Goldschmidt 2021 Abstract
https://doi.org/10.7185/gold2021.7134

Uranium isotopic fractionation in microbial mats forming on marine sands from the Dutchisland Schiermonnikoog

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Modern coastal cyanobacterial mats thrive in harsh environmental conditions caused by the high salinity, low nutrient availability, and variable redox conditions, possibly representing a useful analogue for early life in the geological record. Here we analyse the total carbon (TC), trace element and U isotopic composition, $^{238}U/^{235}U$ and $^{234}U/^{238}U$, of modern biocrusts from cyanobacteria and green algae forming on the supratidal sands and adjacent dunes of the Dutch barrier island Schiermonnikoog, North Sea. Variations in redox-sensitive trace metal concentrations and U isotope signatures may be useful indicators of microbial activity, e.g., reduction. Biocrusts were sampled from four sites with varying degrees of formation. Supratidal sands without visible biocrust development were also sampled to assess the isotopic U composition of the substrate. The $\delta^{238}U$ of biocrust and soil samples ranged from -0.14 to -0.29 ‰, whereas the sand substrate ranged from -0.24 to -0.28 ‰. The highest $\delta^{238}U$ was found in the poorly-developed soil profile, likely as a result of microbial or abiotic U reduction, as indicated by the increasing $\delta^{238}U$ and decreasing Th/U with depth. Moreover, elevated S and Mo concentrations were found in the deepest soil layer, possibly associated with Mo removal under sulfidic conditions due to interactions with the reduced groundwater. Although the biocrusts had TC concentrations of up to 2.7% compared to an average of 0.2% in the sand substrate, the $\delta^{238}U$ of the biocrusts (-0.28 to -0.21 ‰) largely reflect the U isotopic composition of the sand substrate. As the Th/U and $\delta^{234}U$ of all samples ranged from 3.2 to 6.0 and +7.8 to +35.41 ‰, respectively, and the samples were dissolved by strong acid dissolution, we propose that the U isotope fractionation may be masked by the high proportion of U in the (non-redox active) silicate fraction. Therefore, we will isolate the various non-detrital phases by using a sequential extraction procedure to ascertain whether U isotopic fractionation is associated with microbial activity in the biocrusts, or rather the redox gradient across the freshwater-seawater transition zone on the island.