Coccolithophore-associated organic biopolymers for fractionating particle-reactive radionuclides (234Th, 233Pa, 210Pb, 210Po, and 7Be)

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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)

Contributors	Affiliation	Role
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Abstract

Laboratory incubation experiments using the coccolithophore Emiliania huxleyi were conducted in the presence of 234Th, 233Pa, 210Pb, 210Po, and 7Be to differentiate radionuclide uptake to the CaCO3 coccosphere from coccolithophore-associated biopolymers.

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Dataset Description

Laboratory incubation experiments using the coccolithophore Emiliania huxleyi were conducted
in the presence of 234Th, 233Pa, 210Pb, 210Po, and 7Be to differentiate radionuclide uptake to the CaCO3
coccosphere from coccolithophore-associated biopolymers.

Acquisition Description

The seawater (< 1 kDa) was enriched with f/2 nutrients, trace metals and vitamins, and autoclaved in pre-combusted and seawater-preconditioned clear glassware. Then, ~50 Bq of each gamma emitting radionuclide, including 234Th, 233Pa, 210Pb and 7Be, was added. Since 210Po emits no gamma radiation, 210Po was added separately into the seawater. After checking the pH of each radiolabeled medium to be 8.0, 2 mL of laboratory axenic Emiliania huxleyi (CCMP 371) was added to 100 mL of media and incubated at a temperature of 19±1ºC with a light:dark cycle of 14 h:10 h under an irradiation condition of 100 µmol-quanta/m2/s.

Non-attached exopolymeric substances (NAEPS) and exopolymeric substances attached on the coccolithophore cellular surface (AEPS) were extracted followed the procedures described in Chuang et al. (2015) and Xu et al. (2011). In brief, laboratory cultures were centrifuged at 3000 ×g for 30 min, and then the supernatant for the NAEPS fraction was filtered, followed by the concentration and extensive desalting of supernatant against

nanopure water (18.2 Ω) with 3 kDa Microsep centrifugal filter tubes (Milipore). For AEPS extraction, the resultant pellet from the centrifugation was resuspended by 50 mL 3% NaCl solution and stirred gently overnight at 4ºC. Lastly, the solution was centrifuged, and the supernatant containing the AEPS was then filtered before further desalting via the 3 kDa ultrafiltration centrifugation tubes. The pellet from the previous step was thus further digested in the 0.44 M HAc + 0.1 M NaCl solution at 4ºC for 8 h. After the digestion, the mixed solution was centrifuged and filtered, followed by ultrafiltration of the supernatant with 3 kDa Microsep centrifugal filter tubes. The retentate (> 3 kDa) was defined as coccosphere-associated biopolymers. The permeate (<3 kDa), defined as the fraction of digested biogenic calcite. Cells remaining from the last step was further heated in 20 mL of 1% SDS containing 10 mM Tris solution (pH 6.8) at 95 ºC for 1 h. The supernatant was also collected through centrifugation and filtration, followed by desalting and concentration with 3 kDa Microsep centrifugal filter tubes. Subsequently, the pellet was further digested by 0.04 M NH2OH HCl + 4.35 M HAc mixture at 96 ºC for 6 h, with occasional agitation to obtain the intracellular Fe-Mn associated metabolitic biopolymer. The sum of these two fractions represents the intracellular biopolymers after cell breakage.

Subsamples were taken from the concentrated biopolymers for the analysis of protein, total carbohydrate (TCHO) and uronic acid (URA), respectively. In brief, the protein abundance was measured through a modified Lowry protein assay, using bovine serum albumin (BSA) as the standard. For the concentrations of TCHO, samples were hydrolyzed by 0.09 M HCl (final concentration) at 150ºC for 1 h. After neutralization with NaOH solution, the hydrolysate was measured by the 2,4,6-tripyridyl-triazine (TPTZ) method (Hung et al., 2001), with glucose as the standard. URA concentrations were determined by the metahydroxyphenyl method using glucuronic acid as the standard (Hung and Santschi, 2001).

All the solutions from the different extraction steps, including the >3 kDa biopolymer fractions and the permeate (< 3 kDa), were counted for the activity concentrations of 234Th, 233Pa, 210Pb and 7Be by a Canberra ultrahigh purity germanium well gamma detector. In addition, the 210Po activity in different separately incubated fractions was determined by Beckman Model 8100 Liquid Scintillation Counter.

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
* reorganized data from two tables into one table

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Related Publications

Chuang, C.-Y., Santschi, P. H., Xu, C., Jiang, Y., Ho, Y.-F., Quigg, A., … Schumann, D. (2015). Molecular level characterization of diatom-associated biopolymers that bind234Th,233Pa,210Pb, and7Be in seawater: A case study withPhaeodactylum tricornutum. Journal of Geophysical Research: Biogeosciences, 120(9), 1858–1869. doi:10.1002/2015JG002970

Hung, C.-C., & Santschi, P. H. (2001). Spectrophotometric determination of total uronic acids in seawater using cation-exchange separation and pre-concentration by lyophilization. Analytica Chimica Acta, 427(1), 111–117. doi:10.1016/S0003-2670(00)01196-X

Hung, C.-C., Tang, D., Warnken, K. W., & Santschi, P. H. (2001). Distributions of carbohydrates, including uronic acids, in estuarine waters of Galveston Bay. Marine Chemistry, 73(3-4), 305–318. doi:10.1016/S0304-4203(00)00114-6

Lin, P., Xu, C., Zhang, S., Sun, L., Schwehr, K. A., Bretherton, L., … Santschi, P. H. (2017). Importance of coccolithophore-associated organic biopolymers for fractionating particle-reactive radionuclides (234 Th, 233 Pa, 210 Pb, 210 Po, and 7 Be) in the ocean. Journal of Geophysical Research: Biogeosciences, 122(8), 2033–2045. doi:10.1002/2017JG003779

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

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Parameters

Parameter	Description	Units
Biopolymer_Fraction	biopolymer fraction of E. huxleyi cells	unitless
Th234_Activity	percentage of 234Th activity (%)	unitless
Pa233_Activity	percentage of 233Pa activity (%)	unitless
Pb210_Activity	percentage of 210Pb activity (%)	unitless
Po210_Activity	percentage of 210Po activity (%)	unitless
Be7_Activity	percentage of 7Be activity (%)	unitless
Protein_Amount	amount of organic protein component	microMole Carbon (uM-C)
TCHO_Amount	amount of organic total carbohydrate component	microMole Carbon (uM-C)
URA_Amount	amount of organic Uronic acid component	microMole Carbon (uM-C)
Protein_C_TCHO_C	ratio of proteins to total carbohydrates	unitless
URA_pcnt_TCHO	the percentage of the uronic acid in the bulk total carbohydrates pool	unitless

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Instruments

Dataset-specific Instrument Name	Beckman Model 8100 Liquid Scintillation Counter
Generic Instrument Name	Liquid Scintillation Counter
Dataset-specific Description	Beckman Model 8100 Liquid Scintillation Counter
Generic Instrument Description	Liquid scintillation counting is an analytical technique which is defined by the incorporation of the radiolabeled analyte into uniform distribution with a liquid chemical medium capable of converting the kinetic energy of nuclear emissions into light energy. Although the liquid scintillation counter is a sophisticated laboratory counting system used the quantify the activity of particulate emitting (ß and a) radioactive samples, it can also detect the auger electrons emitted from 51Cr and 125I samples.

Dataset-specific Instrument Name	UV-Visible spectrometer
Generic Instrument Name	Spectrometer
Dataset-specific Description	UV-Visible spectrometer, BioTek Instruments Inc Model EPOCH
Generic Instrument Description	A spectrometer is an optical instrument used to measure properties of light over a specific portion of the electromagnetic spectrum.

Dataset-specific Instrument Name	Beckman Coulter Allegra X-12 centrifuge
Generic Instrument Name	Centrifuge
Dataset-specific Description	Beckman Coulter Allegra X-12 centrifuge
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	Canberra ultrahigh purity germanium well gamma detector
Generic Instrument Name	Gamma Ray Spectrometer
Dataset-specific Description	Canberra ultrahigh purity germanium well gamma detector Model GCW3024
Generic Instrument Description	Instruments measuring the relative levels of electromagnetic radiation of different wavelengths in the gamma-ray waveband.

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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 (230,234Th, 231Pa, 210Po, 210Pb and 7,10Be). 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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