



Cd isotopes record changes in biologic productivity of Mesoproterozoic stromatolites

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We studied high resolution trace element abundances and stable C, O and Cd isotope compositions in carbonate leachates of stromatolites from two locals within the Mesoproterozoic Paranoa Formation, Brazil. Marine-like shale normalized REY patterns and lack of correlation between conservative (Hf, Zr, Al) and fluid-mobile (Sr, Mn, Ba) elements and O isotopes in carbonate leachates argue for a negligible syn- and postdepositional overprinting on carbonates. Cd isotopes in carbonates are a novel proxy for studying biogeochemical conditions in paleo-environments under the premise that Cd concentrations and isotopic compositions in modern seawater reflect nutrient utilisation of Cd by photosynthetic organisms. The overall variation in Cd isotopic compositions of the stromatolite localities studied is 7 $\epsilon_{112/110}\text{Cd}$ units and exceeds that of crustal rocks. The Cd isotopic compositions in Sao Gabriel stromatolites are unfractionated and match that of the upper crust, indicating that dissolved terrigenous Cd was delivered via weathering and erosion of the continental hinterland into the Sao Gabriel lagoon. By contrast, the $\epsilon_{112/110}\text{Cd}$ values in carbonate leachates from the Fazenda Funil locality show a wider spread in values and tend to be “heavier” with lower Cd concentrations, arguing for biologically induced uptake of the light Cd isotopes into the organic matter of ambient microbial mats. Unusual light $\epsilon_{112/110}\text{Cd}$ values found in carbonates with high Cd concentrations may be best explained by oxidation of dead microbial remnants followed by subsequent “cannibalism” of the previously incorporated nutrients. We propose that such successive accumulation and isotopic fractionation of bioavailable nutrients happens in a low sedimentation-rate environment. Overall, Cd concentrations and isotope compositions in biogenic carbonates provide a unique geochemical proxy for gathering information about microbial life on the Early Earth.