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Experimental Clumped Isotope Reordering in Dolomite

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The conditions leading to the formation of sedimentary dolomite after decades of research, are still debated. Information on the formation temperature and the $\delta^{18}O$ of the fluid from which dolomite has precipitated is fundamental to constrain the models of dolomitization. Carbonate clumped isotopes are a reliable technique to acquire such information. In order to better constrain the potential of clumped isotopes in dolomite to reconstruct conditions during dolomitization in ancient sequences, however, it is important to determine how resistant the clumped isotope signal is against bond reordering at elevated temperatures during burial. Whereas the general systematic of clumped isotope reordering due to increasing temperatures is widely agreed on, there is further knowledge needed about the kinetic parameters of solid-state reordering dependencies. This is especially true for carbonate systems other than calcite.

In this study we present preliminary results of 50+ heating experiments on two, comparatively 'cold' natural dolomites from Monte San Salvatore, Switzerland (SanSal, Δ_{47} = 0.518 ± 0.015 ‰, 67 ± 8 °C) and from La Roda, Spain (LaRoDo, Δ_{47} = 0.651 ± 0.008 ‰, 19 ± 4 °C). SanSal is a well-ordered replacement dolomite from the middle Triassic and LaRo is a poorly ordered lacustrine dolomite from the Pliocene. Experimental temperatures are 360, 420, and 480 °C.

Experiments were conducted in a Box furnace using pre-evacuated quartz glass tubes with dolomitic sample material + $Ag_2C_2O_4$ (silver oxalate). The silver oxalate decomposes at ca. 140 °C to Ag_2 + CO_2, providing 6-8 bars of pCO_2 which prevents decarbonation of the dolomites whereas the remaining Ag_2 binds sulfuric compounds to prevent Δ_{48} interference. Stable- and clumped isotopic compositions were determined using a Kiel IV carbonate device coupled to a ThermoFisher MAT253+ IRMS. Monitoring of potential recrystallization was done with X-Ray diffraction and SEM.

Our results suggest that clumped isotope reordering proceeds rapidly within the first hour of heating and that there is a significant difference in reordering kinetics between the two materials.