

New views on CaCO₃-H₂O oxygen isotope fractionation

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The processes controlling the CaCO₃-H₂O oxygen isotope fractionation factor ($\alpha_{c/w}$) for biogenic and inorganic carbonates are not fully understood, potentially compromising paleoenvironmental reconstructions based on the carbonate oxygen isotope ratio (¹⁸O/¹⁶O). A major advance in understanding ¹⁸O/¹⁶O in carbonates has been to view carbonate-water fractionation as the result of kinetic and/or equilibrium fractionation steps occurring between water and dissolved inorganic carbon (DIC) species and between the DIC species and carbonate [1]. However, the intermediate fractionation steps have not been fully quantified.

This study presents a comprehensive model of kinetic and equilibrium oxygen isotope fractionation between CaCO₃ and H₂O that accounts for fractionation between both CaCO₃ and the CO₃²⁻ pool, and CO₃²⁻ and H₂O, as a function of temperature, pH, salinity, calcite saturation state (Ω), the residence time of the dissolved inorganic carbon (DIC) in solution, and the activity of the enzyme carbonic anhydrase [2].

The model shows that: (a) The fractionation between CaCO₃ and CO₃²⁻ is controlled by the solution calcite saturation state and salinity, (b) pH and mineral growth rate effects on $\alpha_{c/w}$ observed in nature and in laboratories are likely to originate from disequilibrium fractionation (i.e. kinetic isotope effects) between CO₃²⁻ and H₂O, and (c) the temperature sensitivity of $\alpha_{c/w}$ is caused by the negative effect of temperature on the CO₃²⁻-H₂O fractionation factor and is expected to deviate from the commonly accepted $-0.22 \pm 0.02\text{‰}/^\circ\text{C}$ value [3] where the CO₃²⁻ pool is not at isotopic equilibrium with water (e.g. coral aragonite). In contrast, kinetic isotope effects between CaCO₃ and CO₃²⁻ should have limited effects on the temperature sensitivity of $\alpha_{c/w}$. This explains why the ¹⁸O/¹⁶O of many biogenic carbonates (e.g. CaCO₃ secreted by foraminifers, molluscs, ostracods) display similar temperature sensitivities despite the carbonates forming in conditions far from isotopic equilibrium.

[1] Watkins et al. (2013) *EPSL* **375**, 349; [2] Devriendt et al. (in press) *GCA*; [3] Kim & O'Neil (1997) *GCA* **61**, 3461