

Variations of zinc isotopes in post-Marinoan cap dolostones explained by changes in the early Ediacaran seawater pH

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The Cryogenian-Ediacaran limit marks the sudden transition from a Snowball Earth to a greenhouse Earth, with characteristic cap dolostones directly overlying glacial diamictites from the Marinoan Glaciation. These cap dolostones are the basal members of cap carbonates and are an outstanding stratigraphic window into the immediate post-glacial conditions. The zinc isotope record of cap dolostones appears to be a global signature, with $\delta^{66}\text{Zn}$ values presenting a pronounced decrease, usually from ca. 0.6 to ca. 0.1 ‰, although the magnitude of this decrease varies among sections. Several interpretations have been formulated to explain this Zn isotope pattern, including changes in bioproductivity, diagenetic alteration, effects of global carbonate deposition, and changes in Zn sinks. In this study, we present $\delta^{66}\text{Zn}$ values from the post-Marinoan Morraria do Sul cap dolostone, Brazil. Our results align with the global early Ediacaran zinc record, with a drop from 0.59 to 0.13 ‰ upwards in the 50 m-thick cap dolostone section. Furthermore, we have estimated the seawater pH throughout the section using a recently published rare earth elements (REE)-based pH reconstruction model, which indicates a rise upwards in pH, from ca. 7.6 to 8.2. The correlation with the REE-reconstructed pH and zinc isotopes match strikingly well with the pH-dependent curve of fluid-calcite Zn fractionation ($\Delta^{66}\text{Zn}_{\text{fluid-calcite}}$) obtained through laboratory analyses. This correlation shows that $\Delta^{66}\text{Zn}_{\text{fluid-calcite}}$ clearly decreases with increasing pH within the interval from 6 to 9. Therefore, our data suggests that variations in surface seawater pH were the primary driver of the globally recorded Zn isotope pattern in early Ediacaran cap dolostones. This interpretation agrees with models for Marinoan deglaciation, which shows that volcanic activity would have increased atmospheric CO_2 , enhancing greenhouse effects and consequently terminating the icehouse feedback. This accumulation of atmospheric CO_2 would have lowered the pH of surface seawater. After the full deglaciation, ocean mixture would have driven the pH values back to near-present values, around 8.3. Our study also underscores the potential use of Zn isotopes in marine carbonates as a reliable proxy for reconstructing past seawater pH variations.