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Effect of polymorphic transition on oxygen isotope fractionation between aragonite, calcite, and water: A low-temperature experimental study

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ABSTRACT

The polymorphic transition from aragonite to calcite is a common phenomenon in nature and laboratory experiment, but its effect on O-isotope fractionation between secondary calcite and water is not known. Low-temperature synthesis experiments were carried out in this study to decipher the behavior of O-isotope fractionation between $CaCO_3$ and H_2O during this process. The initial aragonite was synthesized by one- and two-step overgrowth techniques at 50 and 70 °C, respectively, with a difference in the duration of O-isotope exchange between dissolved carbonate and water prior to initial aragonite precipitation. Calcite was then synthesized by in situ polymorphic transition from the precursor aragonite in aqueous solution at the same temperatures. SEM observations show that the phase transition from aragonite to calcite proceeded in the mechanism of dissolution-reprecipitation. Although different approaches were employed to synthesize the starting aragonites, O-isotope analyses of product calcite and coexisting water unanimously yield consistent calcite-water fractionations relative to temperature. This finding demonstrates that calcite derived from polymorphic transition of aragonite can readily achieve O-isotope equilibrium with water regardless of its precursor composition. In particular, not only is the calcite-water fractionation relationship obtained in this study at 50 to 70 °C in agreement with that extrapolated from the literature data by slow precipitation experiments at 0 to 40 °C, but also the experimental calcite-water fractionations available at 25 to 70 °C are in close agreement with theoretically calculated fractionations. These results indicate that O-isotope equilibrium between calcite and water may prevail in calcite formed by the mechanism of dissolution-reprecipitation in aqueous solution despite different reaction paths.