

Po, Pb and Be partition coefficients on nanoparticles from laboratory 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 sorption experiments were carried out to examine the adsorption of ^{210}Po , ^{210}Pb and ^7Be and their fractionation on inorganic nanoparticles, including SiO_2 , CaCO_3 , Al_2O_3 , TiO_2 and Fe_2O_3 , in the presence or absence of macromolecular organic compounds (MOCs) that include humic acids (HA), acid polysaccharides (APS) and proteins (BSA), in natural seawater.

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Dataset Description

Improved applications of ^{210}Po , ^{210}Pb and ^7Be as geochemical proxies require more detailed understanding of their interactions with particles. Here, laboratory sorption experiments were carried out to examine the adsorption of ^{210}Po , ^{210}Pb and ^7Be and their fractionation on inorganic nanoparticles, including SiO_2 , CaCO_3 , Al_2O_3 , TiO_2 and Fe_2O_3 , in the presence or absence of macromolecular organic compounds (MOCs) that include humic acids (HA), acid polysaccharides (APS) and proteins (BSA), in natural seawater. Results showed that nanoparticle sorption was not greatly enhanced over that of microparticles as would be expected from their much higher specific surface areas, likely indicating their aggregation in seawater. It was found that synergistic interactions between inorganic nanoparticles, MOCs, and radionuclides determined the sorption, although their adsorption was particle composition-dependent. MOCs enhanced the sorption of selected nuclides on most nanoparticles. On average, in the presence of MOCs, partition coefficients (K_c) of ^{210}Po , ^{210}Pb , and ^7Be on nanoparticles increased 2.9-, 5.0- and 5.9-fold, respectively. The effect of MOCs could be explained for ^{210}Po and ^{210}Pb from their different log K_c values on inorganic nanoparticles. In addition, fractionation effects between ^{210}Po and ^{210}Pb (or between ^{210}Pb and ^7Be) could be quantified from their relative log K_c values on end-member sorbent components. Applications of both ^{210}Po – ^{210}Pb and ^7Be – ^{210}Pb pairs as particle dynamics tracers could be more quantitative when the nature of the organic coatings is taken into account.

Acquisition Description

Natural seawater from the Gulf of Mexico with a salinity of 35.0 was filtered and ultrafiltered sequentially through a $0.4\ \mu\text{m}$ cartridge (GE-Osmonics) and a 1 kDa ultrafiltration membrane (Millipore-Amicon), to remove suspended particles and colloidal matter. ^{210}Po and ^{210}Pb

(in equilibrium) in 1 N HNO₃-2 N HCl were purchased from Eckert & Ziegler Isotopes Products. ⁷Be tracer was produced at the Paul Scherrer Institute, Switzerland and preserved in 0.5 N HCl. All experiments were conducted in a constant temperature laboratory to avoid the influence of changing temperature.

For sorption experiments, 49 ml of the <1 kDa ultrafiltrate of seawater in a stirred-cell unit was added with 1 ml of non-complexing Tris-HCl buffer solution to maintain a constant pH of 8.1 and to prevent formation of pseudo-colloids during the addition of spikes. For the single-sorbent experiments, 2 mg of inorganic particles was added into the solution while stirring, corresponding to a particle concentration of about 40 mg/l. Successively, a total of 0.2 ml of ²¹⁰Pb, ²¹⁰Pb and ⁷Be spikes, with the activities of 100 Bq, 100 Bq and 150 Bq respectively, were added drop by drop while stirring. The pH value was checked after adding spikes and found to be 8.1. For the single MOC experiments, procedures were the same as described above. The final concentration of HA, APS or BSA was at 1 mg/l.

An equilibrium time of 2 h was consistently used in all experiments. After 2 h, the particulate or colloidal phases were separated through ultrafiltration using a 1 kDa membrane (Amicon YM1). The >1 kDa retentate (final volume of ~4 ml) and aliquot of the <1 kDa ultrafiltrate or permeate solutions (10 ml) were transferred into a counting vial for γ -counting.

For the binary-sorbent experiments, macromolecular organic matter was added after the inorganic nanoparticles. The experimental solution was then stirred for 30 min to allow inorganic particles to interact with MOCs. After that, spikes were added. Other experimental procedures were the same as the single-sorbent experiments.

Retentate and permeate samples were measured for ²¹⁰Pb and ⁷Be by non-destructive gamma counting using a Canberra ultra-high purity germanium well detector. The counting efficiencies at different sample geometries (1-10 ml) at 46.5 keV for ²¹⁰Pb and 477.6 keV for ⁷Be were calibrated using tracers with certified activities.

The activities of ²¹⁰Po in samples were measured using α -spectrometry. For the permeate samples, 5 ml of permeate was acidified to pH <1.5 with HCl, then 4 Bq ²⁰⁹Po was added, followed by ascorbic acid powder, 1 ml of hydroxylamine hydrochloride (20%) and 1 ml of sodium citrate (25%). Finally, the mixed solution was adjusted to a pH of 1.5. Polonium isotopes, including ²⁰⁹Po and ²¹⁰Po, were plated on a silver disc at 90°C for 4 h under stirring. Procedures for the retentate samples were the same, except that the retentate was digested with mixed acids. Then, the solution was dried to near dryness.

Activities of ²⁰⁹Po and ²¹⁰Po on silver disc were counted by a Canberra alpha analyst system. The procedural efficiencies of Po isotopes were determined by the measured ²⁰⁹Po and initially added ²⁰⁹Po activities.

Processing Description

Activities of nuclides were calculated by the counts and counting time. The recoveries were quantified based on the total measured activity of each nuclide (including permeate and retentate phases) and initially added spike activity. The partition coefficient was calculated using the activity of each nuclide in retentate divided by that in permeate and the content of total nanoparticle.

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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Parameters

| Parameter | Description | Units |
|-----------------------------------|---|--|
| System | Type of sorption experiment. | unitless |
| Organic_nanoparticle | organic nanoparticle in solution. | unitless |
| Inorganic_nanoparticle | inorganic nanoparticle in solution. | unitless |
| Pb210_recovery | Chemical recovery of 210Pb in percent (%) | unitless |
| err_Pbrec | Error of chemical recovery of 210Pb in percent (%) | unitless |
| Be7_recovery | Chemical recovery of 7Be in percent (%) | unitless |
| err_Berec | Error of chemical recovery of 7Be in percent (%) | unitless |
| Po210_recovery | Chemical recovery of 210Po in percent (%) | unitless |
| err_Porec | Error of chemical recovery of 210Po in percent (%) | unitless |
| Partition_coefficient_of_210Pb_Kc | The partition coefficient of 210Pb between true solution (| 10 ⁴ Liters per Kilogram (L/kg) |
| err_Kc_Pb | Error of the partition coefficient of 210Pb between true solution (| 10 ⁴ Liters per Kilogram (L/kg) |
| Partition_coefficient_of_7Be_Kc | The partition coefficient of 7Be between true solution (| 10 ⁴ Liters per Kilogram (L/kg) |
| err_Kc_Be | Error of the partition coefficient of 7Be between true solution (| 10 ⁴ Liters per Kilogram (L/kg) |
| Partition_coefficient_of_210Po_Kc | The partition coefficient of 210Po between true solution (| 10 ⁴ Liters per Kilogram (L/kg) |
| err_Kc_Po | Error of the partition coefficient of 210Po between true solution (| 10 ⁴ Liters per Kilogram (L/kg) |

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Instruments

| | |
|---|--|
| Dataset-specific Instrument Name | Alpha-spectrometry |
| Generic Instrument Name | Spectrometer |
| Dataset-specific Description | Alpha-spectrometry, Canberra corporation. |
| 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 | Gamma-spectrometry |
| Generic Instrument Name | Gamma Ray Spectrometer |
| Dataset-specific Description | Canberra ultra-high purity germanium well detector. |
| 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 (^{230,234}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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