Kinetics of δ18O and ▲47 equilibration in the dissolved carbonate system revealed by time-series quantitative inorganic carbonate precipitation experiments and numerical modeling.

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Data Type: experimental
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Project
» Experimental study of CO2 hydration in seawater: Mechanism and kinetic isotope effects (CO2 Hydration Mechanism and KIEs)

Contributors	Affiliation	Role
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Abstract
Kinetics of δ18O and Δ47 equilibration in the dissolved carbonate system revealed by time-series quantitative inorganic carbonate precipitation experiments and numerical modeling.

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Dataset Description

We analyzed oxygen and clumped isotope values of inorganic $BaCO_3$ samples from Uchikawa and Zeebe (2012), which were quantitatively precipitated from $NaHCO_3$ solutions over the course of isotopic equilibration. These time-series quantitative inorganic $BaCO_3$ precipitation experiments were conducted under a normal condition at 25 °C and in the presence of varying amount of carbonic anhydrase enzyme that is known to catalyze CO_2 hydration and known to be possessed by a range of marine calcareous organisms.

Summary of new $\delta^{18}O$ and Δ_{47} values measured on $BaCO_3$ samples from Uchikawa and Zeebe (2012). These $BaCO_3$ samples were quantitatively precipitated from $NaHCO_3$ solutions at various times over the course of isotopic equilibration at 25 °C. Also included in the file are $\delta^{18}O$ and Δ_{47} values of the $NaHCO_3$ used in the experiments and original $\delta^{18}O$ data by Uchikawa and Zeebe (2012) on the $BaCO_3$ samples and experimental $NaHCO_3$ and H_2O.

We also developed a fully open-sourced numerical codes (ExClump38 model) that can simulate the time-course of oxygen and clumped isotope equilibration in the dissolved carbonate system as a function of temperature, pH and carbonic anhydrase concentration by extending the work of Chen et al. (2018). By extending the framework of earlier work (Chen et al., 2018), this model tracks temporal change in the abundance of singly

(i.e., $\delta^{13}C$ and $\delta^{18}O$) and doubly-substituted (i.e., Δ_{47}) aqueous CO_2 and the sum of HCO_3^- and CO_3^{2-} (referred to as the dissolved carbonate pool: DCP) from a given initial condition/state to the expected isotopic equilibrium in the dissolved carbonate system.

Matlab codes for the ExClump38 model and accompanying experimental data. These data are attached to this datapackage as a supplemental file. The zipfile contains 9 different files. Descriptions of the files:

* ExClump38.m: A Matlab m-file for the ExClump38 model, which can simulate the progress of isotopic ($\delta^{18}O$ and Δ_{47}) equilibration in the dissolved carbonate system as a function of temperature, pH and carbonic anhydrase activity.

* IsoEquilibration.m: A Matlab m-file containing a set of differential equations to be solved in the ExClump38 model. This file needs to be downloaded with ExClump.m and stored in the same folder.

* Model_Constants.m: A Matlab m-file containing a set of equilibrium and kinetic rate constants as well as isotope fractionation factors used in the ExClump38 model. This file needs to be downloaded with ExClump.m and stored in the same folder.

* Data_Entry.m: A supplementary Matlab m-file for the entry of our experimental data as well as the initial condition for each experimental series for the ExClump38 model.

* TS2.dat: A supplementary .dat file needed for the entry of isotope data from the “TS-2” experimental series. The TS-2 experiments were conducted at T = 25 °C, pH_{NBS} = 8.9 and in the absence of carbonic anhydrase enzyme.

* TS2_CAmn.dat: A supplementary .dat file needed for the entry of isotope data from the “TS-mnCA” experimental series. The TS-2 experiments were conducted at T = 25 °C and pH_{NBS} = 8.9, with the addition of carbonic anhydrase enzyme to a concentration of 3.7 nM.

* TS2_CA2.dat: A supplementary .dat file needed for the entry of isotope data from the “TS-2CA” experimental series. The TS-2 experiments were conducted T = 25 °C and pH_{NBS} = 8.9, with the addition of carbonic anhydrase enzyme to a concentration of 9.3 nM.

* TS2_CA3.dat: A supplementary .dat file needed for the entry of isotope data from the “TS-3CA” experimental series. The TS-2 experiments were conducted T = 25 °C and pH_{NBS} = 8.9, with the addition of carbonic anhydrase enzyme to a concentration of 19 nM.

* SS18.dat: A supplementary .dat file needed for the entry of isotope data from similar experiments done by Staudigel and Swart (2018) at T = 25 °C.

All of the .dat files are organized as follows:

* 1st column (far left): pH_{NBS} of the experimental $NaHCO_3$ solution.
* 2nd column: Elapsed equilibration time (minutes)
* 3rd column: $\delta^{13}C$ of $BaCO_3$ samples (‰, VPDB)
* 4th column: $\delta^{13}C$ measurement uncertainty for $BaCO_3$ (1σ standard error, ‰ VPDB)
* 5th column: $\delta^{18}O$ of $BaCO_3$ samples (‰, VPDB)
* 6th column: $\delta^{18}O$ measurement uncertainty for $BaCO_3$ (1σ standard error, ‰ VSMOW)
* 7th column: $\delta^{18}O$ of experimental H_2O (‰, VSMOW) from Uchikawa & Zeebe (2012)
* 8th column: $\delta^{18}O$ measurement uncertainty for H_2O (1σ standard error, ‰ VSMOW)
* 9th column: Δ_{47} of $BaCO_3$ samples (‰, ARF)
* 10th column (far right): Δ_{47} measurement uncertainty (1σ standard error, ‰ ARF)

Related publications:

* Data contained original data for d18O of H2O from Uchikawa, J., & Zeebe, R. E. (2012)
* The numerical model is adopted and modified from Chen et al. (2018)

* The model is also applied to (their dataset is attached as SS18): Staudige & Swart (2018)

Methods & Sampling

Carbonate samples (BaCO3 and experimental NaHCO3) were digested with 104% phosphoric acid at 90 °C in a common acid bath. After purification, the CO2 gases liberated from acid digestion of the samples were analyzed by a Thermo Finnigan MAT253 dual-inlet isotope ratio monitoring mass spectrometer for δ13C, δ18O and Δ47 at the California Institute of Technology.

The codes for the ExClump38 model are developed in the Matlab computational software.

Data Processing Description

BCO-DMO processing notes:

* added model code and datafiles as supplemental documentation
* added NACHO3 file as data file
* BaCO3 file is added as main data file and viewable in the dataviewer.
* adjusted data parameter names to comply with database requirements.

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Data Files

File
babco3.csv (Comma Separated Values (.csv), 4.19 KB) MD5:216d396bd076a2310811385cfcdef7db Primary data file for dataset ID 865489
NaHCO3_Isotope_Data filename: NaHCO3_Isotope_Data.xlsx (Octet Stream, 13.55 KB) MD5:534b6f59a9a32d0c72beddb33105ced8 Stable isotope data for the NaHCO3 used for the time-series quantitative BaCO3 precipitation experiments. Parameters: Aiquot ID delta_C_13_BaCO3,"δ13CBaCO3, stable carbon isotope ratio",‰ (per mil),nd,d13C,Float delta_C_13_BaCO3_std,± 1σ S.D.,‰ (per mil),nd,std_dev,Float delta_O_18_BaCO3,"δ18OBaCO3, stable oxygen isotope ration",‰ (per mil),nd,delta18O,Float delta_O_18_BaCO3_std,± 1σ S.D.,‰ (per mil),nd,std_dev,Float cap_47,Δ47 ,‰ (per mil),nd,ratio,Float cap_47_std,± 1σ S.D.,‰ (per mil),nd,std_dev,Float

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Supplemental Files

File
ExClump38_model filename: ExClump38_model.zip (ZIP Archive (ZIP), 10.45 KB) MD5:a3ba558b98d4ba6b67f3458000e65805 Matlab codes for the ExClump38 model and accompanying experimental data, related to dataset 865489.

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Related Publications

Chen, S., Gagnon, A. C., & Adkins, J. F. (2018). Carbonic anhydrase, coral calcification and a new model of stable isotope vital effects. Geochimica et Cosmochimica Acta, 236, 179–197. doi:10.1016/j.gca.2018.02.032 https://doi.org/https://doi.org/10.1016/j.gca.2018.02.032
Methods

Staudigel, P. T., & Swart, P. K. (2018). A Kinetic Difference Between 12 C- and 13 C-Bound Oxygen Exchange Rates Results in Decoupled δ18 O and Δ47 Values of Equilibrating DIC Solutions. Geochemistry, Geophysics, Geosystems, 19(8), 2371–2383. doi:10.1029/2018gc007500 https://doi.org/10.1029/2018GC007500
Methods

Uchikawa, J., & Zeebe, R. E. (2012). The effect of carbonic anhydrase on the kinetics and equilibrium of the oxygen isotope exchange in the CO2–H2O system: Implications for δ18O vital effects in biogenic carbonates. Geochimica et Cosmochimica Acta, 95, 15–34. doi:10.1016/j.gca.2012.07.022
Methods

Uchikawa, J., Chen, S., Eiler, J. M., Adkins, J. F., & Zeebe, R. E. (2021). Trajectory and timescale of oxygen and clumped isotope equilibration in the dissolved carbonate system under normal and enzymatically-catalyzed conditions at 25 °C. Geochimica et Cosmochimica Acta, 314, 313–333. doi:10.1016/j.gca.2021.08.014 https://doi.org/https://doi.org/10.1016/j.gca.2021.08.014
Results

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Parameters

Parameter	Description	Units
Series	series id	unitless
Sample	sample id	unitless
pH	pH, NBS scale	unitless
Time	Elapsed isotopic equilibration time (minutes)	min (minutes)
delta_C_13_BaCO3	δ13CBaCO3, stable carbon isotope ratio	‰ (per mil)
delta_C_13_BaCO3_std	± 1σ S.D.	‰ (per mil)
delta_O_18_BaCO3	δ18OBaCO3, stable oxygen isotope ration	‰ (per mil)
delta_O_18_BaCO3_std	± 1σ S.D.	‰ (per mil)
cap_47	Δ47	‰ (per mil)
cap_47_std	± 1σ S.D.	‰ (per mil)

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Instruments

Dataset-specific Instrument Name	Thermo Finnigan MAT253
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset-specific Description	Thermo Finnigan MAT253 dual-inlet isotope ratio monitoring mass spectrometer.
Generic Instrument Description	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).

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Project Information

Experimental study of CO2 hydration in seawater: Mechanism and kinetic isotope effects (CO2 Hydration Mechanism and KIEs)

Coverage: University of Hawaii at Manoa

NSF Award Abstract:
The chemical reaction of carbon dioxide (CO2) with water in the marine environment is a fundamental process that creates carbonic acid (H2CO3) and all of the associated chemical ions (carbonate (CO3); hydrogen ions (H+), and bicarbonate (HCO3-)) that serve as the dominant buffer for pH in the ocean. Dehydration refers to the opposite reaction that releases CO2 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 CO2 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 CO2 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 CO2 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 CO2 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 CO2 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, HCO3-, from CO2 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
NSF Division of Ocean Sciences (NSF OCE)	OCE-1558699

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