

Apparent mass-independent behavior of Mg isotopes during transformation of amorphous carbonate to crystalline carbonate and its implications

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Crystallization from an amorphous precursor is an important pathway of carbonate precipitation in nature. Understanding the mechanism of the crystallization pathway of amorphous carbonate is important for applications of elemental and isotopic signatures in carbonates as paleo-environmental proxies or indicators of geological processes. Two competing mechanisms have been proposed to explain this transformation process, including solid-state transition and coupled dissolution-reprecipitation.

We investigated the transformation of the amorphous carbonate precursor for norsethite [BaMg(CO₃)₂], a dolomite analogue mineral, by conducting isotope exchange experiments using a ²⁵Mg enriched tracer coupled with high precision isotope analyses of ^{26/24}Mg and ^{25/24}Mg ratios for aqueous and solid phases sampled in time-series.

In exchange experiments, the $\Delta^{26}\text{Mg}_{\text{solid-aq}}$ values decreased while the $\Delta^{25}\text{Mg}_{\text{solid-aq}}$ values increased, indicating near-complete Mg isotope exchange between solid and aqueous phases during transformation of amorphous carbonate to norsethite. It is important to note that in most exchange experiments, the $\delta^{25}\text{Mg}$ value of norsethite became greater than that of aqueous solution, producing positive $\Delta^{25}\text{Mg}_{\text{solid-aq}}$ values while the $\Delta^{26}\text{Mg}_{\text{solid-aq}}$ values remained negative. This apparent non-mass dependent behavior was surprising and not expected in batch isotope equilibrium processes.

We numerically modelled the behaviors of Mg isotopes (in both ^{26/24}Mg and ^{25/24}Mg) for the experimental system according to the two existing amorphous carbonate crystallization mechanisms. The results suggest that the apparent non-mass dependent behavior can only be explained by the coupled dissolution-reprecipitation process, and the solid-state transition mechanism is rigorously ruled out irrespective the degree of possible isotope exchange before the solid-state transition. Our study shows that the “three-isotope method” can provide novel and strong constraints to the mineral growth mechanisms.