CO_2 hydration/hydroxylation and the origin of carbonate kinetic isotope effects

J. D. Boettger* and J. D. Kubicki

Penn State Univ., University Park, PA 16802, USA
(*correspondence: jdb488@psu.edu)

Paleoclimate proxies based on isotopic fractionation in biogenic calcium carbonate minerals constrain paleotemperatures and aid in assessments of the current rate of anthropogenic global warming. Corals and some other calcifiers tend to display $\delta^{13}C$ and $\delta^{18}O$ at isotopic disequilibrium with surrounding waters (so-called "vital effects"), introducing potential errors to paleoproxies [1]. Some research attributes vital effects to slow isotopic exchange during the hydration reaction between CO_2 and H_2O to form H_2CO_3 in the semipermeable membrane-bound calcifying space (the "kinetic" vital effect model) [2].

We present atomistic, *ab initio* simulations to elucidate the potential contribution of kinetic vital effects to non-equilibrium C and O isotope fractionation in the skeletons of calcifying organisms. The model utilizes density functional theory and transition state theory to evaluate isotopologue-specific reaction rates for CO_2 hydration. Model accuracy is tested against experimental, non-isotopologue-specific reaction rates and against equilibrium fractionation factors using both forward and reverse reactions. More accurate results are obtained when using more H_2O molecules in the hydration shell surrounding CO_2, highlighting the importance of accurately modeling the local chemical environment around the reactive species and suggesting the usefulnes of cluster-based *ab initio* models. These ab initio models will show whether or not the kinetics of hydration and hydroxylation reactions can account for vital effects in calcifiers, or whether other models are necessary to account for non-equilibrium fractionation.

Initial thoughts will also be presented on an alternative explanation for the source of vital effects in corals: precipitation via an amorphous calcium carbonate (ACC) intermediate. *Ab initio* models of whole nanoparticles are to computationally demanding to be feasible, but the usefulness of cluster models to describe their properties will be discussed.

[1] Felis *et al* (2003) *Coral Reefs* **22**, 328-336 [2] Cohen & McConnaughey (2003) *Rev. Min. Geoch.* **54**, 151-187