

Carbonate $^{17}\text{O}_{\text{excess}}$ as a paleo-hydrology proxy

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Carbonates are a common paleoclimate archive in both marine and land settings. Land carbonates record both temperatures and hydrological conditions. Paleotemperatures derived from clumped isotopes in land carbonates are often combined with $\delta^{18}\text{O}$ to reconstruct parent water $\delta^{18}\text{O}$. However, the common interpretation of water $\delta^{18}\text{O}$ as rainfall amounts does not reflect the hydrological complexity of moisture sources and evaporation. These gaps can be filled by information from $^{17}\text{O}_{\text{excess}}$ in water, that depends on the conditions in which evaporation occurs, thus reflecting the moisture source in meteoric water or the extent of evaporation in a small water body (e.g., a lake). Water $^{17}\text{O}_{\text{excess}}$ can be reconstructed from three oxygen isotope analysis in the same carbonate in which Δ_{47} and $\delta^{18}\text{O}$ are measured.

We derive the fractionation factor $^{17}\alpha$ between CaCO_3 and water, using freshwater mollusk shells from well constrained spring environments, at a temperature range of 15-28°C. The spring water temperature and isotopic composition are constant year-round, avoiding uncertainty associated with seasonality.

The observed $^{18}\alpha$ and $^{17}\alpha$ between mollusk aragonite and parent water are used to calculate the fractionation slope θ ($=\ln^{17}\alpha/\ln^{18}\alpha$), resulting in $\theta=0.5234\pm 0.0005$. This θ value is only slightly lower than the reference slope of 0.528, implying that $^{17}\text{O}_{\text{excess}}$ in carbonates relative to parent waters is only weakly temperature dependent. It is therefore a straightforward recorder of parent water $^{17}\text{O}_{\text{excess}}$. Speleothem carbonates may be a suitable archive for records of $^{17}\text{O}_{\text{excess}}$ in rainfall and therefore of moisture sources. Preliminary application of this approach to speleothem carbonate will be discussed.