

# The fractionation of Li isotopes into amorphous calcium magnesium carbonate (ACMC) and during its transformation into calcite

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The lithium isotope composition ( $\delta^7\text{Li}$ ) of marine biogenic carbonates is widely used as proxy for reconstructing weathering intensities. However, several recent studies have shown major “vital effects” on  $\delta^7\text{Li}$  in skeletal carbonates of modern marine calcifying organisms, potentially complicating their use as  $\delta^7\text{Li}$  archives.

The underlying mechanisms of these vital effects are still poorly understood; e.g. it is unclear whether these fractionations are biologically-driven or a result of non-classical or kinetic processes during carbonate precipitation. This study aims to elucidate which potential processes during carbonate precipitation affect the fractionation of Li isotopes and thus, should be considered when interpreting  $\delta^7\text{Li}$  data derived from marine biogenic carbonates.

An amorphous precursor phase during biomineralisation has been observed or indirectly inferred in the case of several calcifying groups such as echinoids, corals, and molluscs. Therefore, understanding the fractionation of Li isotopes into such a potential precursor phase, the preservation of the original  $\delta^7\text{Li}$  of the precursor phase, as well as effects of solution chemistry on Li isotope fractionation during the transformation into a crystalline calcium carbonate polymorph should be aimed for. In order to address these aspects, we precipitated amorphous calcium magnesium carbonate (ACMC) from artificial seawater (ASW) (pH 9.2, DIC 17.0 mmol/kg), divided the ACMC into different reaction vessels and let it recrystallize in ASW with different solution compositions. The initial saturation state with respect to calcium carbonate ( $\Omega$ ) was kept constant between the different experiments; pH and dissolved inorganic carbon (DIC) co-varied and cover initial ranges of 7.8-8.4 and 1.8-6.4 mmol/kg, respectively.

For ACMC we obtain a fractionation of  $\Delta^7\text{Li}_{\text{ASW-ACMC}} = -3.0\text{‰}$  ( $\pm 1.3\text{‰}$ , 2SD) at the previously stated conditions. Preliminary data indicates no significant difference from the fractionations observed for the calcites resulting from recrystallizing said ACMC ( $\Delta^7\text{Li}_{\text{ASW-calcite}}$  ranges from  $-3.0\text{‰}$  to  $-3.9\text{‰}$  with an average 2SD of  $>1.6\text{‰}$ ). Furthermore, we do not observe a correlation of  $\Delta^7\text{Li}_{\text{ASW-calcite}}$  with pH or DIC over the previously stated initial ranges. Our preliminary data-set indicates that the