



Quantitative speleo-thermometry? Using clumped-isotopes measurements to correct for kinetic isotope fractionations induced by CO₂ degassing

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Assuming that a given speleothem precipitates near thermodynamic equilibrium, quantitative interpretation of its ¹⁸O record in terms of physical parameters is generally hampered by the lack of robust methods for separating isotopic variations due to paleo-temperatures from those reflecting source water compositions. Moreover, in many settings it appears likely that speleothems form out of equilibrium, due to kinetic isotopic fractionation caused by rapid CO₂ degassing, which further detracts from the reliability of paleo-environmental reconstructions.

By combining (1) an *ab initio* model of the kinetic isotopic fractionation associated with the degassing/precipitation process [Guo *et al.*, 2007], (2) “traditional” oxygen isotopic measurements and (3) “clumped-isotope” measurements of Δ₄₇ (a thermodynamic variable which quantifies the statistical overabundance of ¹³C¹⁸O bonds in the carbonate crystal [Schauble *et al.*, 2006; Ghosh *et al.*, 2006]), it appears possible to determine quantitatively the precipitation temperature of an a priori out-of-equilibrium speleothem.

Initial testing of the method on modern, well-characterized speleothems from settings including the Villars cave (SW France) support the model's predictions. Additionally, significant variations in the amplitude of kinetic isotope effects were observed in different speleothems from the same setting.

P. Ghosh et al., 2006. $^{13}\text{C}^{18}\text{O}$ bonds in carbonate minerals: a new kind of paleothermometer. *Geochimica et Cosmochimica Acta*, 70:1439–1456.

W. Guo et al., 2007. Isotope fractionations associated with degassing of CO_2 aqueous solutions: implications for carbonate clumped isotope thermometry. *AGU Fall Meeting abstract*.

E. Schauble et al., 2006. Preferential formation of $^{13}\text{C}^{18}\text{O}$ bonds in carbonate minerals, estimated using first-principles lattice dynamics. *Geochimica et Cosmochimica Acta*, 70:2510–2529.