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The isotopic composition of carbonate groups during phase transitions from amorphous calcium carbonate to calcite

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The stable isotopic composition of carbonate groups (CO_3^{2-}) within biogenic calcium carbonate minerals ($CaCO_3$) provides valuable information on climate and environmental changes throughout the Phanerozoic. Biominerals form via amorphous precursor phases prior to transformation to aragonite or calcite (1-2). Here we examine whether the conversion of amorphous calcium carbonate (ACC) modifies the isotopic composition of the final crystalline phase.

To examine this, we synthesized inorganic ACC and converted aliquots of it into calcite either via (1) dissolution/reprecipitation in solutions with different initial conditions of pH and oxygen isotopic composition or (2) in an anhydrous system by heating in a vacuum oven.

Surprisingly, the dissolution/reprecipitation phase transitions preserve the isotopic composition ($\delta^{13}C$, $\delta^{18}O$ and Δ_{47}) of the original ACC despite a high solution/mineral ratio ($\sim 10^3$) during the experiments. During phase transitions, the solutions evolved to high pH values (pH > 10.4) and degrees of supersaturation with respect to calcite ($\Omega_{calcite} > 10$). We interpret the results to indicate that this caused rapid and largely quantitative transfer of CO_3^{2-} from ACC to calcite, with negligible time for CO_3^{2-}-H_2O isotopic exchange during the phase transitions.

Dehydration of ACC (i.e., loss of bound and unbound water) by heating up to 170 °C did not significantly affect the carbon and oxygen isotope composition of $CaCO_3$ but led to decreases in Δ_{47} clumped isotope compositions. Further heating from 170 °C to 350 °C resulted in crystallization of ACC to calcite, which was accompanied by a small but measurable ~ 0.5‰ decrease in $\delta^{13}C$, additional decrease in Δ_{47} but no measurable change in $\delta^{18}O$.

Based on these results, we present a conceptual model that supports the idea biogenic $CaCO_3$ likely inherits the isotopic composition of ACC precursors. This model differs from expectations based on growth on crystalline $CaCO_3$.

(1) Beniash et al. (1997) *Proc. R. Soc. Lond.* http://doi.org/10.1098/rspb.1997.0066

(2) Schmidt et al. (2024) *Nat Commun.* https://doi.org/10.1038/s41467-024-46117-x