

## **Clumped isotopes in speleothems: accounting for disequilibrium**

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Speleothems are increasingly used as archive material for paleoclimate reconstruction on land. Deriving past temperatures from speleothems  $\delta^{18}\text{O}$ , however, is limited by uncertainty in the isotopic composition of drip water, associated with hydrological variability, and by kinetic isotope effects that play an important role in the isotopic composition of stalagmites. Carbonate clumped isotope thermometry is designed to overcome the hydrological uncertainty, but also serves as an indicator for non-equilibrium biases. Disequilibrium in speleothems is related to the degassing of  $\text{CO}_2$  from drip water films, with fast  $\text{CaCO}_3$  precipitation that does not allow DIC to regain oxygen and clumped isotopes equilibrium through isotope exchange with water. In some caves the extent of disequilibrium varies spatially and temporally, as observed in Bunker Cave (Germany) and Villars Cave (France). In such cases the co-variance between  $\delta^{18}\text{O}$  and  $\Delta_{47}$  may be used to constrain disequilibrium and infer climatic conditions. In other caves, as observed in Soreq Cave (Israel), the extent of disequilibrium varies with drip rate but is spatially constant within fast drip stalagmites. In such cases, carbonates precipitated in laboratory experiments that mimic thin film conditions can be used as speleothem analogs to constrain paleo-temperatures. The talk will discuss the mechanisms of kinetic isotope effects and their implications to speleothem records; it will illustrate the two approaches for accounting for disequilibrium that allow extraction of terrestrial climatic information.