

Uranium isotope fractionation during incorporation into aragonite and calcite

XINMING CHEN^{1*}, STEPHEN ROMANIELLO²,
ACHIM D. HERRMANN³, LAURA E. WASYLENKI⁴
AND ARIEL D. ANBAR^{1,2}

¹Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ, 85287, USA

(*correspondence: xchen147@asu.edu)

²School of Earth and Space Exploration, Arizona State University, Tempe, AZ, 85287, USA

³Coastal Studies Institute and Department of Geology and Geophysics, Louisiana State University, Baton Rouge, LA, 70803, USA

⁴Department of Geological Sciences, Indiana University, Bloomington, IN, 47405, USA

Natural variations in the $^{238}\text{U}/^{235}\text{U}$ ratio of marine carbonates may provide a useful way of constraining past variations in ocean redox conditions. However, to successfully exploit this novel redox proxy, it is essential to understand fractionation effects that may occur during precipitation of calcite and aragonite from seawater and during the early diagenetic conversion of aragonite to calcite. To explore these effects, we conducted controlled laboratory coprecipitation studies of U(VI) with calcite and aragonite.

Aragonite and calcite experiments were conducted at pH 8.5 ± 0.1 using a constant addition method similar to [1]. Due to design constraints, the calcite experiment was conducted at a higher ionic strength and faster precipitation rate than the aragonite experiment. Dissolved U remaining in solution was collected at various time points throughout the experiments. Experiments were terminated when $>90\%$ of U was incorporated into the solid phase (~ 7 days). Samples were purified using UTEVA chemistry and $\delta^{238/235}\text{U}$ was measured using a ^{233}U - ^{236}U double-spike and MC-ICP-MS, attaining a precision of $\pm 0.10\%$ (2σ) [2]. We find that ^{238}U is preferentially incorporated into aragonite. The data from the aragonite experiment can be fit by a Rayleigh fractionation curve with a $^{238}\text{U}/^{235}\text{U}$ fractionation factor of $\alpha = 1.00008 \pm 0.00002$. In contrast, the calcite experiment demonstrated no resolvable U isotope fractionation ($\alpha = 1.00001 \pm 0.00003$).

Further work is needed to understand the mechanisms leading to the different isotopic fractionation of U(VI) during incorporation into aragonite and calcite. Possible drivers include differences in U coordination in the crystal structures or equilibrium isotopic fractionation between various aqueous U(VI) species prior to incorporation.

[1] Reeder *et al* (2001) *GCA* **65**, 3491-3503 [2] Weyer *et al* (2008) *GCA* **72**, 345-359