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Zn isotope evidence for immediate resumption of primary productivity after snowball Earth

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Regional geology and sedimentology of the sampled section

The Cueuing (pr. "Shoe-ing"; Zone 54J, E 261336, N 6503361 (AGD84)) Yards section is located on the shallow NE-dipping flank of Wilpena Pound, a hanging syncline representing the highest preserved structural levels of the Cambro-Ordovician Delamerian Orogeny in central Flinders Ranges (see Preiss (2000) for a recent and detailed review of the evolution and stratigraphy of the Adelaide Rift Complex.)

This ~ 100 square kilometer sector including Wilpena Pound and most of Flinders Ranges National Park is the freshest and least metamorphosed area of Adelaidean outcrops (Raub et al., 2007).

As noted in Figure DR1, the frontal fault trace of the Delamerian fold-and-thrust belt lies ~ 25 km to the SE of Cueuing Yards, and organic maturation, sulphide magnetism, and iron oxide and silicate metasomatic paragenetic sequences indicate that burial metamorphic grade increases steadily southward and eastward from there. Similarly, Delamerian fault activity was intense at Parachilna Gorge, ~ 50 km north of Cueuing Yards, and further to the north from Parachilna Gorge, burial and regional contact metamorphic grade increase noticeably. Cleavage is closely-spaced to penetrative in Nuccaleena cap carbonate and overlying Brachina Formation in the Elder Range ~ 10 km to the south, while cleavage is open-spaced to nonexistent at Cueuing Yards. Further to the S of Elder Range, the frontal Flinders Ranges transfer to the west, where Neoproterozoic structures are multiply reactivated, exposing deeper-water facies of Nuccaleena Formation in steeply-dipping, tightly-folded and sometimes overturned sections with abundant evidence of penetrative cleavage, Delamerian fluid flow and carbonate recrystallization, and prehnite-pumpelleyite minimum metamorphic facies for older Neoproterozoic basaltic units.

Although Cueuing Yards, like most fresh sections of Nuccaleena Formation in central Flinders Ranges, probably owes its exposure relief in part to local (within 300 m) neotectonic activation of minor Neoproterozoic fault splays originally associated with local diapiric islands emergent during Marinoan glacial time, it should be considered a near-optimal section of Nuccaleena Formation, as it is thicker than Nuccaleena cap carbonate at the Elatina Creek para-stratotype, although the full stratigraphy of Nuccaleena Formation is better exposed at Elatina Creek. Those two sections appear superior to all others in Flinders Ranges for preserving a relatively expanded section with relevant sedimentary features and fresh exposure both laterally and in cross-section.

The basal contact of Nuccaleena cap at Cueuing Yards is covered beneath fluvial gravel, although underlying Elatina Formation sandstone can be excavated within ~ 50 cm beneath the base of the measured section. Nuccaleena cap dolostone crops out as a ~ 5 -10 m high cliff on the NW (up-section) cutbank of a streambed meander at Cueuing Yards, while uppermost Elatina Formation sandstone forms low, red-weathering subcrop in the meander bend and soil regolith to the south of the Nuccaleena cliff. The slope break between cliff-hillside and low plain is very close to the bottom of our section, so even though we were unable to dig out the basal Nuccaleena cap dolostone contact, we believe our section effectively begins in the basal cap carbonate bed.

Shale partings are episodic throughout all of Cueuing Yards cap carbonate section, although they abruptly become measurable (>mm thickness) at 8.34 m in the section (just above "Nucc 55"). Above this level, red shale remains sub-cm thickness but occupies $\sim 30\%$ of the section, i.e. individual carbonate layers are 2-5 cm thick. It is noteworthy that Zn isotopes remain near continental values (0.30, 0.32) at this level. Red shale mixes to 50% by 9.4 m height; Zn isotopes remain 0.44 for 10-50 cm higher still, even though shale now occupies 80-90% of the section. The first strongly Zn isotopic-enriched carbonate sample, at 10.32 m in the section, is a 2.5 cm-thick bed located 75 cm beneath a laterally-persistent carbonate marker doublet. Above 10.32 m, 1-6 cm-thick carbonates occur every 10-50 cm (non-systematically) until 13.88 m. The final carbonate bed is 3.0 cm thick; no further carbonates were observed in the section.

Two intervals of constructional, cuspate antiformal bedforms are exposed in cross-section at Cueuing Yards. These are commonly considered aggradational giant wave ripples in the literature (Allen and Hoffman, 2005). From 3.30 to 3.50 m of the section, a set of ripples with wavelength ~ 4.0 m and amplitude ~ 15 cm have axial traces trending at true 043. Another wave ripple set occurs between samples Nucc 57 and Nucc 58 near ~ 8.7 m of the section. This ripple climbs ~ 18 cm over ~ 25 cm laterally (axial trend evolves from 001 to 043), with consistent amplitude ~ 1.5 cm. It is a unique occurrence within Flinders Ranges, as it contains at least eight 1-3 mm-scale red shale interbeds which persist over, rather than onlap against, its crest. This ripple was not associated with any microfault. Its small volume displacement appeared compensated laterally within the distributed shale beds.

Silicate vs carbonate weathering

Post-snowball weathering does not only include silicate weathering which delivers Zn characterised by the mantle signature (0.2-0.3 %) but also weathering of carbonates on exposed continental shelves (Higgins and Schrag, 2003). There is very little available Zn isotope data on ancient carbonates, but the available data (Pichat et al., 2003; Chen et al., 2008) and the fact that most carbonates form in the surface ocean, which should be enriched in ⁶⁶Zn, suggest that carbonates on average should have δ^{66} Zn compositions that are higher than average continental crust. Based on a compilation of our own Zn concentrations on Neoproterozoic carbonates (n=306), the average concentration of Zn in the carbonates that would have been preferentially weathered during the early deglaciation is 17 ppm. This is about three times lower than average Zn concentration of the continental crust, which is about 50 ppm based on a compilation of data from loess deposits (Tayler et al., 1983). Furthermore, it seems unlikely that a large amount of carbonate was exposed in or around the siliciclastic-dominated Adelaide Rift Complex (Preiss, 2000) during deglaciation. The Elatina glacial deposits contain no carbonate in the central Flinders Ranges (Raub et al., 2007) and the surrounding basement is dominated by Archean to Mesoproterozoic crystalline rocks (Coats and Blisset, 1971; Teale, 1993; Gibson and Nutman, 2004; Hand et al., 2007). Had carbonate-derived Zn been an important source of Zn in the deglacial weathering flux, we expect a near constant, somewhat enriched δ^{66} Zn signal. Consequently, we do not regard the



Figure DR 1: (A) Simplified geological map of the central and northern Flinders Ranges in South Australia showing the location of the sampled section "Cueuing Yards" and the Enorama Creek GSSP. (B) Schematic NW–SE stratigraphic cross-section of the Neoproterozoic strata in the Adelaide Rift Complex. Basal Ediacaran Nuccaleena cap dolostone drapes Marinoan glacial deposits (modified from Rose and Maloof (2010)).

flux of Zn from carbonates as having strongly influenced the isotopic composition of the overall weathering flux of Zn off of the continents.

Additional data and methods

Carbon and oxygen isotopes

Cap dolostone samples were collected while measuring the stratigraphic section "Cueuing Yards" just north of the Moralana track in South Australia. Fresh dolostones with little secondary veining, siliciclastic components, or cleavage were targeted. All samples were cut perpendicular to lamination in order to clarify internal textures. Approximately 5 mg of powder were micro-drilled from individual laminations, with an eye to avoid incorporation of material from fractures, veins, siliciclastic components, or weathered parts.

 δ^{13} C and δ^{18} O isotopic data were measured simultaneously on a Fisons Optima dual inlet gas source isotope ratio mass spectrometer attached to a Fisons Isocarb carbonate preparation device in the Stable Isotope Lab, Department of Geology and Geophysics, University of Adelaide, Australia. Approximately 1 mg micro-drilled carbonate powder was reacted in a common, purified H₃PO₄ bath at ~ 90°C. Evolved CO₂ was purified and collected cryogenically and analyzed against an in-house reference gas. The external error (1 σ) from repeat analysis of standards was better than ± 0.1 ‰ for both δ^{13} C and δ^{18} O. Carbon and oxygen isotope data reported relative to PDB. Memory effect associated with the common acid bath system was minimized by increasing the reaction time for dolomite samples and monitoring of standards between sample runs. Memory effect is estimated at ≤ 0.1 ‰ based on variability of standards.

Zinc isotopes

Splits of the powders were used for Zn isotope measurements.

Several authors have developed and applied methods for Zn isotope analyses of natural samples such as silicates, ores, biological materials (Maréchal et al., 1999); suspended particulate matter and sediments (Petit et al., 2008); ferromanganese nodules, sediment trap samples, sediments, organic samples (Maréchal et al., 2000); and carbonates (Pichat et al., 2003). The latter is a selective dissolution procedure for the carbonate fraction and has been applied in this study with minor modifications.

A $\sim 3 \,\mathrm{mm}$ thick slab from the same samples used for carbon and oxygen isotope analyses were trimmed to remove all weathered and other visibly altered surfaces to yield a 100 % fresh sample. After the cutting-step, no metal tools were used during the remaining sample preparation procedure in order to minimize Zn contamination. The dried samples were hand-crushed in an agate mortar, which was cleaned with ethanol between each sample. The remaining steps were performed in a clean lab. All acids were double distilled. In order to remove hydrosoluble salts and fine clay grains, 100–250 mg of sample powder was agitated and ultrasonicated with 2 mL Milli-Q water $(18.2 \,\mathrm{M\Omega\,cm})$ for 5 min. The supernatant was removed after 5 min of centrifugation. This procedure was repeated three times, twice with Milli-Q water and once with ethanol in between. Carbonates were then selectively dissolved by leaching in 2.5 mL of 1.5 M super-pure acetic acid (Zn blank < 50 ppt) in a closed Teflon perfluoroalkoxy (PFA) beaker for 7 h on a hotplate at 65°C. The supernatant was used for Zn isotopic analyses. To ensure the total dissolution of carbonate in the residual solid, 2 mL of 1.5 M acetic acid was added and the sample spent 4 more hours in a closed PFA beaker on a hotplate at 65°C. If CO₂ bubbles evolved after mechanical shaking, the supernatant was kept and the procedure was repeated a third time. Previous studies have shown that mild selective leaching procedures with acetic acid do not attack the crystal lattice of clay minerals and secondary oxides (Pichat et al., 2003; Frost et al., 2007; von Blankenburg et al., 2008). The supernatants were combined and evaporated to dryness at 65°C under a laminar-flow hood. Samples were recovered in 2.5 mL of 7 M HCl, evaporated again and finally dissolved in 1 mL 7 M HCl. Half of the solution was retained and the other half was passed through previously calibrated Biorad anion-exchange chromatography containing AG-MP 1 resin and Zn separated following established procedures (Maréchal et al., 1999).

Samples were analyzed on a ThermoFinnigan NeptuneTM high-resolution MC-ICP-MS at the University of Adelaide, Australia. The sample solutions were introduced with a low-flow 50 μ l/min PFA nebulizer attached to a quartz-glass spray chamber and a Scott Double-Pass assembly. Samples were run in 2% double distilled HNO₃ to eliminate the possibility of generating Cl molecular species that may interfere with the mass spectrum of Zn (Maréchal et al., 1999). Zn blank of the nitric acid was <1.5 ppb. The concentration of Zn in the sample solution was always 300 ppb to ensure comparable matrix effects. The measurements were performed in static mode (no amplifier rotation), however, prior to each analytical run, a gain calibration was performed to correct for possible amplifier bias. The following isotopes were measured on the respective Faraday cups: L3: ⁶²Ni, L2: ⁶³Cu, L1: ⁶⁴Zn, C: ⁶⁵Cu, H1: ⁶⁶Zn, H2: ⁶⁷Zn, H3: ⁶⁸Zn.⁶²Ni was measured in order to subtract any interference of ⁶⁴Ni on the ⁶⁴Zn beam.

The effects of internal mass fractionation were corrected by using a combination of samplestandard-sample bracketing and addition of a Cu spike. The machine's fractionation factor for Cu is

$$\beta^{Cu} = \frac{ln\left(\frac{\left(\frac{M^{65}Cu}{M^{63}Cu}\right)}{\left(\frac{65}{G_{Cu}}\right)_{m}}\right)}{ln\left(\frac{M^{65}Cu}{M^{63}Cu}\right)}$$
(1)

with M representing the isotope's mass and m the measured isotopic ratio. Applying the instrumental exponential mass bias law, the raw Zn isotope ratios were corrected following the equation

$$\left(\frac{^{66}\mathrm{Z}n}{^{64}\mathrm{Z}n}\right)_{t} = \left(\frac{^{66}\mathrm{Z}n}{^{64}\mathrm{Z}n}\right)_{m} \times \left(\frac{M^{66}\mathrm{Z}n}{M^{64}\mathrm{Z}n}\right)^{\beta^{Zn}}$$
(2)

where t is the true isotopic ratio. Assuming $\beta^{Zn} \approx \beta^{Cu}$, the equation can be reformulated as

$$\left(\frac{{}^{66}\text{Z}n}{{}^{64}\text{Z}n}\right)_{t} = \left(\frac{{}^{66}\text{Z}n}{{}^{64}\text{Z}n}\right)_{m} \times \left(\frac{M^{66}\text{Z}n}{M^{64}\text{Z}n}\right)^{-\frac{\ln\left(\frac{M^{65}\text{C}u}{M^{63}\text{C}u}\right)}{\ln\left(\frac{M^{65}\text{C}u}{M^{63}\text{C}u}\right)}}$$
(3)

Prior to the measurement of each solution, the background was measured for a background subtraction. Each sample analysis consisted of 45 cycles of 4.194 s. The beam size for 64 Zn for the 300 ppb solution was 2 V and kept within 10% of the bracketing standard beam in order to minimize variations in internal mass fractionation between standard and sample runs. The results are reported using the standard delta per mil notation with respect to the JMC-Lyon standard.

$$\delta^{66} Zn = \left[\frac{({}^{66} Zn / {}^{64} Zn)_{sample}}{({}^{66} Zn / {}^{64} Zn)_{JMC}} - 1 \right] \times 1000$$
(4)

An in house Zn standard was run multiple times at the onset of each analytical run and periodically throughout the runs to ensure normal operation of the instrument and accuracy of the procedure.

Where sufficient solution permitted, samples were run at least twice to establish reproducibility. The student's t-test was applied in calculation of 95% confidence interval:

Student's
$$T = 2\sigma = \frac{multiplier \times standard \ deviation}{\sqrt{n}}$$
 (5)

The multiplier depends on the number of repetitions (n) and the chosen confidence interval $(95\%, 2\sigma)$.

Assuming there were no interferences on the Zn beams, variations in the different Zn isotopic ratios should follow the mass-dependent fractionation law (Maréchal et al., 1999) (Fig. DR2), which takes into account the relative difference between the masses of the considered isotopes, in this case ${}^{68}\text{Zn}/{}^{64}\text{Zn}$ and ${}^{66}\text{Zn}/{}^{64}\text{Zn}$:

Theoretical slope =
$$\frac{\ln\left(\frac{M^{68}Zn}{M^{64}Zn}\right)}{\ln\left(\frac{M^{66}Zn}{M^{64}Zn}\right)} = 1.9711$$
(6)



Figure DR 2: Plot of Cu-uncorrected $\ln^{66}Zn/^{64}Zn - \ln^{68}Zn/^{64}Zn$, showing the linear mass-dependent fractionation trend. The slope is slightly steeper than the calculated theoretical slope.

Zinc concentration analyses

Approximately 20 to 50 mg sample material were digested with 0.25 ml 1:1 HCl for 30 min at room temperature. 1.25 ml nanopure water was added and the samples were left undisturbed overnight. The supernatant was carefully separated from the residue in the morning and analyzed.

Analyses were performed on a Perkin Elmer Analyst100 atomic absorption spectrometer with acetylene flame at the Department of Earth & Planetary Sciences, McGill University, Montreal, Canada.

Isotopic data and Zn concentration

A summary of the isotopic results and Zn concentration analyses with corresponding stratigraphic height is listed in Table DR1. Table DR2 lists the δ^{66} Zn values of measured insoluble residues. δ^{13} C- δ^{18} O, δ^{13} C- δ^{66} Zn, δ^{18} O- δ^{66} Zn, and δ^{66} Zn-Zn concentration cross-plots are shown in Figures DR3, DR4, DR5, and DR6.

Sample	Stratigraphic Height [†]	$\delta^{66} Zn$	n	2σ	$\delta^{13}C$	$\delta^{18}O$	Zn
	m	% (JMC)			% (VPDB)	% (VPDB)	ppm
Nucc 01	0	0.47	2	0.02	-0.8	-5.2	56.5
Nucc 02	0.0075	0.42	2	0.03	-1.4	-6.3	50.1
Nucc 03	0.1225	0.36	2	0.03	-1.6	-6.4	58.6
Nucc 04	0.2375				-1.6	-6.7	
Nucc 05	0.3325				-1.8	-6.9	
Nucc 06	0.4550	0.36	2	0.01	-1.8	-6.7	45.6
Nucc 07	0.5375	0.41	2	0.00	-1.8	-6.7	39.6
Nucc 08	0.6585				-1.9	-6.4	
Nucc 09	0.7420				-1.9	-7.0	
Nucc 10	0.8435	0.40	2	0.03	-1.8	-6.8	45.8
Nucc 11	0.9375	0.39	2	0.02	-1.8	-6.9	46.0
Nucc 12	1.0600				-1.9	-7.2	
Nucc 13	1.1680				-1.7	-6.6	
Nucc 14	1.2860	0.49	2	0.04	-1.8	-6.8	46.9
Nucc 15	1.3485	0.34	2	0.02	-2.0	-6.9	56.1
Nucc 16	1.5360				-1.9	-7.1	
Nucc 17	1.7110	0.37	1		-1.9	-6.6	28.0
Nucc 18	1.8875	0.23	2	0.02	-1.9	-6.5	34.2
Nucc 19	2.0415				-1.9	-7.0	
Nucc 20	2.0940				-1.7	-5.9	
Nucc 21	2.2840	0.46	1				11.4
Nucc 22	2.4290	0.25	2	0.05	-2.6	-6.5	22.1
Nucc 23	2.5540				-2.4	-6.5	
Nucc 24	2.6540				-2.3	-7.1	
Nucc 25	2.8690				-2.2	-6.9	
Nucc 26	2.9690	0.22	2	0.01	-2.3	-6.8	29.8
Nucc 27	3.1190	0.27	2	0.02	-2.2	-6.6	28.9
Nucc 28	3.2340						21.8
Nucc 29	3.3690				-2.3	-6.8	
Nucc 30	3.4490				-2.3	-7.0	
Nucc 31	3.6190				-2.5	-6.9	
Nucc 32	3.7690	0.19	2	0.06	-2.4	-6.9	26.9
Nucc 33	3.8740	0.24	2	0.02	-2.33	-6.5	26.8
Nucc 34	4.0690	0.18	1		-2.2	-7.0	24.4

Table DR 1: Isotopic and Zn concentration data for 73 samples of the Nuccaleena cap dolostone measured from the section "Cueuing Yards".

Sample	Stratigraphic Height ^{\dagger}	δ^{66} Zn	n	2σ	$\delta^{13}C$	$\delta^{18}O$	Zn
	m	‰ (JMC)			% (VPDB)	% (VPDB)	ppm
Nucc 35	4.2140				-2.2	-7.3	
Nucc 36	4.3490				-2.2	-7.2	
Nucc 37	4.4890				-2.1	-7.4	
Nucc 38	4.7940				-2.1	-7.5	
Nucc 39	4.9440				-2.1	-7.4	
Nucc 40	5.0790				-2.1	-7.5	
Nucc 41	5.1990				-2.1	-7.6	
Nucc 42	5.4140	0.25	1				39.2
Nucc 43	5.5915	0.07	2	0.17	-2.0	-7.2	44.7
Nucc 44	5.8440				-2.1	-7.6	
Nucc 45	6.1140				-2.1	-7.6	
Nucc 46	6.3790				-2.2	-7.4	
Nucc 47	6.5440	0.33	2	0.02	-2.1	-7.2	
Nucc 48	6.6540				-2.1	-7.2	
Nucc 49	6.9090	0.17	2	0.10	-2.2	-7.3	41.3
Nucc 50	7.1640				-2.2	-7.3	
Nucc 51	7.3990	0.23	1		-2.3	-7.5	37.3
Nucc 52	7.5790	0.25	2	0.04	-2.2	-6.9	39.9
Nucc 53	7.8740	0.04	2	0.04	-2.2	-7.3	41.6
Nucc 54	8.1340				-2.2	-7.3	
Nucc 55	8.3340	0.30	2	0.03	-2.8	-7.0	44.9
Nucc 56	8.4490				-2.6	-7.3	
Nucc 57	8.6040	0.32	1		-2.7	-7.8	44.5
Nucc 58	8.8190				-3.0	-7.5	
Nucc 59	9.0540				-3.2	-5.9	
Nucc 60	9.2340				-2.9	-7.1	
Nucc 61	9.3990				-2.9	-7.2	
Nucc 62	9.5540	0.45	2	0.05	-3.1	-7.1	41.4
Nucc 63	9,8790	0.42	2	0.00	-3.2	-6.6	38.9
Nucc 64	9.9240				-3.8	-6.6	
Nucc 65	10.3190	0.83	2	0.07	-3.8	-6.1	54.4
Nucc 66	12.1965	0.87	1		-4.0	-5.9	77.5
Nucc 67	12.3065	0.83	2	0.00	-3.8	-5.9	103.6
Nucc 68	12.7890	0.83	2	0.08	-4.0	-6.2	55.6
Nucc 69	13.0040	0.68	2	0.01	-4.1	-6.2	54.8

Table DR 1: (continued)

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Sample	Stratigraphic Height [†]	$\delta^{66} Zn$	n	2σ	$\delta^{13}C$	$\delta^{18}O$	Zn
	m	% (JMC)			% (VPDB)	% (VPDB)	ppm
Nucc 70	13.1590				-4.0	-5.9	
Nucc 71	13.4640				-4.1	-6.1	
Nucc 72	13.5990	0.82	2	0.21	-4.0	-6.1	61.1
Nucc 73	13.8840				-4.2	-5.9	

 † The 0 m datum is the base of the outcrop, here assumed to be the base of the Nuccaleena cap dolostone.

Table DR 2: δ^{66} Zn data for insoluble residues.							
Sample	Stratigraphic Height	$\delta^{66} \mathrm{Zn}$	n				
	m	% (JMC)					
Nucc 01-Ins	0	0.16	1				
Nucc 32-Ins	3.7690	0.13	1				
Nucc 71-Ins	13.4640	0.42	1				

The $\delta^{13}C-\delta^{18}O$ cross-plot (Fig. DR 3) does not show the characteristic trend of meteoric diagenesis (Allan and Matthews, 1982), nor any other systematic co-variation, suggesting the conservation of primary signals. Nor do other cross-plots show strong correlations or systematic variations.



Figure DR 3: $\delta^{13}C-\delta^{18}O$ cross-plot. The lack of any correlation or trend is inconsistent with coupled alteration by meteoric fluids and suggests preservation at least of the primary sea water carbon isotope signal.



Figure DR 4: δ^{13} C- δ^{66} Zn cross-plot. The diagram shows a dual pattern of positively negatively correlated data points that intersect at low δ^{66} Zn values. This relationship is also seen in Fig. 2 in the paper. Whereas the rise in Zn isotope values record a vigorous increase of primary productivity in the surface ocean, the δ^{13} C values were controlled by transfer of atmospheric, ¹³C-depleted CO₂ to the ocean (Hoffman et al., 1998) and high alkalinity fluxes into the ocean due to continental weathering. Therefore, the δ^{13} C record was immune to the effect of the biological pump at this stage of cap dolostone deposition (Hoffman and Schrag, 1999). Generally, carbon isotope behaviour during cap dolostone deposition would have been controlled by the consequences of the enormous high atmospheric pCO₂ during the post-glacial supergreenhouse climate (Caldeira and Kasting, 1992; Bao et al., 2008) rather than by primary productivity. Because carbon isotopes in cap dolostones are particularly immune to diagenetic overprinting, the preservation of the coupled positive and negative correlations between δ^{13} C and δ^{66} Zn argue strongly in favor of a primary signature in the Zn isotope data.



Figure DR 6: δ^{66} Zn–Zn cross-plot. The absence of a negative correlation suggests that contamination (a potential problem with Zn due to high environmental Zn levels) cannot account for the variability in Zn isotope ratios.

Major element data and discussion of abiological Zn isotope fractionation

Major element data were acquired on a Panalytical Axios Advanced wavelength dispersive XRF at Actlabs, Canada. The fusion disks were made by mixing the sample powder with lithium metaborate and lithium tetraborate and with lithium bromide as a releasing agent. Results are shown in Tab. DR 3, cross plots versus δ^{66} Zn are shown in Figs. DR 7 and DR 8.

Zn mainly occurs as free Zn, Zn chloride or Zn hydroxide in seawater (e.g. Stanley and Byrne, 1990), which do not fractionate Zn isotopes. However, recent studies suggest Zn isotope fractionation, if Zn occurs in colloidal form, namely as sulfate, carbonate and phosphate (Black et al., 2011; Fujii et al., 2011; Fujii and Albarède, 2012). Our major element data show that Zn isotope ratios do not correlate with P, Al, Fe, Mn, Si, Mg, Na, K, Ca, Cr, and V oxide concentration. Had colloidal Zn that co-precipitated with oxide minerals or that was otherwise incorporated into sediments played a quantitatively significant role in modulating surface water Zn isotope ratios, we would expect to see a clear correlation. Two more arguments speak against this abiological driver of the observed Zn isotope signals. First, we would expect generally enriched Zn isotope values if Zn was bound in colloidal form, not a systematic trend toward lower and than higher isotope ratios. If Zn occurred in colloidal form, this would require a systematic change in the way Zn occurred in the post-glacial ocean, we do not see a process that could cause this. Second, if isotopically fractionated Zn was removed from the ocean by a non-biological mechanisms (other than in carbonates), for example in FeMn oxides or fine clay particles, we should see isotopic evidence of this process in the insoluble residue fraction of our carbonates. However, our insoluble residue data are indistinguishable from values previously reported for siliciclastic sediments and the continental crust. We conclude that the heavy Zn isotope values cannot be explained with fractionation associated with Zn occurrence in colloidal form. Therefore, only biological fractionation can cause the observable high values and we retain our model that the upward positive Zn isotope trends reflects a highly productive post-glacial ocean.



Figure DR 7: Cross plots of $\delta^{66} \rm Zn$ versus $\rm Al_2O_3,\,Fe_2O_3,\,P_2O_5,\,MnO,\,MgO,$ and CaO.



Figure DR 8: Cross plots of $\delta^{66} Zn$ versus SiO_2, Na_2O, K_2O, and TiO_2.

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