Re-Os geochronology for the Cambrian SPICE event: Insights into euxinia and enhanced continental weathering from radiogenic isotopes

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ABSTRACT
The late Cambrian Steptoean positive carbon isotope excursion (SPICE) represents a major perturbation to the global carbon cycle and was associated with trilobite extinctions and expansion of anoxic and/or euxinic water masses during episodes of eustatic sea-level change. We present a new Re-Os age together with Os and Nd isotope stratigraphy and major- and trace-element data from the Alum Shale Formation (Scania, Sweden). The Re-Os age of 494.6 ± 2.9 Ma is from the interval of peak δ¹³Corg values, providing the first radiometric age constraint for this Cambrian carbon isotope excursion, interpreted as a possible pre-Mesozoic ocean anoxia event, and the timing of biomere-level extinctions. The Os isotope chemostratigraphic profile can be explained by an increase in terrigenous weathering prior to the SPICE, potentially driven by sea-level fall, and in agreement with enhanced nutrient supply, primary productivity, and organic matter burial as the driver of the SPICE event. Post-SPICE, the Os isotopes become increasingly unradiogenic; however, invariant εNd values argue against a change in provenance and instead support a decrease in the continental weathering flux, possibly related to eustatic sea-level rise.

INTRODUCTION
The middle–late Cambrian (Miaolingian and Furongian series) was a time of significant paleoenvironmental instability, recorded by extinctions in trilobite species and large-scale perturbations to the oceanic redox state and global carbon cycle (Saltzman et al., 2000, 2011; Gill et al., 2011). Throughout the Cambrian, Baltica, Laurentia, Siberia, and Avalonia drifted away from Gondwana, with ensuing eustatic sea-level changes of at least 100 m despite a warm and stable greenhouse environment with no evidence for sea ice or continental ice sheets, although the abruptness and apparent synchronicity of sea-level change suggest glacioeustasy (Babcock et al., 2015). The onset and termination of the Steptoean positive carbon isotope excursion (SPICE) across the Paibian Stage (ca. 497–494 Ma, lower Furongian) mark one of the largest carbon isotope excursions (CIEs) of the Cambrian. The SPICE has been identified in more than 70 globally distributed sections across multiple paleocontinents with an amplitude of ~+5‰ in δ¹³Corg, although the signal may be time-transgressive and/or facies dependent, and the amplitude in δ¹³Corg is variably dampened (Pulsipher et al., 2021).

The large-scale disruption to carbon and sulfur cycles across the SPICE was coincident with turnover among trilobite biomeres and a proposed increase in atmospheric O2 levels related to enhanced carbon and pyrite burial (Saltzman et al., 2004, 2011). Disturbances to the global ocean uranium, molybdenum, and sulfur cycles and concomitant trilobite extinctions have led to the suggestion that the SPICE was a possible pre-Mesozoic ocean anoxia event (OAE; Gill et al., 2011; Saltzman et al., 2011; Dahl et al., 2014). Although the SPICE shares many features with the canonical OAEs of the Mesozoic (Jenkyns, 2010), some stratigraphic sections lack characteristic sedimentological features, such as distinctive nonbioturbated black shale, during the event (e.g., Egenhoff et al., 2015). The main forcing mechanism of Mesozoic OAEs was increased global temperatures resulting from higher CO2 levels due to increased flux from volcanic or methanogenic sources. Higher temperatures resulted in elevated continental weathering and nutrient fluxes to the oceans under an enhanced hydrological cycle. Mesozoic OAEs have been tied to tectonic drivers such as the emplacement of large igneous provinces (LIPs). Although sea-level change during the late Cambrian may have had a tectonic driver, there is no geologic record or unequivocal geochemical evidence for a LIP coincident with the onset of the SPICE (e.g., Pruss et al., 2019).

Regardless of its classification, the SPICE event represents an interval of remarkable oceanic redox volatility that impacted the evolution of animal life in early Paleozoic oceans (Gill et al., 2011; Dahl et al., 2014, 2019; Gerhardt and Gill, 2016). Much work has focused on documenting the magnitude, fidelity, and dynamics of this disturbance in the ocean-carbonate cycle, and the connection, if any, between faunal turnover rates and redox-sensitive-element cycles. Less is known about the specific mechanism(s) that drove these biogeochemical changes in the late Cambrian. In order to better understand and interrogate the triggers and feedbacks among the carbon cycle, the redox state of the oceans, trilobite biomere turnover, and sea-level changes, radiometric age constraints and time-integrated paleoweathering proxies are required.

Internal boundaries within the Cambrian suffer from a dearth of radioisotopic age constraints, and, in particular, the Furongian Series lacks ages for correlation and establishing rates of evolutionary turnover. We provide a new rhenium-osmium (Re-Os) sedimentary rock age constraint from the Furongian Alum Shale Formation, Sweden, in an effort to strengthen intercontinental correlation schemes and refine the Cambrian time scale. Additionally, we couple
and Gee, 1985). The lower Cambrian of Scania, Sweden, consists primarily of sandstones deposited during a stepwise transgression. The overlying Miaolingian and Furongian series, represented by the Alum Shale Formation, consist of dark-gray to black shale and minor carbonate. The Alum Shale Formation varies in thickness across Baltica from ∼100 m in Scania to <0.1 m in Russia. It is often rich in organic matter (up to 25 wt% total organic carbon [TOC]) with abundant pyrite and generally lacks bioturbation, suggesting deposition under intermittently dysoxic to anoxic conditions in a broad sediment-starved basin (Thoppenny, 1984; Nielsen and Schovsbo, 2006; Egenhoff et al., 2015; Dahl et al., 2019; Nielsen et al., 2020). Although the Alum Shale Formation is richly fossiliferous with agnostoid arthropods and trilobites forming the basis of a detailed biostratigraphy, there are no radiotopic age constraints for this unit.

Materials for this study were taken from the Andrarum-3 drill core from Scania, Sweden (Fig. 1; for core location and geologic setting, see the Supplemental Material). This drill core was completed in 2004 and retrieved >28 m of the Miaolingian and Furongian Alum Shale Formation (Fig. 2; Ahlberg et al., 2009). Extensive sedimentologic, geochemical, and paleontologic investigations divided the core into seven biozones and identified two globally correlated CIEs: the negative Drumian carbon isotope excursion (DICE) and the SPICE (Ahlberg et al., 2009; Egenhoff et al., 2015).

RESULTS

Regression of the Re-Os isotopic data from the Alum Shale Formation yielded a model age of 494.6 ± 2.9 Ma for the peak of the SPICE (n = 7, mean square of weighted deviates [MSWD] = 1.3, initial $^{187}$Os/$^{188}$Os [Os$^i$] = 0.82 ± 0.01; data are reported with 2σ uncertainty, and age uncertainty includes the ±0.31% $^{187}$Re decay constant uncertainty [Smolian et al., 1996]; Fig. 2; Table S1). Samples of the Alum Shale Formation from the Andrarum-3 core are enriched in Re and Os with concentrations ranging from 8 to 105 ng/g and from 467 to 4274 pg/g, respectively (Fig. 3; Table S2). The present-day εNd$^i$ isotopic compositions of Alum Shale Formation samples define a narrow range from −6.5 to −8.4 (Fig. 3; Table S3). Isotopic measurements of Os$^i$ and εNd$^i$ were age-corrected to 495 Ma and plotted against core depth (Fig. 3; see Tables S1, S2, and S3).

Samples for Re-Os geochronology, Os and Nd isotope stratigraphy [Os$^i$ and εNd$^i$, respectively], and major- and trace-element analysis were collected from the Andrarum-3 core based upon suitable material (>20 g) being available for analysis (Fig. 3; Ahlberg et al., 2009).

GLOBAL CORRELATION OF THE SPICE

More than two decades after it was first identified in carbonate strata from the Great Basin, United States, the SPICE has been documented in organic carbon and carbonate carbon records of marine sedimentary rocks worldwide (Brasier, 1993; Saltzman et al., 1998). Our Re-Os age of 494.6 ± 2.9 Ma from the Alum Shale Formation provides the first radioisotopic date for the SPICE, aids in correlating and calibrating biogeographic and biomere extinctions during the early Paleozoic, and can be used to tie the floating astrochronologic time scale of Sørensen et al. (2020). Leveraging this radiometric age and multiple paleoweathering proxy and trace-element data sets, we can now begin to identify and interrogate potential drivers of this interval of biogeochemical upheaval.

PALEOWEATHERING PROXY RECORDS ACROSS THE SPICE

Interpreting Re and Os Concentrations Across the SPICE

Elemental Re and Os concentrations from the Andrarum-3 core can shed light on the...
timings and dynamics of expanding euxinia, because it plays a role in controlling the global inventory of these two elements as well as other redox-sensitive metals. Previous iron speciation work suggested that the Alum basin was locally euxinic before and after the SPICE, with an expansion of euxinic waters during the main event (Gill et al., 2011). In the lead-up to the SPICE, Re and Os concentrations generally declined (Fig. 3; Table S2). The marked decline in Re concentrations across the SPICE may have been related to a shrinking oceanic inventory resulting from the expansion of euxinic sinks, as is the case for Mo (Gill et al., 2021), and/or a reduction in the availability of Fe-Mo-S phases that are thought to regulate Re enrichments in euxinic basins (Helz and Dolor, 2012). During the SPICE, Re and Os concentrations oscillated and then rose rapidly at the end of the SPICE to values more than three times the pre-SPICE levels, as euxinic areas shrank and global inventories of these elements recovered.

Os Isotope Stratigraphy and Continental Weathering Dynamics

The Os isotope composition of the global oceans reflects a balance between two highly distinctive end-member fluxes: radiogenic sources (e.g., hydrothermal flux and mafic weathering) and radiogenic sources (e.g., weathering of continental crust). Os isotope records have been employed to investigate connections between continental weathering dynamics and perturbations to global ocean chemistry and the climate system over a range of geologic time scales (e.g., Turgeon and Creaser, 2008; Rooney et al., 2014; Percival et al., 2016).

The Os isotope composition throughout the Andrarum-3 core overall has a moderately radiogenic composition (median $^{187}$Os/$^{188}$Os = 0.83; Table S1). Adjustment of the age-correction value for a range of sedimentation rates did not substantially alter the Osi values or trends. The isochron Osi value of 0.82 ± 0.01 is comparable to other Osi values for the Cambrian and supports arguments for open-ocean connectivity during Alum Shale Formation deposition (Sturroson et al., 2005; Tripathy et al., 2014). This is a critical assumption for interpreting the evolution of global ocean chemistry during the SPICE using Osi values and the Re and Os concentration data of the Andrarum-3 core (Fig. 3).

The peak of the SPICE in Laurentia has been suggested to have coincided with a sea-level lowstand known as the Sauk II-III boundary (Palmer, 1981; Saltzman et al., 2004). Egenhoff et al. (2015) identified two lowstand intervals in the Andrarum-3 core, and using these two intervals, we evaluated the Osi values in the context of changing continental weathering dynamics. In the lead-up to the SPICE event, as recorded in the Andrarum-3 core, seawater Osi values become increasingly radiogenic (rising from $^{187}$Os/$^{188}$Os = 0.68 to 0.99), matching the trend in $^{13}$C$_{org}$ values and with minimal change in Os concentration (Fig. 3). We interpret this radiogenic Os trajectory to have resulted from an increased flux of continentally sourced material during a global sea-level regression (corresponding to the Sauk II-III boundary lowstand; Fig. 1) rather than a secular decrease in the mantle-osmium input (e.g., increased redox or LIP volcanism), for which there is no independent evidence. In the pre-SPICE interval, a slight decline in common Os ($^{188}$Os) supports the interpretation of an increase in terrigenous-sourced radiogenic Os driving the Osi signal (Fig. 3). This episode of enhanced continental weathering would have increased nutrient supply, elevated primary productivity levels, and ultimately resulted in the transient expansion of euxinic water masses seen during the SPICE (Gill et al., 2011; Dahl et al., 2014).

While other OAEs may have ultimately been driven by LIP emplacement and related forcings, the pre-SPICE radiogenic Os profile does not support LIP-driven enhanced mafic weathering, which would show the opposite trend in Osi values. Our Osi data do not negate the possibility of felsic magmatism, possibly related to the final assembly of Gondwana, as a driver of increased continental weathering (Cawood and Buchan, 2007). Additionally, the lack of change in chemical index of alteration (CIA) values or $\varepsilon$Nd$_{os}$ values (Fig. 3) argues against a change in local provenance driving the pre-SPICE Os trend in the Andrarum-3 core.

Through the main body of the SPICE, the Osi values drop from 0.99 to 0.59 and rise back to 0.92 (Fig. 3). There are multiple and nonexclusive explanations for these oscillating Osi values, including (1) variations in the size of the global Os inventory concomitant with enhanced organic matter and pyrite burial leading to a reduction in the residence time, and/or (2) a reduction in seawater sulfate concentrations resulting in a greater flux of unradiogenic Os reaching seawater from mid-ocean ridges as sulfide mineral formation (the major sink for hydrothermal Os) at the ridges declined (Syverson et al., 2021). Additional globally distributed Osi data are required to evaluate these possibilities and assess their connection to the SPICE.

Post-SPICE, the seawater Osi values consistently trend toward less radiogenic values, reaching a nadir of $^{187}$Os/$^{188}$Os = 0.31 at a location ~3 m up section from the termination of the SPICE. This highly unradiogenic Osi pulse is matched by an increase in common Os, with $^{188}$Os concentrations nearly tripling across the fall in Osi values (Figs. 3C; Table S2). We consider it unlikely that this surge in unradiogenic Os after the SPICE was the result of increased weathering of mafic lithologies, as seen from homogeneous trace-element data (e.g., Th/Sc...
~0.8–1.0; Table S4), and consistent CIA and εNd values (Fig. 3; Table S4). Furthermore, the Osi trend is unlikely to reflect changes in the hydrothermal input on the multimillion-year time scale. Instead, we interpret the decline in Osi values as consistent with an overall reduction in continentally derived material reaching the oceans, possibly related to a combination of Milankovitch-scale climate cycles in the late Cambrian Alum Shale basin and/or transgression (Sørensen et al., 2020).

CONCLUSIONS

Our Re-Os age of 494.6 ± 2.9 Ma for the lower Furongian interval (trilobite Olenus attenuatus Zone) of the Alum Shale Formation provides the first radiometric age constraint for the SPICE, allowing further calibration of correlation schemes for trilobite andagnostoid zones of the Furongian and strengthening global correlations of the SPICE. The Osi data from the Andrumard-3 core identify an interval of increased continentally weathering in the lead-up to the SPICE, which was likely responsible for greater nutrient supply and ultimately the expansion of anoxia and/or euxinia in the global oceans. The Osi profile reveals a marked decline in the flux of radiogenic, continentally sourced material in the aftermath of the SPICE. We consider the trends in Osi values to track changes in the magnitude of the continental weathering flux resulting from the Sauk II-Sauk III regression and transgression across Laurentia. The lack of variation in εNd and trace-element data in the Alum Shale Formation does not provide any support for a volcanic or mafic-weathering driver for the SPICE.

ACKNOWLEDGMENTS

We thank S. Ameenou and D. Skarzynski for laboratory and field assistance. This manuscript was greatly improved after constructive criticism from Ben Gill, David van Acken, Jim Schffbauer, and an anonymous reviewer.

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Printed in USA