

Absorbance from Fourier transform infrared spectroscopy sample characterization experiments.

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Project

» [Biopolymers as carrier phases for selected natural radionuclides \(of Th, Pa, Pb, Po, Be\) in diatoms and coccolithophores](#) (Biopolymers for radionuclides)

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Abstract

Laboratory studies were conducted to examine the sorption of selected radionuclides (^{234}Th , ^{233}Pa , ^{210}Po , ^{210}Pb , and ^7Be) onto inorganic (pure silica and acid-cleaned diatom frustules) and organic (diatom cells with or without silica frustules) particles in natural seawater and the role of templating biomolecules and exopolymeric substances (EPS) extracted from the same species of diatom, *Phaeodactylum tricornutum*, in the sorption process. The range of partition coefficients (K_d , reported as $\log K_d$) of radionuclides between water and the different particle types was 4.78–6.69 for ^{234}Th , 5.23–6.71 for ^{233}Pa , 4.44–5.86 for ^{210}Pb , 4.47–4.92 for ^{210}Po , and 4.93–7.23 for ^7Be , similar to values reported for lab and field determinations. The sorption of all radionuclides was significantly enhanced in the presence of organic matter associated with particles, resulting in K_d one to two orders of magnitude higher than for inorganic particles only, with highest values for ^7Be ($\log K_d$ of 7.2). Results further indicate that EPS and frustule-embedded biomolecules in diatom cells are responsible for the sorption enhancement rather than the silica shell itself. By separating radiolabeled EPS via isoelectric focusing, we found that isoelectric points are radionuclide specific, suggesting that each radionuclide binds to specific biopolymeric functional groups, with the most efficient binding sites likely occurring in acid polysaccharides, iron hydroxides, and proteins. Further progress in evaluating the effects of diatom frustule-related biopolymers on binding, scavenging, and fractionation of radionuclides would require the application of molecular-level characterization techniques.

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Dataset Description

Laboratory studies were conducted to examine the sorption of selected radionuclides (^{234}Th , ^{233}Pa , ^{210}Po , ^{210}Pb , and ^7Be) onto inorganic (pure silica and acid-cleaned diatom frustules) and organic (diatom cells with or without silica frustules) particles in natural seawater and the role of templating biomolecules and exopolymeric substances (EPS) extracted from the same species of diatom, *Phaeodactylum tricornutum*, in the sorption process.

The range of partition coefficients (K_d , reported as $\log K_d$) of radionuclides between water and the different particle types was 4.78–6.69 for ^{234}Th , 5.23–6.71 for ^{233}Pa , 4.44–5.86 for ^{210}Pb , 4.47–4.92 for ^{210}Po , and 4.93–7.23 for ^7Be , similar to values reported for lab and field determinations. The sorption of all radionuclides was significantly enhanced in the presence of organic matter associated with particles, resulting in K_d one to two orders of magnitude higher than for inorganic particles only, with highest values for ^7Be ($\log K_d$ of 7.2). Results further indicate that EPS and frustule-embedded biomolecules in diatom cells are responsible for the sorption enhancement rather than the silica shell itself. By separating radiolabeled EPS via isoelectric focusing, we found that isoelectric points are radionuclide specific, suggesting that each radionuclide binds to specific biopolymeric functional groups, with the most efficient binding sites likely occurring in acid polysaccharides, iron hydroxides, and proteins. Further progress in evaluating the effects of diatom frustule-related biopolymers on binding, scavenging, and fractionation of radionuclides would require the application of molecular-level characterization techniques.

Acquisition Description

Diatom cultures, sample preparation, and EPS extraction
P. tricornutum (UTEX 646) was selected for culturing in autoclaved $f/2$ and $f/2\text{-Si}$ media (salinity of 26) at a temperature of 19 ± 1 °C with a light cycling of 14 h : 10 h under a saturating irradiance of $100 \mu\text{mol quanta m}^{-2} \text{s}^{-1}$. In order to deplete the diatom of Si supply,

cultures were transferred into f/2-Si medium over at least six generations by harvesting cells (2694 g, 30 min) and resuspending them in fresh f/2-Si medium. Sterile polycarbonate bottles were also used to prevent Si supply from glassware. The growth status of *P. tricornutum* was monitored by changes in optical density at 750 nm. Cells, frustules, and EPS were collected when *P. tricornutum* reached the stationary phase.

Laboratory cultures of *P. tricornutum* were centrifuged (2694 x g, 30 min) and filtered (0.2 μm) to collect the whole cells. The frustules were repeatedly treated by using a hydrogen peroxide (30%, room temperature) treatment until bubbles were no longer generated, followed by concentrated nitric acid (HNO_3) digestion (85°C, 1 h) to remove organic matter adopted from Robinson et al. (2004).

The resulting organic carbon (C), nitrogen (N), and sulfur (S) contents of the cleaned frustules were measured using a Perkin Elmer CHNS 2400 analyzer to ensure the removal of organic materials using cysteine as a standard according to Guo and Santschi (1997).

EPS extraction was followed the procedures described in Xu et al. (2011b), which minimize cell rupture and molecular alterations and maximize extraction efficiency. EPS here is referring to those biopolymers that are attached on the diatom frustules. Hereafter, EPS Si⁺ and EPS Si² denote the EPS extracted from diatoms cultured under Si-replete (f/2 medium) and Si-depleted (f/2-Si medium) conditions, respectively. Briefly, laboratory cultures were centrifuged (2694 x g, 30 min) and filtered (0.2 μm) when diatoms reached stationary phase. The diatom cells were soaked with 0.5 mol L⁻¹ sodium chloride (NaCl) solution for 10 min and followed by centrifugation at 2000 x g for 15 min to remove the medium and weakly bound organic material on the cells. The pellet from previous step was resuspended in a new 100 mL 0.5 mol L⁻¹ NaCl solution and stirred gently overnight at 4°C. The resuspended particle solution was ultracentrifuged at 12,000 x g (30 min, 4°C), and the supernatant was then filtered through a 0.2 μm polycarbonate membrane. The filtrate was desalted and collected with a 1 kDa cutoff cross-flow ultrafiltration and diafiltration membrane and then freeze-dried for later use.

Fourier transform infrared spectroscopy (FTIR) was used to characterize samples using a Varian 3100 model interfaced with a single reflection horizontal attenuated total reflectance (ATR) accessory (PIKE Technologies). A diamond plate was used as the internal reflection element. A freeze-dried EPS sample was mounted at the surface of the diamond. Absorbance spectra from 800 to 2000 cm^{-1} were collected and integrated using Varian Resolution Pro 4.0 software. ATR-FTIR spectroscopy provides a noninvasive way to quickly gain information about the contents of major secondary structures of biopolymers (Xu et al. 2011b; Jiang et al. 2012). Major infrared (IR) peaks were assigned according to Xu et al. (2011b) and Jiang et al. (2012). Characteristic bands found in the IR spectra of proteins and polypeptides include the amide I (1652–1648 cm^{-1}) and amide II (1550–1548 cm^{-1}) band. The absorption associated

with the amide I band leads to stretching vibrations of the C=O bond of the amide, and absorption associated with the amide II band leads primarily to bending vibrations of the N-H and C-N bond. The symmetric stretching peak due to deprotonated carboxyl groups is observed at 1400 cm⁻¹ along with the CH₂ bending mode at 1455 cm⁻¹. In the 800–1200 cm⁻¹ regions, responses from C-O, C-O-C, P-O-P, C-O-P, and ring vibrations of the main polysaccharide functional groups are present in polysaccharide mixtures. The peaks at 1241 and 1113 cm⁻¹ correspond to P-O stretching in phosphate groups.

Processing Description

BCO-DMO Processing Notes:

- added conventional header with dataset name, PI name, version date
- modified parameter names to conform with BCO-DMO naming conventions

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Related Publications

Alvarado Quiroz, N. G., Hung, C.-C., & Santschi, P. H. (2006). Binding of thorium(IV) to carboxylate, phosphate and sulfate functional groups from marine exopolymeric substances (EPS). *Marine Chemistry*, 100(3-4), 337–353. doi:[10.1016/j.marchem.2005.10.023](https://doi.org/10.1016/j.marchem.2005.10.023)

Baskaran, M., & Santschi, P. H. (1993). The role of particles and colloids in the transport of radionuclides in coastal environments of Texas. *Marine Chemistry*, 43(1-4), 95–114. doi:[10.1016/0304-4203\(93\)90218-D](https://doi.org/10.1016/0304-4203(93)90218-D)

Chuang, C.-Y., Santschi, P. H., Ho, Y.-F., Conte, M. H., Guo, L., Schumann, D., ... Li, Y.-H. (2013). Role of biopolymers as major carrier phases of Th, Pa, Pb, Po, and Be radionuclides in settling particles from the Atlantic Ocean. *Marine Chemistry*, 157, 131–143. doi:[10.1016/j.marchem.2013.10.002](https://doi.org/10.1016/j.marchem.2013.10.002)

Chuang, C.-Y., Santschi, P. H., Jiang, Y., Ho, Y.-F., Quigg, A., Guo, L., ... Schumann, D. (2014). Important role of biomolecules from diatoms in the scavenging of particle-reactive radionuclides of thorium, protactinium, lead, polonium, and beryllium in the ocean: A case study with *Phaeodactylum tricornutum*. *Limnology and Oceanography*, 59(4), 1256–1266. doi:[10.4319/lo.2014.59.4.1256](https://doi.org/10.4319/lo.2014.59.4.1256)

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Xu, C., Zhang, S., Chuang, C., Miller, E. J., Schwehr, K. A., & Santschi, P. H. (2011). Chemical composition and relative hydrophobicity of microbial exopolymeric substances (EPS) isolated by anion exchange chromatography and their actinide-binding affinities. *Marine Chemistry*, 126(1-4), 27–36. doi:[10.1016/j.marchem.2011.03.004](https://doi.org/10.1016/j.marchem.2011.03.004)

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Parameters

Parameter	Description	Units
wavenumber	wavenumber	unitless
EPS_Si_plus	absorbance EPS Si+	per centimeter
EPS_Si_minus	absorbance EPS Si-	per centimeter
EPS_Si_diff	absorbance difference EPS (Si-)-(Si+)	per centimeter

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Instruments

Dataset-specific Instrument Name	Varian 3100 Excalibur
Generic Instrument Name	Spectrometer
Dataset-specific Description	Fourier transform infrared spectroscopy (FTIR) was used to characterize samples using a Varian 3100 Excalibur model interfaced with a single reflection horizontal attenuated total reflectance (ATR) diamond accessory (PIKE Technologies).
Generic Instrument Description	A spectrometer is an optical instrument used to measure properties of light over a specific portion of the electromagnetic spectrum.

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Project Information

Biopolymers as carrier phases for selected natural radionuclides (of Th, Pa, Pb, Po, Be) in diatoms and coccolithophores (Biopolymers for radionuclides)

NSF Award Abstract: Particle-associated natural radioisotopes are transported to the ocean floor mostly via silica and carbonate ballasted particles, allowing their use as tracers for particle transport. Th(IV), Pa (IV,V), Po(IV), Pb(II) and Be(II) radionuclides are important proxies in oceanographic investigations, used for tracing particle and colloid cycling, estimating export fluxes of particulate organic carbon, tracing air-sea exchange, paleoproductivity, and/or ocean circulation in paleoceanographic studies. Even though tracer approaches are considered routine, there are cases where data interpretation or validity has become controversial, largely due to uncertainties about inorganic proxies and organic carrier molecules. Recent studies showed that cleaned diatom frustules and pure silica particles, sorb natural radionuclides to a much lower extent (by 1-2 orders of magnitude) than whole diatom cells (with or without shells). Phytoplankton that build siliceous or calcareous shells, such as the diatoms and coccolithophores, are assembled via bio-mineralization processes using biopolymers as nanoscale templates. These templates could serve as possible carriers for radionuclides and stable metals. In this project, a research team at the Texas A & M

University at Galveston hypothesize that radionuclide sorption is controlled by selective biopolymers that are associated with biogenic opal (diatoms), CaCO₃ (coccolithophores) and the attached exopolymeric substances (EPS), rather than to pure mineral phase. To pursue this idea, the major objectives of their research will include separation, identification and molecular-level characterization of the individual biopolymers (e.g., polysaccharides, uronic acids, proteins, hydroquinones, hydroxamate siderophores, etc.) that are responsible for binding different radionuclides (Th, Pa, Pb, Po and Be) attached to cells or in the matrix of biogenic opal or CaCO₃ as well as attached EPS mixture, in laboratory grown diatom and coccolithophore cultures. Laboratory-scale radiolabeling experiments will be conducted, and different separation techniques and characterization techniques will be applied. Intellectual Merit : It is expected that this study will help elucidate the molecular basis of the templated growth of diatoms and coccoliths, EPS and their role in scavenging natural radionuclides in the ocean, and help resolve debates on the oceanographic tracer applications of different natural radioisotopes (^{230,234}Th, ²³¹Pa, ²¹⁰Po, ²¹⁰Pb and ^{7,10}Be). The proposed interdisciplinary research project will require instrumental approaches for molecular-level characterization of these radionuclides associated carrier molecules. Broader Impacts: The results of this study will be relevant for understanding biologically mediated ocean scavenging of radionuclides by diatoms and coccoliths which is important for carbon cycling in the ocean, and will contribute to improved interpretation of data obtained by field studies especially through the GEOTRACES program. This new program will enhance training programs at TAMUG for postdocs, graduate and undergraduate students. Lastly, results will be integrated in college courses and out-reach activities at Texas A&M University, including NSF-REU, Sea Camp, Elder Hostel and exhibits at the local science fair and interaction with its after-school program engaging Grade 9-12 students from groups traditionally underrepresented.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1356453

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