

Triple oxygen isotope fractionation during phosphoric acid digestion of carbonates

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Carbonate is one of the most important proxies for reconstructing ancient climate, and triple oxygen isotope compositions in carbonate hold the promise providing additional constraints on carbonate formation environment. To retrieve the information recorded by ¹⁷O in carbonate, high precision measurement is required. Extraction of CO₂ from carbonate by phosphoric acid digestion and measuring ¹⁷O in CO₂ has been used to obtain accurate ¹⁷O isotope compositions in carbonate minerals. However, the triple oxygen isotope fractionation during phosphoric acid digestion is just ignored in literatures, which will limit the usage of small ¹⁷O anomaly recorded in carbonates and bring difficulty in inter-laboratory comparison. In this study, density functional theory (DFT) calculation will be applied to calibrate the triple oxygen isotope fractionation during phosphoric acid digestion.

We suggest that the phosphoric acid digestion reaction can effectively accelerated or catalyzed by the H-bonding. This kind of catalytic reaction has been well-studied in chemistry field (concerted proton transfer reaction). There are only three major H-containing compounds in the system, i.e., phosphoric acid (H₃PO₄), the H₂CO₃ and water (H₂O), showing that there are three different catalyzing pathways. By this way, the energy barriers of proton transfer can be kept as low as possible.

The triple oxygen isotope fractionation relationship θ for three pathways, i.e., i.e. H₂CO₃-catalyzed, H₃PO₄-catalyzed and H₂O-catalyzed pathways, are found to be 0.525, 0.526 and 0.529 at 25°C, respectively. The apparent θ between extracted CO₂ and carbonates is a function of these three intrinsic θ s, and its value changes with the variation of individual contribution. This is one of the main reasons that there is a spreading distribution of clumped isotope calibration lines during phosphoric acid digestion of carbonates.