

# Clumped isotope reordering kinetics in carbonate minerals: Experiments and first-principles atomistic simulations

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Clumped isotope paleothermometry has the potential to resolve the conundrum posed by oxygen isotope data which, depending on interpretation, suggest hot early-mid Ordovician oceans (30 to >40 °C) or a cold (<10 °C) and <sup>18</sup>O-depleted (~-4‰) late Ordovician (Hirnantian) ocean. Clumped isotope data from well-preserved, shallow-buried brachiopod shells suggest relatively high temperatures (30-40 °C), but clumped isotope temperatures may be influenced by reordering during burial heating. Undeniably, better criteria are needed to screen carbonate samples for susceptibility to reordering.

To this end we are conducting heating experiments with various carbonate minerals and constrained *ab initio* molecular dynamics (cAIMD) simulations to evaluate the susceptibility of carbonate minerals to clumped isotope reordering as a function of 1) crystal structure, 2) cation vacancy and substitution, and 3) internal water. Thus far experiments have been conducted on synthetic calcite, strontianite, and witherite precipitated at 5 °C and heated at temperatures ranging from 185 to 385 °C. The *ab-initio* molecular dynamics (AIMD) simulations apply the density functional theory (DFT) method implemented in the Vienna *ab-initio* simulation package.

The heating experiments reveal reordering rates in the following decreasing order: strontianite, witherite, and calcite. Combined with other studies, the order of reordering rates is strontianite > witherite > aragonite > calcite > dolomite. Arrhenius activation energies for reordering follow the order: strontianite < witherite < aragonite < dolomite < calcite. cAIMD simulations show the same order of free energy change to the transition state ( $\Delta A^\ddagger$ ) as the Arrhenius activation energies: strontianite < witherite < calcite. Simulation of atomistic dynamics in calcite reveal the following order of  $\Delta A^\ddagger$  lowering (least to most): cation vacancies, Mg<sup>2+</sup> substitution, H<sup>+</sup> addition, and H<sub>2</sub>O addition. The last two emphasize the key role structural water plays in increasing reordering rates. This role has been suggested in recent experimental studies but has not been demonstrated theoretically. Ongoing studies are combining reordering experiments in calcite and aragonite, additional cAIMD simulations, and measurements of water content and  $\delta D$  to quantify the effect of structural water on clumped isotope reordering and develop water-screening criteria for clumped isotope samples.