

Sulfur isotope fractionations constrain the biological cycling of dimethylsulfoniopropionate (DMSP) in the upper ocean

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The rapid turnover of dimethylsulfoniopropionate (DMSP), likely the most relevant dissolved organic sulfur compounds in the surface ocean, makes it pivotal to understand the cycling of organic sulfur. Dimethylsulfoniopropionate is mostly synthesized by phytoplankton and it can be utilized as carbon and sulfur sources by marine bacteria or cleaved by bacteria or algae to produce the volatile compound dimethylsulfide (DMS), involved in the formation of sulfate aerosols. The fluxes between the consumption (i.e. demethylation) and cleavage pathways are thought to depend on community interactions and the sulfur demand. However, a quantitative assessment on the sulfur partitioning between each of these pathways is still missing. Here, we report for the first time the sulfur isotope fractionations by enzymes involved in DMSP degradation with different catalytic mechanisms, expressed heterologously in *Escherichia coli*. We show that the residual DMSP from the demethylation pathway is 2.7‰ enriched in $d^{34}\text{S}$ relative to the initial DMSP, and that the fractionation factor ($^{34}\epsilon$) of the cleavage pathways varies between -1 and -9‰. The incorporation of these fractionation factors into mass balance calculations constrains the biological fates of DMSP in seawater, supports the notion that demethylation dominates over cleavage in marine environments, and could be used as a proxy for the dominant pathways of degradation of DMSP by marine microbial communities.