

Non-Classical crystallization of calcium carbonate: impact on its isotopic composition

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Carbonates are essential paleoenvironmental archives, recording past conditions through their isotopic and chemical signatures. However, diagenesis and crystallization can alter their original signatures, affecting their reliability to be used as a paleoenvironmental proxies.

This study examines isotopic changes during the transformation of amorphous calcium carbonate (ACC) into crystalline CaCO_3 under varying relative humidity (RH) conditions over five months to shed light into the role of ACC in the calcification process and its effect on the final composition of crystalline polymorphs. With that aim, ACC was synthesized by mixing equimolar CaCl_2 and Na_2CO_3 (+NaOH) solutions, initially separated by a polyethylene sheet and mixed via centrifugation. Two types of ACC were prepared: one using Milli-Q water (MW) and the other with ^{18}O -enriched water (EW). Samples were stored at 20°C in desiccators at 33%, 60%, and 95% RH using saturated salt solutions, with water types swapped between conditions (EW for MW-ACC and vice versa) to track oxygen and carbon isotope fractionation. Analyses were performed by SEM, FTIR, and XRD, with isotope ratios measured via IRMS.

At 95% RH, both MW- and EW-ACC crystallized into CaCO_3 within three days, as indicated by the calcite bands at 872 and 712 cm^{-1} in the FTIR spectra. In contrast, crystallization was slower at lower RH levels; at 60% RH, the ACC band at 862 cm^{-1} persisted even after 30 days, and at 33% RH, the transformation was further delayed.

The initial ACC isotope values ($\delta^{18}\text{O}_{\text{PDB}} = -15.24\text{‰}$ and $\delta^{13}\text{C}_{\text{PDB}} = -12.58\text{‰}$ PDB for EW-ACC and $\delta^{18}\text{O}_{\text{PDB}} = -15.06\text{‰}$ and $\delta^{13}\text{C}_{\text{PDB}} = -12.84\text{‰}$ for MW-ACC) increased rapidly over the first few days, followed by a slower and gradual increase. Overall, our findings indicate that crystalline polymorphs formed from an amorphous precursor at low water/solid ratios can yield isotopic values that may not accurately reflect the original formation conditions. This has significant implications for interpreting the isotopic composition of carbonates.