

Δ_{47} and $\delta^{18}\text{O}$ disequilibria in microbial carbonates as tracers of metabolic activity

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Microbial biomineralisation is a major mechanism inducing carbonate precipitation in environments such as caves, soils and sediments. Provided that carbonate precipitation occurred at isotopic equilibrium (ie., without “vital effects” observed in some carbonates formed by living organisms) their Δ_{47} and $\delta^{18}\text{O}$ values can be used to retrieve informations on their formation conditions (temperature and $\delta^{18}\text{O}$ value of the precipitating fluid). If microbial carbonates Δ_{47} values were affected by vital effects, it would constitute a tracer for the microbial origin of those carbonates.

To adress that question, we performed an isotope study of carbonates precipitated by a soil carbonatogen bacteria, shown to generate carbonates with $\delta^{18}\text{O}$ values in strong disequilibrium with water [1]. Its metabolic activity produces ammonia (increasing pH) and dissolved inorganic carbon (DIC) that precipitates as solid carbonates. We found Δ_{47} offsets down to 0.262‰ lower than expected Δ_{47} equilibrium values (the largest Δ_{47} offset measured to date in biogenic carbonates) –corresponding to a temperature offset of ~200°C from the precipitation temperature. In contrast, a similar experiment conducted with the addition of carbonic anhydrase (an enzyme able to equilibrate the oxygen isotopes between DIC and water) yielded expected equilibrium Δ_{47} and $\delta^{18}\text{O}$ values, despite fast precipitation rates.

Overall, these data demonstrates that bacteria can precipitate carbonates with strong vital effects on Δ_{47} (and $\delta^{18}\text{O}$) compositions, suggesting that Δ_{47} values could also fingerprint a microbial origin. As importantly, our results indicate that most ^{13}C – ^{18}O bonds in solid carbonates are aquired before precipitation (ie., inherited from their distribution within the DIC pool). Thus, when carbonates precipitate from a DIC in disequilibrium with water regarding oxygen isotopes, the abundance of ^{13}C – ^{18}O bonds in the carbonate lattice should not correspond to its abundance expected at equilibrium.. We stress that paired Δ_{47} – $\delta^{18}\text{O}$ data should help to further constrain vital effects, notably to determine if carbonate precipitation occurred at isotopic equilibrium, but also to retrieve information on metabolically produced DIC and porewater (or even body water) $\delta^{18}\text{O}$ values.

[1] Thaler et al. 2017. *GCA*, **199**, 112-127