

The kinetics of clumped isotope reordering of synthetic inorganic carbonates

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In the last decade, the reordering of carbonate clumped isotopes has been applied in reconstructing thermal histories of sedimentary basins based on the kinetics of clumped isotope reordering of calcite, dolomite and aragonite [1,2,3,4]. The activation energies of dissociation of C-O bonds and O diffusion in the lattice vary in the carbonates with different mineral structures, cations, concentration of trace elements and grain sizes. We systematically evaluate how the mineral structure and type of cations affect the reordering rate and associated activation energy by conducting heating experiments on calcite, aragonite, strontianite and witherite at temperatures ranging from 285°C to 485°C under dry conditions. We synthesized carbonates at 5°C in the lab under the same experimental condition for 60 days to control the chemical composition of the starting materials. The initial Δ_{47} values of carbonate precipitates vary between 0.732‰ and 0.752‰. We find that the order of the initial reordering rate of these carbonates at all temperatures is strontianite > witherite > aragonite > calcite. For the 385 °C (30-minute) heating experiment, strontianite underwent 74% (0.392‰) reordering. By contrast, witherite and calcite only underwent 52% (0.500‰) and 19% (0.644‰) reordering respectively. Beyond our expectation, witherite shows a slower reordering rate than the other carbonates in the latter period of heating, causing its apparent equilibrium Δ_{47ap} values to be far off the $\Delta_{47equilibrium}$ values, and varying little with temperature. For instance, the Δ_{47ap} value of witherite at 485 °C is 0.451‰, much higher than 0.339‰ and 0.306‰ for calcite and strontianite, respectively, but close to 0.482‰ for witherite heated at 385°C. Our calcite reordering rate is faster than those in previous studies, which may reflect the smaller grain size of our calcite powders. Experiments are underway to test this. By combining modeling of molecule dynamics with reordering rates obtained from heating experiments, we will show how mineral structure and type of cation control clumped isotope reordering at the atomic scale.

[1] Passey & Henkes (2012), *EPSL* 351, 223-236.

[2] Stolper & Eiler (2015), *AJS* 315, 363-411.

[3] Lloyd et al. (2018), *GCA* 242, 1-20.

[4] Chen et al. (2019), *GCA* 258, 156-173.