Out of equilibrium δ^{18} O CaCO₃ in microbial carbonates: a subsurface biomioneralization tracer?

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Oxygen stable isotope compositions of carbonates are widely used to provide information on their conditions of precipitation. Most carbonates result from a biological activity, which in the case of some skeleton-forming eukaryotic organisms has been shown to lead to isotopic characteristics that differ from those expected for isotope equilibrium. The origin of this difference remains poorly understood and is referred to as the "vital effect". It could be a tracer for the deep microbial communities as it is likely that those microbial communities precipitate carbonates in the subsurface.

So far, potential microbial vital effects have been overlooked and microbial carbonation is considered from an oxygen isotope perspective as occurring at equilibrium with water. We revisit this assumption by performing an isotope study of carbonates precipitation by the strain Sporosarcina pasteurii, a bacterial model of carbonatogen metabolisms. Its ureolytic activity produces ammonia (thus increasing the pH) and dissolved inorganic carbon (DIC) that precipitates as solid carbonates. $\delta^{18}O_{CaCO3}$ results show values up to 20% lower than what was expected for carbonate precipitation in equilibrium with water. The addition of carbonic anhydrase, an enzyme able to equilibrate the oxygen isotopes between DIC and water, yields equilibrium values. This demonstrates that bacteria may precipitate carbonates with a vital effect and highlights the potential of O isotopes as proxies to identify biogenic subsurface carbonates.