of S isotopes in carbonate-associated sulfate (44).

*Wewe Slate, Chocolay Group, Marquette Range Supergroup (ca. 2.2-2.1 Ga)*

The Wewe Slate is in the uppermost Chocolay Group, and is unconformably overlain by the 1874 ± 9 Ma Menominee Group (45). The Kona Dolomite conformably underlies the Wewe Slate, and contains isotopically enriched carbonates (up to +9.5‰ $\delta^{13}$C) associated with the Lomagundi carbon isotope excursion (8, 46). In the Marquette Range of Michigan, the Kona Dolomite lies in unconformable contact with the Menominee Group, indicating the limited geographic extent of the Wewe Slate and suggesting that it was deposited during an episode of basin-deepening (46). A maximum age is derived from detrital zircon U-Pb ages of 2288 ± 15 Ma for the underlying Enchantment Lake Formation in the lowermost Chocolay Group (47). The lack of tight
chronological constraints allows for a wide range of possible ages for the Wewe Slate; however, conformable contact with the underlying Kona Dolomite and cross-basinal correlations with other sections of the Marquette Range Supergroup suggest that an age of ca. 2.2-2.1 Ga seems most likely (46). The Bear Creek Hole 35, drilled by Cliffs Natural Resources, was sampled for this study.

The Wewe Slate was predominantly deposited below fair-weather wave base, but starved ripples suggest occasional sediment delivery by strong currents resulting in erosion overwhelming sediment supply (49). Additionally, the conformably underlying stromatolitic Kona Dolomite and mature Mesnard Quartzite indicate their deposition in a tidally-influenced shallow-marine environment (48). Thus, it seems possible that the Wewe Slate was deposited in a nearer-shore environment than the other shales analyzed in this study. This interpretation is supported by the lower TOC and TSe contents of the Wewe Slate compared to the other formations studied here (Fig. S1). Deposition in a near-shore environment could have allowed the Wewe Slate to capture a different Se isotope signal than that recorded by the outer shelf environments that were sampled in the other formations studied here. Accordingly, both extremely negative and extremely positive $\delta^{32/78}$Se values are seen in a relatively short section of the Wewe Slate section (Fig. S1). The lack of a trend across the drill core section suggests that these different values do not reflect secular evolution of the depositional environment (see main text for further discussion).

**Figure S1. Break Creek Hole 35 stratigraphic column of the Wewe Slate.** Solid symbols represent averages of multiple measurements on a single sample; crosses are samples that had insufficient Se for isotopic analysis. Error bars in Se, Se/TOC and TOC plots are omitted because they are smaller than points. No trend is seen in either $\delta^{32/78}$Se or TSe, suggesting that secular change in redox or depositional environment was not responsible for the spread of values. Rather, a depositional environment that straddled a chemocline with fluctuating depth could have experienced both non-quantitative and quantitative Se oxyanion reduction, causing the occurrence of very negative and very positive $\delta^{32/78}$Se values in <100 m of core. See text for further discussion.
Mass-dependent fractionation of selenium isotopes

Due to the geochemical similarity of selenium and sulfur, it was once hypothesized that selenium compounds might have been subject to significant mass-independent fractionation early in Earth’s history (reviewed in refs. 49, 50). Subsequent work has found no evidence for significant mass-independent fractionation of selenium isotopes (49). This dataset also displays no mass independent fractionation (Fig. S2). All deviations from the mass-dependent fractionation lines can likely be explained via residual isobaric interferences (51).

Figure S2. Three-isotope diagrams of $\delta^{82/76}$Se vs. $\delta^{82/78}$Se (left) and $\delta^{82/77}$Se vs. $\delta^{82/78}$Se (right). Error bars are 1σ; trend lines are plotted for mass-dependent fractionation (MDF). All samples display mass-dependent fractionation, with any deviations from the MDF lines likely deriving from residual interferences (see ref. 51 for discussion of method and corrections for isobaric interferences).
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