

Trajectory and timescale of Δ_{47} equilibration in the $\text{HCO}_3^-/\text{CO}_3^{2-}$ pool under normal and enzymatically catalyzed conditions.

JOJI UCHIKAWA¹, SANG CHEN², JOHN M. EILER², JESS F. ADKINS², RICHARD E. ZEEBE¹

¹Dept. of Oceanography, Univ. of Hawaii.
(uchikawa@hawaii.edu; zeebe@hawaii.edu)

²Division of Geological and Planetary Sciences,
California Institute of Technology.
(scchen@caltech.edu; eiler@gps.caltech.edu;
jess@gps.caltech.edu)

Due to a difference in the equilibrium fractionation, $\delta^{18}\text{O}$ of HCO_3^- is higher than CO_3^{2-} by $\sim 6\text{‰}$ in full ^{18}O equilibrium with H_2O at 25°C . Its equilibration kinetics follows a monotonic and asymptotic path of a first-order exponential function governed by solution pH and kinetic rate constants for CO_2 hydration and hydroxylation. There is also a measurable offset of $\sim 0.06\text{‰}$ in the clumped isotope (Δ_{47}) value between HCO_3^- and CO_3^{2-} . Yet, unlike the first-order kinetics in ^{18}O equilibration, *Staudigel and Swart* (2018) recently showed a non-first-order behavior in the attainment of Δ_{47} equilibrium in the $\text{HCO}_3^-/\text{CO}_3^{2-}$ pool, initially heading toward stronger disequilibrium and then returning toward full equilibrium. That is, an excess Δ_{47} disequilibrium during the initial equilibration phase (“DIP”).

Here, we follow up on the trajectory and timescale of Δ_{47} equilibration using BaCO_3 samples quantitatively precipitated from NaHCO_3 solutions at various times over the course of the equilibration under normal and enzymatically-catalyzed conditions using carbonic anhydrase (CA). As expected for quantitative precipitation, $\delta^{13}\text{C}$ of all the BaCO_3 samples were consistent and agreed with $\delta^{13}\text{C}$ of NaHCO_3 . Under normal conditions, our Δ_{47} dataset shows the “DIP” that is consistent with *Staudigel & Swart* (2018) and a very similar timescale in reaching full equilibrium for both $\delta^{18}\text{O}$ and Δ_{47} . As is the case for ^{18}O equilibration, the presence of CA accelerates Δ_{47} equilibration in the $\text{HCO}_3^-/\text{CO}_3^{2-}$ pool due apparently to the enzymatic catalysis of CO_2 hydration. However, at our examined CA concentrations, the “DIP” is still evident in all cases with no significant difference in its magnitude. Thus, it appears the presence and concentrations of CA influence only the timescale, but not the overall pattern of the Δ_{47} equilibration trajectory.

Staudigel & Swart (2018) G-cubed 10.1029/2018GC007500