

Carbonate clumped isotopes thermometry: equilibrium and kinetic effects

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Clumped isotopes refer to the natural abundance of molecules containing more than one heavy, rare, isotope. In CO₂, this refers to measurements of the isotopologue combination of mass 47, primarily ¹³C¹⁸O¹⁶O. Δ₄₇ measures the abundance of CO₂ of mass 47 relative to that expected from random distribution of ¹³C and ¹⁸O among all isotopologues. As such, Δ₄₇ reflects internal ordering of ¹³C and ¹⁸O atoms with respect to each other, in either CO₂ molecules or a carbonate lattice, and is independent of the absolute abundances of ¹³C and ¹⁸O. At equilibrium, Δ₄₇ approaches zero at high temperatures whereas the abundance of ¹³C-¹⁸O bonds increases at low temperatures, reflecting the thermodynamic preference of two heavy isotopes to bind with each other.

Clumped isotopes measurements in CO₂ extracted from carbonates were first performed in 2004 in the laboratory of John Eiler in Caltech, and recently has been spreading into additional laboratories. The Δ₄₇-temperature relationship has been originally determined through synthetically precipitated calcite at known temperatures, by bubbling N₂ to remove CO₂ from a saturated Ca(HCO₃)₂ solution. A large variety of biogenic carbonates from marine organisms has been shown to conform to the same Δ₄₇-T relationship when considering the growing season temperature for these organisms.

The wide biogenic conformity suggests that this relationship is close to thermodynamic equilibrium. However, the existence of kinetic isotope effects has been recognized and is most notably observed in speleothem carbonates. These effects are likely related to fast CO₂ degassing from a thin film of solution, followed by two competing processes having similar rates: oxygen isotope exchange between DIC and H₂O on one hand and carbonate precipitation on the other.

The talk will discuss the use of clumped isotopes thermometry at equilibrium as well as the processes leading to offsets from equilibrium and the attempts to apply clumped isotopes thermometry in these cases as well.