

# $\Delta_{47}$ – $\Delta_{48}$ disequilibrium in steady state chemical systems: numerical models describing carbonate mineralization in corals and methane seeps

PHILIP STAUDIGEL AND JENS FIEBIG

Goethe University Frankfurt

Presenting Author: staudigel@em.uni-frankfurt.de

Carbonate minerals generally do not form as a result of equilibrium processes; as systems at chemical equilibrium by definition do not result in a net accumulation of minerals. The bio-geochemical systems that result in continuous precipitation of calcium carbonate operate due to sustained perturbation of fluid chemistry. These processes can occur at steady-state, and may do so with residence times for dissolved elements/molecules similar to the rates of CO<sub>2</sub> (de)hydration and (de)hydroxylation reactions, and thus reach a state of sustained isotopic disequilibrium, which is then preserved in carbonate minerals. Identification of these kinetic isotope effects in carbonate samples has relied previously on their correlated effects on isotope ratios, such as  $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$  values in corals [1], or correlated effects between  $\delta^{18}\text{O}$  and  $\Delta_{47}$  values in methane seeps[2, 3] and corals[4]. These effects make unambiguous determination of paleotemperatures using these values difficult, as there must exist *a priori* knowledge of water  $\delta^{18}\text{O}$  values. This assumption precludes applications in systems with variable salinity or epochs with potentially variable water composition. The use of coupled  $\Delta_{48}$ - $\Delta_{47}$  values in carbonates may present a solution to this problem, as these values are affected differently by these kinetic processes, but possess a single, thermodynamically predictable, point of agreement. Thus, these values can be used not only to identify these kinetics, but also to correct for them to reconstruct water composition and temperature. To this end, we have constructed numerical models that simulate the extent of isotopic disequilibrium in carbonates precipitated under steady state conditions at methane seeps and by corals. Model output data is compared to dual clumped isotope data of carbonates with known formation temperatures to identify key parameters that control the extent of observed isotopic disequilibrium.

[1] Chen, Gagnon & Adkins (2018), *Geochim Cosmochim Acta* **236**, 179–197.

[2] Savard, Jautzy, Lavoie, Dhillon & Defliese (2021), *Geochim Cosmochim Acta* **298**, 43–54.

[3] Thiagarajan, *et al.*, (2020), *Geochim Cosmochim Acta* **279**, 204–219.

[4] Thiagarajan, Adkins & Eiler (2011), *Geochim Cosmochim Acta* **75**, 4416–4425.