Zn and C Isotopic Variations Associated with Neoproterozoic Ice Ages.
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Abstract: The "Snowball Earth" events of the Cryogenian period (850-635 Ma) are renowned for their chemical and isotopic signatures in the geological record[1,2]. Glacial deposits from tropical paleolatitudes are found in multiple locations around the world and provide strong evidence for episodes when Earth's surface was covered in ice[3]. These glaciations are thought to be responsible for periods of rapid evolution as evidenced by increased organism complexity post glaciation, including the Cambrian explosion[1]. In particular the Marinoan glaciation, the final event of the Cryogenian before the Ediacaran, precedes the appearance of the first metazoan, large shifts in the biogeochemical carbon cycle, and rise in atmospheric oxygen[4]. The glaciations, as a result of changes in CO_2, are a superb example of extreme climate events, and can provide insight to other planets. By correlating alternate elements (such as Zn) with the trends found in these samples for other elements (e.g. C), we gain a new tool for understanding the processes which drive other worlds.

The Snowball Earth model explains glacial deposits which, through paleomagnetic analysis, are found to have formed within ten degrees of latitude[4]. Glaciation was thus postulated to have extended from the poles to the equator, and further identifications of these deposits were undertaken[4]. Sediments from these deposits were found to contain dropstones, glacial striations, and varves[3]. Further corroboration of the Snowball Earth effect was made through C isotope measurements. A decrease in $^{13}C/^{12}C$ ratios between pre and post snowball depositions indicates events which killed off the majority of the photosynthetic oceanic life in the neoproterozoic[2]. The appearances of Banded Iron Formations, indicative of an anoxic environment, further suggest massive glaciation[1].

Deglaciation occurs through buildup of CO_2, which in turn leads to a rapid return to a greenhouse environment. A variant theory, the "slushball Earth,"[3] holds that the world would not have entirely frozen and that bands of the equatorial ocean would have remained unglaciated. The duration of the Snowball Earth in either case is 17 million years (±13 My) based on the assumption of a CO_2 outgassing from volcanism, a dimmer sun, and reduced pelagic deposition of carbonates[5].

Zn shows little to no fractionation in most terrestrial rock samples[5]. Zn fractionation is primarily a function of biological processes, creation of carbonates, or formation of sedimentary sulfides[7]. However, changing redox states in the ocean will affect the biological pool of Zn and indirectly affect Zn isotopic composition during carbonate burial[7,8]. Living organisms seem to preferentially utilize and uptake light isotopes of Zn[9].

Samples and methods:

We perform multi-isotopic analysis of boundary layer samples dated to the Marinoan glaciations event from the Fransfontain, Naraachamspos, Entrance South Valley, and the Khowarib Valley of Namibia for Zn isotopic composition.

We dissolve the carbonate fraction in 1.5 M acetic acid, and then centrifuge to separate the solid from the dissolve carbonate. Zn is then purified by anion-exchange chomatography following the protocol described in [10].

The isotopic composition was measured on a Multicollector-Inductively Coupled Plasma Mass Spectometer (MC-ICPMS) Thermo-Fisher Neptune Plus at Washington University in St Louis.

C and O data is analyzed at the Thiemens laboratory at UCSD, using a Thermo-Finnigan MAT 253 isotope ratio mass spectrometer. Sample preparation is done through acidification and degassing, followed by vacuum extraction and purification system. The $\delta^{13}C$ of isolated calcite and dolomite were measured.

Results:

Most Marinoan carbonates have a homogeneous Zn isotopic composition, typical of the terrestrial value ($\delta^{66}Zn=0.3\pm0.1$). However several sites are enriched in heavy isotopes, up to 0.6‰ (in $\delta^{66}Zn$) in the Khowarib Valley and up to 0.7‰ in the clays at the entrance to the south Valley. These enrichments correlate in inverse to the characteristic C excursion (See Figure 1).

A moderate depletion of $\delta^{13}C$ in calcite ($\delta^{13}C$ <0 V-PDB) has been observed, confirming the event. Associated dolomites also show a $\delta^{13}C$ depletion, however in some places the concentrations were too low to measure. The dolomites generally track with the calcites (Figure 2), however in some places the negative C excursion is not matched by the dolomites, indicative of potential alteration or a difference in depositional times between the two. Measurements of O in turn tells us that these were not the result of post deposition alteration.

Discussion

The post glaciation event would contribute large amounts of cations to the ocean such as Ca, Mg, and Zn. These provide nutrients for any organisms, allowing large amounts of life to flourish. Furtheremore, as neither the weathering or precipitation would fractionate Zn the observed fractionation must be biological in nature. Comparisons of the Zn and C directly (figure 1) show the increase in heavy Zn to correlate with the C depletion.

The correlation of Zn with biological fractionation thus shows promise, and can be used as a proxy for biological life in places where life has long been absent.

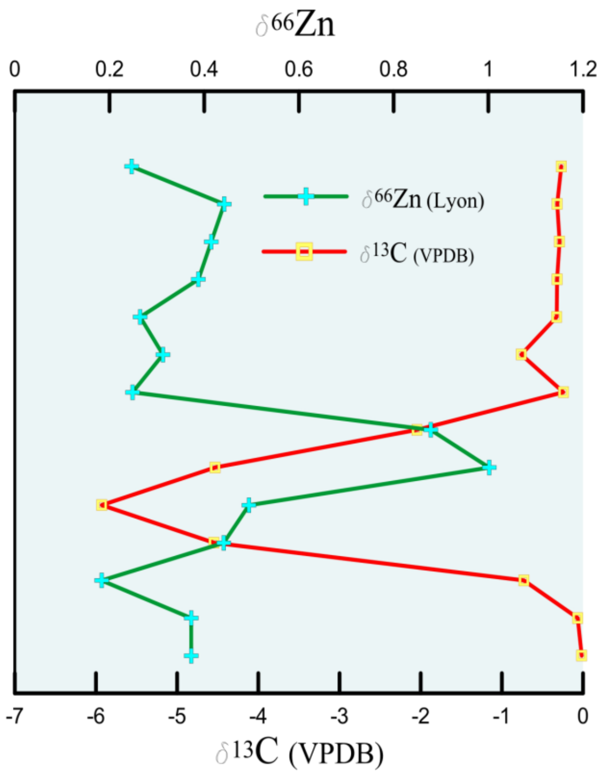

Figure 1: Comparison between C and Zn. Note that standard terrestrial values for Zn lie between 0.2 and 0.4

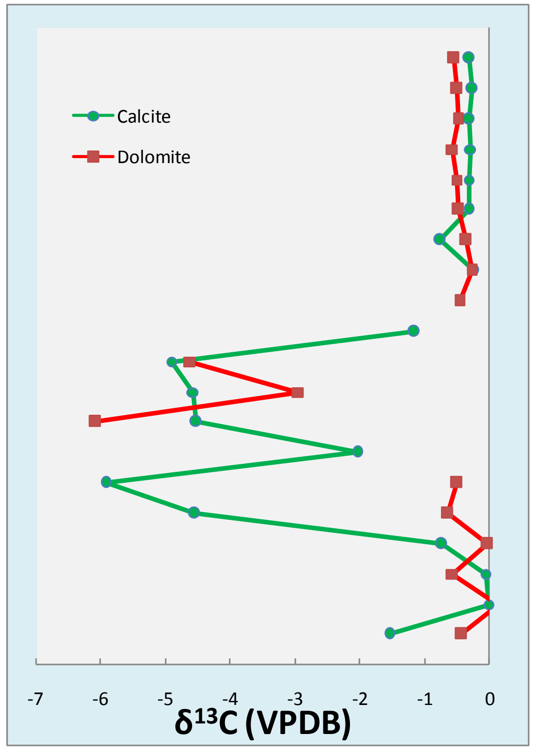

Figure 2: Correlative trend between Calcite (green) and Dolomite (red) in the strata. Missing points are where concentrations were too low to measure.

References: [1] Fairchild, I.J. and M.J. Kennedy (2007) Journal of the Geological Society, 164, 895-921. [2] Rothman, D.H et al. (2003) PNAS, 100(14), 8124-8129. [3] Kirschvink, J.L. (1992) *The Proterozoic Biosphere*, 51-52. [4] Hoffman, P.F., et al (1998) Science 281, 1342-46. [5] Bodiselitsch, B., et al. (2005) Science, 308(5719), 239-242 [6] Fike, D.A. and J.P. Grotzinger, (2008) Geochimica Et Cosmochimica Acta, 72(11), 2636-2648 [7] Fike, D.A., et al., (2006), 444(7120), 744-747 [8] Moynier, F., Fike,D. and Pichat,S (2009) Geochimica Et Cosmochimica Acta, 73(13), p. A910-A910. [9] John, S.G. et al (2007) Chemical Geology, 245(1-2): 61-69, [10] Moynier, F. et al (2006) Geochimica et Cosmochimica Acta, 70, 4287-4294.