Dissolved Th/Pa measurements from CTD Niskin collected depth profiles from a GEOTRACES transect cruise along the Mid-Atlantic Ridge in the North Atlantic (GA13/JC156)

Website: https://www.bco-dmo.org/dataset/987617
Data Type: Cruise Results
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Contributors	Affiliation	Role
Hayes, Christopher T.	University of Southern Mississippi (USM)	Principal Investigator
Redmond, Neil	University of Southern Mississippi (USM)	Co-Principal Investigator
Rauch, Shannon	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

Abstract
This dataset contains concentrations of dissolved thorium and protactinium isotopes (Th-232, Th-230, Pa-231) in seawater collected during the GEOTRACES transect cruise GA13 (JC156) in winter 2017-2018. Dissolved thorium and protactinum isotopes (Th-232, Th-230, and Pa-231) were analyzed as core parameters on GEOTRACES cruise transect GA13. This cruise transect focused on known hydrothermal venting sites along the mid-Atlantic ridge of the North Atlantic. The Th/Pa isotopes are excellent tracers of inorganic scavenging (chemical adsorption) onto hydrothermal particualte material and help demonstrate the impact particles can have on scavenging other trace metals of biogeochemical interest. A start-up grant from the University of Southern Missisippi funded the analysis at USM. The cruise was funded by the UK NERC.

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Coverage

Location: Mid-Atlantic Ridge
Spatial Extent: **N**:37.842 **E**:-31.521 **S**:25.93 **W**:-45.118
Temporal Extent: 2017-12-29 - 2018-01-27

Methods & Sampling

Sampling Methods at Sea:
The GA13 team followed cookbook methods for sampling from the conventional Niskin rosette. To sample for ^{230}Th, ^{232}Th, and ^{231}Pa, samples were taken from the stainless steel rosette and filtered directly from the niskin bottle through a 0.45 micron AcroPak 500 filter. Tygon tubing was used to attach the filter to the opening of the niskin bottle. The samples were collected into 4-liter (L) cubitainers. These cubitainers were then double bagged into plastic bags. These samples will then be shipped back to the lab, and stored until analysis.

Samples were not acidified at sea, but once returned to the lab in Mississippi, the samples were acidified to a pH < 2 with Optima HCl and left to equilibrate at least 3 months before analysis.

Analytical Methods:
In the on-shore laboratory, seawater samples were weighed to determine sample size, taking into account the

weight of the cubitainer and of the added acid. Then, weighed aliquots of the artificial isotope yield monitors Th-229 (10 picograms (pg)) and Pa-233 (~0.8 pg) and 10 milligrams (mg) dissolved Fe were added to each sample. After allowing 1 day for spike equilibration, the pH of each sample was raised to 8-9 by adding ~10-14 milliliters (mL) of concentrated NH4OH (Fisher Scientific OPTIMA grade) which caused iron (oxy)hydroxide precipitates to form. Each sample cubitainer was fitted with a nozzle cap, inverted, and the Fe precipitate was allowed to settle for 2 days. After 2 days, the nozzle caps were opened and the pH~8-9 water was slowly drained, leaving only the iron oxyhydroxide precipitate and 250-500 mL of water. The Fe precipitate was transferred to centrifuge tubes for centrifugation and rinsing with Milli-Q H2O (>18 MΩ) to remove the major seawater ions. The precipitate was then dissolved in 8M HNO3 (Fisher Scientific OPTIMA grade) and transferred to a Teflon beaker for acid digestions. First the nitric sample solution was dried to near dry at 180-200°C. The sample was then taken up in 1-2 mL 8 M HNO3, the beakers capped and the samples refluxed at 180°C for at least 3 hours. The sample was then cooled, uncapped, retaining all sample drops in the beaker, heated again to 180°C for an HF (Optima) addition of 1 mL. This solution was dried at 180°C to a white precipitate that is dissolvable in optima HCl. After total dissolution of the sample, another precipitation of iron (oxy)hydroxide followed and the precipitate was washed with Milli-Q H2O, centrifuged, and dissolved in 8M HCl (Fisher Scientific OPTIMA grade) for a series of anion-exchange chromatography using 6 mL polypropylene columns each containing a 1 mL bed of Bio-rad resin (AG1-X8, 100-200 mesh size) and a 45 µm porous polyethylene frit (Anderson et al., 2012). The final column elutions were dried down at 180-200°C in the presence of 2 drops of concentrated HNO3 (Fisher Scientific OPTIMA grade) and taken up in 1.0 mL of 0.32 M HNO3 (Fisher Scientific OPTIMA grade) for mass spectrometric analysis. Digestions and columns were done in a standard fume hood, but whenever samples were sealed (i.e., no acid fumes) they were handled in a benchtop HEPA-filtered laminar flow hood.

Concentrations of Th-232, Th-230, and Pa-231 were calculated by isotope dilution, relative to the calibrated tracers Th-229 and Pa-233 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™), but we did utilize the specially designed sample (Jet) and skimmer (X) cones which increased sensitivity. All measurements were made in low resolution mode (Δm/M≈300), peak jumping in Escan mode across the central 5% of the flat-topped peaks. Measurements were made on a MasCom™ SEM; Th-229, Th-230, Pa-231, and Pa-233 were measured in Counting mode, while the Th-232 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 U-238 and U-235 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, U-238 was measured in Analog mode and U-235 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 Th-232 into the minor Th and Pa isotopes was monitored by counting at the half-masses surrounding Th-230 and Pa-231. Tailing corrections were typically small (<0.5% and often negligible).

Water samples were analyzed in batches of 12 to 20 (5 batches total). Procedural blanks were determined by processing 4-5 L of Milli-Q H2O in an acid-cleaned cubitainer acidified to pH ~2 with 6 M HCl (Fisher Scientific OPTIMA grade) as a sample in each batch (n = 10 total procedural blanks). In addition to the procedural blanks, with every batch 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, were added to acidified MQ-H2O and treated like a sample. Samples were corrected using the procedural blank analyzed during within each batch. Procedural blank, limit of detection and the results of the reference material solutions are reported in the Supplemental File "987617_v1_ga13_dissolved_th_pa_LODs.pdf". 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 and we have scaled the limit of detection into the equivalent concentration in a 5 liter sample. Our results for SWS2010-1 are within the consensus range from the intercalibration exercise (Anderson et al., 2012). Consensus values for SWS2015-1 have not been yet been coordinated but they agree with the reports of the LDEO lab. A total of 134 samples were collected. Human error during the beginning of the analysis period caused a certain number of batches/elemental fractions to be lost during column chromatography (in the case of Pa-231) or clearly contaminated (in the case of Th-232/Th-230) and this resulted in 34 Pa-231 samples, 12 Th-232 samples and 2 Th-230 samples to be reported as missing data (flag = 9).

Data Processing Description

Data Processing:
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.

Analysis of all samples was completed over the course of several years. A correction was made to account for the ingrowth of Th-230 and Pa-231 due to the decay of the natural U-234 and U-235 preserved in the acidified samples during the period of time between sample collection and U-Th/Pa separation during anion exchange chromatography. Thus, the reported Th-230 and Pa-231 concentrations have been corrected to represent their concentrations at the time of sampling. U concentrations in the samples were estimated using the bottle salinity (S) measured from the CTD and the U-Salinity relationship in seawater (Owens et al., 2011), [U] = (0.100 * S – 0.326) ng U (g seawater)-1. We used seawater U-isotopic compositions of U-234/U-238 = 1.1468 activity ratio (Andersen et al., 2010), and U-238/U-235 = 137.824 mole ratio (Weyer et al., 2008), to calculate [U-234] and [U-235] respectively based on [U].

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 2015-1 standards. Reproducibility metrics on these standard measurements are reported in the Analytical Methods section.

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.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.

Naming Conventions:
Parameter names in the form such as "Th_232_D_CONC_BOTTLE" are adopted based on a recommendation from the GEOTRACES community (https://www.geotraces.org/parameter-naming-conventions/).

"Dissolved" (D) here refers to that which passed through stacked 0.8/0.45 µm Acropak™ 500 filter capsules sampled from conventional Niskin bottles on a CTD rosette. All seawater samples were weighed directly in the on-shore laboratory to determine sample size, taking into account acid during acidification.

Units of Measurement:
Radionuclide concentrations are given as micro-Becquerel (10e-6 Bq, µBq or micro-Bq) per kilogram water for Th-230 and Pa-231, and picomole (10e-12 mol, pmol) per kilogram water for Th-232. A Becquerel is the SI unit for radioactivity and is defined as 1 disintegration per second. These units are recommended by the GEOTRACES community.

BCO-DMO Processing Description

- Imported original file "JC156_dataTemplate.xlsx" into the BCO-DMO system.
- Flagged "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.
- Removed empty/unused columns.

- Converted date field to YYYY-MM-DD format.
- Saved the final file as "987617_v1_ga13_dissolved_th_pa.csv".
- Extracted the table of blank, LOD, etc. information from the original .docx file and saved as a PDF, "987617_v1_ga13_dissolved_th_pa_LODs.pdf".

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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

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Parameters

Parameter	Description	Units
Station_ID	Station number	unitless
Event_ID	Event number	unitless
Start_Date_UTC	Date at start of sample collection	unitless
Start_Latitude	Latitude at start of sample collection	decimal degrees
Start_Longitude	Longitude at start of sample collection	decimal degrees
Rosette_Position	Rosette position	unitless
Sample_ID	Sample ID number	unitless
Sample_Depth	Sample depth	meters (m)
Pa_231_D_CONC_BOTTLE_h01akr	Concentration (or activity) of dissolved 231Pa	micro-Becquerel per kilogram (uBq/kg)
SD1_Pa_231_D_CONC_BOTTLE_h01akr	Standard deviation of Pa_231_D_CONC_BOTTLE_h01akr	micro-Becquerel per kilogram (uBq/kg)
Flag_Pa_231_D_CONC_BOTTLE_h01akr	Quality flag for Pa_231_D_CONC_BOTTLE_h01akr	unitless

Th_230_D_CONC_BOTTLE_iiujzv	Concentration (or activity) of dissolved 230Th	micro-Becquerel per kilogram (uBq/kg)
SD1_Th_230_D_CONC_BOTTLE_iiujzv	Standard deviation of Th_230_D_CONC_BOTTLE_iiujzv	micro-Becquerel per kilogram (uBq/kg)
Flag_Th_230_D_CONC_BOTTLE_iiujzv	Quality flag for Th_230_D_CONC_BOTTLE_iiujzv	unitless
Th_232_D_CONC_BOTTLE_xpr9pd	Concentration (or activity) of dissolved 232Th	picomole per kilogram (pmol/kg)
SD1_Th_232_D_CONC_BOTTLE_xpr9pd	Standard deviation of Th_232_D_CONC_BOTTLE_xpr9pd	picomole per kilogram (pmol/kg)
Flag_Th_232_D_CONC_BOTTLE_xpr9pd	Quality flag for Th_232_D_CONC_BOTTLE_xpr9pd	unitless

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Instruments

Dataset-specific Instrument Name	centrifuge
Generic Instrument Name	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	conventional Niskin rosette
Generic Instrument Name	Niskin bottle
Generic Instrument Description	A Niskin bottle (a next generation water sampler based on the Nansen bottle) is a cylindrical, non-metallic water collection device with stoppers at both ends. The bottles can be attached individually on a hydrowire or deployed in 12, 24, or 36 bottle Rosette systems mounted on a frame and combined with a CTD. Niskin bottles are used to collect discrete water samples for a range of measurements including pigments, nutrients, plankton, etc.

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	Analyses were carried out on a Thermo-Finnigan ELEMENT XR Single Collector Magnetic Sector ICP-MS. This instrument lacks the high-performance Interface pump (Jet Pump Aridus I™), but we did utilize the specially designed sample (Jet) and skimmer (X) cones, which increased sensitivity.
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 x 10^7 to 1 x 10^12 counts per second (cps), and allows simultaneous measurement of elements at concentrations over 1000 ug/g.

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Deployments

JC156

Website	https://www.bco-dmo.org/deployment/923071
Platform	RRS James Cook
Report	https://www.bodc.ac.uk/resources/inventories/cruise_inventory/reports/jc156.pdf
Start Date	2017-12-20
End Date	2018-02-01
Description	See more about this cruise at: https://www.bodc.ac.uk/resources/inventories/cruise_inventory/report/16349/

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