S4 Summer School on Speleothem Science

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Lecture Abstract:

Kinetic and equilibrium fractionation in speleothem carbonate 'clumped isotopes'

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Carbonate clumped isotopes provide a paleo-thermometer that is based on the abundance of ^{18}O-^{13}C bonds in the carbonate lattice relative to that expected at a random distribution of isotopes among all isotopologues. The Δ47 parameter measures the thermodynamic ordering preference of two heavy isotopes to bind with each other and it does not depend on the absolute concentrations of ^{13}C and ^{18}O in the carbonate mineral. At equilibrium, this preference is temperature dependent and potentially records the temperature of mineral growth, independent of the oxygen isotope composition of the solution in which it grows. Clumped isotopes generally agree well with synthetic Δ47 thermometer calibrations for a wide variety of biogenic, primarily marine, carbonates. This conformity is consistent with the notion that the Δ47-T relationship reflects mineral formation from a solution that is at, or close to, isotopic equilibrium. Nevertheless, marked deviations from the equilibrium Δ47-T relationship have been observed in speleothems. Early measurements of Δ47 in the Soreq cave (Israel) speleothems yielded a value for a modern stalagmite that is lower than that expected at equilibrium with the local bedrock temperature. Subsequent Δ47 studies of fossil speleothems in Villars cave (France) and Bunker cave (Germany) confirm this observation, which reflects a Kinetic Isotope Effect (KIE) associated with CO2 degassing.

The talk reviews the history of the application of carbonate clumped isotope thermometry to speleothems: the theory, the experimental calibrations, and the mechanisms and magnitude of kinetic isotope effects. Attention is placed on the coupling between Δ47 and $\delta^{18}O$ in speleothem carbonate and how this can be utilized in to the determination of $\delta^{18}O$ of cave waters.

Selected references:

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