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Dual clumped isotope data for amorphous carbonates and transformation products reveal novel mechanisms for nonequilibrium effects

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Transient amorphous precursors to minerals have been observed in a range of laboratory materials and in nature including across diverse phyla. These metastable phases can allow for the incorporation of cations at higher concentrations than classical crystallization pathways. Thus their chemistry and behavior have implications in an array of disciplines across the geosciences and chemical, health, and material sciences. However, there are major knowledge gaps in characterization of the isotopic composition of the anion in amorphous carbonates and behavior during transformation. Here, we examined the evolution of the isotopic composition of amorphous carbonates and transformation products to constrain reaction mechanisms and potential origins of non-equilibrium isotopic compositions in carbonate minerals. We measured dual clumped isotopes ($^{13}C^{18}O^{16}O$ - δ_{47}; $^{12}C^{18}O^{18}O$ - δ_{48}), bulk stable isotope ratios ($\delta^{13}C$, $\delta^{18}O$), and chemical and structural data before, during, and after the transformation of an amorphous calcium magnesium carbonate (ACMC) precursor into high Mg-calcite (HMC) over 1 year, with crystallization occurring in solutions at different temperatures (10 to 60 °C). ACMC synthesized from an unequilibrated dissolved inorganic carbon (DIC) pool at 10 °C had lower δ_{47} and higher δ_{48} than equilibrium HMC. At all temperatures, δ_{47}, δ_{48}, and $\delta^{18}O$ evolved considerably during transformation of ACMC to HMC. δ_{47} and δ_{48} values achieved a non-equilibrium steady-state, while $\delta^{18}O$ continued to evolve after crystallization. Observations and modeling simulations were consistent with the dissolution of ACMC altering the chemistry of the solution and driving disequilibrium in the DIC pool, which was then recorded during subsequent crystallization of HMC. Clumped isotope results may also reflect mixing effects due to ACMC progressively dissolving and reprecipitating over time while the DIC pool has an evolving isotopic composition. These results have implications for applied studies as they demonstrate new mechanisms where nonequilibrium isotope effects could be produced in minerals formed from amorphous precursors, but with expression of the effects dependent on the conditions during transformation.