



Zn isotope composition of Neoproterozoic cap dolostones from South Australia: Evidence for the resumption of primary productivity after Snowball Earth?

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Zinc is an essential micronutrient that is taken up in the surface ocean by primary producers and exported to the deep ocean via remineralization. It is also incorporated in carbonate minerals in trace quantities and with apparently no measurable isotopic fractionation (Pichat et al., 2003). Because assimilatory uptake of Zn appears to fractionation its isotopes, the biological pump generates a surface-to-deep isotope gradient (Maréchal et al., 2000) akin to that of the $\delta^{13}\text{C}$ composition of dissolved inorganic carbon, such that Zn isotope ratios measured in carbonate precipitated in the surface ocean should track variations in primary productivity (Maréchal et al., 2000; Pichat et al., 2003). Little work has been done to date to exploit this novel proxy, but the work of Pichat et al. (2003) has demonstrated a promising correlation between oxygen and zinc isotopes in deep sea carbonates spanning the past six marine oxygen isotope stages.

Carbonates that directly overlie glacial deposits of the ca. 635 Ma Marinoan glaciation, the best candidate for a Neoproterozoic "Snowball Earth", offer a unique opportunity to test the application of the Zn isotope proxy to reconstructing ancient ocean conditions. Glaciogenic strata were globally superseded by a *cap dolostone* which represents the basal, transgressive portion of the post-glacial depositional sequence and is characterized by a suite of unique geochemical and sedimentological features. Importantly, the cap dolostone in most locations bears evidence of very early if not primary dolomitization, making it relatively robust against subsequent diagenetic alteration and an important archive for the unusual environmental conditions that prevailed after the snowball glaciation. We have measured and sampled, at high resolution, an exceptionally well-preserved, ≈ 14 m-thick section of the Nucaleena Formation (10 m), the cap dolostone associated with the Marinoan age Elatina glaciation in the Adelaide Rift Complex of South Australia and of the lowermost part of the following Brachina Formation (4 m).

C and O isotopic profiles and the sedimentology of our section are homologous to other well-characterized Marinoan cap dolostones. The $\delta^{66}\text{Zn}$ data ($^{66}\text{Zn}/^{64}\text{Zn}$) profile of the carbonate fraction (acetic acid leach) of the cap dolostone display a systematic trend. $\delta^{66}\text{Zn}$ (‰ versus JMC-Lyon) begins with 0.47‰ and decrease to a nadir of 0.07‰ near the middle of the dolostone. Zn isotope data then rises in the upper half of the profile to a maximum of 0.87‰ at the top of the section. In contrast, selected insoluble residues yield values similar to average continental crust (≈ 0.25 ‰).

This profile cannot be easily explained in terms of analytical artefacts (i.e. spectral interferences) or diagenetic re-equilibration, and thus we argue that it records the evolution of the Zn isotope composition of the surface ocean during the post-glacial sea level rise. We interpret the decline in $\delta^{66}\text{Zn}$ data in the bottom half of the cap dolostone to record input of Zn to the surface ocean by intense surface runoff from the continents due to post-snowball supergreenhouse conditions. The subsequent rise in $\delta^{66}\text{Zn}$ data is then interpreted to record the effect of the biological pump, and the export of isotopically light Zn to the deep ocean. Given that intense physical and chemical weathering of the continents would have continued long past deposition of the cap dolostone (Le Hir et

al., 2009), delivering relatively ^{66}Zn -depleted zinc to the surface ocean, the sharp rise in $\delta^{66}\text{Zn}$ data is testament to a vigorous photosynthetic biota in the aftermath of the snowball glaciation.

References

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