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Constraints on triple oxygen isotope kinetics

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Triple oxygen isotope methods have been used to classify meteorites, to constrain atmospheric chemistry, and to estimate primary productivity, among other uses. Such utility relies on predictable mass-dependent isotopic relationships for most chemical reactions. While constraints on mass dependency are well established for equilibrium isotope effects, similar constraints for kinetic isotope effects are lacking. Using a Monte Carlo approach we find the range of kinetic isotope effects (i.e., resulting from unidirectional chemical reactions) contains and exceeds the range of model-accessible equilibrium isotope effects for the ^{16}O-^{17}O-^{18}O system (Hayles and Killingsworth, 2022; Figure 1). In some cases, a single kinetic step could fractionate oxygen-17 to such a degree that it could be mistaken for mass-independent fractionation, such as when a solid thermally decomposes into a product with a relatively small molecular mass. For example, comparison of density functional theory 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.

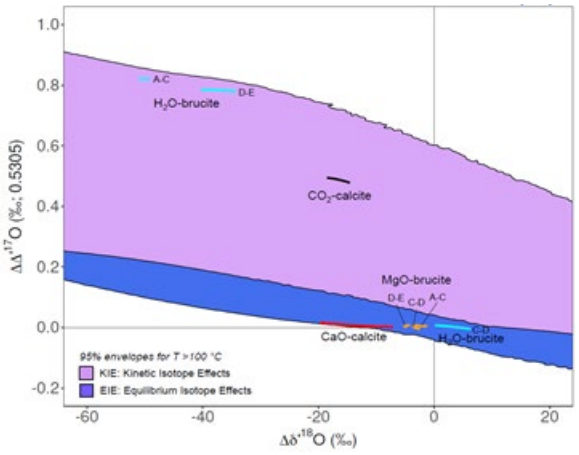

Figure 1: Oxygen isotope fractionations from DFT models of calcite thermal decomposition and brucite thermal decomposition, are compared to the envelope containing fractionations accessible to the Monte Carlo model. For brucite thermal decomposition three transition states were modeled, “A-C”, “C-D” and “D-E”. Reaction products shown in the figure are MgO: orange, H2O: light blue, CO2: black, CaO: red. Please see Hayles and Killingsworth (2022) for further details on the figure and isotopic definitions.