Biologic controls on clumped isotope signatures in cultured corals

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The abundance of ^{13}C-^{18}O 'clumps' in calcite or aragonite of corals skeletons are a potentially valuable tool for reconstructing past ocean temperatures. However, corals are known to exhibit significant "vital effects" (i.e., non-equilibrium mineral compositions) in $\delta^{18}O$, which complicates its application in paleoclimate studies, and may also exhibit clumped isotope disequilibrium. Here we determined mass 47 anomalies (Δ_{47}) in CO_2 derived from both field collected and cultured shallow water and deep-sea coral. In two species of live-collected scleractinian (*Enallopsammia* sp.) and gorgonian (Isididae and Coralliidae) deep-sea corals that respectively have aragonitic and calcitic mineralogy, we find distinct clumped isotope signatures and temperature calibration slopes. This difference is an indication that different types of materials can yield unique clumped isotope calibrations. In cultured surface water coral (*Oculina arbuscula*), we find disequilibrium Δ_{47} and $\delta^{18}O$ values that are consistent with a pH effect driving disequilibrium isotopic signatures. We go on to show that culturing specimens at elevated CO_2 conditions drives changes in both Δ_{47} and $\delta^{18}O$ that follows the same relationship defined for pH effects in inorganic carbonate precipitation experiments. This suggests that dissolved inorganic carbon speciation at the site of calcification and therefore fluid pH can effect the clumped isotope composition of biogenic minerals.