Effects of water on carbonate clumped isotope bond reordering kinetics

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Carbonate clumped isotope geothermometry is a powerful tool for reconstructing past temperatures. The overabundance of doubly substituted isotopologues can change at elevated temperatures (ca. > 100 °C) without altering the individual C and O bulk isotopic composition of a mineral owing to solid-state reordering reactions through the crystal lattice [Dennis and Schrag, 2010; Passey and Henkes, 2012]. Understanding the kinetics of this clumped isotope reordering process is a prerequisite for application to geological questions involving samples that have been heated in the subsurface.

The effect of water on reordering kinetics has not been thoroughly explored. The presence of water dramatically increases rates of oxygen self-diffusion in calcite [Farver, 1994, Kronenberg et al., 1984], but whether water-enhanced diffusion is limited to the mineral surface or extends into the bulk crystal lattice is not clear. Here we present experimentally determined Arrhenius parameters for reordering rates in optical calcite heated under wet high pressure (100 MPa) conditions. We observe marginal increases in reordering rates under these conditions relative to rates observed for the same material reacted under dry, low pressure conditions. This contrasts with the orders of magnitude increase in oxygen diffusivity at the mineral surface when water is present, suggesting the latter effect arises from surface reactions that have minimal influence on the diffusivity of C or O in the bulk mineral. Our results imply that previously published reordering kinetics determined under dry, low pressure experimental conditions are generally applicable to geological samples that have been heated in the presence of water.