

Isotope exchange mechanisms between CaCO₃ and fluid at chemical equilibrium

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The isotopic composition of carbonate minerals (e.g., C, O) is widely used as a record of conditions at the time of mineral formation. The robust interpretation of the isotopic composition of minerals requires that the composition of the mineral is not altered since deposition and that the mechanisms of isotope fractionation are relatively understood. Textural evidence of recrystallization can be used to indicate lack of preservation of isotopic compositions, but recent studies have revealed that certain minerals may experience isotopic exchange with their surrounding fluid at chemical equilibrium without any obvious morphological alteration [1,2]. Recently, Harrison et al (2022) [3] exposed abiotic calcite to a fluid at chemical equilibrium but enriched in ¹⁸O and ¹³C at 25°C and tracked the resultant isotopic exchange between fluid and solid. The experiments revealed that extensive alteration of the solid isotopic composition occurred, but the mechanism of exchange could not easily be identified. Here, we conducted a further set of experiments at 90°C to promote a greater extent of reaction. Both the 90°C and select 25°C-reacted samples were analyzed by nanoSIMS to visualize the distribution of ¹³C and ¹⁸O in the solids and shed light on the mechanism of isotope exchange at the sub-micron scale. Preliminary findings indicate that isotope exchange was heterogeneously distributed (at the scale of observation) and tended to be localized along crystal edges and cracks. These findings are consistent with the observation that isotope exchange may occur predominantly at sites of higher reactivity (e.g., defects). Moreover, in experiments conducted with aragonite at chemical equilibrium with a fluid [4], Ca isotope exchange occurred rapidly due to extensive Ostwald ripening of the needle-like crystals, in contrast to calcite crystals which demonstrated no observable ripening. Combined, these results highlight that isotope exchange likely proceeds as a heterogeneous process at highly reactive sites, the distribution of which depends on the mineral type and morphology, and the elementary mechanisms controlling mineral formation.

[1] Cisneros-Lazaro et al (2022) *Nat Commun.* **13**, 113; [2] Gorski and Fantle (2017) *GCA* **198**, 439-465; [3] Harrison et al (2022) *GCA* **335**, 369-382; [4] Harrison et al (2023) *EPSL* **603**, 117985.