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Solution to an enigma: Explaining the slope of carbon vs. oxygen isotopic disequilibrium in biogenic and inorganic carbonates

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A widespread phenomenon in biogenic and inorganic carbonates that are formed out of isotopic equilibrium is a nearly ubiquitous co-variation (slope) of carbon vs. oxygen isotopes, in e.g., speleothem and cryogenic carbonates, shells and skeletons of foraminifera, corals etc. For proxy calibrations, it is critical to understand such isotope variations (often labeled kinetic or vital effects) in proxies widely used for paleo-reconstructions. Given that this phenomenon is observed in inorganic carbonates and biogenic carbonates across different phyla suggest a common underlying mechanism, possibly independent of biological controls, that is, likely of inorganic origin. Here we present results from laboratory experiments on synthetic carbonate precipitation to constrain the kinetic isotope fractionation factor (KFF) of carbon and oxygen during CO2 hydration. We used an experimental setup similar to that of an earlier study but with important modifications and tight temperature and pH control. The average d13C and d18O values of our carbonate samples (BaCO3) produced at 25 deg C and pH = 8.0 (NBS) are -29.7 +- 0.71 per mil (VPDB) and 18.8 +- 0.56 per mil (VSMOW), respectively. From the isotope data, we calculate our experimental 13KFF and 18KFF, which refer to the 13C/12C and 18O/16O fractionation between CO2(g) and BaCO3, where the d13C and d18O values of CO2(g) were calculated using known equilibrium fractionation factors. Our results show that our KFFs are the largest values compared to previously reported experimental KFFs (except for one study), suggesting that our values are closest to the full isotopic disequilibrium during CO2 hydration. Based on our KFFs, we will present the expected slope of carbon vs. oxygen isotopic disequilibrium from kinetic effects during CO2 hydration. We will also discuss the expected slope from equilibrium effects of solution pH on oxygen isotopes. Comparison with field and culture data will reveal the origin of the slope of carbon vs. oxygen isotopic disequilibrium in biogenic and inorganic carbonates.