Diagenesis on uranium isotopes ($^{238}U/^{235}U$) in ancient marine carbonates

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Uranium isotopic ratios ($^{238}U/^{235}U$) of ancient marine carbonates have been increasingly explored as an effective paleoredox proxy for evaluating the extent of oceanic anoxia throughout geological time. The fidelity of this proxy relies heavily on the well-characterization of the U isotope fractionation induced by carbonate diagenesis. An isotope fractionation of up to 0.3‰ has been reported for $^{238}U/^{235}U$ in modern shallow-water carbonates from the Bahamas during early diagenesis (Romaniello et al., 2013; Chen et al., 2018; Tissot et al., 2018), however, diagenetic alterations on $^{238}U/^{235}U$ in ancient carbonates remains poorly constrained. Here, we measured $^{238}U/^{235}U$ in the uppermost Middle Triassic Leikoupo formation and explored the effects of dolomitization, meteoric diagenesis, and closed system marine burial diagenesis in organic-rich carbonates, on modifying of U isotopic signals in these ancient carbonates. Our results show that seawater dolomitization occurring in shallow burial environment preserves seawater-like $\delta^{13}C$ signatures but display lighter $\delta^{238}U$ values (–0.53 to –0.71‰). In contrast, meteoric diagenesis exhibited marked negative $\delta^{13}C$ (down to –6.3‰) and $\delta^{18}O$ (down to –12.1‰) values, and a positive shift of up to 0.5‰ in $\delta^{238}U$ relative to modern seawater. The lighter $\delta^{238}U$ values during dolomitization most likely resulted from reservoir that experienced partial U(VI) reduction. Further, carbonate $\delta^{238}U$ may help testing the viability of mixing dolomitization models. The heavier $\delta^{238}U$ values during meteoric diagenesis is linked to authigenic enrichment of isotopically heavy U(IV) during U(VI) reduction and/or incorporation of isotopically heavy U(VI) species into recrystallized carbonates.