

Sediment core porewater and particulate measurements from three sites on the Louisiana Shelf sampled during R/V Pelican cruises in August 2021

Website: <https://www.bco-dmo.org/dataset/945927>

Data Type: Cruise Results

Version: 1

Version Date: 2024-12-12

Project

» [Collaborative Research: Understanding substrate limitation and Lithium and Silicon isotope fractionation during secondary clay formation in marine systems](#) (Marine Secondary Clay Formation)

Contributors	Affiliation	Role
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Abstract

Thirteen days prior to Hurricane Ida's landfall in Port Fourchon, Louisiana in August 2021, sediment cores were collected at three sites in the topset delta sediment between the Southwest Pass (major Mississippi River distributary) and Cocodrie, LA aboard the R/V Pelican. All sites experienced Category 4 hurricane conditions from Ida with maximum sustained winds of 130 knots (67 m/s). Using a multi-proxy approach, this project analyzed the initial conditions prior to the storm event, and a companion project ("Sediment porewater and particulates on the Louisiana Shelf during December 2021 through August 2022") examined how the storm altered properties in the subsequent 12 months. These data include operational particulate silica pools, particulate organic carbon/nitrogen and their stable isotopes, porewater constituents and general characteristics (e.g. porosity).

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Coverage

Location: Northern Gulf of Mexico, specifically the Louisiana Shelf region dominated by the discharge of the Mississippi River plume

Spatial Extent: N:28.942 E:-89.763 S:28.9398 W:-90.4793

Temporal Extent: 2021-08-17

Dataset Description

This dataset provides information on initial conditions from topset delta sediment prior to a major storm event. Less than two weeks after this initial sampling, Hurricane Ida made landfall on August 29th, 2021.

A companion project allowed for additional sampling after the event to study important aspects of silica cycling in coastal sediments. For post-storm data, please see related dataset <https://www.bco-dmo.org/dataset/915912>.

Methods & Sampling

I. Field sampling

Sample collection took place during R/V Pelican cruise PE22-05 in the northern part of the Gulf of Mexico, specifically the Louisiana Shelf region dominated by the discharge of the Mississippi River plume. At each site, an 8-spot Ocean Instruments Multi-corer collected sediment that was sectioned in 2 cm intervals and placed into 50mL metal clean, acid washed tubes, pre-weighed and labeled microcentrifuge tubes for porosity, and freezer-safe Ziploc bags. Tubes were centrifuged at 3500 rpm for 10 minutes to extract and filter supernatant. The filtered supernatant was placed into a metal clean/acid washed tube and frozen for later analysis of metal and dissolved silica. The 50mL tube of sediment was frozen at -20°C for further analysis.

II. Porewater Dissolved Constituents

Where there was sufficient supernatant (porewater) from the centrifuged sediment sample, it was divided for three different analyses: dissolved silica analysis (DSi), nutrient analysis (Skalar), and metal concentrations (ICPMS).

1. **DSi analysis:** 50uL of porewater was analyzed for dissolved $\text{Si}(\text{OH})_4$ concentration using a spectrophotometric molybdate-blue method (Brzezinski & Nelson, 1986).

2. **Skalar Analysis (N+N, NH₄, PO₄):** Porewater was diluted with Milli-Q (18.2 MΩ * cm) water and run through a Skalar Analyzer for Nitrate and Nitrite, Phosphorus, and Ammonia. For detection limits, please refer to the descriptions in the Parameters section below.

3. **ICPMS (Metal Concentrations):** Porewater was reconstituted in dilute HNO₃ and diluted to minimize salt interferences before analysis on a Thermo Scientific Element XR High Resolution-ICP-MS housed at the University of Southern Mississippi at the Stennis Space Center. The following elements are reported in the data from the ICPMS analysis: magnesium (Mg), sulfur (S), calcium (Ca), manganese (Mn), iron (Fe), potassium (K), cesium (Cs), uranium (U), lithium (Li), vanadium (V), cobalt (Co), nickel (Ni), copper (Cu), strontium (Sr), molybdenum (Mo), barium (Ba), phosphorus (P), and aluminum (Al), along with phosphorus (P) and silica (Si). For each element's detection limit, please see the description in the Parameters section below.

Sediments

Sediments were analyzed for physical properties, chemical properties, phases of silica, and isotopic composition. Each section below describes the specific methods in greater detail.

III. Sediment properties

Porosity

For porosity measurements, microcentrifuge tubes were placed in a drying oven at 60°C until the sediment was dry. Once dried, tubes were weighed. Porosity was calculated as in Comeaux et al. (2012).

Loss on ignition (LOI)

For loss on ignition (LOI) analysis, dried sediment was ground into a fine consistency using a mortar and pestle. Then 1g of the ground sediment was weighed into pre-muffled and pre-weighed porcelain crucibles. To remove any carbon from the presence of calcium carbonate, samples were fumed by adding 1mL of milli-Q to each crucible and placing samples into a desiccator with 10 mL of 12M HCl for 6 hours (Harris et al. 2001, Ramnarine et al. 2011, Walthert et al. 2010). After 6 hours, samples were placed in a vacuum oven for roughly 16 hours, until dry (Ramnarine et al. 2011, Walthert et al. 2010). Once dry, samples were kept in the oven and weighed one at a time to keep moisture out of samples. If sample was still acidic (yellow in color), 1 mL of milli-Q was added and the sample was dried again. Sediment was ground again into a fine powder.

After the above preparation, fumed and ground sediment was weighed (100 mg) in triplicate into pre-weighed and muffled liquid scintillation (LSC) vials. Samples were combusted at 550°C for 6 hours (Kemp et al. 2021).

After combustion, weights were recorded, and loss of organic matter was calculated (Kemp et al. 2021).

IV. Sediment Silica Pools

Sequential Extractions

Frozen samples were thawed, homogenized, and 50 mg were weighed in triplicates (per depth) into pre-labeled 50 mL centrifuge tubes (Krause et al., 2017; Pickering et al., 2020). Samples with procedural blanks (in triplicate) then went through the sequential extraction process. The sequential extraction methodology separates silica into operationally defined pools based on kinetics, reaction conditions and reaction sequence (DeMaster, 1981; Michalopoulos and Aller, 2004; Rahman et al., 2016; Pickering et al., 2020).

Operational Definitions

Based on prior studies, we use the following nomenclature:

1. **Si-HCl**: Mild acid-leachable pre-treatment; Highly reactive silica associated with authigenic clays and metal oxide coatings (Michalopoulos and Aller, 2004).
2. **Si-Alk**: Mild alkaline-leachable digestion completed after acid pretreatment; Frees reactive silica associated with the biogenic silica pool (Michalopoulos and Aller, 2004).
3. **Si-NaOH (Alk)**: Harsh NaOH digestion done after Si-HCl and Si-Alk (Rahman et al., 2016; Rahman et al., 2017); Associated with the reactive lithogenic Si (LSi) pool and the comparatively refractory "dark bSiO₂" (e.g. sponge spicules and Rhizaria).
4. **TbSi**: Following the traditional definition of biogenic silica (DeMaster, 1981), with no acid pre-treatment.
5. **Si-NaOH (TbSi)**: Harsh NaOH digestion done after T-bSi.

V. Sediment Organic matter

Preparation

Same preparation as that listed above for Loss on Ignition

Particulate Organic Carbon and Nitrogen content and isotopes ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$)

After fumigation (explained above), ~60 to 70 mg of sediment were packed in 5x9mm silver capsules, which were then packed in tin 5x9mm capsules in triplicate (UC Davis protocol recommendation). Samples were placed in a 96 well plate and kept in a desiccator until shipped to UC Davis for isotopic ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) analysis (Krause et al. 2017).

Results from UC Davis had an absolute accuracy for calibrated reference materials of ± 0.04 ‰ (± 0.05 ‰ SD) for $\delta^{13}\text{C}$ and ± 0.05 ‰ (± 0.05 ‰ SD) for $\delta^{15}\text{N}$. Core depth 24-26cm was the only sample below detection (9.7ug) for $\delta^{15}\text{N}$, which is represented as 0 on the data sheet.

Data Processing Description

Raw data were input into Microsoft Excel (Version 2302) to calculate final reported values.

- Porosity was calculated as in Comeaux et al. (2012).
- Loss of organic matter was calculated as in Kemp et al. (2021).

BCO-DMO Processing Description

- Imported data from source file "BCO-DMO_SiLi_Sediment.Summary-Broken Links.xlsx" into the BCO-DMO data system.
- Added R/V Pelican official cruise IDs corresponding to the submitted cruise name.
- Combined separate date and time columns into a single datetime column
- Kept local datetime but added a column for ISO8601 formatted UTC datetime
- Removed percent (%) signs from the column values

- Modified parameter (column) names to conform with BCO-DMO naming conventions. The only allowed characters are A-Z,a-z,0-9, and underscores. Replaced spaces with underscores.

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Related Publications

Brzezinski, M. A., & Nelson, D. M. (1986). A solvent extraction method for the colorimetric determination of nanomolar concentrations of silicic acid in seawater. *Marine Chemistry*, 19(2), 139–151. doi:[10.1016/0304-4203\(86\)90045-9](https://doi.org/10.1016/0304-4203(86)90045-9)

Methods

Comeaux, R. S., Allison, M. A., & Bianchi, T. S. (2012). Mangrove expansion in the Gulf of Mexico with climate change: Implications for wetland health and resistance to rising sea levels. *Estuarine, Coastal and Shelf Science*, 96, 81–95. <https://doi.org/10.1016/j.ecss.2011.10.003>

Methods

DeMaster, D. J. (1981). The supply and accumulation of silica in the marine environment. *Geochimica et Cosmochimica Acta*, 45(10), 1715–1732. doi:[10.1016/0016-7037\(81\)90006-5](https://doi.org/10.1016/0016-7037(81)90006-5)

Methods

Harris, D., Horwath, W. R., & van Kessel, C. (2001). Acid fumigation of soils to remove carbonates prior to total organic carbon or CARBON-13 isotopic analysis. *Soil Science Society of America Journal*, 65(6), 1853–1856.

doi:[10.2136/sssaj2001.1853](https://doi.org/10.2136/sssaj2001.1853)

Methods

Kemp, E., Rosebrough, R., Elliott, E., & Krause, J. (2021). Spatial Variability of Sediment Amorphous Silica and its Reactivity in a Northern Gulf of Mexico Estuary and Coastal Zone. *Gulf and Caribbean Research*, 32, SC6–SC11. <https://doi.org/10.18785/gcr.3201.14>

Methods

Krause, J. W., Darrow, E. S., Pickering, R. A., Carmichael, R. H., Larson, A. M., & Basaldua, J. L. (2017). Reactive silica fractions in coastal lagoon sediments from the northern Gulf of Mexico. *Continental Shelf Research*, 151, 8–14. doi:[10.1016/j.csr.2017.09.014](https://doi.org/10.1016/j.csr.2017.09.014)

Methods

Michalopoulos, P., & Aller, R. C. (2004). Early diagenesis of biogenic silica in the Amazon delta: alteration, authigenic clay formation, and storage. *Geochimica et Cosmochimica Acta*, 68(5), 1061–1085.

doi:[10.1016/j.gca.2003.07.018](https://doi.org/10.1016/j.gca.2003.07.018)

Methods

Pickering, R. A., Cassarino, L., Hendry, K. R., Wang, X. L., Maiti, K., & Krause, J. W. (2020). Using Stable Isotopes to Disentangle Marine Sedimentary Signals in Reactive Silicon Pools. *Geophysical Research Letters*, 47(15). doi:[10.1029/2020gl087877](https://doi.org/10.1029/2020gl087877)

Methods

Rahman, S., Aller, R. C., & Cochran, J. K. (2016). Cosmogenic ³²Si as a tracer of biogenic silica burial and diagenesis: Major deltaic sinks in the silica cycle. *Geophysical Research Letters*, 43(13), 7124–7132.

doi:10.1002/2016gl069929 <https://doi.org/10.1002/2016GL069929>

Methods

Rahman, S., Aller, R. C., & Cochran, J. K. (2017). The Missing Silica Sink: Revisiting the Marine Sedimentary Si Cycle Using Cosmogenic ³²Si. *Global Biogeochemical Cycles*, 31(10), 1559–1578. doi:10.1002/2017gb005746

<https://doi.org/10.1002/2017GB005746>

Methods

Ramnarine, R., Voroney, R. P., Wagner-Riddle, C., & Dunfield, K. E. (2011). Carbonate removal by acid fumigation for measuring the $\delta^{13}\text{C}$ of soil organic carbon. *Canadian Journal of Soil Science*, 91(2), 247–250.

<https://doi.org/10.4141/cjss10066>

Methods

Walther, L., Graf, U., Kammer, A., Luster, J., Pezzotta, D., Zimmermann, S., & Hagedorn, F. (2010). Determination of organic and inorganic carbon, $\delta^{13}\text{C}$, and nitrogen in soils containing carbonates after acid fumigation with HCl. *Journal of Plant Nutrition and Soil Science*, 173(2), 207–216. Portico.

<https://doi.org/10.1002/jpln.200900158>

Methods

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Related Datasets

IsContinuedBy

Lemke, L. R., Roseburrough, R., Rahman, S., Krause, J. W. (2023) **Sediment core porewater and particulate measurements from three sites on the Louisiana Shelf sampled during R/V Pelican cruises from December 2021 through August 2022.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2023-12-11 <http://lod.bco-dmo.org/id/dataset/915912> [[view at BCO-DMO](#)]

Lemke, L. R., Roseburrough, R., Siersma, A., Rahman, S., Krause, J. W. (2024) **Sediment core porewater and particulate measurements from three sites on the Louisiana Shelf sampled during R/V Pelican cruises in August 2021.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2024-12-12 <http://lod.bco-dmo.org/id/dataset/945927> [[view at BCO-DMO](#)]

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Parameters

Parameters for this dataset have not yet been identified

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Instruments

Dataset-specific Instrument Name	Box core
Generic Instrument Name	Box Corer
Dataset-specific Description	A box core was used on the December 2021 cruise to sample sediments
Generic Instrument Description	<p>General description of a box corer: A box corer is a marine geological tool that recovers undisturbed soft surface sediments. It is designed for minimum disturbance of the sediment surface by bow wave effects. Traditionally, it consists of a weighted stem fitted to a square sampling box. The corer is lowered vertically until it impacts with the seabed. At this point the instrument is triggered by a trip as the main coring stem passes through its frame. While pulling the corer out of the sediment a spade swings underneath the sample to prevent loss. When hauled back on board, the spade is under the box. (definition from the SeaVox Device Catalog)</p> <p>Box corers are one of the simplest and most commonly used types of sediment corers. The stainless steel sampling box can contain a surface sediment block as large as 50cm x 50cm x 75cm with negligible disturbance. Once the sediment is recovered onboard, the sediment box can be detached from the frame and taken to a laboratory for subsampling and further analysis. The core sample size is controlled by the speed at which the corer is lowered into the ocean bottom. When the bottom is firm, a higher speed is required to obtain a complete sample. A depth pinger or other depth indicator is generally used to determine when the box is completely filled with sediment. Once the core box is filled with sediment, the sample is secured by moving the spade-closing lever arm to lower the cutting edge of the spade into the sediment, until the spade completely covers the bottom of the sediment box. (definition from Woods Hole Oceanographic Institution).</p>

Dataset-specific Instrument Name	centrifuge
Generic Instrument Name	Centrifuge
Dataset-specific Description	Multicorer samples were placed into tubes and centrifuged at 3500 rpm for 10 minutes to extract and filter supernatant, which was later used for dissolved silica analysis.
Generic Instrument Description	A machine with a rapidly rotating container that applies centrifugal force to its contents, typically to separate fluids of different densities (e.g., cream from milk) or liquids from solids.

Dataset-specific Instrument Name	Skalar San++ Automated Wet Chemistry Analyzer
Generic Instrument Name	Continuous Flow Analyzer
Dataset-specific Description	The Skalar San++ Automated Wet Chemistry Analyzer, also known as continuous flow analyzer, was used to analyze porewater for nitrate, nitrite, phosphorus, and ammonia.
Generic Instrument Description	A sample is injected into a flowing carrier solution passing rapidly through small-bore tubing.

Dataset-specific Instrument Name	continuous flow interface at UC Davis
Generic Instrument Name	Continuous Flow Interface for Mass Spectrometers
Dataset-specific Description	Samples measured at University of California Davis were run on an elemental analyzer interfaced to a continuous flow isotope ratio mass spectrometer. See Stable Isotope Facility instrument descriptions here: https://stableisotopefacility.ucdavis.edu
Generic Instrument Description	A Continuous Flow Interface connects solid and liquid sample preparation devices to instruments that measure isotopic composition. It allows the introduction of the sample and also reference and carrier gases. Examples: Finnigan MATConFlo II, ThermoScientific ConFlo IV, and Picarro Caddy. Note: This is NOT an analyzer

Dataset-specific Instrument Name	Elemental analyzer at UC Davis
Generic Instrument Name	Elemental Analyzer
Dataset-specific Description	Samples measured at University of California Davis were run on an elemental analyzer interfaced to a continuous flow isotope ratio mass spectrometer. See Stable Isotope Facility instrument descriptions here: https://stableisotopefacility.ucdavis.edu
Generic Instrument Description	Instruments that quantify carbon, nitrogen and sometimes other elements by combusting the sample at very high temperature and assaying the resulting gaseous oxides. Usually used for samples including organic material.

Dataset-specific Instrument Name	Thermo Scientific Element XR high resolution inductively coupled plasma-mass spectrometer (HR-ICP-MS)
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Dataset-specific Description	Porewater was reconstituted in dilute HNO ₃ and diluted to minimize salt interferences before analysis on a Thermo Scientific Element XR High Resolution-ICP-MS housed at the University of Southern Mississippi at the Stennis Space Center.
Generic Instrument Description	An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer.

Dataset-specific Instrument Name	CF-IRMS at UC Davis (continuous flow isotope ratio mass spectrometer)
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset-specific Description	Samples measured at University of California Davis were run on an elemental analyzer interfaced to a continuous flow isotope ratio mass spectrometer. See Stable Isotope Facility instrument descriptions here: https://stableisotopefacility.ucdavis.edu
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).

Dataset-specific Instrument Name	Ocean Instruments Multicorer
Generic Instrument Name	Multi Corer
Dataset-specific Description	At each site, an 8-spot Ocean Instruments Multi-corer collected sediment that was sectioned in 2 centimeter intervals
Generic Instrument Description	The Multi Corer is a benthic coring device used to collect multiple, simultaneous, undisturbed sediment/water samples from the seafloor. Multiple coring tubes with varying sampling capacity depending on tube dimensions are mounted in a frame designed to sample the deep ocean seafloor. For more information, see Barnett et al. (1984) in Oceanologica Acta, 7, pp. 399-408.

Dataset-specific Instrument Name	Thermo Scientific Genesys 10S UV-Vis Spectrophotometer
Generic Instrument Name	Spectrophotometer
Dataset-specific Description	Porewater was analyzed for dissolved Si(OH) ₄ concentration using a spectrophotometric molybdate-blue method and a Thermo Scientific Genesys 10S UV-Vis Spectrophotometer.
Generic Instrument Description	An instrument used to measure the relative absorption of electromagnetic radiation of different wavelengths in the near infra-red, visible and ultraviolet wavebands by samples.

Deployments

PE22-05

Website	https://www.bco-dmo.org/deployment/945957
Platform	R/V Pelican
Start Date	2021-08-17
End Date	2021-08-17

Project Information

Collaborative Research: Understanding substrate limitation and Lithium and Silicon isotope fractionation during secondary clay formation in marine systems (Marine Secondary Clay Formation)

Coverage: Northern Gulf of Mexico & Laboratory-based work

NSF Award Abstract:

A long-standing topic of investigation in the field of chemical oceanography is understanding the processes that deliver elements to, and remove them from, seawater. There has long been a "missing sink" in the global marine silicon (Si) budget in that removal to sediments did not appear to balance the inputs from rivers. Several decades ago, it was postulated that "reverse weathering" in marine sediments could be this missing sink. In this process, the weathering process that takes place on land, whereby silicon is removed from minerals and dissolved in water, would be reversed and these minerals would be reconstituted in marine sediments through the formation of clays. Evidence for this process was very difficult to obtain, and only recently have studies using advanced measurement techniques shown that the global magnitude of marine reverse weathering could account for all the missing sink term in the global Si budget. If validated, this means reverse weathering would represent the largest individual sink for marine Si identified to date, with most of this burial occurring in a relatively small area of the ocean, the land-sea interface. Moreover, the continued upward revision of the marine reverse weathering rate has implications for the sequestration of other elements (e.g. iron, aluminum) and for other coastal processes (e.g. ocean acidification, as carbon dioxide is a byproduct of the reverse weathering process). This project aims to understand the most important factors affecting how fast reverse weathering occurs, and developing new approaches to evaluate this process in the field environment. Beyond the scientific pursuits, this project will support an early career researcher, a postdoctoral investigator, a graduate student, and undergraduate interns. It will also support high school outreach through science fair participation and annual scholarships for students wishing to pursue Marine Science education. This project will develop a community outreach activity to be used annually during the Atlanta Science Festival, Georgia's biggest science fair that showcases science and technology to the public. Finally, it will build capacity for silicon isotope measurements in the U.S.

In this project, the investigators propose to understand the driving factors of marine secondary clay formation and facilitate the determination of reaction degree in the field using a novel dual silicon and lithium stable isotope approach. The overarching goals are: 1) to better constrain the geochemical factors, kinetics, and mechanisms involved in secondary clay formation from diatom-produced silica ($bSiO_2$); this will be done by conducting controlled laboratory experiments using pure mineral phases, diatom $bSiO_2$, and artificial seawater; 2) to test the validity of the isolated geochemical factors by conducting mesocosm incubation experiments using field sediment materials, diatom $bSiO_2$, and seawater; and 3) to experimentally determine whether laboratory-derived Li and Si isotope fractionations are valid during secondary clay formation under marine sediment conditions. This work addresses one of the eight Ocean Sciences Priorities identified in The National Research Council's 2015-2025 Decadal Survey of Ocean Sciences, specifically "How have ocean biogeochemical and physical processes contributed to today's climate and its variability, and how will this system change over the next century?" These results have fundamental importance to understanding the factors regulating marine elemental sequestration (e.g. Si, C, Fe, Al, Mg, K) and those driving global climate

through oceanic CO₂ evolution, a byproduct of the reverse weathering reaction, in marine sediments.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1924585
NSF Division of Ocean Sciences (NSF OCE)	OCE-1923802

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