A numerical framework for interpreting clumped isotope ‘vital effects’ in scleractinian coral skeletons

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The carbonate clumped isotope thermometer constrains carbonate formation temperature based on the extent of $^{13}$C and $^{18}$O clumping in the carbonate mineral lattice ($\Delta_{47}$), and is a promising tool in paleoclimate and paleoceanographic research. However, there is growing evidence that biological processes (‘vital effects’) can cause deviations in the clumped isotope compositions of scleractinian coral skeletons from the expected thermodynamic equilibrium values in certain coral genera. This finding complicates the application of this thermometer in corals.

Based on existing models of stable isotope vital effects in corals, we present a numerical framework for interpreting clumped isotope vital effects in scleractinian coral skeletons. This framework takes into account both the kinetic isotope effects associated with CO$_2$ hydration/hydroxylation reactions and isotope equilibration of dissolved inorganic carbon (DIC) in the coral’s calcifying fluid. It allows quantitative evaluation of the effects of a variety of factors on the oxygen isotope and clumped isotope vital effects in corals. These factors include temperature, pH of the calcifying fluid, the source of carbon for calcification, concentration of carbonic anhydrase and residence time of DIC in the calcifying fluid. Our model results suggest the source of carbon for calcification (i.e. CO$_2$ diffused across cell membrane versus DIC from seawater leakage) and the isotope exchange kinetics of DIC in the calcifying fluid place the first-order control on the magnitude of clumped isotope vital effects present in coral skeletons. A higher fraction of diffused CO$_2$ as the carbon source and a smaller extent of isotope exchange within the calcifying fluid are expected to lead to larger clumped isotope vital effects. Our model reproduces the different types of relations observed between clumped isotope and oxygen isotope vital effects in different coral genera, and supports the idea that genus- or species- specific calibrations could be a promising approach for future application of the clumped isotope thermometer in coral skeletons.

The accuracy of our model predictions is limited by the lack of constraints on the values of model parameters. To enable better comparison between model results and experimental observations, future studies should aim to place better experimental constraints on these model parameters in different coral genera.