Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.36644

# Evaluating the effects of dolomitization on the uranium isotope paleoredox proxy

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Uranium isotopic ratios ($^{238}U/^{235}U$; denoted as $\delta^{238}U$) have emerged as a paleoredox proxy that is increasingly applied to reconstruct the redox evolution of Earth's oceans and atmosphere. The proxy is based on the mass-independent isotopic fractionation that occurs between reduced U(IV) and oxidized U(VI). If reliably preserved in marine carbonates, variations in $\delta^{238}U$ track global changes in ocean oxygenation because uranium reduction is closely coupled to benthic redox conditions. However, studies of shallow marine limestones have demonstrated that early diagenetic processes can produce a positive offset from contemporaneous seawater due to the incorporation of isotopically heavier U(IV), complicating paleoredox reconstructions. Although this effect is increasingly recognized in limestones, uranium isotope systematics in dolostones remain poorly constrained despite their ubiquity in the sedimentary record, particularly in the Precambrian.

Here we present preliminary results from a well-preserved 'dolomitization front' on Grand Cayman (Cayman Formation; Miocene), where the $\delta^{238}U$ of limestone (-0.039 ± 0.056‰) evolves laterally to dolostone (-0.234 ± 0.081‰). Such results imply that (i) calcite and dolomite have different fractionation factors, or (ii) they formed from diagenetic fluids with distinct $\delta^{238}U$ compositions. To test these hypotheses, our results are bolstered by a series of high-temperature, replacement dolomitization experiments that track the partitioning and isotopic fractionation of U(VI) between the $CaCO_3$ reactant, diagenetic fluid, and $CaMg(CO_3)_2$ product. Resolving whether dolomitization retains the $\delta^{238}U$ signal of the precursor $CaCO_3$ or overprints it in a predictable manner is essential for refining the uranium isotope paleoredox proxy and may provide new insights into the geochemical conditions that accompany the formation of ancient dolostones.