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The vital aspects of reconstructing seawater Li isotope composition: insights from modern shells and cultured organisms

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In this study, we constrain the fractionation of Lithium (Li) isotopes between calcite or aragonite and seawater ($\Delta^7\text{Li}_{\text{carbonate-seawater}}$) during the precipitation of carbonate shells. There is currently a growing interest in measuring Li isotopes in sedimentary carbonates to determine paleo-weathering conditions, with implications for understanding the carbon cycle over geologic time. While the incorporation of Li isotopes in foraminifera is now better understood, these are absent from most of the geologic record, and little is known about the preservation of seawater Li isotope compositions ($\delta^7\text{Li}$) in other types of biogenic carbonates.

Here, we investigate the $\delta^7\text{Li}$ of various organisms (mollusc, echinoderms and corals) abundant in Phanerozoic carbonates, in order to understand which geologic archives might allow us to reconstruct past seawater composition. The range of measured samples includes (i) modern calcite and aragonite shells from variable natural environments, and (ii) shells from organisms grown under controlled conditions (temperature, salinity, pCO_2). This dataset will make it possible to evaluate the influence of environmental parameters on Li isotope fractionation during biogenic calcification and to determine the magnitude of inter-species variability. To separate the carbonate fraction, we use a leaching protocol that includes removal of the exchangeable Li and weak HCl leach to avoid potential silicate contamination.

Our initial results show a preferential incorporation of ^7Li in calcitic shells compared to seawater. The measured values of $\Delta^7\text{Li}_{\text{calcite-seawater}}$ for bivalve species range from +2 to +15‰ with some interspecies variability. These values are higher than inorganic calcite fractionation ($\Delta^7\text{Li}_{\text{calcite-seawater}} = -2$ to -5 ‰) [1], suggesting a strong influence of vital effects on Li isotopes during bio-calcification of bivalve shells. Cultured experiments of *Pecten Maximum* (bivalve) show little change of $\Delta^7\text{Li}_{\text{calcite-seawater}}$ as a function of temperature. On the contrary, the $\Delta^7\text{Li}_{\text{aragonite-seawater}}$ measured in aragonitic bivalves range from -8 to -13 ‰ and is close to but slightly more positive than the $\Delta^7\text{Li}_{\text{aragonite-seawater}}$ determined from abiogenic aragonite precipitation experiments ($\Delta^7\text{Li}_{\text{aragonite-seawater}} \approx -12$ ‰) [1] suggesting less fractionation due to vital effects for aragonite than for calcite. This work has important implications for using Li isotopes in carbonates to quantify paleo-weathering in the geological record.

[1] Marriott et al., (2004) *Chemical Geology*, **212**(1), 5-15