A revised model for clumped isotope bond reordering in dolomite based on experimental constraints and field observations

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Carbonate clumped isotope ($\Delta47$) thermometry is used to constrain formation temperatures and oxygen-isotope compositions of fluids involved in the precipitation of carbonate minerals. It exploits the preference of $^{13}\text{C-}^{18}\text{O}$ bonds in carbonate molecules to form with decreasing temperature. This method has important applications in reconstructing paleoclimate through time, paleoaltimetry, diagenesis, and tectonics. Here, we specifically focus on the mineral dolomite, which can form as a primary precipitate in seawater, during early diagenesis, or during burial diagenesis. Depending on its origin, dolomite can thus either provide information on Earth-surface temperatures or on the diagenetic and tectonic history of carbonate sequences.

The use of clumped isotopes to reconstruct dolomitization conditions in ancient sequences requires determining if the temperatures reconstructed from clumped isotopes reflect the original signal or subsequent alteration caused by 13C-18O bond reordering at elevated temperatures during burial. Current reordering models use Arrhenius parameters for reordering that are based only a small number of heating experiment and are thus poorly constrained. Here, we reevaluate the published experiment, combined with additional heating experiment data at temperatures between 360 and 480 °C as well as natural dolomites with a well constrained thermal history, to redetermine the Arrhenius parameters for dolomite reordering. We show that existing reordering models underestimate the activation energy, highlighting the need for further experimental temperature-time series experiments to further constrain dolomite $\Delta 47$ reordering over geologic timescales.