Unpacking “vital effects” in biogenic carbonates using deep-sea corals

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Offsets from isotopic equilibrium in biogenic carbonates have complicated paleoclimate reconstructions for decades. We use a new archive of climate, deep-sea corals, to evaluate the calcification processes, independent of photosynthesis, that contribute to these offsets. Carbon and oxygen stable isotope data from six modern deep-sea corals show strong linear trends between $\delta^{13}C$ and $\delta^{18}O$. Slopes of these trends between samples are similar and range between 2.1-2.6 for $\Delta\delta^{13}C/\Delta\delta^{18}O$. Linear trends intersect isotopic equilibrium for $\delta^{18}O$ and are slightly depleted for $\delta^{13}C$. Variations in the isotopic ratios are strongly correlated with the density banding structure. Isotopically depleted aragonite is associated with light, fast precipitating bands, while isotopically enriched points correspond to slowly accumulating less dense aragonite. The densest, white band at the trabecular center is furthest from isotopic equilibrium for both carbon and oxygen. Data from this region fall off the linear trend between $\delta^{18}O$ and $\delta^{13}C$. This deviation, where $\delta^{13}C$ is anomalously heavy for the $\delta^{18}O$, does not support “vital effect” mechanisms that call upon kinetic fractionation to explain offsets from isotopic equilibrium. We propose a new mechanism for “vital effects” in biogenic carbonates that is based on a thermodynamic response to a biologically induced pH gradient in the calcifying region. We also present a numerical model of the calcifying region that can explain many of the observed features of stable isotope “vital effects” in a variety of marine organisms.

The temperature, salinity and $\delta^{18}O$ of the LGM deep ocean

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We have measured the sediment pore fluid profiles of $\delta^{18}O$ and chloride ion concentration at five ODP sites covering the North Atlantic, the Southern and the South Pacific oceans. Combining high precision data with samples at high depth resolution, we can constrain the amplitude and location of the pore water salinity and $\delta^{18}O$ maximum that results from glacial extension during the LGM. A 1-D diffusion/advection model, forced at the top boundary with the shape of the global sea level curve, allows us to reconstruct the size of bottom water change from LGM to today at each site. Combined with benthic foraminiferal $\delta^{18}O$ this data allows us to reconstruct the temperature, salinity and $\delta^{18}O$ of the LGM deep waters.

The resulting temperature versus salinity plot for the LGM shows several important features. First, outside of the shallow high latitude North Atlantic (site 981), all of our sites are within error of the seawater freezing point. Second, the Southern Ocean (site 1093) is the saltiest water in the LGM deep ocean, by over 1 psu compared to the deep North Atlantic (site 1063). Third, the mean salinity of the ocean, if our deep south Pacific site (1123) is representative of the mean ocean, is larger than the 35.8 psu implied by ~125 meters of global eustatic sea level change. This last point needs to be confirmed with cores from the deep equatorial and deep north Pacific ocean. The water $\delta^{18}O$ versus salinity plot indicates that the salty Southern Ocean deep waters were formed in large part by sea ice formation and export from the sinking region. Overall the LGM deep waters were at or near the freezing point and reversed from the modern salinity gradient in the Atlantic Ocean.