Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.35408

Simulating solid state isotope reordering of C-O bonds in the framework of trigonal carbonate mineral: a probabilistic approach

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Solid-state isotopic reordering of C–O bonds has been shown to alter the clumped isotope values of carbonate minerals subjected to elevated temperatures in both controlled heating experiments and geological settings. Understanding the kinetics of this process is imperative for reconstructing both the initial formation temperatures and the thermal histories experienced by carbonate mineral samples. Previous studies have considered increasingly complex mechanisms and reaction networks to explain the non–first-order reaction progress trends revealed by laboratory and natural experiments. Recent observations and models associate such deviations from first-order kinetics with differences in the activation energy required for isotope exchange along specific vectors connecting oxygen sites within the crystal lattice. The underlying atomistic mechanisms and activation energies of some of these vectors have recently been investigated using computationally expensive constrained ab initio molecular dynamics and density functional theory (cAIMD+DFT) models.

Here, we develop a computationally efficient probabilistic model that tracks the reaction progress of clumped isotope values through isotope exchange reactions among oxygen sites within the framework of trigonal carbonate minerals. When informed by vector-specific activation energies derived from cAIMD+DFT simulations for a defect-free lattice, our model fails to predict the reaction progress trends observed in controlled heating experiments. Fitting these data requires that lower activation energies persist between a limited number of oxygen sites within the crystal lattice. Such a scenario may be enabled by lattice defects. Our model bridges the gap between atomistic- and mineral-scale kinetics of solid-state reordering and can serve as a platform for predicting the effects of mineral cation composition, lattice impurities, cation ordering, and deformation on observed clumped isotope compositions.