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Kinetic triple oxygen isotope fractionation during phosphoric acids digestion of carbonates

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Triple oxygen isotope ($\Delta^{17}O$) in carbonates serve as valuable proxies for reconstructing past environments, ranging from humidity and temperature to hydrological cycles and diagenetic history. High precision $\Delta^{17}O$ measurements are essential to validate these applications, with the measurement of $\Delta^{17}O$ on CO_2 extracted through phosphoric acid digestion of carbonates being a common practice. However, since this process does not achieve 100% oxygen extraction, kinetic isotope fractionation factors, i.e. $^{18}\alpha$ and θ ($\ln^{17}\alpha/\ln^{18}\alpha$), are critical for accurately translating the measured $\Delta^{17}O$ to that of the associated carbonate samples. Notably, a significant discrepancy exists between the theoretically predicted θ (0.528)[1, 2] and the experimentally observed one (0.523)[3], even though the $^{18}\alpha$ values align between the two approaches. We propose that this discrepancy stems from an insufficient consideration of solvation effects in the theoretical calculations, and employ quantum mechanical calculations to test this hypothesis.

Molecular clusters consisting of up to 12 phosphoric acid molecules and a single carbonic acid molecule were used to simulate the reaction system. Our results show that the cluster with 12 phosphoric acid molecules is sufficiently large to account for the solvation effects. Along the reaction pathway, we identified two transition states and one intermediate state, which differ from previously proposed reaction mechanisms[1, 2] and are critical for determining the probable kinetic isotope fractionation factors. Our calculated values for $^{18}\alpha$ and θ are 0.9891 ±0.0008 (2SE) and 0.5233±0.0008 (2SE) at 25℃, respectively, and are consistent with experimental results. Additionally, we present the temperature-dependent relationships of $^{18}\alpha$ and θ, as shown in Fig. 1.

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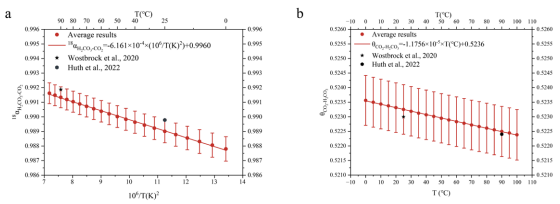

Fig 1. $^{18}\alpha$ and θ values varied with temperature ranging from 0 ℃ to 100 ℃