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

GEOLOGIC CONTEXT FOR THE ALUM SHALE FORMATION AND SAMPLES FROM THE ANDRARUM-3 CORE

Cambrian sedimentary successions outcrop across Scandinavia and consist predominantly of siliciclastics deposited under shallow to moderately deep marine conditions during much of the early Paleozoic. The upper Cambrian of Scandinavia is entirely hosted within the Alum Shale Formation which consists of dark grey to black organic-rich (>25% TOC) shales with a minor number of thin (<0.15 m) limestone beds (Thickpenny, 1984; Ahlberg et al., 2009). Disseminated and macroscopic (mm-scale) pyrite is abundant throughout the Alum Shale Formation. The absence of sedimentary structures (e.g., ripples) indicative of current reworking is suggestive of deposition below wave base and under sub-oxic to dysoxic conditions supported by the lack of evidence for bioturbation as well as range of redox proxy data (Egenhoff et al., 2015; Gill et al., 2011; Table DR4). Despite these indicators, the Alum Shale basin, was sufficiently oxygenated intermittently to allow benthic life to colonize portions of the basin. Fossils are common on many bedding planes within the Alum Shale Formation and allow for a detailed biostratigraphy (Terfelt et al., 2008; Ahlberg et al., 2009; Rasmussen et al., 2017). Fossiliferous portions of the Alum Shale Formation are host to conodonts, brachiopods, sponge spicules as well as a range of trilobite and phosphatocopine genera including the index fossil *Glyptagnostus reticulatus.*

The Andrarum-3 core, a new drilling that targeted the middle Cambrian of Scania (Skåne), Sweden and was completed in 2004 (55.715486"N, 13.978125"E; Ahlberg et al., 2009; Fig. 1). The Andrarum-3 core reached a total depth of 31.30 m and penetrated the *Parabolina brevispina*

Subzone (Furongian Series) down into the *Ptychagnostus atavus* Zone (Drumian Stage). Samples were taken throughout the core for $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ with the Steptoean Positive Carbon Isotope Excursion (SPICE) and the DrumIan Carbon isotope Excursion (DICE) identified for the first time from Baltica (Ahlberg et al., 2009). The $\delta^{13}C_{org}$ data for the SPICE is presented alongside our geochemical data in Figure 3 and Table DR4. Samples for Re-Os geochronology were taken from 11.00 to 10.28 m of the core and samples for Osi and ϵNd geochemistry were sampled throughout the core with heights provided in Tables DR2 and DR3.

METHODOLOGY

Rhenium-Osmium Geochronology

Individual Re-Os samples weighing 20-30 g were collected for Re-Os geochronology over a 0.72 m vertical interval of the Andrarum-3 core (10.32 to 11.00 m). Any weathered or altered core surfaces were removed using a diamond-coated rock saw and samples were then hand-polished with a diamond-plated polishing pad to remove potential contamination from the saw blade. Samples were dried overnight at room temperature and then crushed to a fine (~70 μm) powder in a SPEX 8500 Shatterbox using a zirconium grinding container and puck in order to homogenize any Re and Os heterogeneity present in the samples.

Re and Os isotopic abundances and compositions were determined at the Yale Geochemistry and Geochronology Center. Between 0.50 and 0.62 g of sample was digested and equilibrated in 8 ml of $Cr^{VI}O_3$-H_2sSO_4 together with a mixed tracer (spike) solution of ^{190}Os and ^{185}Re in carius tubes at 220°C for 48 hours. The $Cr^{VI}O_3$-H_2SO_4 digestion was employed as it has been shown to preferentially liberate hydrogenous Re and Os yielding more accurate and precise age determinations than other dissolution techniques (Selby and Creaser, 2003; Kendall et al., 2004). Rhenium and osmium were extracted and purified using solvent extraction (NaOH,

(CH$_3$)$_2$CO, and CHCl$_3$,), micro-distillation, anion column chromatography methods, and negative mass spectrometry as outlined by Selby and Creaser (2003).

Total procedural blanks during this study were 43.2 ± 2.1 pg and 0.13 ± 0.1 pg for Re and Os respectively, with an average ^{187}Os/^{188}Os value of 0.15 ± 0.01 (1σ, n = 2). Isotopic measurements were performed using a ThermoFisher TRITON PLUS mass spectrometer via static Faraday collection for Re and ion-counting using a secondary electron multiplier in peak-hopping mode for Os (Creaser et al., 1991; Volkening et al., 1991). In-house Re and Os solutions were continuously analyzed during the course of this study to ensure and monitor long-term mass spectrometer reproducibility. The Yale Geochemistry and Geochronology Center Re standard solution measured on the Faraday cups yields an average ^{185}Re/^{187}Re value of 0.598014 ± 0.02 (2σ, n = 3), which is identical to the accepted value (Gramlich et al., 1973). The measured difference in ^{185}Re/^{187}Re values for the Re solution and the accepted ^{185}Re/^{187}Re value (0.5974) (Gramlich et al., 1973) is used to correct the Re sample data. The Os isotope standard solution used at Yale Metal Isotope Center is the Durham Romil Osmium Standard (DROsS; Luguet et al., 2008). Over the past three years on this Triton, the runs yield a ^{187}Os/^{188}Os ratio of 0.16089 ± 0.000173 (2σ, n = 302) that is identical, within uncertainty, to the value reported by other laboratories (e.g., Luguet et al., 2008; Liu and Pearson, 2014). The Os samples were loaded onto 99.995% Pt wire (H-Cross, NJ) in 9 N HBr and covered with a saturated solution of Ba(OH)$_2$ in 0.1 N NaOH as activator and analyzed as oxides of Os. Interference of ^{187}ReO$_3$ on ^{187}OsO$_3$ was corrected by the measured intensity of ^{185}ReO$_3$. Mass fractionation was corrected with ^{192}Os/^{188}Os = 3.0826, using the exponential fractional law.

Uncertainties for ^{187}Re/^{188}Os and ^{187}Os/^{188}Os are determined by error propagation of uncertainties in Re and Os mass spectrometry measurements, blank abundances and isotopic

compositions, spike calibrations, and reproducibility of standard Re and Os isotopic values. The Re-Os isotopic data, 2σ calculated uncertainties for $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$, and the associated error correlation function (rho) are regressed to yield a Re-Os date using Isoplot v. 4.15 with the λ ^{187}Re constant of $1.666 \times 10^{-11}yr^{-1}$ (Ludwig, 1980; Smoliar et al., 1996; Ludwig, 2008).

Major and Trace Element Chemistry

Aliquots of powdered samples used for radiogenic isotope geochemistry were also analyzed for major and trace element chemistry at Activation Laboratories Ltd (Actlabs) in Ancaster, Ontario Canada. Complete digestion of sample powders was preformed using lithium metaborate/tetraborate fusion and then beads were dissolved using nitric acid. Solutions were analyzed using ICP-MS. Precision and accuracy were assessed by replicate analyses of samples and standards, with less than 5% error for major elements (Table DR4). We calculate Chemical index of alteration (CIA) (Table DR4) using the molar proportion of oxides using the formula $[Al_2O_3 / (Al_2O_3 + Na_2O + K_2O + CaO^*)] * 100$ (Nesbitt & Young, 1982) where CaO* denotes the CaO from the silicate mineral fraction and was obtained by excluding the carbonate- and phosphate-associated CaO (McLennan, 1993). CaO was first corrected for phosphate CaO by subtracting moles of P_2O_5. When the phosphate-corrected CaO was greater than the moles of Na_2O we assumed CaO* = Na_2O, and when the phosphate-corrected CaO was less than moles of Na_2O we assumed CaO* = phosphate-corrected CaO.

Chemical index of alteration (CIA) values for the Andrarum-3 Alum shale samples are ~76, similar to that of an average shale (Nesbitt and Young, 1982). Rare earth element (REE) concentrations normalized to chondritic value (Taylor and McLennan, 1985) for both sample sets are comparable to that of the average shale (Fig. DR4; Taylor and McLennan, 1985).

Nd Isotope Geochemistry

Each powdered sample was ignited at ~600 °C for 24 hours to remove volatiles and organic matter. ~25 mg of the resulting powder was weighed into a 10 mL Teflon beaker, spiked with ~85 µl of enriched ^{150}Nd-^{149}Sm tracer, and dissolved with a HF-HNO$_3$ mixture (1:3, 29N HF- 7N HNO$_3$) for five days and then evaporated. The resulting solid was dissolved in aqua regia (3:1, 6N HCl- 7N HNO$_3$) for two days and then evaporated and redissolved in 6N HCl for column chemistry. Geological standards (BHVO-2), as well as total procedural blanks, were digested along with samples.

For each sample of pure Nd and Sm separates were isolated through three-stage gravity and vacuum driven column chromatography based on procedures from Pin et al. (1997) and Yang et al. (2010). In the first set of columns Fe was removed, as it is shown to negatively affect Sm and Nd recovery (Pin et al., 1997), by passing the sample solution through columns filled with 5ml of 200–400 mesh AG1-X8 anion exchange resin. To isolate the light rare earth elements the sample was passed through columns filled with 0.4 ml of Eichrom TRU Resin (50–100 µm). Third, the Sm and Nd fractions were purified by passing the samples through columns filled with 180 µl of Eichrom LN Resin (20-50 µm) under pressure in a vacuum box at 10 Hg. Separates of Nd and Sm were evaporated and redissolved in 4 mL of 0.8N HNO$_3$ to ensure sample voltages between 0.1-10V for each isotope of interest. For the Nd separate of each sample voltages of ^{140}Ce, ^{142}Nd, ^{143}Nd, ^{144}Nd, ^{145}Nd, ^{146}Nd, ^{147}Sm, ^{148}Nd, and ^{150}Nd were measured. Isotopic interference of ^{144}Sm on ^{144}Nd was corrected for assuming a ^{147}Sm/^{144}Sm of 4.83871 and isotopic ratios relative to ^{144}Nd were calculated. Replicate measurements of the Nd isotopic reference JNdi-1 yielded values within error of the value obtained by Tanaka et al. (2000) (average ^{143}Nd/^{144}Nd = 0.512114, n=7). BHVO-2 yielded values slightly higher (0.1 εNd units) than the accepted value (average ^{143}Nd/ ^{144}Nd = 0.512908 ± 0.000037, n=3 compared to 0.512957 ± 0.000010 from Raczek et al. [2003]). On the

Sm separate isotopic ratios $^{147}Sm/^{152}Sm$ and $^{149}Sm/^{152}Sm$ were measured for each sample. For each sample, the $^{147}Sm/^{144}Nd$ ratio and Sm and Nd concentrations were calculated using these measurements along with the sample and spike masses. The $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios and Sm and Nd concentrations combined with the approximate depositional age of the sample (495 Ma) were used in a Goldstein recalculation to calculate the εNd at the time of sedimentation, or initial Nd isotopic composition. In this calculation, the chondritic reference values used are $^{143}Nd/^{144}Nd$ CHUR = 0.512638 and $^{147}Sm/^{144}Nd$ CHUR = 0.1966, and the decay constant for ^{147}Sm to ^{143}Nd was assumed to be 6.54 E^{-12} (Goldstein et al, 1984). The reported Sm and Nd concentrations and $^{147}Sm/^{144}Nd$ ratios have less than 0.5% error, corresponding to an error of less than 0.3 εNd units. Results are shown in table DR4,

εNd Isotope Stratigraphy of the Andrarum-3 core

The Sm/Nd ratios of bulk sedimentary rocks are not fractionated by processes such as weathering or diagenesis and thus the Nd-isotopic composition ($εNd_{(t)}$ for age-corrected samples) of these units can provide insight into the general average composition of source terranes as well as changes in sediment sourcing due to tectonism (e.g., Gleason et al., 2002; Hurowitz and McLennan, 2005). The short marine residence time of Nd (<1 kyr) results in a provenance proxy that can provide a baseline for the local source region of a sedimentary basin. The $εNd_{(t)}$ of the Andrarum-3 core provides a snapshot of local weathering dynamics during deposition of the Alum Shale Formation defining a narrow range from -6.5 to -8.4 as well as largely homogenous t_{DM} of 1.80 Ga suggestive of sourcing from a provenance with a Paleoproterozoic Nd signal (Fig. 3D; Table DR2). This uniformity in $εNd_{(t)}$ values for the Alum shales coupled with invariant CIA values (75-76) is typical for fine-grained sedimentary packages deposited during a transgression in an epicontinental sea (Table DR3). Additionally, the lack of large-scale shifts in either $εNd_{(t)}$ space or trace element

ratios further supports the notion that the decline in Os*i* values post-SPICE is related to an overall decrease in continental weathering, and not related to a shift to weathering mafic lithologies.

DATA REPOSITORY TABLE AND FIGURE CAPTIONS

Table DR 1: Re and Os isotopic composition and element abundance data for Alum Shale isochron 11.00 – 10.32 m.

Table DR 2: Re and Os isotopic composition and elemental abundance data for the Andraum-3 core including Osi values for samples with a running age change based upon sedimentation rates of 5 mm/ka and 10 mm/ka.

Table DR 3: Sm and Nd isotopic composition and elemental abundance data for the Andraum-3 core

Table DR 4: Major and trace element data for Andrarum-3 samples

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