

## Table 2. Elemental ratios and partition coefficients for CaCO<sub>3</sub> in deepsea conditions: Mg, S, Sr, and Ba between crystallized solids and fluid.

Website: <https://www.bco-dmo.org/dataset/806957>

Data Type: experimental

Version: 1

Version Date: 2020-03-25

### Project

» [Biologically induced methane oxidation and precipitation of carbonate minerals: An experimental study](#) (Deep Sea Geochem CaCO<sub>3</sub>)

### Program

» [Center for Dark Energy Biosphere Investigations](#) (C-DEBI)

Contributors	Affiliation	Role
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### Abstract

Trace elements in CaCO<sub>3</sub> and fluid. Table 2. Elemental ratios and partition coefficients for CaCO<sub>3</sub> in deepsea conditions: Mg, S, Sr, and Ba between crystallized solids and fluid.

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## Coverage

**Temporal Extent:** 2014 - 2014

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## Dataset Description

Table 1: Experimental conditions and fluid carbonate chemistry for RPI-3 run where only aragonite precipitated

## Acquisition Description

### X-ray diffraction (XRD)

Powdered samples were examined for mineral presence using a Rigaku Ultima III X-ray Diffraction (XRD) System at the Institute of Imaging and Analytical Technologies (i2AT) at Mississippi State University. These analyses were conducted at 40 kV and 40 mA.

### Elemental analysis of experimental aragonite crystals and experimental fluids with ICP-MS

Crystals were dissolved and solutions were analyzed by ICP-MS. Experimental fluids were also analyzed with ICP-MS, as well. Analyses were conducted on an Agilent 7900 quadrupole ICP-MS equipped with a glass nebulizer at the University of Rochester (Rochester, NY). Prior to analysis, fluid samples were diluted with 2% trace metal grade HNO<sub>3</sub> (Fisher) in the volume proportion of 1:100. Aragonite crystals were dissolved in HNO<sub>3</sub> in the mass proportion of 1:1000. Experimental fluid samples were analyzed using a 5-point calibration curve (one blank and four standards). Seawater standards were prepared by diluting a seawater certificate reference material (CRM-SW; High-Purity Standards) to a final concentration of ~300, 200, 150, and 80 ppm. Experimental crystals were analyzed using a 5-point calibration curve (one blank and four standards). Calcium carbonate standards were prepared by dissolving and diluting the original MACS-3 powder to a final concentration of ~111, 55, 27, and 11 ppm. Because S concentration was not reported in the certificate of analysis provided by the USGS, we added a small amount of sulfur single element standard (Inorganic Ventures) to a final concentration of ~1.5, 0.75, 0.375, and 0.150 ppm, in each MACS-3 standard we prepared. Samples, blanks, and standards were also spiked with 2 ppb indium, which was used as the internal standard to

check for possible instrumental drift during each analytical session.

The instrument was tuned at the beginning of each analytical session (two analytical sessions in two consecutive days).  $^{24}\text{Mg}$ ,  $^{34}\text{S}$ ,  $^{43}\text{Ca}$ ,  $^{88}\text{Sr}$ ,  $^{138}\text{Ba}$ , and  $^{238}\text{U}$  were analyzed. Integration times were the following: 0.3 s for  $^{24}\text{Mg}$ ; 0.12 s for  $^{43}\text{Ca}$ ,  $^{88}\text{Sr}$ , and  $^{138}\text{Ba}$ ; 0.99 s for  $^{238}\text{U}$ . The calibration curve was run before analyzing each set of samples. For each element analyzed, the correlation among standards was 0.9923 or better. Elements were identified using three peaks. Each analysis included three replicates, with 100 sweeps/replicate. The carrier gas (argon) flow was set at 1.15 L/min. In addition, we used helium flow of 4.2 milliliters per minute in the collision reaction cell in the ICP-MS to minimize oxide interference. At the end of each tuning, oxides and doubly-charged ion interferences were below 0.8% and 1.4%, respectively. Data were computed automatically during the run using the Agilent Mass Hunter 4.1 workstation software v. C.01.01.

## Results

XRD spectra identified the presence of aragonite and monohydrocalcite (Table 2). Only aragonite crystallized at intermediate pressure (110 bars). Calculations of fluid carbonate chemistry were conducted with a CO2SYS spreadsheet (Lewis and Wallace, 1998) and presented in Table 1. There, measured pH and total alkalinity (TA) were used to calculate the concentration of  $\text{CO}_3^{2-}$ , which together with  $\text{Ca}^{2+}$  is necessary to calculate fluid saturation states with respect to aragonite (Omega-Ar). Precipitation started at saturation state, which exceeds that of artificial seawater (ASW) by the factor of ~25. Over the course of the experiments, Omega-Ar decreased back to 2, i.e. Omega-Ar value of ASW prior to the addition of  $\text{Na}_2\text{CO}_3$ . Table 2 contains E/Ca of experimental products (solids and liquids) as well as the Doerner-Hoskins apparent partition coefficients between solid and fluid (KE). Fluid composition changed during individual experiments, and therefore, values of KE were calculated using the Doerner-Hoskins relationship:

$$KE = \log(1 + m^{\text{E}}_{\text{aragonite}} / m^{\text{E}}_{\text{fluid}}) / \log(1 + m^{\text{Ca}}_{\text{aragonite}} / m^{\text{Ca}}_{\text{fluid}}) \quad (1)$$

where  $m^{\text{E}}_{\text{aragonite}}$  is the total number of moles of element (i.e., Mg, S, Sr, Ba, or U) or Ca in the final precipitate, and  $m^{\text{E}}_{\text{fluid}}$  is the total number of moles of element or Ca in the final fluid (Doerner and Hoskins, 1925).

### Software products used:

XRD: Jade and Microsoft Excel

ICP-MS: Agilent Mass Hunter 4.1 workstation software v. C.01.01 and Microsoft Excel

## Processing Description

## BCO-DMO Data Manager Processing Notes:

- added a conventional header with dataset name, PI name, version date
- modified parameter names to conform with BCO-DMO naming conventions
- blank values in this dataset are displayed as "nd" for "no data." nd is the default missing data identifier in the BCO-DMO system.
- reformatted table so each column represent only one parameter
- removed quotes, replaced commas with semicolons

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## Related Publications

Doerner, H. A., & Hoskins, W. M. (1925). Co-Precipitation of radium and barium sulfates<sup>1</sup>. *Journal of the American Chemical Society*, 47(3), 662-675.

<https://pubs.acs.org/doi/pdf/10.1021/ja01680a010> [details]

Gabitov, R., Borrelli, C., Buettner, J., Kirkland, B., Skarke, A., Trail, D., ... Zverkova, I. (2019). Characterization of Carbonate Crust from a Recently Discovered Methane Seep on the North Atlantic Continental Margin of the USA. *Minerals*, 9(3), 138. doi:[10.3390/min9030138](https://doi.org/10.3390/min9030138) [details]

Pytkowicz, R. M. (1965). Rates of Inorganic Calcium Carbonate Nucleation. *The Journal of Geology*, 73(1), 196–199. doi:[10.1086/627056](https://doi.org/10.1086/627056) [details]

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## Parameters

Parameter	Description	Units
analysis	The type of analysis: solids; fluids; or KE (Doener-Hoskins partition coefficients between solid and fluid)	unitless
run	experimental run identifier	unitless
press	pressure	bars
minerals	minerals identified with X-ray diffraction technique: aragonite; monoclinic carbonate (CaCO <sub>3</sub> -II)	unitless
Mg_Ca	magnesium to calcium ratio in carbonate crystals (solids) or in fluid at end of experiment	millimole per mole of calcium

Mg_Ca_2sd	two standard deviations from the mean of magnesium to calcium ratio	millimole per mole of calcium
S_Ca	sulfur to calcium ratio in carbonate crystals (solids) or in fluid at end of experiment	millimole per mole of calcium
S_Ca_2sd	two standard deviations from the mean of sulfur to calcium ratio	micromole per mole of calcium
Sr_Ca	strontium to calcium ratio in carbonate crystals (solids) or in fluid at end of experiment	millimole per mole of calcium
Sr_Ca_2sd	two standard deviations from the mean of strontium to calcium ratio	millimole per mole of calcium
Ba_Ca	barium to calcium ratio in carbonate crystals (solids) or in fluid at end of experiment	millimole per mole of calcium
Ba_Ca_2sd	two standard deviations from the mean of barium to calcium ratio	micromole per mole of calcium
KMg	Doener-Hoskins partition coefficients of magnesium multiplied by 1000	unitless
KMg_2sd	two standard deviations from the mean of Doener-Hoskins partition coefficients of magnesium multiplied by 1000	unitless
KS	Doener-Hoskins partition coefficients of sulfur multiplied by 1000	unitless
KS_2sd	two standard deviations from the mean of Doener-Hoskins partition coefficients of sulfur multiplied by 1000	unitless
KSr	Doener-Hoskins partition coefficients of strontium	unitless
KSr_2sd	two standard deviations from the mean of Doener-Hoskins partition coefficients of strontium	unitless
KBa	Doener-Hoskins partition coefficients of barium	unitless
Kba_2sd	two standard deviations from the mean of Doener-Hoskins partition coefficients of barium	unitless

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## Instruments

<b>Dataset-specific Instrument Name</b>	high-pressure apparatus
<b>Generic Instrument Name</b>	unknown
<b>Dataset-specific Description</b>	Custom designed pressure chamber used to simulate the high-pressure conditions at the seafloor for this set of experiments (designed at Rensselaer Polytech Institute, Department of Earth and Environmental Sciences).
<b>Generic Instrument Description</b>	No relevant match in BCO-DMO instrument vocabulary.

<b>Dataset-specific Instrument Name</b>	Rigaku Ultima III X-ray Diffraction (XRD) System at the Institute of Imaging and Analytical Technologies (i2AT)
<b>Generic Instrument Name</b>	X-ray diffractometer
<b>Dataset-specific Description</b>	Located at at Mississippi State University
<b>Generic Instrument Description</b>	Instruments that identify crystalline solids by measuring the characteristic spaces between layers of atoms or molecules in a crystal.

<b>Dataset-specific Instrument Name</b>	Agilent 7900 quadrupole ICP-MS equipped with a glass nebulizer at the University of Rochester (Rochester, NY)
<b>Generic Instrument Name</b>	Inductively Coupled Plasma Optical Emission Spectrometer
<b>Generic Instrument Description</b>	Also referred to as an Inductively coupled plasma atomic emission spectroscope (ICP-AES). These instruments pass nebulised samples into an inductively-coupled gas plasma (8-10000 K) where they are atomised and excited. The de-excitation optical emissions at characteristic wavelengths are spectroscopically analysed. It is often used in the detection of trace metals.

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## Project Information

### **Biologically induced methane oxidation and precipitation of carbonate minerals: An experimental study (Deep Sea Geochem CaCO<sub>3</sub>)**

**Website:** <https://www.darkenergybiosphere.org/award/biologically-induced-methane-oxidation-and-precipitation-of-carbonate-minerals-an-experimental-study/>

Biologically-mediated CaCO<sub>3</sub> precipitation widely occurs in aquatic systems and is often directly linked to the metabolic activity of microorganisms, which could significantly affect the local environment. An example is oxidation of methane and reduction of sulfate mediated by a consortium of Bacteria and Archaea. In order to investigate geochemistry of CaCO<sub>3</sub> precipitated abiotically and under microbial activity experimental work was initiated. The abiotic experiments were performed at different temperatures and pressures (nitrogen and nitrogen-methane mixture). Further geochemical analyses will allow evaluating of the effect of total pressure and methane partial pressure on the geochemistry of CaCO<sub>3</sub>. Sulfate reducing bacterial (*Desulfovibrio salexigens*) was successfully cultured and precipitation experiments on microbially mediated CaCO<sub>3</sub> are in progress. This work is relevant to C-DEBI Research Theme I (Activity in the Deep Subseafloor Biosphere: function & rates of global biogeochemical processes) because carbonate growth rate is linked to microbial activity and the rate of methane oxidation.

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## Program Information

### **Center for Dark Energy Biosphere Investigations (C-DEBI)**

**Website:** <http://www.darkenergybiosphere.org>

**Coverage:** Global

The mission of the Center for Dark Energy Biosphere Investigations (C-DEBI) is to explore life beneath the seafloor and make transformative discoveries that advance science, benefit

society, and inspire people of all ages and origins. C-DEBI provides a framework for a large, multi-disciplinary group of scientists to pursue fundamental questions about life deep in the sub-surface environment of Earth. The fundamental science questions of C-DEBI involve exploration and discovery, uncovering the processes that constrain the sub-surface biosphere below the oceans, and implications to the Earth system. What type of life exists in this deep biosphere, how much, and how is it distributed and dispersed? What are the physical-chemical conditions that promote or limit life? What are the important oxidation-reduction processes and are they unique or important to humankind? How does this biosphere influence global energy and material cycles, particularly the carbon cycle? Finally, can we discern how such life evolved in geological settings beneath the ocean floor, and how this might relate to ideas about the origin of life on our planet? C-DEBI's scientific goals are pursued with a combination of approaches: (1) coordinate, integrate, support, and extend the research associated with four major programs—Juan de Fuca Ridge flank (JdF), South Pacific Gyre (SPG), North Pond (NP), and Dorado Outcrop (DO)—and other field sites; (2) make substantial investments of resources to support field, laboratory, analytical, and modeling studies of the deep seafloor ecosystems; (3) facilitate and encourage synthesis and thematic understanding of submarine microbiological processes, through funding of scientific and technical activities, coordination and hosting of meetings and workshops, and support of (mostly junior) researchers and graduate students; and (4) entrain, educate, inspire, and mentor an interdisciplinary community of researchers and educators, with an emphasis on undergraduate and graduate students and early-career scientists. Note: Katrina Edwards was a former PI of C-DEBI; James Cowen is a former co-PI. Data Management: C-DEBI is committed to ensuring all the data generated are publically available and deposited in a data repository for long-term storage as stated in their Data Management Plan (PDF) and in compliance with the NSF Ocean Sciences Sample and Data Policy. The data types and products resulting from C-DEBI-supported research include a wide variety of geophysical, geological, geochemical, and biological information, in addition to education and outreach materials, technical documents, and samples. All data and information generated by C-DEBI-supported research projects are required to be made publically available either following publication of research results or within two (2) years of data generation. To ensure preservation and dissemination of the diverse data-types generated, C-DEBI researchers are working with BCO-DMO Data Managers make data publicly available online. The partnership with BCO-DMO helps ensure that the C-DEBI data are discoverable and available for reuse. Some C-DEBI data is better served by specialized repositories (NCBI's GenBank for sequence data, for example) and, in those cases, BCO-DMO provides dataset documentation (metadata) that includes links to those external repositories.

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## Funding



Funding Source	Award
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-0939564</a>

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