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Uptake of metal cofactors in enzymes as a fingerprint for deep-time microbial C-fixation - Lessons learned from the Cd isotope system in stromatolitic carbonates

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Microbial habitats record the intricate interactions of the biosphere, atmosphere, and hydrosphere. The evolution of C-fixation in microbial ecosystems is directly linked to their metallome, i.e., the availability of dissolved metals used as enzymatic cofactors for diverse metabolisms. One of the key metalloenzymes in the microbial world is carbonic anhydrase (CA), which plays an essential role in the carbon cycle of aqueous ecosystems by regulating the balance of dissolved CO_2 and HCO^{3-}. In a microbial mat, diurnal fluctuation in light penetration causes steep chemical gradients and variable gas exchange between microbes and ambient pore fluids on a millimeter scale. While phototrophic microbes in the upper layers create favorable conditions for authigenic carbonate precipitation, fermentation in the deeper layers causes partial carbonate dissolution, necessitating efficient carbon utilization across diverse microbial communities. Carbonic anhydrase is an enzyme that commonly uses Zn^{2+} as a cofactor; however, Cd^{2+} is relatively more accessible in a Zn-limited niche where the operational use of Cd is mechanistically linked to the specific environmental conditions of microbial habitats, i.e., evaporative settings with high salinity, high pH, and localized sulfide formation via bacterial sulfate reduction. Stable Cd isotope fractionation during CA-uptake by modern phototrophs is readily recorded in authigenic carbonates. Here, we tested whether this proxy can be expanded to trace CA in the microbial rock record. We analyzed Cd isotopic compositions in stromatolite occurrences spanning the Archean to the Holocene and report fractionated Cd isotopic compositions that correlate with macro- and micronutrients P and Zn, suggesting enzymatic metal cycling from the Paleoarchean onwards. Rayleigh-type isotope fractionation indicates that Cd was used as a cofactor from as early as the Mesoarchean, with long-term evolution in Cd/Zn ratios and Cd isotopic compositions approaching modern surface-ocean values before the GOE. We further show that the temporal restriction of a marine basin during the Badenian Salinity Crisis is recorded in the Cd isotope compositions of stromatolitic carbonates deposited under lagoon-like conditions. Our work on Cd isotope compositions in stromatolites offers new insights into the microbial metallome and its role in habitability, adding a new isotope-biomarker perspective to the study of deep-time microbial evolution.