

A tale of two Archean microbial habitats – on the Cd uptake and isotope fractionation by Earth's earliest life

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Abundant Paleo- to Neoproterozoic stromatolites have been described in the strata of the Pilbara Craton and the Fortescue Basin in W.-Australia. While one of the earliest evidence of fossilized microbial mats has been recorded in the ~3.4 Ga-old Strelley Pool Formation representing shallow marine shelf conditions on a carbonate platform, the ~2.7 Ga-old Tumbiana Formation stromatolites likely formed in a lacustrine environment.

This study confirms the formation of stromatolitic carbonates in the presence of possible Cd-cycling microbes before the great oxygenation event in two Archean environments under reducing atmosphere-hydrosphere conditions that differed in salinity, alkalinity, and nutrient supply. The environments and microbial metabolism at the two sites reveal significant disparities in stable Cd and C isotope compositions, and carbonate-associated Zn, Cd, P, Fe, and S concentrations.

At Strelley Pool, uniform Cd isotope compositions in stromatolitic carbonates ($\delta^{112}\text{Cd} = 0.11 \pm 0.03 \text{ ‰}$, 2SD) overlap heavy fractionated values in Phanerozoic marine photic-zone carbonates. Although the absence of correlations with P, Zn, or Cd may argue against a Cd-uptake mechanism, positive C and Cd isotope compositions do not generally exclude a phototrophic metabolism such as Cd-carbonic-anhydrase and potentially extend its presence before the currently described oxygen oases into the Early Archean rock record.

In the Tumbiana stromatolites, highly fractionated $\delta^{112}\text{Cd}$ (up to $0.34 \pm 0.06 \text{ ‰}$, 2SE), negative correlations between stable Cd and C isotope compositions, and carbonate-associated Cd and P concentrations ($R^2 = 0.4, 0.4$ and 0.9 , respectively) strongly support the use of these elements as nutrients or enzymatic cofactors in phototrophic metabolisms. The lack of correlations with carbonate-associated Ni and S levels at this site disqualifies previously documented anaerobic methane oxidizers or bacterial sulphate reducers as the main drivers for Cd isotope fractionation.

The late Archean microbiome may have achieved the pinnacle of metabolic complexity and variety in a suboxic world dominated by prokaryotes, making the Tumbiana Formation a fascinating analogue for ancient Martian settings that may have been home to comparable biota. This study offers new insights into metallome evolution and its role in advancing enzymatic processes in microbes at the dawn of life on planet Earth and beyond.