Stable isotopes in reactive silica pools of Mississippi River plume sediments collected aboard the R/V Pelican in May 2017

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

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Abstract
Stable isotopes in reactive silica pools of Mississippi River plume sediments collected aboard the R/V Pelican in May 2017

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Coverage

Spatial Extent: **N**:28.94688 **E**:-89.75004 **S**:28.49884 **W**:-90.83464
Temporal Extent: 2017-05-05 - 2017-05-06

Dataset Description

Stable isotopes in reactive silica pools of Mississippi River plume sediments collected aboard the R/V Pelican in May 2017

Methods & Sampling

Stable silicon isotopes (e.g. δ30Si) in sediment biogenic silica (bSi) are widely used as a paleoproxy for marine silicic acid usage by pelagic diatoms. Despite the growing body of work that uses bSi δ30Si signals, there are a lack of δ30Si data on other reactive pools of Si in sediments. This oversight misses valuable information on

early diagenetic products and potentially biases existing sedimentary bSi δ30Si, which only quantified bSi fractions not altered by diagenesis. For the first time, we quantified δ30Si among operationally defined reactive Si pools (using a pre-leach of mild acid prior to alkaline digestion) in Mississippi River plume sediments. We compared the δ30Si signal within these reactive Si pools to a traditional alkaline-only digestion of sedimentary bSi. These data offer proof of concept that δ30Si is a higher throughput approach for quantifying isotopic properties among reactive Si pools marine sediments vs. the more laborious (albeit powerful) examination of natural silicon radioisotopes in these chemical leaches.

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 N2 gas and frozen at -20o C for further analysis.

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 bSiO2” (e.g. sponge spicules and Rhizaria, Maldonado et al., 2019).
4. T-bSi: 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

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).

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)

The remaining sediment from the acid pre-treatment was subsequently digested with 0.1 M Na2CO3 (Fisher Scientific Certified ACS) for 20 mins in a 85o C water bath. Following the 20 min timepoint, samples were placed on ice and neutralized to stop the digestion. Following centrifugation, the Si-Alk leachate was removed and stored for further use. The process was stopped after 20 mins to ensure the absence of lithogenic material (DeMaster, 1981; Michalopoulos and Aller, 2004) and certify that the clear majority of solubilized silica present is biogenic. Fresh 0.1 M Na2CO3 was added to the samples and the digestions were continued for a total of 5 hrs (DeMaster, 1981) to completely remove the bSi phase. Concluding after 5 hrs, samples were placed on ice and 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 Na2CO3 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-bSi)

Additionally, a second treatment following the traditional definition of biogenic silica (DeMaster, 1981), with no acid pre-treatment was used to derive δ30Si from traditional bSi measurements. New subsamples of sediment were weighed out. 0.1 M Na_2CO_3 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 $SiOH_4$ 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 concentrated via evaporation at 100o C and stored following DeMaster (1980) in preparation for stable isotope analysis.

Stable Isotope Analysis

Sample purification and isotope analysis were carried out at the University of Bristol Isotope Group laboratories. Concentrated sample fluids were purified via cation ion exchange chromatography (Bio-Rad AG50W-X12, 200-400 mesh cation exchange resin in H+ form). Purified solutions were analyzed in duplicate for Si isotopes (28Si, 29Si, 30Si) using a multi collector-inductively coupled plasma-mass spectrometer (MC-ICP-MS, Finnigan Neptune s/n 1002), equipped with CETAC PFA spray chamber and PFA nebulizer (100ul/min). A standard-sample-standard bracketing procedure with Mg doping following Cardinal et al., (2003) was used to correct for both instrumental mass bias and matrix effects. Additionally, sample and standard solutions were both doped with 0.1 M H_2SO_4 (ROMIL UpA) and 1 M HCl (in-house distilled) to reduce any matrix effects from anion loading and guarantee matrix matching between sample and standard (Hughes et al., 2011). All isotopic composition results are expressed as δ30Si, corresponding to the silicon isotopic abundances in samples relative to the international reference standard NBS-28 (NIST RM8546, purified quartz sand). Reference standards Diatomite (Reynolds et al., 2007) and LMG08 (sponge) (Hendry et al., 2011) were run in tandem with samples to assess long- term reproducibility. Average measured values are reported as +1.27 ± 0.09‰ (n=75) and -3.47 ± 0.16‰ (n=27) (±SD) respectively, which are well within agreement with published values (Reynolds et al., 2007; Hendry et al., 2011). All samples and standards are consistent with the kinetic mass fractionation law (Reynolds et al., 2007) with the $\delta^{29}Si = 0.518 \times \delta^{30}Si$. Procedural blanks were lower than the detection limit and thus considered negligible on δ30Si of the samples.

Major Metal Compositions and Corrections

Additional thawed/wet sediment subsamples were used for duplicate sequential extractions and digestions (Si-HCl, Si-Alk, Si-NaOH and T-bSi) run as previously described. Supernatants were concentrated via evaporation at 100o C and fluids were reconstituted in 2% HNO_3 (in-house distilled) to determine major ion concentrations on an Agilent 7700 Series ICP-MS. The instrument was calibrated using a blank and seven matrix-matched, mixed standards. Internal standardization during analysis was monitored via the addition of (50 µl, 10,000 ppb) 115In and 4Be to all standards and samples. Using Aluminum (Al):Si corrections (Kamatani and Oku, 2000; Ragueneau et al., 2005), both Si-Alk and T-bSi δ30Si signals (‰) and mass of Si released (µmol/g) were adjusted for bias from lithogenic material (however, this was more important for the mass of Si, as isotopic content was derived from 30-minute digestions, opposed to 5 hour digestions for the former).

Organic Matter

Sediment total organic carbon (TOC) and total organic nitrogen (TON) 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 TOC/TON analyses (Yamamuro and Kayanne, 1995).

Data 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. Added ND as a missing data identifier.
* removed all spaces in headers and replaced with underscores
* removed all units from headers
* created an ISO_DateTime_UTC column from the Date_Collected and Time_Collected columns
* set Types for each data column

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Data Files

File
isotope.csv (Comma Separated Values (.csv), 13.12 KB) MD5:8b7cb2a1e9f5590ac51028c42f79cbe9 Primary data file for dataset ID 786508

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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
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
Methods

Demaster, D. J. (1980). The half life of32Si 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
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
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
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
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
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
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
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 32 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
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
Methods

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Parameters

Parameter	Description	Units
Cruise_Collected	local name chosen by project investigators for a research expedition on a vessel as opposed to the formal/official cruise ID	dimensionless
MultiCore	core number/identification	number/identification
Station_Number	station identifier	dimensionless
Bottom_Depth	bottom depth in meters	meters

Latitude_N	latitude in decimal degrees	decimal degrees
Longitude_W	longitude in decimal degrees	decimal degrees
Date_Collected	date when core was collected in the format mmddyyyy	unitless
Time_Collected	time GMT when core was collected	HHMM
Sample_Depth	subsection used for analysis	centimeters
Nominal_Depth	depth used for data plots	centimeters
Porewater	concentration of dissolved silica acid Si(OH)4 in porewater collected	uM
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
Reactive_Pool_Treatment	which reactive pool the following data is for	unitless
Avg_d30Si	Average d30Si (n=3) for each corresponding reactive Si Pool (- per mille)	0/00
Avg_d30Si_2_Stdev	Average d30Si (n=3) for each corresponding reactive Si Pool including 2 standard deviations of sample variation	dimensionless
Avg_Si_Released	Average Si released (n=3) for each corresponding reactive Si Pool (- micromoles per gram dry sediment)	umol/g
Avg_Si_Released_2_Stdev	Average Si released (n=3) for each corresponding reactive Si Pool including 2 standard deviations of sample variation	dimensionless

Mg	magnesium concentration for each corresponding reactive Si pool	ppm
Al	aluminum concentration for each corresponding reactive Si pool	ppm
K	potassium concentration for each corresponding reactive Si pool	ppm
V	vanadium concentration for each corresponding reactive Si pool	ppm
Cr	chromium concentration for each corresponding reactive Si pool	ppm
Mn	manganese concentration for each corresponding reactive Si pool	ppm
Fe	iron concentration for each corresponding reactive Si pool	ppm
Ni	nickel concentration for each corresponding reactive Si pool	ppm
Cu	copper concentration for each corresponding reactive Si pool	ppm
Ti	titanium concentration for each corresponding reactive Si pool	ppm
ISO_DateTime_UTC	Date/Time (UTC) ISO formatted	YYYY-MM-DDTHH:MM:SS[.xx]Z

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Instruments

Dataset-specific Instrument Name	
Generic Instrument Name	Costech International Elemental Combustion System (ECS) 4010
Generic Instrument Description	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.

Dataset-specific Instrument Name	Finnigan Neptune s/n 1002 multi collector-inductively coupled plasma-mass spectrometer
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
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	Genesys 10S UV-Vis Spectrophotometer
Generic Instrument Name	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.

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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:
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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