Constraints on triple oxygen isotope kinetics

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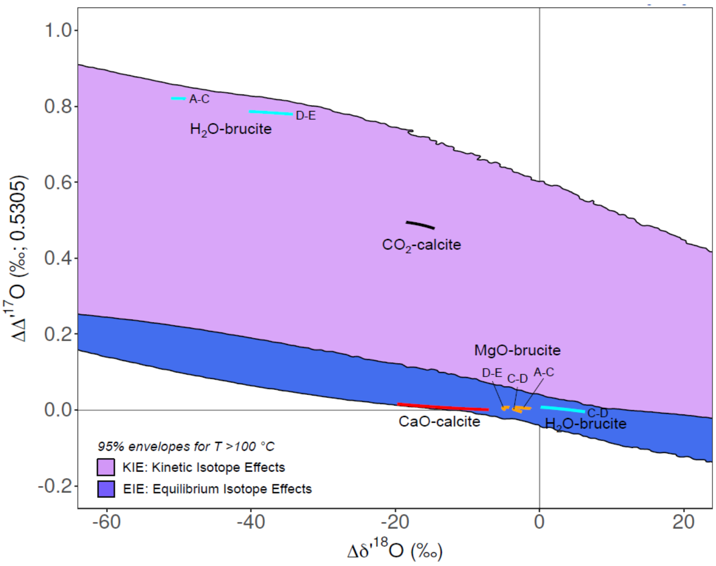
Triple oxygen isotope methods (e.g., using $\delta^{18}O$, and $\Delta'^{17}O$) have been used to classify meteorites, to constrain atmospheric chemistry, and to estimate primary productivity, among other uses. Such utility relies on the mass dependency of most chemical reactions: $\delta^{17}O$ is proportional to $\delta^{18}O$ by roughly a factor of 0.5. However, in detail, mass-dependency factors vary. While constraints on mass dependency are well established for equilibrium isotope effects, similar constraints for kinetic isotope effects are lacking. Using an *ab initio* Monte Carlo approach (see envelopes in Figure 1), we find the range of kinetic isotope effects (i.e., resulting from unidirectional chemical reactions) contains and exceeds the range of accessible equilibrium isotope effects for the ^{16}O-^{17}O-^{18}O system (Hayles and Killingsworth, 2022). Accessible kinetic isotope effects can yield $\Delta'^{17}O$ variations as large 0.8 ‰ from a single kinetic fractionation step. Reactions that yield the largest deviations from equilibrium are those with the largest molecular mass difference between decomposition fragments, typically the two products such as a gas and solid generated from the thermal decomposition of an initial solid. Comparison of DFT transition state model results against previously published experiments on the thermal decomposition of calcite ($CaCO_3$) (Miller et al., 2002) and dehydroxylation of brucite ($Mg(OH)_2$) (Clayton and Mayeda, 2009) show they are matched with mass-dependent kinetic isotope effects. This approach can be applied to any system with more than two isotopes.

Included figure: Calcite thermal decomposition and brucite thermal decomposition fractionations A-C, C-D and D-E, corresponding to different modelled transition states over a range of temperatures, are compared to the envelope containing Monte Carlo results. Reaction products shown in the figure are MgO: orange, H2O: light blue, CO2: black, CaO: red.



References:

Hayles, Justin A., and Bryan A. Killingsworth. "Constraints on triple oxygen isotope kinetics." Chemical Geology 589 (2022): 120646.

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