Results from a laboratory-based investigation into sediment Silicon sorption capacities using standardized clay samples and the radioactive tracer 32Si

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Data Type: experimental
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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
These data are from a laboratory-based investigation into sediment Silicon sorption capacities using standardized clay samples (KGa-2 and SWy-3) and the radioactive tracer silicon-32 (32Si). Water for the project incubations was collected during the 2017 CLASiC Cruise (R/V Pelican PE17-20). Sampling spans sacrificial triplicate timepoints over 6 days. The data presented in this overall summary file include the location and depth of the water collection, which clay standard was used in each sample (KGa-2 vs. SWy-3), the salinity of the water used, sacrificial collection timepoint, initial radioactive tracer 32Si added to each individual sample, the final raw data for dissolved Si in solution, 32Si DPM found in the solution, and 32Si DPM found in the particles for each individual sample. The scope of the data was defined by the sampling scheme using triplicate sacrificial sampling over 6 days for the different clay types.

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Coverage

Location: Northern Gulf of Mexico Shelf
Spatial Extent: **Lat**:28.5 **Lon**:-90.8167
Temporal Extent: 2017-05-06 - 2018-10-14

Methods & Sampling

Source Materials: The clay standards used were sourced from The Clay Minerals Society Source Clays Repository, and they have well-known chemical compositions. As the materials are a natural clay, these substances are assumed to be slightly impure, e.g. <7% Ti and/or Fe-oxides (Guggenheim, 2001). Montmorillonite and kaolinite were selected due to their environmental relevance, e.g. river plume systems in northern Gulf of Mexico (Grim and Johns, 1954; Pinsak, 1958; Scafe and Kunze, 1971; Sionneau et al., 2008;

Ghaisas et al., 2021). SWy-3 is a Na-rich Montmorillonite sourced from Crook County, Wyoming, USA. KGa-2 is a Kaolinite sourced from Warren County, Georgia, USA. Before use, clays were sterilized for 30 minutes inside an Ultraviolet (UV) light box to degrade bacteria and avoid confounding results due to biotic activity. Samples were not ground, chemically- or heat-treated prior to experiments, as these processes are known to increase reactivity by decreasing surface crystallinity. Clays were not size fractionated as little variation in reactivity occurs when separating the < 2 micrometer (µm) size fraction from bulk clays (Siever and Woodford, 1973).

Seawater Collections: Natural seawater, which contains a complicated blend of dissolved organic and inorganic chemical compounds and species (e.g. macronutrients, trace metals) was used in these experiments as in previous studies (Siever, 1968a; Siever and Woodford, 1973). Bottom water (33 meters) was collected just above the sediment-water interface during Spring 2017 aboard the R/V Pelican (cruise ID: PE17-20) in the northern Gulf of Mexico (Krause et al., 2023); the sample location (28°30’ N, 90°50’ W) is ~150 kilometers west of the main Mississippi River outflow channel (Southwest Pass). The samples in this dataset were collected on May 6, 2017. Water was collected using 10-liter (L) Niskin bottles attached to an Ocean Instruments MC-900 Multi-corer; Niskin bottles were triggered concurrently with the multi-corer release and thus did not capture significant resuspended sediment from the Multi-corer landing. Shortly after recovery, the water was gravity-filtered directly from the Niskin through a 0.2 µm Whatman polycap filter into acid pre-cleaned 10 L carboys for storage (in the dark, room temperature) and future use. In the lab, the salinity (ppt) of the filtered seawater was checked and adjusted with 18.2 MΩ *cm deionized water to either 4 ppt or 32 ppt. The water was then sterilized with a UV Steripen (Adventure Opti Model) for 10 minutes to degrade bacteria and a subsample was analyzed for dSi using a commonly used spectrophotometric molybdate-blue method (e.g. Pickering et al., 2020).

Laboratory Experiments: Laboratory experiments were conducted from October 1 to October 14, 2018. In the lab, homogenized clay standard samples were weighed and mixed with 250 milliliters (mL) of adjusted seawater to achieve sediment dry-weight solid-to-solution ratios (SSR, grams per liter (g L-1)) of 0.1, 3 and 10; this was done for both clays (SWy-3 and KGa-2) and both salinities (4 ppt and 32 ppt). Procedural blanks were also prepared without the addition of sediment. A Teflon-coated stir bar and stir plate were used to keep the sediment suspended during subsampling. 7 mL of suspended sediment slurry was pipetted into 15 mL polypropylene plug seal centrifuge tubes and 10,000 DPM (167 Bq) of 32Si(OH)4 (104 Bq (µg Si)-1) was then added to each tube. Following the addition of 32Si to each tube, samples were sealed and immediately inverted to ensure the complete mixing of the radioisotope tracer into the slurry. Tubes were placed sideways on a shaker table and incubated in the dark at 15 degrees Celsius (°C) for 144 hours. Samples were vented every 12 hours to ensure oxygenation (i.e. exchange 8-mL ambient air headspace). Triplicate sacrificial sampling of each SSR occurred at the following time points; 0, 12, 24, 48, 72, 96, 120, and 144 hours as described below (i.e., for each clay type and SSR, 24 individual tubes sampled over time).

For each time point, individual samples were partitioned to quantify particulate and dissolved constituents. After mixing thoroughly using a vortex mixer, 3 mL of suspended sediment solution was filtered onto a polycarbonate membrane filter (25-millimeters (mm) diameter - 0.6 µm pore size). This filter was placed on a nylon disk planchette, dried overnight, covered with a mylar film, and both the filter and mylar were secured to the planchette using a nylon ring. Next, the tube was centrifuged for 10 minutes at 1500 x g. Following centrifugation, 2 mL of supernatant was subsampled in 1-mL aliquots. The first 1 mL was placed into a 20 mL plastic liquid scintillation vial. The second 1 mL was analyzed for dSi using a spectrophotometric molybdate-blue method as described above. The remaining 2 mL of solution was frozen for future analysis and contained ~57% of the original sediment, as liquid was removed without sediment from the sample tube for the two 1-mL aliquots. Blanks were treated in the same manner and run in tandem with each sediment (SWy-3, KGa-2) type totaling 48 - 4 ppt and 48 - 32 ppt blanks.

32Si Quantification: 32Si activity was quantified after the samples were aged into secular equilibrium with 32P, the short-lived (t½ = 14.28 days) and high energy (Emax = 1709 keV) daughter isotope of 32Si (t½ = 144 years, Emax = 227 keV). While the International System derived unit of radioactivity is the becquerel (Bq), we report activity in disintegrations per minute (DPM) (1 Bq = 60 DPM) as it is a functional unit that relates directly to instrument-derived counts per minute (CPM) and counting efficiency. For particulate 32Si, activity was measured using a GM-24 Multicounter (Risø DTU National Laboratory, Denmark) following Krause et al. (2011). For solution 32Si, sample activity was quantified using liquid scintillation counting (LSC). Given the quantity of samples, we chose a more commonly used and inexpensive liquid scintillation cocktail than traditionally used for LSC, e.g. Ultima GoldTM XR (Brzezinski and Phillips, 1997). To the 1 mL solution subsamples, 9 mL of EcoLumeTM (MP Biomedicals LLC, USA) was added, mixed, and total counts in solution were quantified after samples sat 2 hours (to reduce chemoluminescence) using a TriCarb 3110 TR liquid scintillation counter (Perkin Elmer).

Data Processing Description

Dixon's Q-Test was used to identify outliers among triplicate replicates (Dean and Dixon, 1951), and these values were removed from the dataset, (32Si particulates; n = 8 out of 288 samples, 32Si solution; n = 6 out of 288 samples). Two factor ANOVA with replication on Microsoft Excel was used to examine differences among treatments; an alpha value of 0.05 was assigned a priori. An F value represents how much the variability between averages, exceeds those expected, while a FCritical value determines if the averages between two populations are significant.

BCO-DMO Processing Description

- Imported original file "Pickering et al_Data _Overall_Summary.xlsx" into the BCO-DMO system.
- Renamed fields to comply with BCO-DMO naming conventions.
- Converted latitude and longitude from degrees and decimal minutes to decimal degrees, and rounded values to 5 decimal places.
- Saved the final file as "925041_v1_estuarine_sediment_si_sorption_capacities.csv".

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Data Files

File
925041_v1_estuarine_sediment_si_sorption_capacities.csv (Comma Separated Values (.csv), 40.87 KB) MD5:d37959ff57fe21f180d5420ecc956269 Primary data file for dataset ID 925041, version 1

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Related Publications

Brzezinski, M. A., & Phillips, D. R. (1997). Evaluation of 32Si as a tracer for measuring silica production rates in marine waters. Limnology and Oceanography, 42(5), 856–865. Portico. https://doi.org/10.4319/lo.1997.42.5.0856
Methods

Dean, R. B., & Dixon, W. J. (1951). Simplified Statistics for Small Numbers of Observations. Analytical Chemistry, 23(4), 636–638. https://doi.org/10.1021/ac60052a025
Methods

Ghaisas, N. A., Maiti, K., & Roy, A. (2021). Iron-Mediated Organic Matter Preservation in the Mississippi River-Influenced Shelf Sediments. Journal of Geophysical Research: Biogeosciences, 126(4). Portico. https://doi.org/10.1029/2020jg006089
Methods

Grim, R. E., & Johns, W. D. (1953). Clay Mineral Investigation of Sediments in the Northern Gulf of Mexico. Clays and Clay Minerals (National Conference on Clays and Clay Minerals), 2, 81–103. https://doi.org/10.1346/ccmn.1953.0020107
Methods

Guggenheim, S., & Koster van Groos, A. F. (2001). Baseline Studies of the Clay Minerals Society Source Clays: Thermal Analysis. Clays and Clay Minerals, 49(5), 433–443. https://doi.org/10.1346/ccmn.2001.0490509
Methods

Krause, J. W., Boyette, A. D., Marquez, I. A., Pickering, R. A., & Maiti, K. (2023). Drivers of diatom production and the legacy of eutrophication in two river plume regions of the northern Gulf of Mexico. Frontiers in Marine Science, 10. https://doi.org/10.3389/fmars.2023.1162685
Methods

Krause, J. W., Brzezinski, M. A., & Jones, J. L. (2011). Application of low-level beta counting of 32Si for the measurement of silica production rates in aquatic environments. Marine Chemistry, 127(1-4), 40–47.

doi:10.1016/j.marchem.2011.07.001
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
Methods

Pinsak, A. P., & Murray, H. H. (1958). Regional clay Mineral Patterns in the Gulf of Mexico. Clays and Clay Minerals (National Conference on Clays and Clay Minerals), 7, 162–177. https://doi.org/10.1346/ccmn.1958.0070109
Methods

Scafe, D. W., & Kunze, G. W. (1971). A clay mineral investigation of six cores from the Gulf of Mexico. Marine Geology, 10(1), 69–85. https://doi.org/10.1016/0025-3227(71)90077-6
Methods

Siever, R. (1968). Establishment of equilibrium between clays and sea water. Earth and Planetary Science Letters, 5, 106–110. https://doi.org/10.1016/s0012-821x(68)80023-8 https://doi.org/10.1016/S0012-821X(68)80023-8
Methods

Siever, R., & Woodford, N. (1973). Sorption of silica by clay minerals. Geochimica et Cosmochimica Acta, 37(8), 1851–1880. https://doi.org/10.1016/0016-7037(73)90146-4
Methods

Sionneau, T., Bout-roumazeilles, V., Biscaye, P.E., van Vliet-Lanoe, B., & Bory, A. (2008). Clay mineral distributions in and around the Mississippi River watershed and Northern Gulf of Mexico: sources and transport patterns. Quaternary Science Reviews, 27 (17-18), pp.1740-1751. hal-03290439 https://hal.science/hal-03290439
Methods

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Parameters

Parameter	Description	Units
Sample_Number	Unique sample ID for each sample incubation	unitless
Sample_Description	Overall description for solid-to-solution ratio (SSR), salinity, and clay type used for each unique sample	unitless
Latitude_water_collection	Latitude location in which incubation water was collected; positive values = North	decimal degrees
Longitude_water_collection	Longitude location in which incubation water was collected; negative values = West	decimal degrees
Depth_water_collection	Depth in which incubation water was collection	meters (m)
Sediment_Type_Used	Clay Mineral Society source clay standard type used (KGa-2 or SWy-3)	unitless

SSR_g_L_1	Sediment to solution ratio	grams per liter (g L-1)
Salinity_ppt	Corrected salinity used	ppt
Time_Elapsed_Hrs	Time elapsed from starting 32Si isotope addition until stopping the incubation	hours
Si32_Initial_isotope_Added_DPM	Total starting 32Si isotope added to individual sample	disintegrations per minute (DPM)
dSi_in_solution_umol_L_1	Final dissolved Si(OH)4 in solution at unique timepoint indicated	micromoles per liter (umol L-1)
Average_dSi_in_solution_umol_L_1	Average final dissolved Si(OH)4 in solution for 3 sacrificial triplicate timepoints	micromoles per liter (umol L-1)
Stdev_dSi_in_solution_umol_L_1	Standard deviation of final dissolved Si(OH)4 in solution for 3 sacrificial triplicate timepoints	micromoles per liter (umol L-1)
Si32_DPM_in_Solution	Final DPM of 32Si in solution at unique timepoint indicated	disintegrations per minute (DPM)
Average_32Si_in_solution_DPM	Average final DPM of 32Si in solution for 3 sacrificial triplicate timepoints	disintegrations per minute (DPM)
Stdev_32Si_in_solution_DPM	Standard deviation of final DPM of 32Si in solution for 3 sacrificial triplicate timepoints	disintegrations per minute (DPM)
Si32_in_Particles_DPM	Final DPM of 32Si in sediment particles at unique timepoint indicated	disintegrations per minute (DPM)
Si32_in_Particles_Blank_Corrected_DPM	Blank corrected (using the average of the 3 blanks for this timepoints) final DPM of 32Si in sediment particles at unique timepoint indicated	disintegrations per minute (DPM)
Average_32Si_in_Particles_Blank_Corrected_DPM	Blank corrected average final DPM of 32Si in sediment particle for 3 sacrificial triplicate timepoints	disintegrations per minute (DPM)

Stdev_32Si_in_Particles_Blank_Corrected_DPM	Blank corrected standard deviation final DPM of 32Si in sediment particle for 3 sacrificial triplicate timepoints	disintegrations per minute (DPM)

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Instruments

Dataset-specific Instrument Name	GM-24 Multicounter (Risø DTU National Laboratory, Denmark)
Generic Instrument Name	GM multicounter
Generic Instrument Description	A gas flow multicounter (GM multicounter) is used for counting low-level beta doses. GM multicounters can be used for gas proportional counting of 32Si to 32P. For more information about GM multicounter usage see Krause et. al. 2011.

Dataset-specific Instrument Name	Ocean Instruments MC-900 Multi-corer
Generic Instrument Name	Multi Corer
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	10 L Niskin bottles attached to an Ocean Instruments MC-900 Multi-corer
Generic Instrument Name	Niskin bottle
Generic Instrument Description	A Niskin bottle (a next generation water sampler based on the Nansen bottle) is a cylindrical, non-metallic water collection device with stoppers at both ends. The bottles can be attached individually on a hydrowire or deployed in 12, 24, or 36 bottle Rosette systems mounted on a frame and combined with a CTD. Niskin bottles are used to collect discrete water samples for a range of measurements including pigments, nutrients, plankton, etc.

Dataset-specific Instrument Name	TriCarb 3110 TR liquid scintillation counter (Perkin Elmer)
Generic Instrument Name	PerkinElmer Tri-Carb 3110TR low activity liquid scintillation analyzer
Generic Instrument Description	The PerkinElmer Tri-Carb 3110TR is a benchtop liquid scintillation analyzer for detecting small amounts of alpha, beta, and gamma radioactivity. It features a Multichannel Analyzer with an effective resolution of 1/10 keV and an extended dynamic quench range. Sample capacity is either 408 standard 20 mL vials, or 720 small 4 or 7 mL vials. The instrument includes a barium-133 low-energy external standard source centered under the sample vial which eliminates the effects of volume variations. It has an energy range of 0-2000 keV and an operating ambient temperature range of 15-35 degrees Celsius.

Dataset-specific Instrument Name	UV Steripen - Adventure Opti Model
Generic Instrument Name	Ultraviolet Light Sterilization Device
Generic Instrument Description	Ultraviolet (UV) light sterilization is a sterilization process that uses short wavelength radiation to kill microorganisms.

Dataset-specific Instrument Name	Ultraviolet (UV) Light Box
Generic Instrument Name	Ultraviolet Light Sterilization Device
Generic Instrument Description	Ultraviolet (UV) light sterilization is a sterilization process that uses short wavelength radiation to kill microorganisms.

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Deployments

PE17-20

Website	https://www.bco-dmo.org/deployment/792830
Platform	R/V Pelican
Start Date	2017-05-03
End Date	2017-05-13
Description	More information about this cruise can be found in R2R: https://www.rvdata.us/search/cruise/PE17-20

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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:

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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
NSF Division of Ocean Sciences (NSF OCE)	OCE-1558957

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