Goldschmidt 2024 Abstract
https://doi.org/10.46247/gold2024.23476

Process-based modeling of kinetic clumped (Δ_{47} and Δ_{48}) isotope effects: from inorganic to biogenic carbonates

JAMES M WATKINS[1], QICUI JIA[2], SHUO ZHANG[2] AND LAURENT DEVRIENDT[3]

[1]University of Oregon
[2]Tsinghua University
[3]Lawrence Berkeley National Laboratory
Presenting Author: watkins4@uoregon.edu

We developed a generalizable box model [1] that tracks the non-equilibrium carbon, oxygen, and clumped (D_{47}, D_{48} and D_{49}) isotope compositions of chemical species in the full $CaCO_3$-DIC-H_2O system. The model is calibrated against inorganic calcite precipitation experiments and can be adapted to include processes (e.g., alkalinity pumping, ion-selective channels, vacuolization) known to affect the stable isotope composition of biominerals [2].

We will present an overview of the model as well as the first adaptation for modeling carbonate biomineralization. Specifically, recently published dual clumped (D_{47} and D_{48}) isotope data from corals grown at nearly constant temperature exhibit strong covariations in $d^{13}C$-$d^{18}O$ as well as D_{47}-D_{48} [3]. We use the $d^{13}C$-$d^{18}O$ data to constrain model parameters and then calculate D_{47} and D_{48}. We show that the model successfully predicts the observed large deviations from equilibrium in D_{47} and D_{48}, supporting the idea that temperatures can be retrieved from samples thought to be compromised by nonequilibrium isotope effects. The model outputs also provide constraints on parameters such as the activity of the enzyme carbonic anhydrase, the coral growth rate, and the composition of the calcifying fluid.

We will discuss some general approaches and progress towards adapting the model to other situations involving CO_2 absorption (e.g., corals, foraminifera, high-pH travertines) or degassing (e.g., speleothems, low-pH travertines, cryogenic carbonates) and/or mixing with other DIC sources.

[1] Watkins & Devriendt (2022), Geochem. Geophys. Geosystems. 23, e2021GC010200.

[2] Chen, Gagnon & Adkins (2018), Geochim. Cosmochim. Acta 236, 179-197.

[3] Davies, Guo, Bemecker, Tagliavento, Raddatz, Gischler, Flogel & Feibig (2022), Geochim. Cosmochim. Acta 338, 66-78.