

EGU2020-10573

<https://doi.org/10.5194/egusphere-egu2020-10573>

EGU General Assembly 2020

© Author(s) 2020. This work is distributed under the Creative Commons Attribution 4.0 License.



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

Richard Zeebe, Lauren Yumol, and Joji Uchikawa

University of Hawaii, School of Ocean and Earth Science and Technology, Oceanography, Honolulu, United States of America (zeebe@hawaii.edu)

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 δ¹³C and δ¹⁸O 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 δ¹³C and δ¹⁸O 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.