

Oxygen Isotopic Fingerprints on the Phosphorus Cycle Within the Subseafloor Biosphere

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The oxygen isotopic composition of phosphate holds important information on P cycling and microbial activity due to the distinct oxygen isotopic fractionations accompanying multiple P pathways and metabolic processes. Here we report the oxygen isotopic compositions ($\delta^{18}\text{O}$) of both dissolved inorganic phosphate (DIP) and sedimentary phosphate in deep-sea sediments to over 200m depths at ODP Site 1230. We have placed the results into a quantitative framework and found that the $\delta^{18}\text{O}$ value of DIP ($\delta^{18}\text{O}_{\text{DIP}}$) is mainly controlled by three pathways of P cycling at Site 1230: (1) release of DIP by enzymatic degradation of organic matter, (2) removal of DIP by the precipitation of authigenic apatite, and (3) enzyme-catalyzed O-isotopic exchange between phosphate and water. In particular, there is a shift of $\delta^{18}\text{O}_{\text{DIP}}$ towards equilibrium around 140m below seafloor, in parallel with a change in microbial communities. This suggests $\delta^{18}\text{O}$ of phosphate as a potential proxy for microbial activities in the subseafloor deep biosphere. Our model simulations also suggest that the rate of O-isotopic exchange is correlated with the rate of organic matter decomposition, implying microbially and enzymatically controlled isotopic exchange. Lastly, bulk sediment $\delta^{18}\text{O}_p$ values as well as the abundance of each sediment phosphate phase (detrital apatite, authigenic apatite and Fe-bound phosphate) suggests that authigenic apatite and/or Fe-bound phosphate can record the $\delta^{18}\text{O}$ value of porewater DIP during their formation.