Clumped isotopes in speleothems: accounting for disequilibrium

Speleothems are increasingly used as archive material for paleoclimate reconstruction on land. Deriving past temperatures from speleothems δ^{18} 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 CO_2 from drip water films, with fast $CaCO_3$ precipitation that does not allow DIC to regain oxygen and clumped isotopes equilibrium through isotope exchange with water. The talk will discuss the mechanisms of kinetic isotope effects and their implications to speleothem records. It will further describe a laboratory based approach that we develop in order to account for accounting for disequilibrium that allow extraction of terrestrial climatic information.