

# New experimental constraints on the magnitude of kinetic C and O isotope fractionation for CO<sub>2</sub> hydration

**Website:** <https://www.bco-dmo.org/dataset/865161>

**Data Type:** experimental

**Version:** 1

**Version Date:** 2021-11-17

## Project

» [Experimental study of CO<sub>2</sub> hydration in seawater: Mechanism and kinetic isotope effects](#) (CO<sub>2</sub> Hydration Mechanism and KIEs)

Contributors	Affiliation	Role
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## Abstract

These are experimental data on kinetic C and O isotope fractionation of CO<sub>2</sub> hydration. These data were published in Yumol et al., 2020 (doi: 10.1016/j.gca.2020.03.041).

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## Coverage

**Temporal Extent:** 2017 - 2019

## Methods & Sampling

We quasi-instantaneously precipitated BaCO<sub>3</sub> by bubbling CO<sub>2</sub> gas that was in full isotopic equilibrium with NaHCO<sub>3</sub> solution through highly concentrated BaCl<sub>2</sub> solutions buffered at alkaline pH. As the CO<sub>2</sub> gas entered the BaCl<sub>2</sub> solution through a fritted disk, a small fraction of it was transformed into HCO<sub>3</sub><sup>-</sup> via diffusion and hydration across the thin-film of the bubbles. The resultant HCO<sub>3</sub><sup>-</sup> immediately reacted with Ba<sup>2+</sup> in the solution and precipitated as BaCO<sub>3</sub>. By measuring  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of the BaCO<sub>3</sub> samples and experimental NaHCO<sub>3</sub> and H<sub>2</sub>O and applying oxygen mass-balance, we constrained kinetic C and O isotope effect associated with the hydration of CO<sub>2</sub>.

All carbonate samples (BaCO<sub>3</sub> and NaHCO<sub>3</sub>) were analyzed at the University of California Santa Cruz for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , using a Thermo Finnigan MAT-253 dual-inlet isotope ratio monitoring mass spectrometer (irm-MS) coupled to a Kiel IV carbonate device. The samples were reacted with orthophosphoric acid and the resultant CO<sub>2</sub> gas was analyzed by the irm-MS. Note that all samples were treated as if they are calcite, which means that we did not apply the corrections to account for BaCO<sub>3</sub>-specific and NaHCO<sub>3</sub>-specific acid fractionation factor.

All H<sub>2</sub>O samples were analyzed for  $\delta^{18}\text{O}$  at the University of Hawaii on a PICARRO L2130-*i* isotope and gas

concentration analyzer.

## Data Processing Description

### BCO-DMO Processing:

- renamed fields to comply with BCO-DMO naming conventions;
- created separate columns for standard deviations.

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## Data Files

File
<b>kinetic_C_and_O_isotope_fract.csv</b> (Comma Separated Values (.csv), 935 bytes) MD5:1449d437600f04a9675adeea093a8591 Primary data file for dataset ID 865161

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## Related Publications

Yumol, L. M., Uchikawa, J., & Zeebe, R. E. (2020). Kinetic isotope effects during CO<sub>2</sub> hydration: Experimental results for carbon and oxygen fractionation. In *Geochimica et Cosmochimica Acta* (Vol. 279, pp. 189–203). Elsevier BV. <https://doi.org/10.1016/j.gca.2020.03.041>  
*Results*

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## Parameters

Parameter	Description	Units
Sample	sample number	unitless
T	temperature	degrees Celsius
pH	pH (NBS)	unitless
d13C	delta 13C, VPDB	per mil (‰)
d13C_stdev	standard deviation of d13C	per mil (‰)
d18O	delta 18O, VSMOW	per mil (‰)
d18O_stdev	standard deviation of d18O	per mil (‰)
KIF13_CO2g_BaCO3	13KIFCO2(g)-BaCO3 refers to the 13C/12C fractionation between CO2(g) and BaCO3, where the d13C values of CO2(g) were calculated using known equilibrium fractionation factors	per mil (‰)
KIF13_CO2g_BaCO3_stdev	standard deviation of KIF13_CO2g_BaCO3	per mil (‰)
KIF18_CO2g_BaCO3	18KIFCO2(g)-BaCO3 refers to the 18O/16O fractionation between CO2(g) and BaCO3, where the d18O values of CO2(g) were calculated using known equilibrium fractionation factors	per mil (‰)
KIF18_CO2g_BaCO3_stdev	standard deviation of KIF18_CO2g_BaCO3	per mil (‰)
KIF18_Inst	kinetic isotope fractionation (KIF)between instantaneously formed HCO3 (inst) and BaCO3	per mil (‰)
KIF18_Inst_stdev	standard deviation of KIF18_Inst	per mil (‰)

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## Instruments

<b>Dataset-specific Instrument Name</b>	Thermo Finnigan MAT-253 dual-inlet isotope ratio monitoring mass spectrometer (irm-MS)
<b>Generic Instrument Name</b>	Isotope-ratio Mass Spectrometer
<b>Dataset-specific Description</b>	All carbonate samples (BaCO3 and NaHCO3) were analyzed at the University of California Santa Cruz for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ , using a Thermo Finnigan MAT-253 dual-inlet isotope ratio monitoring mass spectrometer (irm-MS) coupled to a Kiel IV carbonate device.
<b>Generic Instrument Description</b>	The Isotope-ratio Mass Spectrometer is a particular type of mass spectrometer used to measure the relative abundance of isotopes in a given sample (e.g. VG Prism II Isotope Ratio Mass-Spectrometer).

<b>Dataset-specific Instrument Name</b>	PICARRO L2130-i isotope and gas concentration analyzer
<b>Generic Instrument Name</b>	Picarro L2130-I deltaD/delta18O Isotopic Water Analyzer
<b>Dataset-specific Description</b>	All H2O samples were analyzed for $\delta^{18}O$ at the University of Hawaii on a PICARRO L2130-i isotope and gas concentration analyzer.
<b>Generic Instrument Description</b>	A portable analyser designed for laboratories or field based isotope analysis. It uses Cavity Ring-Down Spectroscopy (CRDS) to measure the spectral signature of the molecule of interest. The instrument includes a closed-loop temperature and pressure control. The L2130-i can be used in all aspects of the water cycle: water vapor, liquid water, or water trapped in solids. It has a typical precision of 0.25 per mil for $d^{18}O$ and 1.20 per mil for $dD$ in solid samples. Corresponding typical values for liquid samples are 0.011 per mil for $d^{18}O$ and 0.038 per mil for $dD$ .

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## Project Information

### Experimental study of CO<sub>2</sub> hydration in seawater: Mechanism and kinetic isotope effects (CO<sub>2</sub> Hydration Mechanism and KIEs)

**Coverage:** University of Hawaii at Manoa

#### *NSF Award Abstract:*

The chemical reaction of carbon dioxide (CO<sub>2</sub>) with water in the marine environment is a fundamental process that creates carbonic acid (H<sub>2</sub>CO<sub>3</sub>) and all of the associated chemical ions (carbonate (CO<sub>3</sub>); hydrogen ions (H<sup>+</sup>), and bicarbonate (HCO<sub>3</sub><sup>-</sup>)) that serve as the dominant buffer for pH in the ocean. Dehydration refers to the opposite reaction that releases CO<sub>2</sub> gas. By entering into important reactions and serving to control pH, these species govern a wide variety of chemical and biological processes in the ocean. Surprisingly, while the important reactions that involve CO<sub>2</sub> hydration and its resulting products have been extensively studied in the ocean, some of the fundamental mechanisms remain poorly understood and datasets are sparse. In particular, almost nothing is known about how the natural isotopes of the carbon and oxygen atoms are involved and this is critically needed to explain observed changes in chemical species and solid calcium carbonate such as that created by coral reefs. This research aims to carefully produce novel experimental data that includes critical measurements of carbon and oxygen isotopes before and after the hydration of CO<sub>2</sub> in the ocean. Because these resulting carbonate species are used widely in many studies in the ocean sciences, particularly those examining past climates, this research will have far-reaching influences. Additionally, the results will provide new fundamental insight on exactly how the ocean will take up and respond to changing concentrations of atmospheric CO<sub>2</sub> in a changing climate. The research will fund an early-career scientist who is dedicated to graduate and undergraduate education as well as scientific outreach to the community.

While hydration/dehydration of CO<sub>2</sub> in the ocean critically influences a variety of marine chemical and biological processes, there are certain aspects of the reaction that are poorly understood. The molecular mechanism is not yet clear, as there are two possible pathways that have been proposed. Additionally, kinetic isotope effects during CO<sub>2</sub> have not been well studied, and the data regarding this topic is inconsistent. This research aims to study the carbon and oxygen isotope fractionation, which will not only clarify the molecular mechanism of the reaction but also will add a consistent dataset on kinetic isotope effects. The main challenge in this study is separating the product, HCO<sub>3</sub><sup>-</sup>, from CO<sub>2</sub> before re-equilibration, but the researcher will resolve this by rapidly precipitating dissolved carbon as carbonate. Since carbonates formed from the process of hydration are considered critical indicators of water chemistry, biological processes, and the inorganic carbon cycle as a whole and are used in a wide variety of oceanographic research, particularly as paleo-proxies, this research will provide fundamental mechanistic data that will greatly advance studies reaching beyond the physical chemical measurements that will be made here.

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## Funding

Funding Source	Award
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1558699</a>

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