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Kinetic isotopic fractionation versus thermodynamic equilibrium in modern speleothems: new insights from clumped isotopes

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Speleothems offer excellent conditions to record climate change over various time scales, because they can be precisely and absolutely dated, and because several environmental parameters directly or indirectly affect their isotopic composition. In particular, if, as commonly assumed, speleothem carbonate precipitates at thermodynamic equilibrium, its oxygen composition (δ^{18}Oc) is a function of two variables only: the composition of local drip water and the crystallization temperature. It has long been recognized, however, that a speleothem's carbon and oxygen compositions can also be affected by isotopic fractionation caused by rapid CO2 degassing and/or crystallization, resulting in δ^{18}Oc values heavier than predicted by equilibrium thermodynamics. Although many of the caves described in the literature have been reported as producing speleothems in quasi-equilibrium with their parent waters, δ^{18}Oc values are still typically 0.5-1.5 permil heavier than expected using published inorganic carbonate-water ^{18}O fractionation factors [McDermott et al., 2006].

Based on 'clumped isotope' measurements of 13 well-constrained modern speleothems, we determined that none of them appear to precipitate in thermodynamic equilibrium, neither with respect to ^{18}O nor to Δ_{47}. Based on a new theoretical model of kinetic isotopic fractionation affecting speleothem growth, we propose a quantitative interpretation of the physical processes affecting the isotopic composition of speleothems [Guo, 2008], and discuss the implications on past climate reconstructions using fossil speleothem records.

Guo (2008): *Carbonate clumped isotope thermometry: application to carbonaceous chondrites and effects of kinetic isotope fractionation*. PhD thesis, Caltech.