

# **The effect of pH, [DIC], precipitation rate, and polymorphism on lithium isotope fractionation between calcium carbonate and seawater – Insights from inorganic carbonate precipitation experiments conducted under biologically-relevant solution conditions**

VANESSA SCHLIDT<sup>1</sup>, DAVID EVANS<sup>2,3</sup>, HANS-MICHAEL SEITZ<sup>4</sup> AND SILKE VOIGT<sup>5</sup>

<sup>1</sup>Goethe University Frankfurt

<sup>2</sup>FIERCE, Frankfurt Isotope & Element Research Center, Goethe University

<sup>3</sup>Institute of Geosciences, Goethe University

<sup>4</sup>Institute of Geosciences

<sup>5</sup>Institute for Geosciences, Goethe University Frankfurt

Presenting Author: [schlidt@em.uni-frankfurt.de](mailto:schlidt@em.uni-frankfurt.de)

The use of Li isotopes in marine carbonates as proxy for reconstructing chemical weathering intensities has increased over the last decade. Originally, marine carbonates were considered to record the Li isotope composition of seawater ( $\delta^7\text{Li}$ ) without being affected by vital effects as Li is likely not bioessential. However, recent studies on modern marine calcifying organisms report substantial taxon-specific vital effects on Li isotope fractionation raising the question of which processes mechanistically control Li uptake and incorporation into skeletal  $\text{CaCO}_3$ . Previous precipitation experiments tackled this issue, but were broadly not conducted under conditions relevant to marine calcifiers. Therefore, we addressed this issue by precipitating inorganic  $\text{CaCO}_3$  from artificial seawater to assess a range of potential factors affecting Li isotope fractionation. Specifically, we analysed the effects of pH, precipitation rate and [DIC] in three sets of experiments across ranges (pH = 7.6-9.0; [DIC] = 2.3-19.2mmol/kgSW) that are likely to cover the carbonate chemistry conditions at the biomineralisation site of marine calcifiers. For each set one parameter was kept constant by co-varying the other two. In contrast to previous work, our results show that the effects of the aforementioned factors are negligible for biologically relevant precipitation rates at a pH range typical for biomineralisation. Therefore, the spread in  $\delta^7\text{Li}$  values reported for different groups of calcifying organisms seems to be almost solely inflicted by taxon-specific vital effects, hinting towards the importance of biomineralisation pathways for isotopic fractionation. For calcite, we obtain a fractionation between water and calcite of  $\Delta^7\text{LiH}_2\text{O-calcite} = -5.6\text{‰}$  ( $\pm 1.3\text{‰}$ , 2SE). Compared to our results, Marriott et al.[1], who precipitated from solutions with enriched Li concentrations, observed a fractionation of  $-3\text{‰}$  and Day et al.[2], who simulated cave-analogue conditions, of  $-8.5\text{‰}$ . Preliminary results from aragonite precipitation experiments show a Li isotope

fractionation towards lighter values compared to calcite. We observed a slightly larger fractionation of  $\Delta^7\text{LiH}_2\text{O-aragonite} = -13.4\text{‰}$  ( $\pm 2.4\text{‰}$ , 2SE) compared to the fractionations obtained in previous studies[3].

References: [1] Marriott et al., 2004a EPSL 222, 615-624; [2] Day et al., 2021 GCA 305, 243-262; [3] Gabitov et al., 2011 Geochemistry Geophysics Geosystems Technical Brief vol. 12 no. 3