

Experimental calibration of the triple oxygen isotope fractionation between CaCO₃ and H₂O

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Calcium carbonates have the potential to preserve various geochemical signatures reflecting their environmental conditions at the time they formed. They are ideal archives for paleoclimate and paleoenvironmental studies. Recently, it has been shown that, beyond the conventional stable isotopes, the three isotopes of oxygen in carbonates can help us better reconstruct processes associated with past changes in hydrology, climate, and environment.

Here, we inorganically precipitate calcite and aragonite to calibrate the triple oxygen fractionation in the CaCO₃-H₂O system under well-constrained laboratory conditions. Our results suggest that the triple isotope equilibrium fractionation between CaCO₃ and H₂O between 10 °C and 35 °C, as reflected by the proportionality factor $\theta = \ln^{17}\alpha / \ln^{18}\alpha$ (1) shows a slight temperature-dependence, (2) is polymorph independent, and (3) is independent of the molarity of the precipitating solution. We also found that, the carbonates are strongly depleted in ¹⁷O relative to their parent water, as reflected in their ¹⁷O_{excess} values.

However, while comparing our experimental results with predictions from theoretical studies, two important discrepancies were revealed. First, the direction of the trendline of the proportionality factor θ as a function of temperature shows opposite direction. Second, the absolute θ values for experimental studies are relatively lower than those determined from simulations. The causes of such differences are still poorly understood, but will be discussed.