

U(VI) reduction in an oligotrophic ferruginous ocean analog?

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The fidelity of the uranium isotope paleoredox proxy depends in large part on our mechanistic understanding of the pathways that induce U isotope fractionation during the reduction of U(VI) to U(IV). Most early applications of the U isotope proxy did not clearly distinguish between U reduction occurring under anoxic Fe(II)-bearing ferruginous conditions and sulfide-bearing euxinic conditions. In contrast, laboratory experiments suggest that the magnitude and even the direction of U isotope fractionation accompanying U reduction may depend on a variety of factors including reaction kinetics, U speciation, and/or the identity of the reductant. While U isotope fractionation has been extensively studied in modern euxinic freshwater and marine settings, U geochemistry in equivalent ferruginous environments remains poorly understood.

In order to address this gap, we collected water column and sediment profiles from Canyon Lake, a naturally-occurring oligotrophic ferruginous lake located in northern Michigan, USA. Dissolved U concentrations increased from 0.24 ppb in the oxic mixolimnion to 0.83 ppb in the ferruginous monimolimnion, paralleling increases in conductivity. Mixing relationships and $\delta^{234}\text{U}$ profiles suggest that dissolved U is being provided by one or more unique groundwater sources, but did not show definitive evidence for a reductive sink of dissolved U even in the presence of 1.5 mM $\text{Fe(II)}_{\text{aq}}$. Water column samples as well as oxic and anoxic sediments were all characterized by a uniform $\delta^{238}\text{U}$ value of -0.38 ± 0.06 ‰. In contrast with predictions that U(VI) should be rapidly reduced and scavenged from the water column in the presence of Fe(II), our preliminary data suggest a limited role for U(VI) reduction under oligotrophic ferruginous conditions.