Size-fractionated particulate thorium and protactinium isotopes in seawater from Leg 2 (Hilo, HI to Papeete, French Polynesia) of the US GEOTRACES Pacific Meridional Transect (PMT) cruise (GP15, RR1815) on R/V Roger Revelle from Oct-Nov 2018

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Project

» US GEOTRACES Pacific Meridional Transect (GP15) (U.S. GEOTRACES PMT)

» <u>Collaborative Research: U.S. GEOTRACES Pacific Meridional Transect: Thorium-232, Thorium-230 and Protactinium-231 as tracers of trace element supply and removal</u> (PMT Thorium Isotopes)

Program

» U.S. GEOTRACES (U.S. GEOTRACES)

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Abstract

This dataset contains concentrations of size-fractionated particulate thorium and protactinium isotopes (Th-232, Th-230, Pa-231) in seawater collected during the U.S. GEOTRACES Pacific Meridional Transect GP15; Alaska to Tahiti) on the Roger Revelle (RR1814 and RR1815) from 18 September – 24 November 2018. This is compiled data produced by three laboratories with the following associations: Lamont-Doherty Earth Observatory of Columbia University (LDEO), the University of Southern Mississippi (USM) and the University of Minnesota (UMN). A report will be submitted for review by the International GEOTRACES Standards and Intercalibration (S&I) Committee. This dataset contains data from Leg 2 of the expedition (RR1815). Data from leg 1 are available in a separate BCO-DMO dataset.

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Coverage

Spatial Extent: N:17.5 E:-151.969 S:-20 W:-152.029 Temporal Extent: 2018-10-27 - 2018-11-23

Methods & Sampling

Sampling Methods at Sea:

Sampling methods at sea followed the GEOTRACES cookbook (Cutter et al., 2017). Large-volume size-fractionated particulate samples were collected using McLane Research in-situ pumps (WTS-LV) that had been modified to accommodate two flowpaths (Lam and Morris, 2013). The wire-out was used to target depths during deployment and both a self-recording Seabird 19plus CTD deployed at the end of the line and an RBR pressure logger attached to the pump at the middle of the line were used to correct for actual depths during pumping.

Filter holders used were 142 mm-diameter "mini-MULVFS" style filter holders with two stages for two size fractions and multiple baffle systems designed to ensure even particle distribution and prevent particle loss (Bishop et al., 2012). One filter holder/flowpath was loaded with paired 0.8 μ m Pall Supor800 polyethersulfone filters behind a 51 μ m Sefar polyester mesh prefilter ("Supor-side") and the other filter holder/flowpath was loaded with paired 1 μ m Whatman QMA quartz fiber filters behind a 51 μ m Sefar polyester mesh prefilter ("QMA-side") (see Xiang and Lam, 2020 for particulate sampling methodology). Each cast also had "dipped" filter blanks deployed. These were the full filter sets (prefilter followed by paired Supor or paired QMA filters) sandwiched within a 1 μ m polyester mesh filter, loaded into perforated polypropylene containers, attached with plastic cable ties to a pump frame, and deployed. "Dipped" filter blanks were exposed to seawater for the length of the deployment, processed and analyzed as regular samples, and thus functioned as full seawater particulate procedural blanks. For the "small particulate" dataset, we analyzed a 0.3125 fraction of each top (or bottom) Supor filter sample, or a 0.3125 fraction from the "dipped" Supor filter blanks for nearly every station. For the "large particulate" dataset, UMN analyzed eighth filter cuts from selected samples and from the "dipped" Sefar prefilter blanks from 1 or more depths for every station where samples were selected for analysis.

All filters and filter holders were acid leached prior to use according to methods recommended in the GEOTRACES cookbook (Cutter et al., 2017).

<u>Analytical Methods at LDEO:</u> Sample Digestion

The acids used in all the procedures below were as follows: Hydrochloric and Nitric Acids were redistilled in separate Savillex DST-1000 sub-boiling stills. The feed stock was Fisher Scientific Trace Metal grade acids. Hydrofluoric Acid, Perchloric Acid and Ammonium Hydroxide were all Fisher Scientific Optima Grade reagents.

Samples analyzed consisted of 5/16 pie slices of the top 142mm diameter, 0.8µm pore size Supor filters ("Small Particulate Matter", 0.8-51 µm particle size class, "suspended" size fraction). Bottom filters and Dipped Blanks were the same fractional portion of a filter [our experience has been that the Th isotopes and Pa concentrations of bottom filters and dipped blanks were statistically indistinguishable]. Samples were folded onto themselves and placed into 60 ml Teflon jars. Weighed aliquots of artificial isotope yield monitors, Th-229 (1 pg) and Pa-233 (0.05-0.12 pg), and 5 mg of dissolved Fe were added to each jar.

In addition to the samples and blank filters (dipped blanks and bottom filters), spikes were also prepared for 1) a procedural blank that was treated exactly as the samples and filter blanks, 2) a spiked blank that was only carried through the anion column chemistry, and 3) two or three aliquots of inhouse Th isotope and Pa-231 standards. We made two of these standards, designed to mimic the Th-232, Th-230 and Pa-231 amounts expected in a 1-10 liter seawater sample at 2km water depth. The main difference between SW Std 2010-1 and SW Std 2015-1 is that the Th-232 in SW Std 2010-1 was designed to match the Th-232 concentrations expected in the North Atlantic Ocean, where Th-232 is higher than the Central Pacific Ocean by about a factor of 5. We used these standards as an internal check that the ICP-MS was giving reproducible results at the concentrations we expected from our samples.

After addition of 5 ml concentrated Nitric Acid, jars were capped and heated at 150°C overnight. The next day, samples were cooled. After ensuring that filters were not sticking to the walls or bottom of jar, 4ml concentrated Perchloric Acid was added to each jar and then heated at 180°C for about 30 minutes. At that point the hot plate temperature was increased to 220°C Samples were heated until dense white perchloric fumes appeared. After 10-20 minutes, the samples were covered with a Teflon watch glass. After 60-90 minutes, rapid oxidation of the Supor material would occur, at which point the Supor material was almost completely broken down. The watch glasses were removed and the covers and jar walls were rinsed down with 2 ml concentrated Nitric Acid and placed back on the hot plate at 220°C.Once the samples were back to fuming Perchloric, 0.5 ml of concentrated Hydrofluoric Acid was added to the samples and heated at 220°C back to perchloric fumes before another 0.25-0.50 ml of concentrated Hydrofluoric Acid were added. Following the second addition of concentrated HF, the samples were dried down at 220°C to a viscous residue. Samples were then removed from the hot plate and 0.5ml concentrated Hydrochloric Acid was added to each jar, followed by 5ml Milli-Q water. This solution was heated for a few minutes on the hot plate, and then transferred to a clean 50ml Teflon centrifuge tube. The 60ml jar was rinsed several times with 5ml aliguots that were added to the 50ml centrifuge tube. More Milli-Q water was added directly to the centrifuge tubes, and then Ammonium Hydroxide was added to bring the solution to pH~8.5 to precipitate Fe as an oxyhydroxide. Centrifugation separated the Fe oxyhydroxide from the supernatant, which was discarded. The precipitate was dissolved in 0.5 concentrated Nitric Acid and transferred to a 15ml Teflon vial. The centrifuge tubes were rinsed twice more with 0.5ml aliguots of concentrated Nitric Acid and combined in the 15ml vials. These solutions were then processed to purify Th isotopes and Pa.

Th Isotopes and Pa Purification Chemistry

The solutions from the sample digestion procedure, were dried at 150°C. When totally dry, 0.5ml concentrated Nitric Acid was added, and samples were heated dry again. Then, 0.5ml concentrated Hydrochloric Acid was added and samples were heated at 120°C to dry. More Hydrochloric Acid was added and samples were heated dry again at 150°C. At this point, 2 ml concentrated Hydrochloric Acid was added, samples were capped tightly and the solutions were heated at 100°C for about an hour to ensure complete dissolution. Samples were then cooled to room temperature while the anion exchange resin columns were washed and conditioned.

Columns were polypropylene with 45-90 μ m frits with a total volume of ~8ml. Resin bed was 1ml of BioRad AG1-X8 (100-200 mesh) strong Anion exchange resin.

Columns were stored between uses with dilute Hydrochloric Acid. Columns were drained and then filled with 3ml Concentrated Hydrochloric Acid/0.14M Hydrofluoric Acid. Columns were then rinsed with a full reservoir (~7ml) of Milli-Q water. Finally, the resin was conditioned with two 2ml aliquots of Concentrated Hydrochloric Acid.

Thorium Fraction (Column 1)- Samples (2ml Concentrated Hydrochloric Acid) were loaded onto the columns, collected in 7ml Teflon vials. Vials were rinsed twice with 1ml Concentrated Hydrochloric Acid. Then the resin was washed twice with 1ml Concentrated Hydrochloric Acid. Total volume was 6ml. This fraction contains Th isotopes and the major elements carried over from the Fe oxyhydroxide precipitation step, including Beryllium.

Pa Fraction (Column 1)-A new 7ml Teflon vial was placed under the anion column. Pa was eluted from the resin with three 2ml additions of Concentrated Hydrochloric Acid/0.14M Hydrofluoric Acid.

Columns were washed and stored with 0.24M Hydrochloric Acid.

The Th and Pa fractions were both heated down on a hot plate after the addition of 3 drops of Perchloric Acid. The Th and Pa fractions were further purified, reusing the same anion resin columns for the next steps.

The Th and Pa fractions were dried overnight at 125°C. The next morning 200µm of concentrated Nitric Acid was added and the temperature was increased to 200°C to decompose any organic matter extracted from the resin and drive off the Perchloric Acid, except for a tiny drop.

Pa purification (Column 2)- 200µl of concentrated Hydrochloric Acid was added to the vials, capped and heated at 150°C for 10 minutes. 1ml of Hydrochloric Acid was added to vials, which were recapped and cooled to room temperature.

Columns were drained and the resin was conditioned with two aliquots of 2ml Concentrated Hydrochloric Acid.

Samples were loaded onto the columns collecting the effluent as waste. Beakers were rinsed and loaded onto columns twice with 1ml Concentrated Hydrochloric Acid each time. The resin was then washed twice with 1ml Concentrated Hydrochloric Acid. All of this was collected as waste.

Pa was eluted into the 7ml Pa vial with three 2ml aliquots of Concentrated Hydrochloric Acid/0.14M Hydrofluoric Acid. The time of elution was noted as that was the time of the final separation of Pa-233 from U -233. Columns were washed and stored with 0.24M Hydrochloric Acid.

The purified Pa fraction had 3 drops Perchloric Acid added and was heated down overnight at 125°C. The next morning 200µl of concentrated Nitric Acid was added, the temperature was raised to 200°C and the solution was heated to a tiny drop of fuming Perchloric Acid. 500µl of 0.48M Nitric Acid/0.08M Hydrofluoric Acid was added and the vial was capped. This solution was then transferred to acid-cleaned 2ml µcentrifuge tubes, ready for ICP-MS analysis.

Th Fraction (Column 3) 100µl Concentrated Nitric Acid was added to the Th fractions, which often had some precipitated solids mixed with the small amount of Perchloric Acid. Samples were heated at 200°C to a tiny drop of Perchloric Acid again, at which point 100µl Milli-Q Water and 100µl of concentrated Nitric Acid were added to the vial. If all the solids were not dissolved at this point samples were capped and heated at 100°C for 30 minutes before continuing to the next step. Usually, everything was dissolved and 1ml 8N Nitric Acid was added to the vials, which were then capped and cooled as the resin was prepared.

Columns were drained and conditioned with two 2ml aliquots of 8M Nitric Acid.

Samples were loaded onto the columns collecting the effluent as waste. Vials were rinsed with 1ml 8M Nitric Acid and loaded onto columns. The resin was then washed twice with 1ml 8M Nitric Acid. All of the rinses and washes were collected as waste. [If samples were spiked with Be carrier for Be-10 analysis, all of the 8M Nitric acid was collected in an 8ml acid-washed LDPE bottle]

Th was eluted into the 7ml Th vial with 200µl concentrated Hydrochloric Acid, followed by three 2ml aliquots of Concentrated Hydrochloric Acid. Columns were washed and stored with 0.24M Hydrochloric Acid.

The purified Th fraction had 3 drops Perchloric Acid added and was heated down overnight at 125°C. The next morning 200µl of concentrated Nitric Acid was added, the temperature was raised to 200°C and the solution was

heated to a tiny drop of fuming Perchloric Acid. 500µl of 0.48M Nitric Acid/0.08M Hydrofluoric Acid was added and the vial was capped. This solution was then transferred to acid-cleaned 2ml µcentrifuge tubes, ready for ICP-MS analysis.

ICP-MS Analyses

Analyses were carried out on a Thermo-Finnigan ELEMENT XR Single Collector Magnetic Sector ICP-MS, equipped with a high-performance Interface pump (Jet Pump), and enhanced sensitivity sample (Jet) and skimmer (X) cones. The sample introduction system consisted of a 50µl/min pfa nebulizer, attached to a Cetac Aridus II desolvation unit. Sensitivity was 25-35 Mcps/ppb based on repeated measurements of a 2ppt Th-232/U-238 standard solution. All measurements were made in low resolution mode (M/ $\Delta m \approx 300$), peak jumping in Escan mode across the central 5% of the flat-topped peaks (100 points/peak). All samples and standards were bracketed by instrument blanks to correct for possible changes in the background counting intensities. Natural U standards were run to correct for mass biasing (both Th and Pa analyses), and for the Analog/Counting mode correction factor (Th analyses only).

Samples were run on the ICP-MS in batches of 20 (not including instrument blanks, Th-232 tailing corrections, or Mass bias/Analog-Counting correction factors); 15 samples, and a combination of internal seawater standards (to check Th isotope and Pa analysis reproducibility), dipped blanks, bottom filters, chemical procedure blanks, and column chemistry-only blanks.

Pa measurements- For Pa analyses, the masses monitored were Pa-231, Th-232, and Pa-233. The dwell times used were 125msec, 5msec, and 30msec, respectively. As a precaution, external Th-232 standards were run within the Pa analysis sequence (0.25-1pg/g Th-232) to constrain Th-232 tail contributions to the signals at mass 231and 233. This was never the case, and no Th-232 tailing correction on Pa-231 or Pa-233 was required.

Every 4-6 months, a new Pa-233 spike was prepared due to its relatively short half-life (26.975 days). At that time, a mixed Pa solution was prepared (mixture of an inhouse Pa-231 standard solution and the Pa-233 spike being used at the time. The starting Pa-231/Pa-233 ratio was about 0.2 and increased with each batch of samples, as larger amounts of the mixed Pa solution was used as a way to keep the amount of Pa-233 measured constant over the useful lifetime of the Pa spike. An aliquot of this mixed Pa solution was processed through column chemistry at the same time as samples, and was used to calibrate the Pa spike for each sample batch, while taking into account the amount of U-233 ingrowth that occurred between the final Pa purification column and running samples on the ICP-MS.

Th measurements- For Th analyses, the masses monitored were Th-229, Th-230, and Th-232. The dwell times used were 25msec, 125msec, and 10msec, respectively. Th-229 and Th-230 were measured in counting mode, and Th-232 was measured in Analog mode. A series of Th-232 standards covering the expected range of Th-232 concentrations expected in the samples were run to assess the Th-232 tailing into the Th-230 and Th-229 peaks.

Data reduction

Average instrumental blanks, mass bias, and Analog-Counting correction factor were calculated. The raw data for samples, internal seawater standards, and various blanks were corrected for the instrumental blank for each isotope. Blank corrected count rates that were more than 3-sigma away from the mean for each isotope were excluded from further analysis. These isotope data were then block-averaged into groups of 5, conforming to the 5 points/peak measurement cycles. At this point the Th-229 and Th-230 data were corrected for Th-232 tailing into those peaks. Isotope ratios were calculated, and then subjected to another screening for outliers at the 3-sigma level. These corrected isotope ratios were then block averaged into groups of ten.

The mean values of the isotope ratios were then corrected for mass biasing, and for the calculation of Th-232 concentrations, Analog-Counting correction factors.

Standard isotope dilution calculations for Th isotopes were made using an externally calibrated Th-229 solution. As described above, given its short half-life, the Pa-233 spike was calibrated each time it was run. Consistency of the run to run calibration was monitored by decay correcting the Pa-233 concentration back to the initial separation date of that particular Pa-233 spike.

Blank and Standard Results

Samples were corrected using the pooled average of all procedural blanks ("dipped" filter blanks) analyzed during processing of GP15 particulate samples at LDEO. The average procedural blanks ("dipped" filter blanks) for the "small particulate" data from GP15 for a 5/16 filter cut of top (or bottom) Supor filters for Th-232, Th-230, and Pa-231 were 11 ± 5 pg, 0.96 ± 0.51 fg, and 0.097 ± 0.074 fg, respectively. The limit of detection (LOD) is the smallest quantity of each isotope in samples that can reliably be detected or that can be statistically distinguished from a procedural blank. The LOD was considered to be 2 standard deviations above the average of the procedural blanks. Our LOD for Th-232, Th-230, and Pa-231 were 20 pg, 2 fg, and 0.25 fg, respectively.

See Table 1 (in the Supplemental Files section).

Further details on analysis of seawater radionuclides are given by Anderson et al. (2012).

Analytical Methods at UMN:

Filter cuts (5/16) of the paired (top and bottom) Supor filters ("small particulate", 0.8-51 µm particle size class, "suspended" size fraction) and 1/8 cuts of the Sefar prefilters ("large particulate", > 51 µm particle size class, "sinking" size fraction) were folded into 30 mL Savillex Teflon (PFA) beakers and weighed aliguots of the artificial isotope yield monitors Th-229 (1 pg) and Pa-233 (30-60 fg) were added to the filters. Filters were then completely submerged in 20-25 mL of 8 M HNO3 combined with 10 drops of concentrated HF, tightly covered with a Teflon threaded cap and heated for 24 hours at $\sim 100^{\circ}$ C so that the particulate sample was dissolved/leached under pressure. The leachate was transferred to a second acid-cleaned Teflon beaker separate from the residual filter. Another round of 5-10 mL of 8 M HNO3 with 5 drops of concentrated HF was added onto the residual filter, tightly covered with a threaded cap and heated for 12 hrs at \sim 100°C and the leachate was combined with the leachate of previous round in the same clean beaker separate from the residual filter. The second round of leaching was performed to increase the overall quantitative yields. A wash of the filter was done using a rinse solution (rinsed twice with ICP-MS solution, 0.16 M HNO3/0.026 M HF) and combined with the leachate. Five drops of concentrated HCIO4 were then added to the leach solution in the second beaker (the beaker with combined leachate). The original beaker walls and caps were washed with small amounts of weak HNO3 (2 M) and the resulting solution added to the second beaker. The solution was then dried down and taken up in dilute (2 M) HCl and transferred to 15 mL centrifuge tubes along with a dilute (2 M) HCl rinse. About 0.5 mg of dissolved Fe (one drop of iron chloride solution with Fe concentration of $\sim 1\%$) and five to ten drops of concentrated NH4OH were added to raise the pH to 8.0-8.5 at which time iron (oxy)hydroxide precipitated. This precipitate was then centrifuged, decanted, washed with deionized H2O (>18 M Ω), centrifuged, dissolved in 14 M HNO3, and transferred to a clean Teflon beaker.

This solution was then dried down and taken up in 8 M HNO3 for anion-exchange chromatography using Bio-rad resin (AG1-X8, 100-200 mesh size) and a polyethylene frit. Initial separation was done on Teflon columns (internal diameter \sim 0.35 cm) with a 0.55 mL column volume (CV). The sample was loaded in 0.55 mL (1 CV) of 8 M HNO3, followed by 0.825 mL (1.5 CV) of 8 M HNO3 (to wash Fe and other undesired elements off the resin), 1.65 mL (3 CV) of 9 M HCl (to collect Th fraction), and 1.65 mL (3 CV) of 9 M HCl + 0.015 M HF (to collect Pa fraction). The Pa and Th fractions were then dried down in the presence of 2 drops of concentrated HClO4 and taken up in 8 M HNO3. They were individually passed through second and third columns (each with 0.55 mL column volumes) using similar elution schemes. The final Pa and Th fractions were then dried down in the presence of 2 drops of the mass spectrometer.

"Small particulate" (0.8-51 μ m particle size class, "suspended" size fraction) and "large particulate" (>51 μ m particle size class, "sinking" size fraction) samples were analyzed in batches of 25-30. Analysis of the paired Supor filters represents a particle size class approximating 0.45-51 μ m (Bishop et al., 2012), while the top filter alone represents 0.8-51 μ m and it is this size class referred to here as "small particulate". Previously, a selection of 14 top and bottom Supor filters were measured separately for radionuclides at LDEO and it was found that the bottom filters had radionuclide levels that were indistinguishable from procedural blanks ("dipped" filter blanks). Therefore, whether or not samples were analyzed as paired Supor filters, or the top Supor filter alone, the "small particulate" data was inferred to represent the 0.8-51 μ m particle size class or "suspended" size fraction. "Small particulate" samples and procedural blanks ("dipped" filter blanks) were analyzed as paired Supor filters.

Blanks and Standards

Procedural blanks were determined by analyzing "dipped" filter blanks, mentioned above, which represent the total blank associated with the sample collection and handling in addition to the laboratory procedure. An aliquot of one of two intercalibrated working standard solutions of Th-232, Th-230, and Pa-231, SW STD 2010-1 referred to by Anderson et al. (2012) and SW STD 2015-1 which has ~6 times lower Th-232 activity, was added to a separate acid-cleaned Teflon beaker along with weighed aliquots of Th-229 and Pa-233 spike. Spikes and SW STD were equilibrated for 2 days. They were then dried down and taken up in 8 M HNO3 for anion-exchange chromatography and processed like a sample with each batch.

Mass Spectrometry

Concentrations of Th-232, Th-230, and Pa-231 were calculated by isotope dilution using nuclide ratios determined on a Thermo-Finnigan Neptune Multicollector ICP-MS. Machine was tuned for torch positions and gas flows for maximum U sensitivity using dilute U standard (112a) before the sample measurements. All measurements were done using a peak jumping routine in ion counting mode on the discreet dynode multiplier behind the retarding potential quadrupole. A solution of U-233-U-236 tracer was run to determine the mass bias correction (assuming that the mass fractionation for Th and Pa are the same as for U). Each sample measurement was bracketed by measurement of an aliquot of the run solution (weak nitric acid) used to correct for the instrument background count rates on the masses measured.

Blank and Standard Results

Sample Th and Pa concentrations were corrected using the pooled average of all procedural blanks ("dipped" filter blanks) analyzed during processing of GP-15 particulate samples. The average procedural blanks ("dipped" filter blanks) for the GP15 "small particulate" dataset for a 5/16 filter cut of paired Supor filters for Th-232, Th-230, and Pa-231 were 19 ± 6 pg, 1.47 ± 0.49 fg, and 0.13 ± 0.07 fg, respectively. The average procedural blanks ("dipped" filter blanks) for the GP-15 "large particulate" dataset for an eighth filter cut of Sefar prefilters for Th-232, Th-230, and Pa-231 were 12.55 ± 8.26 pg, 0.35 ± 0.15 fg, and 0.13 ± 0.14 fg, respectively. The limit of detection (LOD) is the smallest quantity of each isotope in samples that can reliably be detected or that can be statistically distinguished from a procedural blank. The LOD was considered at 2 standard deviations above the average of the procedural blanks. For the GP-15 "small particulate" dataset, our LOD for Th-232, Th-230, and Pa-231 were 32 pg, 2.4 fg, and 0.14 fg, respectively. The average procedural blanks ("dipped" filter blanks) for the GP15 "large particulate" dataset for a 1/8 filter cut for Th-232, Th-230, and Pa-231 were 8.0 ± 1.9 pg, 0.29 ± 0.08 fg, and 0.025 ± 0.017 fg, respectively. For the

GP-15 "large particulate" dataset, our LOD for Th-232, Th-230, and Pa-231 were 12 pg, 0.45 fg, and 0.06 fg, respectively.

Further details on Pa and Th analysis at University of Minnesota are given in Shen et al. (2002, 2003, 2012), and Cheng et al. (2000, 2013).

See Table 2 (in the Supplemental Files section).

Analytical Methods at USM:

Processing of Supor Th/Pa particle samples at USM for GP15

This method was based on the method used for Supor samples at the University of Minnesota with minor modifications. The procedure also contains steps so that Nd and Be isotopes could be measured on the same sample digests, but further analysis of Nd or Be are not documented here. Supor filter samples were generally analyzed as a 5/16 slice of the filter. During sample collection the filters are loaded into the pump as 2 stacked Supor filters. Only the top filter was analyzed based on previous work that showed that the bottom filter was generally not distinguishable from "dipped" filter blanks. "Dipped" blanks were blank filters deployed on the in situ pumps in mesh bags to check for adsorption from seawater and any blanks associated with filter handling on the cruise.

Each Supor sample was folded into a 30 mL Teflon beaker, and isotope yield monitors were added (Th-229, Pa-233 and Be-9). All acids used were Optima grade unless otherwise noted. A procedural blank was analyzed using an empty beaker and spikes and a standard was analyzed using weighed aliquots of standard seawater solution made at LDEO (SWS2015-1). Filter samples were completely submerged with 8M HNO3 (~8 mL), then concentrated HF was added (1.5 mL) and the beaker was tightly capped and heated for 10 hours total at 95°C. Usually the 10 hours was broken up into 2 sessions so hot plates did not need to be left on overnight.

The leach solution was decanted into a new 15 mL Teflon beaker, leaving the residual filter behind. The original beaker walls and caps were washed 2 x 1 mL with 1 M HNO3 and added to the 15 mL beaker. The leach solution was dried down at 150°C. The residue was taken up in 0.5 mL 8M HNO3 and then 0.5 mL HF was added. The solution was dried down again and residue fully dissolved in 0.5 mL 8M HCl. The solution was dried down once more and taken up in 2 mL 2M HCl. If at this point any filter fragments were visible (occurred for 3 of the 88 samples analyzed), they would be physically removed with plastic tweezers.

The 2 mL 2M HCl was transferred to 15 mL centrifuge tubes along with 2 x 2M HCl rinses and filled with Milli-Q water to 10 mL. Then dissolved Fe was added as 80 micro-liters of a 60 mg/ml iron chloride solution. pH was raised to 8-8.5 with concentrated ammonium hydroxide (~40 drops). The precipitate was centrifuged, decanted, washed with Milli-Q water and dissolved with 8M HCl (2 mL) and transferred back to the 15 mL Teflon beaker with water rinses. That solution was dried down and taken up in 1 mL 8M HCl for column chemistry, using Dowex 1-X8 anion exchange resin, 100-200 mesh (1 mL resin bed) and polyethylene frit.

A first column was performed to separate (Th+Nd+Be) from Pa and the added Fe. At this point a mixed Pa solution (containing a known amount of Pa-231 and the same amount of Pa-233 samples received) is made and run as a sample so that the Pa-233 concentration at the time of column separation can be accurately calculated. Samples are loaded as 1 mL 8 M HCl and Th/Nd/Be pass through the column to be collected in a new 15 mL Teflon beaker. Sample beakers were rinsed with 2 column volumes 8 M HCl, which were added to columns, and columns rinsed further with 2 column volumes 8 M HCl. Pa is eluted next with 4 x 1mL 8N HCl/0.13 M HF into the original 15 mL beakers, cleaned with 8 M HNO3 and brief heating. Fe is then washed off the column with 5-10 mL water and transferred to waste.

A second column is performed to separate Th and Nd/Be and also to collect any Pa that went through with the 8 M HCI fraction. We found by gamma counting of Pa-233 in the sample fractions that in approximately 30% of samples, up to 50% of the Pa went through the first HCl column, but can be reclaimed and added to the first collected Pa fraction for increased yield. The Th-Nd-Be fraction collected in 8 M HCl needs to be dried down and converted to 2 mL 8 M HNO3. Loaded as 2 mL sample onto column, collecting the elution in a 15 mL HDPE bottle that is saved for further analysis of Nd (and Be) isotopes. Columns rinsed with 5 column volumes of 8 M HNO3. Thorium is eluted with $0.2 + 4 \times 1.5$ mL HCl into cleaned beakers. Any residual Pa is then eluted with 4×1 mL 8 M HCl/0.18 M HF and added to the Pa fraction collected off the first column. Both Th and Pa fractions are dried down to near dry, taken up in 2 drops HNO3, dried again, then 1 drop HNO3, dried again and taken up in 1 mL 2%HNO3 for ICP-MS analysis. ICP-MS procedures were identical to those reported previously for the dissolved phase GP15 measurements.

Concentrations of 232Th, 230Th and 231Pa were calculated by isotope dilution, relative to the calibrated tracers 229Th and 233Pa added at the beginning of sample processing. Analyses were carried out on a Thermo-Finnigan ELEMENT XR Single Collector Magnetic Sector ICP-MS. This model lacks the high-performance Interface pump (Jet Pump Aridus I^m) mentioned above, but we did utilize the specially designed sample (Jet) and skimmer (X) cones which increased sensitivity. All measurements were made in low resolution mode ($\Delta m/M \approx 300$), peak jumping in Escan mode across the central 5% of the flat-topped peaks. Measurements were made on a MasCom^m SEM; 229Th, 230Th, 231Pa, and 233Pa were measured in Counting mode, while the 232Th signals were large enough that they were measured in Analog mode. Two solutions of SRM129, a natural U standard, were run multiple times throughout each run. One solution was in a concentration range where 238U and 235U were both measured in Counting mode, allowing us to determine the mass bias/amu (typical values varied from -0.5%/amu to +0.2%/amu). In the other, more concentrated solution, 238U

was measured in Analog mode and 235U was measured in Counting mode, yielding a measurement of the Analog/Counting Correction Factor (typical values varied from 0.9 to 1.1). These corrections assume that the mass bias and Analog/Counting Correction Factor measured on U isotopes can be applied to Th and Pa isotope measurements. Each sample measurement was bracketed by measurement of an aliquot of the run solution (0.32 M HNO3), which was used to correct for the instrumental background count rates. Tailing of 232Th into the minor Th and Pa isotopes was monitored by counting at the half-masses surrounding 230Th and 231Pa. Tailing corrections were typically small (<0.5% and often negligible).

Procedural blanks were generally < 10% of sample signals measured. Mean and standard deviation of procedural blanks (n = 4) were 11 \pm 2 pg 232Th, 1.9 \pm 0.5 fg 230Th, and 0.24 \pm 0.23 fg 231Pa. Limits of detection were defined using 3 times the standard deviation of these blank measurements, which given a typical sample volume analyzed of ~120L equates to concentration detection limits of 0.05 pg/kg 232Th, 0.015 fg/kg 230Th and 0.007 fg/kg 231Pa. Dipped blanks analyzed (n = 8) were not significantly different than procedural blanks and therefore only procedural blanks were used to blank correct measured samples.

See Table 3 (in the Supplemental Files section).

Data Processing Description

The reported errors for radionuclide concentrations represent the propagation of one sigma errors based on the standard isotope ratios collected by ICP-MS, estimated error in the Th-229 or Pa-233 spike concentration, and the blank correction of the individual isotopes. For each laboratory (LDEO, USM and UMN), samples were corrected for blanks using the pooled average of all procedural blanks (or "dipped" filter blanks) analyzed during processing of GP15 seawater particulate samples.

Individual uncertainties for protactinium and thorium were calculated to include contributions from (a) blank correction using the variance of the blanks measured over the course of the analyses, (b) standard error of the ratios of the analysis (typically close to counting statistics) and (c) spike calibration. For protactinium we also included assessment of the correction from the yield correction, mass bias and instrument background. In order to assess the reproducibility of the procedure, repeat analyses were performed on the GEOTRACES 2010-1 and/or 2015-1 standards. For standards run alongside GP15 particulate samples at LDEO, the reproducibility for each isotope based on 10 analyses SW STD 2010-1 was 1.9% for Th-232, 2.0% for Th-230 and 2.1% for Pa-231. At UMN, the reproducibility for each isotope based on 11 analyses of SW STD 2015-1 was 1.2% for Th-232, 1.7% for Th-230 and 2.3% for Pa-231. At USM, the reproducibility for each isotope based on 5 analyses of SW STD 2015-1 was 7% for Th-232, 3% for Th-230 and 3% for Pa-231.

Quality Flags:

SeaDataNet quality flags have been assigned to all measured and derived parameters. More information on SeaDataNet quality flags is available from GEOTRACES at https://www.geotraces.org/geotraces-quality-flag-policy/ and from SeaDataNet at https://www.geotraces.org/geotraces-quality-flag-policy/ and from SeaDataNet at https://www.geotraces.org/geotraces-quality-flag-policy/ and from SeaDataNet at https://www.seadatanet.org/Standards/Data-Quality-Control. In summary:

- 0 = no quality control;
- 1 = good value;
- 2 = probably good value;
- 3 = probably bad value;
- 4 = bad value;
- 5 = changed value;
- 6 = value below detection;
- 7 = value in excess;
- 8 = interpolated value;
- 9 = missing value;
- A = value phenomenon uncertain.

Notes on DERIVED PARAMETERS:

Th_230_SPT_XS_CONC_PUMP: The small particulate excess Th-230 refers to the measured small particulate Th-230 corrected for a contribution of Th-230 originating from U-bearing minerals or lithogenic Th-230. Some of this lithogenic Th-230 will be still intact within minerals and some after partial dissolution will have adsorbed to particle surface to contribute in part to the total adsorbed Th-230. Using the measured small particulate Th-232 and a lithogenic Th-230/Th-232 ratio of 4.0e-6 (atom ratio) as determined by Roy-Barman et al. (2002), and not taking into account the fact that some of the measured particulate Th-232 is adsorbed, corrects for all of the lithogenic Th-230 whether it be adsorbed or within intact minerals. This excess Th-230 is what should be used in scavenging or particle flux studies where it is desired to compare particulate Th-230 concentrations to Th-230 production by decay of uranium dissolved in seawater. An additional conversion factor (1.7473e5) converts picomoles (the units of 232Th) to micro-Becquerels (the units of 230Th).

Th_230_SPT_XS_CONC_PUMP = Th_230_SPT_CONC_PUMP - 4.0e-6 * 1.7473e5 * Th_232_SPT_CONC_PUMP

Pa_231_SPT_XS_CONC_PUMP: The small particulate excess Pa-231 refers to the measured small particulate Pa-231 corrected for a contribution of Pa-231 originating from U-bearing minerals or lithogenic Pa-231. Some of this lithogenic Pa-231 will be still intact within minerals and some after partial dissolution will have adsorbed to particle surface to contribute in part to the total adsorbed Pa-231. Using the measured small particulate Th-232 and a lithogenic Pa-231/Th-232 ratio of 8.8e-8 (atom ratio) which is derived from assuming an average upper continental crustal U/Th ratio (Taylor and McClennan, 1995) and secular equilibrium between Pa-231 and U-235 in the lithogenic material, and not taking into account the fact that some of the measured particulate Th-232 is adsorbed, corrects for all of the lithogenic Pa-231 whether it be adsorbed or within intact minerals. This excess Pa-231 is what should be used in scavenging or particle flux studies where it is desired to compare particulate Pa-231 concentrations to Pa-231 production by decay of uranium dissolved in seawater. An additional conversion factor (4.0370e5) converts picomoles (the units of 232Th) to micro-Becquerels (the units of 231Pa).

Pa_231_SPT_XS_CONC_PUMP = Pa_231_SPT_CONC_PUMP - 8.8e-8 * 4.0370e5 * Th_232_SPT_CONC_PUMP

Th_230_LPT_XS_CONC_PUMP: The large particulate excess Th-230 refers to the measured large particulate Th-230 corrected for a contribution of Th-230 originating from U-bearing minerals or lithogenic Th-230. Some of this lithogenic Th-230 will be still intact within minerals and some after partial dissolution will have adsorbed to particle surface to contribute in part to the total adsorbed Th-230. Using the measured large particulate Th-232 and a lithogenic Th-230/Th-232 ratio of 4.0e-6 (atom ratio) as determined by Roy-Barman et al. (2002), and not taking into account the fact that some of the measured particulate Th-232 is adsorbed, corrects for all of the lithogenic Th-230 whether it be adsorbed or within intact minerals. This excess Th-230 is what should be used in scavenging or particle flux studies where it is desired to compare particulate Th-230 concentrations to Th-230 production by decay of uranium dissolved in seawater. An additional conversion factor (1.7473e5) converts picomoles to (the units of 232Th) to micro-Becquerels (the units of 230Th).

Th_230_LPT_XS_CONC_PUMP = Th_230_LPT_CONC_PUMP - 4.0e-6 * 1.7473e5 * Th_232_LPT_CONC_PUMP

Pa_231_LPT_XS_CONC_PUMP: The large particulate excess Pa-231 refers to the measured large particulate Pa-231 corrected for a contribution of Pa-231 originating from U-bearing minerals or lithogenic Pa-231. Some of this lithogenic Pa-231 will be still intact within minerals and some after partial dissolution will have adsorbed to particle surface to contribute in part to the total adsorbed Pa-231. Using the measured large particulate Th-232 and a lithogenic Pa-231/Th-232 ratio of 8.8e-8 (atom ratio) which is derived from assuming an average upper continental crustal U/Th ratio (Taylor and McClennan, 1995) and secular equilibrium between Pa-231 and U-235 in the lithogenic material, and not taking into account the fact that some of the measured particulate Th-232 is adsorbed, corrects for all of the lithogenic Pa-231 whether it be adsorbed or within intact minerals. This excess Pa-231 is what should be used in scavenging or particle flux studies where it is desired to compare particulate Pa-231 concentrations to Pa-231 production by decay of uranium dissolved in seawater. An additional conversion factor (4.0370e5) converts picomoles (the units of 232Th) to micro-Becquerels (the units of 231Pa).

Pa_231_LPT_XS_CONC_PUMP = Pa_231_LPT_CONC_PUMP - 8.8e-8 * 4.0370e5 * Th_232_LPT_CONC_PUMP

Th_230_SPT_ADS_CONC_PUMP: The small particulate adsorbed Th-230 concentration refers to the measured small particulate Th-230 corrected for a contribution of Th-230 locked within mineral lattices. To estimate the particulate Th-230 supported by decay of U within mineral lattices, we use measured small particulate Th-232 and a lithogenic Th-230/Th-232 ratio of 4.0e-6 (atom ratio) as determined by Roy-Barman et al. (2002). However, because some fraction of the Th-232 is also adsorbed (and not merely found within mineral lattices), we use the dissolved Th-232/Th-230 ratio to estimate the fraction of the small particulate Th-232 that is adsorbed and furthermore to calculate the correction for adsorbed Th-230. In this calculation it is assumed that dissolved 230Th derived from decay of dissolved 234U adsorbs to the same extent as dissolved 230Th derived from dissolution of lithogenic material. A conversion factor (1.7473e5) is also necessary to convert picomoles (the units of 232Th) to micro-Becquerels (the units of 230Th). When dissolved Th data do not exist at the same depth as the particulate samples, we linearly interpolated the dissolved data onto the depths of the particulate samples. See Hayes et al. (2015) for more details.

Th_230_SPT_ADS_CONC_PUMP = [Th_230_SPT_CONC_PUMP - 4.0e-6 * 1.7473e5 * Th_232_SPT_CONC_PUMP] / [1 - 4.0e-6 * 1.7473e5 * Th_232_D_CONC_BOTTLE / Th_230_D_CONC_BOTTLE]

Pa_231_SPT_ADS_CONC_PUMP: The small particulate adsorbed Pa-231 concentration refers to the measured small particulate Pa-231 concentration corrected for a contribution of Pa-231 locked within mineral lattices (as opposed to adsorbed onto particle surfaces). To estimate the adsorbed particulate Pa-231, we divide particulate excess 231Pa (calculated above as Pa_231_SPT_XS_CONC_PUMP) by the fraction of total dissolved 231Pa (Pa_231_D_CONC_BOTTLE) that is excess, or produced by 235U decay in seawater. In this process we use measured small particulate Th-232 and a lithogenic Pa-231/Th-232 ratio of 8.8e-8 (atom ratio) which is derived from assuming an average upper continental crustal U/Th ratio (Taylor and McClennan, 1995) and secular equilibrium between Pa-231 and U-235 in the lithogenic material. However, because some fraction of the Th-232 is also adsorbed (and not merely found within mineral lattices), we use the dissolved 231Pa/232Th (Pa_231_D_CONC_BOTTLE and Th_232_D_CONC_BOTTLE) ratio to

calculate the concentration of adsorbed Pa-231. In this calculation it is assumed that dissolved 231Pa derived from decay of dissolved 235U adsorbs to the same extent as dissolved 231Pa derived from dissolution of lithogenic particles, and that 231Pa dissolves from lithogenic material to the same extent as 232Th dissolves from lithogenic material. A conversion factor (4.0370e5) is also necessary to convert picomoles (the units of 232Th) to micro-Becquerels (the units of 231Pa). When dissolved Pa data do not exist at the same depth as the particulate samples, we linearly interpolate the dissolved data onto the depths of the particulate samples. See Hayes et al. (2015) for more details.

Pa_231_SPT_ADS_CONC_PUMP = [Pa_231_SPT_CONC_PUMP - 8.8e-8 * 4.0370e5 * Th_232_SPT_CONC_PUMP] / [1 - 8.8e-8 * 4.0370e5 * Th_232_D_CONC_BOTTLE / Pa_231_D_CONC_BOTTLE]

Th_230_LPT_ADS_CONC_PUMP: The large particulate adsorbed Th-230 concentration refers to the measured large particulate Th-230 corrected for a contribution of Th-230 locked within mineral lattices. To estimate the particulate Th-230 supported by decay of U within mineral lattices, we use measured large particulate Th-232 and a lithogenic Th-230/Th-232 ratio of 4.0e-6 (atom ratio) as determined by Roy-Barman et al. (2002). However, because some fraction of the Th-232 is also adsorbed (and not merely found within mineral lattices), we use the dissolved Th-232/Th-230 ratio to estimate what fraction of the large particulate Th-232 that is adsorbed and furthermore to calculate the correction for adsorbed Th-230. In this calculation it is assumed that dissolved 230Th derived from decay of dissolved 234U adsorbs to the same extent as dissolved 230Th derived from dissolution of lithogenic material. A onversion factor (1.7473e5) is also necessary to convert picomoles (the units of 232Th) to micro-Becquerels (the units of 230Th). When dissolved data do not exist at the same depth as the particulate samples, we linearly interpolated the dissolved data onto the depths of the particulate samples. See Hayes et al. (2015) for more details.

Th_230_LPT_ADS_CONC_PUMP = [Th_230_LPT_CONC_PUMP - 4.0e-6 * 1.7473e5 * Th_232_LPT_CONC_PUMP] / [1 - 4.0e-6 * 1.7473e5 * Th_232_D_CONC_BOTTLE / Th_230_D_CONC_BOTTLE]

Pa 231 LPT ADS CONC PUMP: The large particulate adsorbed Pa-231 concentration refers to the measured large particulate Pa-231 concentration corrected for a contribution of Pa-231 locked within mineral lattices (as opposed to adsorbed onto particle surfaces). To estimate the adsorbed particulate Pa-231, we divide particulate excess 231Pa (calculated above as Pa 231 LPT XS CONC PUMP) by the fraction of total dissolved 231Pa (Pa 231 D CONC BOTTLE) that is excess, or produced by 235U decay in seawater. In this process we use measured large particulate Th-232 and a lithogenic Pa-231/Th-232 ratio of 8.8e-8 (atom ratio) which is derived from assuming an average upper continental crustal U/Th ratio (Taylor and McClennan, 1995) and secular equilibrium between Pa-231 and U-235 in the lithogenic material. However, because some fraction of the Th-232 is also adsorbed (and not merely found within mineral lattices), we use the dissolved 231Pa/232Th (Pa 231 D CONC BOTTLE and Th 232 D CONC BOTTLE) ratio to calculate the concentration of adsorbed Pa-231. In this calculation it is assumed that dissolved 231Pa derived from decay of dissolved 235U adsorbs to the same extent as dissolved 231Pa derived from dissolution of lithogenic particles, and that 231Pa dissolves from lithogenic material to the same extent as 232Th dissolves from lithogenic material. A conversion factor (4.0370e5) is also necessary to convert picomoles (the units of 232Th) to micro-Becquerels (the units of 231Pa). When dissolved Pa data do not exist at the same depth as the particulate samples, we linearly interpolate the dissolved data onto the depths of the particulate samples. See Hayes et al. (2015) for more details.

Pa_231_LPT_ADS_CONC_PUMP = Pa_231_LPT_CONC_PUMP - 8.8e-8 * 4.0370e5 * Th_232_LPT_CONC_PUMP] / [1 - 8.8e-8 * 4.0370e5 * Th_232_D_CONC_BOTTLE / Pa_231_D_CONC_BOTTLE]

BCO-DMO Processing Description

- Imported original file "RR1815_PartThPa_DoordataTemplate_Anderson_submitted.xlsx" into the BCO-DMO system.

- Marked "nd" as a missing data value (missing data are empty/blank in the final CSV file).
- Renamed fields to comply with BCO-DMO naming conventions.
- Created the Start ISO DateTime UTC field in ISO 8601 format.
- Removed empty columns: End_Date_UTC, End_Time_UTC, End_Latitude, End_Longitude, Rosette_Position.
- Converted the Sample Depth Flag column to integers.
- Saved the final file as "954626_v1_gp15_particulate_th_pa_leg2.csv".

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Related Publications

Anderson, R. F., Fleisher, M. Q., Robinson, L. F., Edwards, R. L., Hoff, J. A., Moran, S. B., ... Francois, R. (2012). GEOTRACES intercalibration of 230Th, 232Th, 231Pa, and prospects for 10Be. Limnology and Oceanography: Methods, 10(4), 179–213. doi:10.4319/lom.2012.10.179

Methods

Auro, M. E., Robinson, L. F., Burke, A., Bradtmiller, L. I., Fleisher, M. Q., & Anderson, R. F. (2012). Improvements to 232-thorium, 230-thorium, and 231-protactinium analysis in seawater arising from GEOTRACES intercalibration. Limnology and Oceanography: Methods, 10(7), 464–474. doi:<u>10.4319/lom.2012.10.464</u> *General*

Bishop, J. K. B., Lam, P. J., & Wood, T. J. (2012). Getting good particles: Accurate sampling of particles by large volume in-situ filtration. Limnology and Oceanography: Methods, 10(9), 681–710. doi:<u>10.4319/lom.2012.10.681</u> *Methods*

Chen, J. H., Edwards, R. L., & Wasserburg, G. J. (1986). 238U, 234U and 232Th in seawater. Earth and Planetary Science Letters, 80(3-4), 241–251. doi:<u>10.1016/0012-821x(86)90108-1</u> *General*

Cheng, H., Edwards, R. L., Hoff, J., Gallup, C. D., Richards, D. A., & Asmerom, Y. (2000). The half-lives of uranium-234 and thorium-230. Chemical Geology, 169(1-2), 17–33. doi:<u>10.1016/s0009-2541(99)00157-6</u> *Methods*

Cheng, H., Edwards, R. L., Shen, C.-C., Polyak, V. J., Asmerom, Y., Woodhead, J., ... Alexander Jr., E. C. (2013). Improvements in 230Th dating, 230Th and 234U half-life values, and U–Th isotopic measurements by multi-collector inductively coupled plasma mass spectrometry. Earth and Planetary Science Letters, 371-372, 82–91. doi:10.1016/j.epsl.2013.04.006

Methods

Cutter, Gregory, Casciotti, Karen, Croot, Peter, Geibert, Walter, Heimbürger, Lars-Eric, Lohan, Maeve, Planquette, Hélène, van de Flierdt, Tina (2017) Sampling and Sample-handling Protocols for GEOTRACES Cruises. Version 3, August 2017. Toulouse, France, GEOTRACES International Project Office, 139pp. & Appendices. DOI: http://dx.doi.org/<u>10.25607/OBP-2</u> *Methods*

Hayes, C. T., Anderson, R. F., Fleisher, M. Q., Vivancos, S. M., Lam, P. J., Ohnemus, D. C., ... Moran, S. B. (2015). Intensity of Th and Pa scavenging partitioned by particle chemistry in the North Atlantic Ocean. Marine Chemistry, 170, 49–60. doi:<u>10.1016/j.marchem.2015.01.006</u> *General*

Lam, P. J., & Morris, P. J. (2013). In situ marine sample collection system and methods (U.S. Patent Application No. 20130298702). Washington, DC: U.S. Patent and Trademark Office. https://patents.google.com/patent/US20130298702 Methods

Roy-Barman, M., Coppola, L., & Souhaut, M. (2002). Thorium isotopes in the western Mediterranean Sea: an insight into the marine particle dynamics. Earth and Planetary Science Letters, 196(3-4), 161–174. doi:<u>10.1016/s0012-821x(01)00606-9</u>

General

Shen, C.-C., Cheng, H., Edwards, R. L., Moran, S. B., Edmonds, H. N., Hoff, J. A., & Thomas, R. B. (2003). Measurement of Attogram Quantities of 231Pa in Dissolved and Particulate Fractions of Seawater by Isotope Dilution Thermal Ionization Mass Spectroscopy. Analytical Chemistry, 75(5), 1075–1079. doi:<u>10.1021/ac026247r</u> *Methods*

Shen, C.-C., Edwards, R. L., Cheng, H., Dorale, J. A., Thomas, R. B., Moran, S. B., ... Edmonds, H. N. (2002). Uranium and thorium isotopic and concentration measurements by magnetic sector inductively coupled plasma mass spectrometry. Chemical Geology, 185(3-4), 165–178. doi:<u>10.1016/s0009-2541(01)00404-1</u> *Methods*

Shen, C.-C., Wu, C.-C., Cheng, H., Edwards, R. L., Hsieh, Y.-T., Gallet, S., ... Spötl, C. (2012). High-precision and highresolution carbonate 230Th dating by MC-ICP-MS with SEM protocols. Geochimica et Cosmochimica Acta, 99, 71–86. doi:<u>10.1016/j.gca.2012.09.018</u>

Methods

Taylor, S. R., & McLennan, S. M. (1995). The geochemical evolution of the continental crust. Reviews of Geophysics, 33(2), 241. doi:<u>10.1029/95rg00262</u> *General*

Xiang, Y., & Lam, P. J. (2020). Size-Fractionated Compositions of Marine Suspended Particles in the Western Arctic Ocean: Lateral and Vertical Sources. Journal of Geophysical Research: Oceans, 125(8). doi:<u>10.1029/2020jc016144</u> *Methods*

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Related Datasets

Continues

Anderson, R. F., Edwards, R. L., Hayes, C. T., Fleisher, M. Q., Cheng, H., Shaikh, J. (2025) **Size-fractionated particulate thorium and protactinium isotopes in seawater from Leg 1 (Seattle, WA to Hilo, HI) of the US GEOTRACES Pacific Meridional Transect (PMT) cruise (GP15, RR1814) on R/V Roger Revelle from September to October 2018.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2025-02-24 http://lod.bco-dmo.org/id/dataset/954271 [view at BCO-DMO] *Relationship Description: GP15 was made up of two cruise legs, RR1814 (Leg 1) and RR1815 (Leg 2)*

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Parameters

Parameter	Description	Units
Cruise_ID	Cruise identifier	unitless
Station_ID	Station number	unitless
Cast_ID	Cast number	unitless
Event_ID	GEOTRACES event number	unitless
Gear_ID	Pump number	unitless
Start_Date_UTC	Date (UTC) at start of sample collection	unitless
Start_Time_UTC	Time (UTC) at start of sample collection	unitless
Start_ISO_DateTime_UTC	Date and time (UTC) at start of sample collection in ISO 8601 format	unitless
Start_Latitude	Latitude at start of sample collection; negative values = South	decimal degrees
Start_Longitude	Longitude at start of sample collection; negative values = West	decimal degrees
Sample_ID	GEOTRACES sample number	unitless
Lab_ID_SPT	Lab identifier for small particulate (SPT) sample analysis	unitless
Lab_ID_LPT	Lab identifer for large particulate (LPT) sample analysis	unitless
Sample_Depth	Sample depth	meters (m)

Sample_Depth_Flag	Sample depth flag. (Depths are incorrect for deep SPT samples at Station 18 (Leg 1). The nature and source of the problem are unknown. The depth of each of these samples is flagged as bad.)	unitless
Th_232_SPT_CONC_PUMP_lpmi1m	Concentration of small particulate Th-232 in seawater collected using a McLane large volume in situ pump	picomoles per kilogram (pmol/kg)
SD1_Th_232_SPT_CONC_PUMP_lpmi1m	One standard deviation of Th_232_SPT_CONC_PUMP_lpmi1m	picomoles per kilogram (pmol/kg)
Flag_Th_232_SPT_CONC_PUMP_lpmi1m	SeaDataNet quality flag for Th_232_SPT_CONC_PUMP_lpmi1m	unitless
Th_230_SPT_CONC_PUMP_29jynq	Concentration of small particulate Th-230 in seawater collected using a McLane large volume in situ pump	micro- Becquerel per kilogram (uBq/kg)
SD1_Th_230_SPT_CONC_PUMP_29jynq	One standard deviation of Th_230_SPT_CONC_PUMP_29jynq	micro- Becquerel per kilogram (uBq/kg)
Flag_Th_230_SPT_CONC_PUMP_29jynq	SeaDataNet quality flag for Th_230_SPT_CONC_PUMP_29jynq	unitless
Pa_231_SPT_CONC_PUMP_hhdaou	Concentration of small particulate Pa-231 in seawater collected using a McLane large volume in situ pump	micro- Becquerel per kilogram (uBq/kg)
SD1_Pa_231_SPT_CONC_PUMP_hhdaou	One standard deviation of Pa_231_SPT_CONC_PUMP_hhdaou	micro- Becquerel per kilogram (uBq/kg)
Flag_Pa_231_SPT_CONC_PUMP_hhdaou	SeaDataNet quality flag for Pa_231_SPT_CONC_PUMP_hhdaou	unitless
Th_232_LPT_CONC_PUMP_g03dki	Concentration of large particulate Th-232 in seawater collected using a McLane large volume in situ pump	picomoles per kilogram (pmol/kg)
SD1_Th_232_LPT_CONC_PUMP_g03dki	One standard deviation of Th_232_LPT_CONC_PUMP_g03dki	picomoles per kilogram (pmol/kg)
Flag_Th_232_LPT_CONC_PUMP_g03dki	SeaDataNet quality flag for Th_232_LPT_CONC_PUMP_g03dki	unitless
Th_230_LPT_CONC_PUMP_ngh1t4	Concentration of large particulate Th-230 in seawater collected using a McLane large volume in situ pump	micro- Becquerel per kilogram (uBq/kg)

SD1_Th_230_LPT_CONC_PUMP_ngh1t4	One standard deviation of Th_230_LPT_CONC_PUMP_ngh1t4	micro- Becquerel per kilogram (uBq/kg)
Flag_Th_230_LPT_CONC_PUMP_ngh1t4	SeaDataNet quality flag for Th_230_LPT_CONC_PUMP_ngh1t4	unitless
Pa_231_LPT_CONC_PUMP_mpkma1	Concentration of large particulate Th-230 in seawater collected using a McLane large volume in situ pump	micro- Becquerel per kilogram (uBq/kg)
SD1_Pa_231_LPT_CONC_PUMP_mpkma1	One standard deviation of Pa_231_LPT_CONC_PUMP_mpkma1	micro- Becquerel per kilogram (uBq/kg)
Flag_Pa_231_LPT_CONC_PUMP_mpkma1	SeaDataNet quality flag for Pa_231_LPT_CONC_PUMP_mpkma1	unitless
Th_230_SPT_XS_CONC_PUMP	Concentration of large particulate Th-230 in seawater collected using a McLane large volume in situ pump	micro- Becquerel per kilogram (uBq/kg)
SD1_Th_230_SPT_XS_CONC_PUMP	One standard deviation of Th_230_SPT_XS_CONC_PUMP	micro- Becquerel per kilogram (uBq/kg)
Flag_Th_230_SPT_XS_CONC_PUMP	SeaDataNet quality flag for Th_230_SPT_XS_CONC_PUMP	unitless
Pa_231_SPT_XS_CONC_PUMP	Concentration of small particulate excess Pa-231 in seawater collected using a McLane large volume in situ pump (see metadata for full explanation)	micro- Becquerel per kilogram (uBq/kg)
SD1_Pa_231_SPT_XS_CONC_PUMP	One standard deviation of Pa_231_SPT_XS_CONC_PUMP	micro- Becquerel per kilogram (uBq/kg)
Flag_Pa_231_SPT_XS_CONC_PUMP	SeaDataNet quality flag for Pa_231_SPT_XS_CONC_PUMP	unitless
Th_230_LPT_XS_CONC_PUMP	Concentration of large particulate excess Th-230 in seawater collected using a McLane large volume in situ pump (see metadata for full explanation)	micro- Becquerel per kilogram (uBq/kg)
SD1_Th_230_LPT_XS_CONC_PUMP	One standard deviation of Th_230_LPT_XS_CONC_PUMP	micro- Becquerel per kilogram (uBq/kg)
Flag_Th_230_LPT_XS_CONC_PUMP	SeaDataNet quality flag for Th_230_LPT_XS_CONC_PUMP	unitless
1		

Pa_231_LPT_XS_CONC_PUMP	Concentration of large particulate excess Pa-231 in seawater collected using a McLane large volume in situ pump (see metadata for full explanation)	micro- Becquerel per kilogram (uBq/kg)
SD1_Pa_231_LPT_XS_CONC_PUMP	One standard deviation of Pa_231_LPT_XS_CONC_PUMP	micro- Becquerel per kilogram (uBq/kg)
Flag_Pa_231_LPT_XS_CONC_PUMP	SeaDataNet quality flag for Pa_231_LPT_XS_CONC_PUMP	unitless
Th_230_SPT_ADS_CONC_PUMP	Concentration of small particulate adsorbed Th-230 in seawater collected using a McLane large volume in situ pump (see metadata for full explanation)	micro- Becquerel per kilogram (uBq/kg)
SD1_Th_230_SPT_ADS_CONC_PUMP	One standard deviation of Th_230_SPT_ADS_CONC_PUMP	micro- Becquerel per kilogram (uBq/kg)
Flag_Th_230_SPT_ADS_CONC_PUMP	SeaDataNet quality flag for Th_230_SPT_ADS_CONC_PUMP	unitless
Pa_231_SPT_ADS_CONC_PUMP	Concentration of small particulate adsorbed Pa-231 in seawater collected using a McLane large volume in situ pump (see metadata for full explanation)	micro- Becquerel per kilogram (uBq/kg)
SD1_Pa_231_SPT_ADS_CONC_PUMP	One standard deviation of Pa_231_SPT_ADS_CONC_PUMP	micro- Becquerel per kilogram (uBq/kg)
Flag_Pa_231_SPT_ADS_CONC_PUMP	SeaDataNet quality flag for Pa_231_SPT_ADS_CONC_PUMP	unitless
Th_230_LPT_ADS_CONC_PUMP	Concentration of large particulate adsorbed Th-230 in seawater collected using a McLane large volume in situ pump (see metadata for full explanation)	micro- Becquerel per kilogram (uBq/kg)
SD1_Th_230_LPT_ADS_CONC_PUMP	One standard deviation of Th_230_LPT_ADS_CONC_PUMP	micro- Becquerel per kilogram (uBq/kg)
Flag_Th_230_LPT_ADS_CONC_PUMP	SeaDataNet quality flag for Th_230_LPT_ADS_CONC_PUMP	unitless
Pa_231_LPT_ADS_CONC_PUMP	Concentration of large particulate adsorbed Pa-231 in seawater collected using a McLane large volume in situ pump (see metadata for full explanation)	micro- Becquerel per kilogram (uBq/kg)

SD1_Pa_231_LPT_ADS_CONC_PUMP	One standard deviation of Pa_231_LPT_ADS_CONC_PUMP	micro- Becquerel per kilogram (uBq/kg)
Flag_Pa_231_LPT_ADS_CONC_PUMP	SeaDataNet quality flag for Pa_231_LPT_ADS_CONC_PUMP	unitless

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Instruments

Dataset- specific Instrument Name	Dual-flow McLane Research in-situ pumps (WTS-LV)
Generic Instrument Name	McLane Large Volume Pumping System WTS-LV
Dataset- specific Description	The Large Volume Pumping System-WTS-LV can be one of several different models of Water Transfer Systems (WTS) Large Volume (LV) pumping systems designed and manufactured by McLane Research Labs (Falmouth, MA, USA). The Large Volume Water Transfer System (WTS-LV) is a large volume single-event sampler that collects suspended and dissolved particulate samples in situ into a 142mm membrane filter. The WTS-LV allows for a choice of pump size and filter porosity for a range of specimen collection. Collection targets include chlorophyll maximum, particulate trace metals, and phytoplankton.
Generic Instrument Description	The WTS-LV is a Water Transfer System (WTS) Large Volume (LV) pumping instrument designed and manufactured by McLane Research Labs (Falmouth, MA, USA). It is a large-volume, single-event sampler that collects suspended and dissolved particulate samples in situ. Ambient water is drawn through a modular filter holder onto a 142-millimeter (mm) membrane without passing through the pump. The standard two-tier filter holder provides prefiltering and size fractioning. Collection targets include chlorophyll maximum, particulate trace metals, and phytoplankton. It features different flow rates and filter porosity to support a range of specimen collection. Sampling can be programmed to start at a scheduled time or begin with a countdown delay. It also features a dynamic pump speed algorithm that adjusts flow to protect the sample as material accumulates on the filter. Several pump options range from 0.5 to 30 liters per minute, with a max volume of 2,500 to 36,000 liters depending on the pump and battery pack used. The standard model is depth rated to 5,500 meters, with a deeper 7,000-meter option available. The operating temperature is -4 to 35 degrees Celsius. The WTS-LV is available in four different configurations: Standard, Upright, Bore Hole, and Dual Filter Sampler. The high-capacity upright WTS-LV model provides three times the battery life of the standard model. The Bore-Hole WTS-LV is designed to fit through a narrow opening such as a 30-centimeter borehole. The dual filter WTS-LV features two vertical intake 142 mm filter holders to allow simultaneous filtering using two different porosities.

Dataset- specific Instrument Name	Thermo-Finnigan Neptune Multicollector ICP-MS
Generic Instrument Name	Thermo Finnigan Neptune inductively coupled plasma mass spectrometer
Dataset- specific Description	A Thermo-Finnigan Neptune Multicollector ICP-MS, equipped with a high-performance Interface pump (Jet Pump Aridus II [™]), and specially designed sample (Jet) and skimmer (X) cones to ensure the highest possible sensitivity in the Newton Horace Winchell School of Earth and Environmental Sciences at the University of Minnesota was used.
Generic Instrument Description	A laboratory high mass resolution inductively coupled plasma mass spectrometer (ICP-MS) designed for elemental and isotopic analysis. The instrument is based on a multicollector platform, comprising eight moveable collector supports and one fixed center channel equipped with a Faraday cup and, optionally, an ion counter with or without a retardation lens. The Faraday cup is connected to a current amplifier, whose signal is digitized by a high linearity voltage to frequency converter. The instrument was originally manufactured by Thermo Finnigan, which has since been replaced by Thermo Scientific (part of Thermo Fisher Scientific). This model is no longer in production.

Dataset- specific Instrument Name	Thermo-Finnigan ELEMENT XR Single Collector Magnetic Sector ICP-MS
Generic Instrument Name	Thermo Scientific ELEMENT XR high resolution inductively coupled plasma mass spectrometer
Dataset- specific Description	A Thermo-Finnigan ELEMENT XR Single Collector Magnetic Sector ICP-MS, equipped with a high- performance Interface pump (Jet Pump Aridus I [™]), and specially designed sample (Jet) and skimmer (X) cones to ensure the highest possible sensitivity, was used in the ICP-MS Labs at the Lamont-Doherty Earth Observatory of Columbia University and at the University of Southern Mississippi.
Generic Instrument Description	A high-resolution (HR) inductively coupled plasma (ICP) mass spectrometer (MS) composed of a dual mode secondary electron multiplier (SEM) and a Faraday detector. The ELEMENT XR instrument has a dynamic range of 5×10^7 to 1×10^12 counts per second (cps), and allows simultaneous measurement of elements at concentrations over 1000 ug/g.

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Deployments

RR1815	
Website	https://www.bco-dmo.org/deployment/776917
Platform	R/V Roger Revelle
Report	https://datadocs.bco- dmo.org/docs/geotraces/GEOTRACES_PMT/casciotti/data_docs/GP15_Cruise_Report_with_ODF_Report.pdf
Start Date	2018-10-24
End Date	2018-11-24
Description	Additional cruise information is available from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/RR1815

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Project Information

US GEOTRACES Pacific Meridional Transect (GP15) (U.S. GEOTRACES PMT)

A 60-day research cruise took place in 2018 along a transect form Alaska to Tahiti at 152° W. A description of the project titled "*Collaborative Research: Management and implementation of the US GEOTRACES Pacific Meridional Transect*", funded by NSF, is below. Further project information is available on the <u>US GEOTRACES website</u> and on the <u>cruise blog</u>. A detailed <u>cruise report is also available</u> as a PDF.

Description from NSF award abstract:

GEOTRACES is a global effort in the field of Chemical Oceanography in which the United States plays a major role. The goal of the GEOTRACES program is to understand the distributions of many elements and their isotopes in the ocean. Until quite recently, these elements could not be measured at a global scale. Understanding the distributions of these elements and isotopes will increase the understanding of processes that shape their distributions and also the processes that depend on these elements. For example, many "trace elements" (elements that are present in very low amounts) are also important for life, and their presence or absence can play a vital role in the population of marine ecosystems. This project will launch the next major U.S. GEOTRACES expedition in the Pacific Ocean between Alaska and Tahiti. The award made here would support all of the major infrastructure for this expedition, including the research vessel, the sampling equipment, and some of the core oceanographic measurements. This project will also support the personnel needed to lead the expedition and collect the samples.

This project would support the essential sampling operations and infrastructure for the U.S. GEOTRACES Pacific Meridional Transect along 152° W to support a large variety of individual science projects on trace element and isotope (TEI) biogeochemistry that will follow. Thus, the major objectives of this management proposal are: (1) plan and coordinate a 60 day research cruise in 2018; (2) obtain representative samples for a wide variety of TEIs using a conventional CTD/rosette, GEOTRACES Trace Element Sampling Systems, and in situ pumps; (3) acquire conventional CTD hydrographic data along with discrete samples for salinity, dissolved oxygen, algal pigments, and dissolved nutrients at micro- and nanomolar levels; (4) ensure that proper QA/QC protocols are followed and reported, as well as fulfilling all GEOTRACES intercalibration protocols; (5) prepare and deliver all hydrographic data to the GEOTRACES Data Assembly Centre (via the US BCO-DMO data center); and (6) coordinate all cruise communications between investigators, including preparation of a hydrographic report/publication. This project would also provide baseline measurements of TEIs in the Clarion-Clipperton fracture zone (~7.5°N-17°N, ~155°W-115°W) where large-scale deep sea mining is planned. Environmental impact assessments are underway in partnership with the mining industry, but the effect of mining activities on TEIs in the water column is one that could be uniquely assessed by the GEOTRACES community. In support of efforts to communicate the science to a wide audience the investigators will recruit an early career freelance science journalist with interests in marine science and oceanography to participate on the cruise and do public outreach, photography and/or videography, and social media from the ship, as well as to submit articles about the research to national media. The project would also support several graduate students.

Collaborative Research: U.S. GEOTRACES Pacific Meridional Transect: Thorium-232, Thorium-230 and Protactinium-231 as tracers of trace element supply and removal (PMT Thorium Isotopes)

NSF Award Abstract:

The goal of the international GEOTRACES program is to understand the distributions of trace chemical elements and their isotopes in the oceans. Many trace elements are essential for life and their extremely low concentrations in seawater are thought to limit biological productivity (fertility) throughout much of the ocean. This limitation, in turn, partially constrains the level of fisheries that can be supported by marine ecosystems as well as the ocean's capacity to absorb carbon dioxide from the atmosphere. Whereas the importance of these trace-element micronutrients is well established, many basic features of their ocean distribution remain unknown. Measurements of other elements and isotopes can be used to understand the processes that influence the distributions of the micronutrient elements. Two naturally-occurring radioactive isotopes that are particularly important in this regard are thorium-230 and protactinium-231, which have been designated as key parameters to be measured as part of GEOTRACES. This project will focus on the measurement of these two isotopes in order to provide critical information about the processes that supply iron to the Pacific Ocean, as well as the rates of those processes. The project will support an early career investigator, a postdoctoral researcher, and students at the undergraduate and graduate levels.

Samples of seawater and of suspended particulate material will be collected along a north-south transect between Alaska and Tahiti to examine the processes that supply and remove trace elements. These samples will be analyzed for naturally-occurring radionuclides thorium-232, thorium-230 and protactinium-231. Aerosol samples and sediments collected along the transect will be analyzed as well. In collaboration with other investigators involved in the expedition, this project will:

1) Interpret the distributions of thorium-232 and thorium-230 to quantify the supply of iron and other trace elements

delivered by dust as well as the trace elements supplied by chemical reactions in volcanic sediments along the Alaskan margin,

2) Determine the sinking flux of major particulate phases and of particulate trace elements throughout the water column to quantify their rate of removal from the ocean, and

3) Compare the rate of trace element removal among contrasting environmental regimes to be encountered along the Alaska to Tahiti transect to identify the key physical, chemical and biological factors, such as dust supply and biological productivity, that regulate the rate of trace element removal from the ocean.

Note: Additional datasets from cruises PE17-24 and PS1718 were collected as complementary activities to this project and were supported by NSF award OCE-1737023.

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Program Information

U.S. GEOTRACES (U.S. GEOTRACES)

Website: http://www.geotraces.org/

Coverage: Global

GEOTRACES is a <u>SCOR</u> sponsored program; and funding for program infrastructure development is provided by the <u>U.S. National Science Foundation</u>.

GEOTRACES gained momentum following a special symposium, S02: Biogeochemical cycling of trace elements and isotopes in the ocean and applications to constrain contemporary marine processes (GEOSECS II), at a 2003 Goldschmidt meeting convened in Japan. The GEOSECS II acronym referred to the Geochemical Ocean Section Studies To determine full water column distributions of selected trace elements and isotopes, including their concentration, chemical speciation, and physical form, along a sufficient number of sections in each ocean basin to establish the principal relationships between these distributions and with more traditional hydrographic parameters;

* To evaluate the sources, sinks, and internal cycling of these species and thereby characterize more completely the physical, chemical and biological processes regulating their distributions, and the sensitivity of these processes to global change; and

* To understand the processes that control the concentrations of geochemical species used for proxies of the past environment, both in the water column and in the substrates that reflect the water column.

GEOTRACES will be global in scope, consisting of ocean sections complemented by regional process studies. Sections and process studies will combine fieldwork, laboratory experiments and modelling. Beyond realizing the scientific objectives identified above, a natural outcome of this work will be to build a community of marine scientists who understand the processes regulating trace element cycles sufficiently well to exploit this knowledge reliably in future interdisciplinary studies.

Expand "Projects" below for information about and data resulting from individual US GEOTRACES research projects.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-1737023</u>
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-1737224</u>
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-1736677</u>

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