

# An investigation into the characteristics of the reactive pools of Mississippi River plume sediments collected August to September of 2016 and May 2017 aboard the R/V Pelican.

**Website:** <https://www.bco-dmo.org/dataset/823190>

**Data Type:** Cruise Results

**Version:** 1

**Version Date:** 2020-09-04

## Project

» [The biotic and abiotic controls on the Silicon cycle in the northern Gulf of Mexico](#) (CLASiC)

Contributors	Affiliation	Role
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## Abstract

An investigation into the characteristics of the reactive pools of Mississippi River plume sediments collected August to September of 2016 and May 2017 aboard the R/V Pelican.

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## Coverage

**Spatial Extent:** N:29.01 E:-89.57833 S:28.49563 W:-91.60927

**Temporal Extent:** 2016-08-28 - 2017-05-11

## Acquisition Description

### Core Sampling

Briefly, samples were acquired from the study area using an Ocean Instruments MC-900 Multi-corer, which preserved the sediment-water interface during recovery. Overlying bottom water was removed, cores were sectioned into 1cm slices, homogenized, packed under N<sub>2</sub> gas and frozen at -20o C for further

analysis. On select cores, pore waters were collected prior to core sectioning using Rhizons (0.15  $\mu\text{m}$  pore size; Rhizosphere Research Products) attached to syringes, and inserted into the core (1-cm sediment intervals) through pre-drilled holes. Porewater nutrients were analyzed at the Dauphin Island Sea Lab Analytical Laboratory, via a Skalar San++ Auto Analyzer based on standard Environmental Protection Agency methodologies, including dSi, nitrate plus nitrite ( $\text{NO}_3 + \text{NO}_2$ ), soluble reactive phosphate ( $\text{PO}_4$ ) and nitrite ( $\text{NO}_2$ ) ( $\mu\text{mol L}^{-1}$ ).

## Operational Definitions

Operational reactive Si pools have previously been defined by Rahman et al. (2016) but for consistency and clarity with previous literature (DeMaster, 1981; Michalopoulos and Aller, 2004; Qin et al., 2012; Wang et al., 2015; Rahman et al., 2016; Krause et al., 2017) it has been restated here. Therefore 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: 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 bSiO<sub>2</sub>" (e.g. sponge spicules and Rhizaria, Maldonado et al., 2019).
4. T-bSiO<sub>2</sub>: Following the traditional definition of biogenic silica (DeMaster, 1981), with no acid pre-treatment.

## Reactive Silica Pools

Frozen sediment samples were thawed to room temperature (22o C) and triplicate ~50-100 mg subsamples were immediately weighed into 50 mL polyethylene centrifuge tubes. Samples were never dried or ground before/during extractions. Procedural blanks were also prepared in triplicate. Additional subsamples of sediment were dried at 60o C to obtain correction for water content.

### *Sequential Extractions*

#### *Acid Leachable Silica (Si-HCl)*

Sediment extractions occurred at room temperature (22o C) using Honeywell Fluka Trace SELECT 0.1 N HCl for 12 hrs, while keeping particles suspended via constant motion. Following centrifugation, the Si-HCl leachate was removed and neutralized. Remaining sediment was rinsed in triplicate with Milli-Q water to remove any residual acid (Michalopoulos and Aller, 2004). As it had previously been demonstrated by Rahman et al. (2016) that the rinses contained minor amounts of Si these rinses were discarded. A weak HCl molarity was purposely chosen to remove metal coatings, authigenic phases, and activate bSi surfaces while not affecting the sequential Si-Alk digestion (Michalopoulos and Aller, 2004).

#### *Mild Alkaline Leachable Si (Si-Alk)*

Following the acid pre-leach, the remaining sediment was sequentially digested with 25 ml Fisher Scientific Certified ACS 0.1 M Na<sub>2</sub>CO<sub>3</sub> in an 85o C water bath for a total of 5 hrs. (dry weight SSR ~1-2). Time-point subsamples were taken at 20 min., 1, 2, 3, and 5 hrs. following (DeMaster, 1981). The individual acidified Si-Alk leachates were analyzed for dSi and the intercept from a regression of individual timepoints (DeMaster, 1981) represents the bSiO<sub>2</sub> content without LSi interference. After the 5 hrs. aliquot was removed, whole samples were neutralized to stop the digestion. Following centrifugation, the leachate was removed and discarded. Remaining sediment was rinsed in triplicate with Milli-Q water to remove any residual Na<sub>2</sub>CO<sub>3</sub> and again the rinses were discarded.

#### *Harsh NaOH Digestion (Si-NaOH)*

The remaining sediment from the Si-Alk treatment was subsequently digested with Honeywell Fluka 4 M NaOH for 2 hrs in a 85o C water bath. After 2 hrs, samples were placed on ice and neutralized to stop the digestion. Following centrifugation, the Si- NaOH leachate was removed, the remaining sediment was rinsed with Milli-Q water to remove any residual leachate and this rinse was added to the Si-NaOH

leachate and stored for further analysis (Rahman et al., 2016).

### *Traditional bSi Digestion (T-bSiO<sub>2</sub>)*

Additionally, a second treatment following the traditional definition of biogenic silica (DeMaster, 1981), with no acid pre-treatment was used. New subsamples of sediment were weighed out. 0.1 M Na<sub>2</sub>CO<sub>3</sub> was added to samples and heated in a 85o C water bath for 20 mins to remove the bSi phase. Following the 20 min timepoint, samples were placed on ice and neutralized to stop the digestion. Following centrifugation, leachate was removed and stored for further use. Similar to the Si-Alk digestions, the process was stopped after 20 mins to ensure the absence of lithogenic material.

A 1 ml aliquot of each resulting liquid (Si-HCl, Si-Alk, Si-NaOH and T-bSi) was analyzed for dissolved SiOH<sub>4</sub> concentration (dSi) as described by Brzezinski and Nelson (Brzezinski and Nelson, 1986) using the molybdate-blue method on a Genesys 10S UV-Vis Spectrophotometer. The remaining supernatants were stored following DeMaster (1980) in preparation for future analysis.

### **Major Metal Compositions and Corrections**

Leachate supernatants were evaporated to dryness in Teflon beakers on a hotplate at 100o C and samples were reconstituted in 2% HNO<sub>3</sub> (in-house distilled). Major ion concentrations were determined on an Agilent 7700 Series ICP-MS at the Dauphin Island Sea Lab, following calibration using a blank and seven matrix-matched, mixed standards. Internal standards 115In and 4Be (50 µl, 10 ppm) were added to all standards and samples. Samples which could not be resolved from the blank solution were considered operationally undetectable.

### **Organic Matter**

Sediment Particulate organic carbon (POC) and total organic nitrogen (PON) content were analyzed at the Dauphin Island Sea Lab using a Costech elemental combustion system (4010 ECS) following vapor phase acidification to remove carbonates. Briefly, dried sediment samples were placed in a glass desiccator and reacted with reagent-grade 12N HCl vapor for 24 hrs at room temperature. Samples were then dried at 60o C overnight to remove remaining HCl and water content before POC/PON analyses (Yamamuro and Kayanne, 1995).

### **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.
- \* removed all spaces in headers and replaced with underscores
- \* removed all units from headers
- \* converted dates to ISO Format yyyy-mm-dd
- \* set Types for each data column

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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*

Cardinal, D., Alleman, L. Y., de Jong, J., Ziegler, K., & André, L. (2003). Isotopic composition of silicon

measured by multicollector plasma source mass spectrometry in dry plasma mode. *Journal of Analytical Atomic Spectrometry*, 18(3), 213–218. doi:10.1039/b210109b <https://doi.org/10.1039/B210109B>  
*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*

Demaster, D. J. (1980). The half life of  $^{32}\text{Si}$  determined from a varved Gulf of California sediment core. *Earth and Planetary Science Letters*, 48(1), 209–217. doi:10.1016/0012-821x(80)90182-x  
[https://doi.org/10.1016/0012-821X\(80\)90182-X](https://doi.org/10.1016/0012-821X(80)90182-X)  
*Methods*

Hendry, K. R., Leng, M. J., Robinson, L. F., Sloane, H. J., Blusztjan, J., Rickaby, R. E. M., ... Halliday, A. N. (2010). Silicon isotopes in Antarctic sponges: an interlaboratory comparison. *Antarctic Science*, 23(1), 34–42. doi:10.1017/s0954102010000593 <https://doi.org/10.1017/S0954102010000593>  
*Methods*

Hughes, H. J., Delvigne, C., Korntheuer, M., de Jong, J., André, L., & Cardinal, D. (2011). Controlling the mass bias introduced by anionic and organic matrices in silicon isotopic measurements by MC-ICP-MS. *Journal of Analytical Atomic Spectrometry*, 26(9), 1892. doi:10.1039/c1ja10110b  
<https://doi.org/10.1039/C1JA10110B>  
*Methods*

Kamatani, A., & Oku, O. (2000). Measuring biogenic silica in marine sediments. *Marine Chemistry*, 68(3), 219–229. doi:10.1016/s0304-4203(99)00079-1 [https://doi.org/10.1016/S0304-4203\(99\)00079-1](https://doi.org/10.1016/S0304-4203(99)00079-1)  
*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*

Maldonado, M., López-Acosta, M., Sitjà, C., García-Puig, M., Galobart, C., Ercilla, G., & Leynaert, A. (2019). Sponge skeletons as an important sink of silicon in the global oceans. *Nature Geoscience*, 12(10), 815–822. doi:[10.1038/s41561-019-0430-7](https://doi.org/10.1038/s41561-019-0430-7)  
*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*

Qin, Y.-C., Weng, H.-X., Jin, H., Chen, J., & Tian, R.-X. (2011). Estimation of authigenic alteration of biogenic and reactive silica in Pearl River estuarine sediments using wet-chemical digestion methods. *Environmental Earth Sciences*, 65(6), 1855–1864. doi:[10.1007/s12665-011-1168-8](https://doi.org/10.1007/s12665-011-1168-8)  
*Methods*

Ragueneau, O., Savoye, N., Del Amo, Y., Cotten, J., Tardiveau, B., & Leynaert, A. (2005). A new method for the measurement of biogenic silica in suspended matter of coastal waters: using Si:Al ratios to correct for the mineral interference. *Continental Shelf Research*, 25(5-6), 697–710. doi:[10.1016/j.csr.2004.09.017](https://doi.org/10.1016/j.csr.2004.09.017)  
*Methods*

Rahman, S., Aller, R. C., & Cochran, J. K. (2016). Cosmogenic  $^{32}\text{Si}$  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  $^{32}\text{Si}$ . *Global Biogeochemical Cycles*, 31(10), 1559–1578. doi:10.1002/2017gb005746 <https://doi.org/10.1002/2017GB005746>  
*Methods*

Reynolds, B. C., Aggarwal, J., André, L., Baxter, D., Beucher, C., Brzezinski, M. A., ... Cardinal, D. (2007). An inter-laboratory comparison of Si isotope reference materials. *J. Anal. At. Spectrom.*, 22(5), 561–568. doi:10.1039/b616755a <https://doi.org/10.1039/B616755A>  
*Methods*

Wang, C., Zhu, H., Wang, P., Hou, J., Ao, Y., & Fan, X. (2015). Early diagenetic alterations of biogenic and reactive silica in the surface sediment of the Yangtze Estuary. *Continental Shelf Research*, 99, 1–11. doi:[10.1016/j.csr.2015.03.003](https://doi.org/10.1016/j.csr.2015.03.003)  
*Methods*

Yamamuro, M., & Kayanne, H. (1995). Rapid direct determination of organic carbon and nitrogen in carbonate-bearing sediments with a Yanaco MT-5 CHN analyzer. *Limnology and Oceanography*, 40(5), 1001–1005. doi:[10.4319/lo.1995.40.5.1001](https://doi.org/10.4319/lo.1995.40.5.1001)  
*Methods*

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## **Parameters**

<b>Parameter</b>	<b>Description</b>	<b>Units</b>
Cruise_Collected	Crusie name and year of collection	unitless
MultiCore	Multicore identifer for corresponding cruise	unitless
Station_Number	Station identifier for corresponding cruise	unitless
Bottom_Depth	Largest veritcal distance below the surface	Meters
Latitude	Decimal Degrees	Decimal Degrees
Longitude	Decimal Degrees	Decimal Degrees
Date_Collected	When was the core collected	yyyy-mm-dd
Sample_Depth	Subsection used for analysis	centimeters
Nominal_Depth	Depth used for data plots	centimeters
Porewater_SiOH_4	Concentration of dissolved silica acid in porewater collected	micromoles per liter
Porewater_NO3_NO2	Concentration of dissolved nitrate-nitrite in porewater collected	micromoles per liter
Porewater_PO4	Concentration of dissolved phosphate in porewater collected	micromoles per liter
Porewater_NO2	Concentration of dissolved nitrite in porewater collected	micromoles per liter
Porewater_NH4	Concentration of dissolved ammonium in porewater collected	micromoles per liter
Vapor_Phase_Carbonate	% of Carbonates present in the sediment sample via vapor phase acidification	%
POC	Particular Organic Carbon	%
POC_2_Stdev	2 standard deviations of sample variation	dimensionless
PON	Particular Organic Nitrogen	%
PON_2_Stdev	2 standard deviations of sample variation	dimensionless
Si_HCl	Average Si released (n=3) for each corresponding reactive Si Pool	micromoles per gram dry sediment umol/g
Si_HCl_2_Stdev	2 standard deviations for the corresponding reactive Si Pool	dimensionless
Si_Alk	Average Si released (n=3) for each corresponding reactive Si Pool	micromoles per gram dry sediment umol/g
Si_Alk_2_Stdev	2 standard deviations for the corresponding reactive Si Pool	dimensionless
Si_NaOH	Average Si released (n=3) for each corresponding reactive Si Pool	micromoles per gram dry sediment umol/g
Si_NaOH_2_Stdev	2 standard deviations for the corresponding reactive Si Pool	dimensionless
T_bSiO2	Average Si released (n=3) for each corresponding reactive Si Pool	micromoles per gram dry sediment umol/g
T_bSiO2_2_Stdev	2 standard deviations for the corresponding reactive Si Pool	dimensionless

## Instruments

<b>Dataset-specific Instrument Name</b>	Skalar San++ Auto Analyzer
<b>Generic Instrument Name</b>	Nutrient Autoanalyzer
<b>Generic Instrument Description</b>	Nutrient Autoanalyzer is a generic term used when specific type, make and model were not specified. In general, a Nutrient Autoanalyzer is an automated flow-thru system for doing nutrient analysis (nitrate, ammonium, orthophosphate, and silicate) on seawater samples.

<b>Dataset-specific Instrument Name</b>	Genesys 10S UV-Vis Spectrophotometer.
<b>Generic Instrument Name</b>	Spectrophotometer
<b>Generic Instrument Description</b>	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.

<b>Dataset-specific Instrument Name</b>	
<b>Generic Instrument Name</b>	Costech International Elemental Combustion System (ECS) 4010
<b>Generic Instrument Description</b>	The ECS 4010 Nitrogen / Protein Analyzer is an elemental combustion analyser for CHNSO elemental analysis and Nitrogen / Protein determination. The GC oven and separation column have a temperature range of 30-110 degC, with control of +/- 0.1 degC.

## Deployments

### PE17-20

<b>Website</b>	<a href="https://www.bco-dmo.org/deployment/792830">https://www.bco-dmo.org/deployment/792830</a>
<b>Platform</b>	R/V Pelican
<b>Start Date</b>	2017-05-03
<b>End Date</b>	2017-05-13

## Project Information

### The biotic and abiotic controls on the Silicon cycle in the northern Gulf of Mexico (CLASiC)

**Coverage:** Northern Gulf of Mexico, specifically the Louisiana Shelf region dominated by the discharge of the Mississippi River on the western side of the delta

NSF Award Abstract: The Louisiana Shelf system in the northern Gulf of Mexico is fed by the Mississippi River and its many tributaries which contribute large quantities of nutrients from agricultural fertilizer to the region. Input of these nutrients, especially nitrogen, has led to eutrophication. Eutrophication is the process wherein a body of water such as the Louisiana Shelf becomes enriched in dissolved nutrients that increase phytoplankton growth which eventually leads to decreased oxygen levels in bottom waters. This has certainly been observed in this area, and diatoms, a phytoplankton which represents the base of the food chain, have shown variable silicon/nitrogen (Si/N) ratios. Because diatoms create their shells from silicon, their growth is controlled not only by nitrogen inputs but the availability of silicon. Lower Si/N ratios are showing that silicon may be playing an increasingly important role in regulating diatom production in the system. For this reason, a scientist from the University of South Alabama will determine the biogeochemical processes controlling changes in Si/N ratios in the Louisiana Shelf system. One graduate student on their way to a doctorate degree and three undergraduate students will be supported and trained as part of this project. Also, four scholarships for low-income, high school students from Title 1 schools will get to participate in a month-long summer Marine Science course at the Dauphin Island Sea Laboratory and be included in the research project. The study has significant societal benefits given this is an area where \$2.4 trillion gross domestic product revenue is tied up in coastal resources. Since diatoms are at the base of the food chain that is the biotic control on said coastal resources, the growth of diatoms in response to eutrophication is important to study. Eutrophication of the Mississippi River and its tributaries has the potential to alter the biological landscape of the Louisiana Shelf system in the northern Gulf of Mexico by influencing the Si/N ratios below those that are optimal for diatom growth. A scientist from the University of South Alabama believes the observed changes in the Si/N ratio may indicate silicon now plays an important role in regulating diatom production in the system. As such, understanding the biotic and abiotic processes controlling the silicon cycle is crucial because diatoms dominate at the base of the food chain in this highly productive region. The study will focus on following issues: (1) the importance of recycled silicon sources on diatom production; (2) can heavily-silicified diatoms adapt to changing Si/N ratios more effectively than lightly-silicified diatoms; and (3) the role of reverse weathering in sequestering silicon thereby reducing diffusive pore-water transport. To attain these goals, a new analytical approach, the PDMPO method (compound 2-(4-pyridyl)-5-((4-(2-dimethylaminoethylamino-carbamoyl)methoxy)phenyl)oxazole) that quantitatively measures taxa-specific silica production would be used.

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## Funding

Funding Source	Award
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1558957</a>

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