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A Novel Biomarker for Deep-Time Methanogenesis – Perspectives from Nickel Isotope Fractionation in Modern Stromatolites

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Stromatolitic carbonates are key archives of ancient microbial environments, preserving chemical signatures of the fluids in which they formed. In particular, during the transition from an anoxic to an oxic atmosphere during the early Proterozoic era, stromatolites were proposed to have formed under increased methanogenic activity. In modern stromatolites, methanogenesis is directly observed by the presence of methane, and methanogenic archaea are typically identified via biomarkers or DNA analyses, but the absence of methane and organic matter in ancient stromatolites limits these approaches. Methanogens rely on nickel (Ni) as a co-factor for CH_4 production, and Ni isotopes ($\delta^{60}Ni$) fractionate in methanogenic biomass to lower values [1]. This process may leave a unique Ni isotope signature in fluids within microbial habitats, the chemistry of which is directly trapped in stromatolite carbonates, and Ni isotopes offer a unique method to trace methanogenesis in deep-time environments. However, this concept remains speculative without support from modern systems.

To explore this idea, we present Ni isotope analyses of microbial carbonates from Lagoa Salgada, a Holocene coastal ephemeral lake in Brazil with sporadic seawater influx, where methanogenic stromatolites are abundant. These carbonates display strong positive $\delta^{13}C_{carb}$ values (up to 20‰) typically derived from ^{12}C methanogen uptake [2]. $\delta^{60}Ni$ values (-1.36 ‰) are significantly negative relative to ambient benthic gastropod shells and authigenic, unlithified carbonate sediments, forming in the water column, that show higher $\delta^{60}Ni$ values (+1.72 ‰, and +1.1 to +1.58 ‰, respectively). Our results indicate that negative Ni isotope values, linked to methanotrophic metabolism, can be preserved in stromatolite carbonate and serve as a proxy for methanogenesis in the deep-time geological record.

This study lays the groundwork for future investigations into microbial diversity within stromatolitic carbonates and the development of essential metabolic processes in microbial environments. Its findings hold significance for comprehending Earth's historical biosphere and have applications in astrobiology.

[1] Cameron et al. (2009), PNAS 106, 10944-10948.

[2] Birgel et al. (2015), Geobiology 13, 245-266.