

A new look at the fractionation of the clumped isotopes of CO₂ as a function of technique and temperature

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The first measurements of Δ_{47} in carbonates were carried out with CO₂ produced by the reaction of carbonates with phosphoric acid at 25°C in a sealed reaction vessel (SV). Later, various workers carried out the reaction at higher temperatures (75 to 90°C) using either a common acid bath (CAB) or a drip method. Although these higher temperatures are used in order to speed up the reaction and ensure complete yield, a correction is needed in order to compare data generated at the different temperatures with the data generated at 25°C. This value has been reported to be between 0.08 and 0.09‰ when comparing 90°C to 25°C. However, a further factor to consider is nature of the reaction method. In the CAB, the CO₂ is continuously removed as the sample reacts, while in the SV it remains in contact with the acid for hours to days. Hence it would be expected that the CO₂ has a significantly greater periods of time to equilibrate with the H₂O present in the acid and that produced in the reaction. In attempts to determine the fractionation associated with the different reaction temperatures, some studies have combined data produced at low temperature using the SV with data generated at high temperature using the CAB. We consider that this confounds the understanding of the processes leading to the fractionation and the determination of its magnitude. Here we present fractionation factors measured on different minerals at a range of temperature for both the CAB and the SV. These show that the CAB shows larger differences as a function of temperature than the SV and that different minerals show different changes in Δ_{47} as a function of temperature.