

## In search of processes driving clumped-isotope (dis)equilibrium

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“Clumped-isotope” thermometry is based on measurements of the proportion of <sup>13</sup>C and <sup>18</sup>O isotopes that are bound to each other within carbonate minerals in <sup>13</sup>C<sup>18</sup>O<sup>16</sup>O<sub>2</sub> groups, and most applications of the thermometer implicitly presume attainment of mineral equilibrium. However, it is known that the oxygen isotopic compositions of dissolved inorganic carbon (DIC) species vary significantly and that in some cases carbonate minerals can preserve a signature of the δ<sup>18</sup>O of the total DIC pool. Therefore determining clumped isotope signatures of DIC species and exploring their potential to be preserved in the solid phase is a key area that needs to be explored in order to develop a realistic assessment of the uncertainties associated with the application of this temperature proxy.

We report evidence from theoretical calculations and precipitation experiments that proportions of multiply-substituted isotopologues in CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> ions are significantly different. Values for calcite are similar to HCO<sub>3</sub><sup>-</sup> and may be intermediate to these two DIC species. Factors influencing DIC speciation (pH, salinity) and the timescale for DIC equilibration, as well as reactions at the solid-solution interface, have the potential to influence clumped isotope signatures and the δ<sup>18</sup>O of carbonate minerals. If a crystal grows too rapidly to come to internal equilibrium (i.e., achieve the value for the temperature-dependent mineral equilibrium), it may inherit the clumped-isotope signature of a DIC species (e.g., the temperature-dependent equilibrium of HCO<sub>3</sub><sup>-</sup>) or a mixture of DIC species, and hence record a disequilibrium mineral composition. However, DIC speciation effects on the occurrence of multiply-substituted isotopologues in carbonate minerals are likely to be relatively small or even negligible for slow-growing crystals, and for samples grown at a HCO<sub>3</sub><sup>-</sup>-dominated pH from a DIC pool at equilibrium. Solution chemistry may be an important factor when examining fast-growing carbonate minerals; over extremes of pH and salinity these effects could be significant. We suggest that growth environment, solution chemistry, surface equilibria, reordering in the interfacial region, and precipitation rate may all play a role in dictating whether a crystal achieves equilibrium or disequilibrium clumped isotope signatures.