

Triple oxygen isotopes as paleoenvironmental tool

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Classic $\delta^{18}\text{O}$ analyses in chemical sediments are widely applied within the geosciences. The most successful isotopic tools such as the classic carbonate thermometer are based on simple systematics with few variables often allowing a unique interpretation of the isotope data. Highly successful target materials typically record near-equilibrium conditions. As soon as kinetic processes come into play, interpreting isotope data becomes challenging obscuring potential applications.

Equilibrium fractionation adjusts both $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ (expressed as $\delta^{17}\text{O}$), so that fully equilibrated samples are expected to fall on equilibrium curves in triple oxygen isotope space. Samples that do not fall on these material specific curves did not form in equilibrium with the water, providing a simple test for equilibrium (or the water isotopic composition).

Emerging $\delta^{17}\text{O}$ data for chemical sediments show considerable scatter pointing to kinetic isotope effects, alteration and mixing. Respective examples and theoretical models to explain such data will be reviewed. I will show how $\delta^{17}\text{O}$ of such unequilibrated samples can be used for paleoenvironmental reconstructions, to better understand reaction pathways and mineral formation mechanisms.

The combination of deuterium and classic oxygen isotopes has been incredibly successful in the hydrological community, mainly because the d-excess parameter allows to identify kinetic effects. The combination of $\delta^{18}\text{O}$, d-excess and ^{17}O -excess ($=\delta^{17}\text{O}_{\text{H}_2\text{O}}$) now enables to reconstruct e.g. absolute paleo relative humidity and pale wind conditions. This example shows how the additional $\delta^{17}\text{O}$ dimension can resolve the processes responsible for the fractionation. Arrays of $\delta^{18}\text{O}$ vs. $\delta^{17}\text{O}$ samples fall on a process dependent slope. The identification of the mechanism is key to i) quantify and correct for the kinetic isotope effect; ii) to unravel the mineral formation mechanisms; and iii) to constrain the respective physico-chemical conditions within the paleoenvironment.