

Oxygen isotope fractionation in carbonates: the role of amorphous calcium carbonate

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The isotopic compositions of calcium carbonates have been used extensively for decades to reconstruct Earth's past environmental conditions. However, carbonate isotope compositions are frequently modified during mineral precipitation, burial, and mineral transformations, which can hamper their use as paleoclimate proxies.

Recently, it has been reported that the formation of many carbonates begins with the precipitation of an amorphous calcium carbonate (ACC) precursor that subsequently transforms into crystalline phases through non-classical nucleation pathways. This transformation may also be accompanied by changes in the isotopic composition of the resultant crystalline calcium carbonates (CC), which could impact their use as accurate paleoenvironmental proxies. To investigate if the final oxygen isotopic composition of calcite is modified when the calcification process involves an amorphous precursor, we performed controlled ACC recrystallization experiments under conditions of 33 to 95 % relative humidity (RH) at 5 and 20 °C for up to 145 days. During the experiments, the solids were characterized by attenuated total reflection–Fourier transform infrared (FTIR) and X-ray diffractometry (XRD), and the oxygen stable isotope ratios were measured by isotope ratio mass spectrometry (IRMS).

Our results show that at low RH and temperatures (e.g., RH ≤ 45 % and 5 °C), no ACC–CC transformation occurs and ACC $d^{18}\text{O}$ values do not change significantly over our experimental times. In contrast, when ACC–CC transformation occurs (e.g., at RH ≥ 60%), calcium carbonate $d^{18}\text{O}$ values initially rapidly increase followed by a slower but consistent increase to reach an almost constant value, up to -8.15 ‰, at the end of the experiments. The results suggest that neither temperature nor pH are the sole drivers of changes in the oxygen isotope compositions. Calculated fractionation factors between the carbonates and the surrounding fluids, from the humidity and the synthesis fluid retained in the ACC, indicate that the recrystallizing calcite moves towards isotopic equilibrium with the expelled 'structural' synthesis fluid; although, some of fractionation factors even exceeded the equilibrium values. This suggests that the carbonate exchanged oxygen during crystallization with an ^{18}O -enriched component probably due to nonequilibrium kinetic effects during evaporation as a function of RH and temperature.