Activities of size-fractionated particulate thorium isotopes and total Thorium-234 from the U.S. GEOTRACES Arctic cruise, HLY1502, on USCGC Healy from August to October 2015

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Project
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» Collaborative Research: GEOTRACES Arctic Section: Radium and Thorium Isotopes as Natural Geochemical Tracers in the Arctic Ocean (Arctic GEOTRACES Ra Th)

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Contributors	Affiliation	Role
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Abstract
This dataset contains activities of size-fractionated particulate thorium isotopes and total Thorium-234 from the U.S. GEOTRACES Arctic cruise, HLY1502 (GN01), on USCGC Healy from August to October 2015.

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Coverage

Spatial Extent: **N**:89.997 **E**:180 **S**:60.178 **W**:-180
Temporal Extent: 2015-08-12 - 2015-10-08

Dataset Description

This dataset contains activities of size-fractionated particulate thorium isotopes and total Thorium-234 from the U.S. GEOTRACES Arctic cruise, HLY1502 (GN01), on USCGC Healy from August to October 2015. Please contact Erin Black (University of Rochester) prior to reuse.

Methods & Sampling

Sampling and analytical procedures:

The sampling methodology followed the GEOTRACES cookbook guidelines. Large and small particle particulates were collected using dual-filter head in situ McLane pumping systems (also see Lam datasets from HLY1502 for additional pumping system details). Generally, shallow total Th-234 samples (<1000 m) were collected from Niskins on the ODF Rosette and deep total Th-234 samples (>1000 m) were collected from Niskin bottles hung above the in situ pumps. However, on occasions where pump associated Niskins did not close prior to recovery, the ODF Rosette was used to obtain deep water for total Th-234. The following sampling methods used on HLY1502 for total and particulate Th-234 followed closely those detailed in Black et al., 2018. Where cruise-specific differences exist, they have been noted here.

Total Thorium-234 (Bottle, Pump, Sub-ice Pump, UW) Sampling:

Total Th-234 samples were taken at 31 of the 66 stations occupied on the HLY1502 campaign. Typically, these samples came from single Niskin bottles attached to a wire (i.e. above the McLane pumps) or Niskins in the standard ODF rosette configuration These totals are listed under 'Th_234_T_CONC_BOTTLE. At shallow shelf and near-slope stations (2, 3, 6, 10, 60, 61, 66), total Th-234 samples were taken at only 4 to 12 discrete depths, typically using the ODF rosette. The Pacific endmember Station 1 similarly had a single ODF cast for total Th-234 with 12 depths. A single sample was also taken at this location from the ship's underway system (0.5 m). At most of the deeper basin stations (14, 19, 26, 30, 32/34, 38, 43, 46, 48, 52, 56, and 57), the full water column was sampled with either 2 casts (1 ODF and 1 Niskin above pumps, 20 depths total) or 3 casts (1 ODF and 2 Niskin above pumps, 28 depths total).

For better resolution within the marginal ice zone and areas with permanent ice cover, total Th-234 samples were taken from the ODF rosette and 'Th_234_T_CONC_PUMP' or 'Th_234_T_CONC_SUBICE_PUMP' samples were taken using the Be-7 submersible pumping system. In the marginal ice zone on the northern transect (stations 7, 8, 9, 12, 17), additional samples at 1-2 depths were taken using the submersible pumping system (See the Be-7 report by Kadko group for more details). On the southbound transect, marginal ice zone samples came from 4 depths at stations 51, 53, 54 using the ODF rosette. For under-ice samples, a hole was made using a gas-powered ice auger and the submersible pump was lowered into the hole. Samples were taken at three discrete depths at ice stations 31 and 33. Note that the beryllium pump samples were not given GEOTRACES numbers and this field in the datasheet has 'NaN'.

At each discrete depth, ~4 L of water was taken from the corresponding Niskin bottle or pump tubing after rinsing the sample bottle three times. The 4L sample bottles were mass-volume calibrated prior to the cruise and were filled to the marked calibration line.

Particulate Thorium-234 and Thorium-228 (SPT and LPT) Sampling:

Size-fractionated particulate Th-234 and Th-228 samples were taken at 20 of the 66 stations occupied using high-volume McLane pumps. The filter heads each contained a 51 µm pore size pre-filter followed by either a Supor filter or a pre-combusted and acid-leached QMA filter with a nominal pore size of 1 µm. Filter heads were pumped down and removed from the filter heads in the designated trace metal clean 'bubble' space by the Lam group (see particulate trace metal dataset information from Lam group). The filters were placed in plastic 142 mm petri dishes and brought to the short-lived radionuclide van (Café Thorium) for processing. The material on the 51 µm pre-filter from the Supor filter head was rinsed onto silver (Ag) filters using 0.1 µm filtered seawater and dried. The 142 mm QMA filter was oven dried and subsampled with a 25 mm punch for Th-234 analysis. The remainder of the 142 mm filter was sealed with tape and stored for Th-228 counting months later. The average sample volume through the 51 µm pre-filter was 402 L and for the area of the QMA subsample was 34 L. The average sample volume through the area of the entire 142 mm QMA was 871 L. These volume averages only include samples flagged as (2) or (3), and not (4) or (9). See data flags section for further information.

Total Thorium-234 General Analytical Procedures:

Th-234 was determined by the widely-adopted 4 L method (Buesseler et al., 2001), which has been utilized previously for other GEOTRACES efforts (e.g. Owens et al., 2015 and Black et al., 2018). An exact 1 mL aliquot of Th-230 (50.39 dpm per g) was used as the yield monitor and added during initial acidification of the samples. QMAs (25 mm) were used to collect the precipitate from the 4L process and immediately dried. Once dried, they were mounted onto plastic 25 mm discs, covered with a mylar layer and 2 layers of aluminum foil, and immediately beta counted at sea. The filters were counted again 5 to 6 months later to quantify the background radioactivity due to the beta decay of long-lived natural radionuclides that are also precipitated. The mean value of the at-sea counts (decay-corrected to the time of collection) minus the background value for each filter is reported as the Th-234 activity (mBq per kg). Activities for Th-234 are generally reported in dpm per L, but have been converted here using a standard density of 1.025 kg per L and 1 dpm = 16.667

mBq. Data are decay corrected to the mid-point time between when bottles 1 and 12 were fired for shallow ODF casts and when the messenger was dropped for deep pumping casts.

To determine Th-234 activity deficits, U-238 (its parent isotope) activities were calculated using a standard uranium-salinity relationship (Owens et al., 2011). Salinities measured on this campaign ranged from 24.4 to 35.1 and calculated U-238 activities from 1.60 dpm per L to 2.44 dpm per L. While this salinity range is rather large compared to those found on previous GEOTRACES campaigns in the Pacific and Atlantic, Not et al. (2012) showed that the relationship held for sea ice, sea ice brine, and subsurface water samples from the Arctic ranging in salinity from ~0 to 135. The efficiency of the beta detectors was determined by minimizing the Th-234 deviation from U-238 for samples collected from regions of the water column where Th-234 and U-238 are expected to be at equilibrium. These included depths below 1000 m and above 400 m off the seafloor that were not near the coastal shelf. For these sample depths (n= 42) the mean derived U-238 activity and standard deviation (s.d.) were 2.431 ± 0.002 dpm per L, a value well within observed natural ranges (Owens et al., 2011).

The reported Th-234 activities were corrected for the chemical recovery efficiency of the 234Th-Mn precipitate method. To determine the percent recovery of the added Th-230 tracer, the method detailed in Pike et al. (2005) was followed without the initial ion exchange column chemistry steps. Filters were leached in a nitric acid-hydrogen peroxide solution and 2 g of a Th-229 yield monitor (activity of either 68.87 dpm per g or 76.27 dpm per g) was added. Samples were then sonicated for 20 min, allowed to stand covered overnight, diluted, and prepared for analysis by ICP-MS. The mean chemical recovery for all reported values was 88.7% and the median recovery was 92%.

Particulate Thorium-234 and Thorium-228 General Analytical Procedures:
Once the silver filters and the 25 mm QMA subsamples were dried, they were mounted onto plastic 25 mm discs, covered with a mylar layer and 2 layers of aluminum foil, and immediately beta counted at sea. They were counted again 5 to 6 months later at the Buesseler beta counting facility at Woods Hole Oceanographic Institution. All data were decay corrected back to the mid-pumping times.

The basic analytical methodology for small particle Th-228 (142 mm QMA filters) has been detailed in Maiti et al. (2014). This method was adapted to measure Th-228 on large particle Ag filters (25 mm) by Dr. Black and the members of the Buesseler and Charette labs at Woods Hole Oceanographic Institution. Details of the measurement chamber construction and the calibration of the Radium Delayed Coincidence Counters can be found in the appendices of Black (2017). The RaDeCC is an alpha scintillation counter that distinguishes decay events of short-lived radium daughter products based on their contrasting half-lives. This system was pioneered by Giffin et al. (1963) and adapted for radium measurements by Moore and Arnold (1996). The RaDeCC method was chosen here because it is well suited for sequential measurements that involve Th-228 as an intermediate (e.g. Th-234, Th-228, particulate carbon), as there is no sample loss or chemical interaction. Large particle samples (Ag filters) were used for Th-234 beta counting at-sea and in the lab 5-6 months later. They were then demounted, weighed, and placed into a 25-mm chamber for use with the RaDeCC systems. The 142 mm QMA filters were removed from the petri storage dishes and individually counted in larger chambers made for the RaDeCC systems. All particulate samples were counted for an average of 23 hours. After measurement of the 25 mm Ag filters, masses were recorded again to ensure than any mass loss could be monitored (although no significant mass loss was found).

Blanks, uncertainties, internal consistency, and detection limits:
Particulate and total Thorium-234:
Thirty-three blank particulate samples (dipped blanks) were collected for each particle size using extra filter heads deployed with the McLane pumps, but without a connection to the pumping systems. On ship, blank QMA filters averaged, in counts per minute, 0.33 cpm ± 0.05 (s.d.) and after 5 to 6 months the background count average was 0.29 cpm ± 0.04. The on-ship cpm values were within 1 s.d. of the final cpm values, typical 'empty' detector cpm (see below), and cpm for non-dipped blank filters (i.e. unused QMA filters for total and small particle analysis and unused Ag filters for large particle analysis)

There was a minute difference between the Ag filter blanks when first measured on-ship (0.30 cpm ± 0.04) and after 5 to 6 months (0.25 cpm ± 0.03), however, no correction was made to the data. These blank averages fall about the average for empty detectors (i.e. the detectors are run with no samples inside for a period of 24-48 hours). The average and s.d. of the empty detectors just prior to the running of any samples on this campaign were 0.28 cpm ± 0.04, which is indistinguishable from the initial blank filter measurement average. Furthermore, there has been no evidence of significant addition (e.g. sorption) of Th-234 to the blank Ag filters on previous GEOTRACES campaigns and a 'blank' value of 0.05 cpm is only 1% of the average (3.7 cpm) and 2% of the median (2.1 cpm) for the sample Ag filters. Only 10 Ag sample filters had cpm less than 0.5 (potential blank adjustment = 10%). Our uncertainties, which are discussed more in the next section, are set at a minimum of 5% even when propagated counting uncertainties are lower. While we don't think the data supports a significant Ag filter blank, a slight increase in the cpm would be within our assumed uncertainties for almost all of the samples.

Limits of detection are not reported because they are not applicable to the Th-234 beta counting method and for total Th-234, specifically, there is never an instance where the 4L volume results in a shipboard sample activity that is anywhere close to the limits of the detectors or a ‘blank’ or unused QMA value. A 'non-detect' for Th-234 or a case where there is no Th-234 present (initially or after 6 months of decay) will still result in a measurable amount of background radioactivity due to the beta decay of long lived natural radionuclides that are also collected on the pump filters. These background values are utilized and therefore, they are not reported as a non-detection of Th-234. The net cpm for total and particulate Th-234 samples here was always higher than 0.05 cpm and in almost all cases was well above this value. Only 4 particulate samples had net cpm between 0.06 cpm and 0.2 cpm. See the previous data flag explanation for our sample volume limits (i.e. the pump volume below which the data are likely unreliable and unrepresentative).

Five 'low-level' uranium standards, with activities close to those measured for total and particulate samples, and five 'high-level' standards ranging from 238 dpm to 365 dpm were run on the RISØ detectors to confirm correct operation and to determine detector to detector variability. These uranium standards have been used for all GEOTRACES cruises performed by the Buesseler lab. These standards were run at the beginning and end of this cruise, as well as periodically during the cruise when sample demands were lower. Analysis of the lower activity uranium standard data suggested that a minimum 5% detector uncertainty should be used. Since the counting uncertainty for total Th-234 samples was always below 5% (square root of the number of counts), the uncertainty on each total Th-234 measurement was set at 5%. Some of the particulate Th-234 samples with relatively low activities had counting uncertainties above 5% and in these cases the counting uncertainty was used as the final measurement uncertainty.

Counting uncertainty is generally the largest source of uncertainty so whenever possible samples were counted until errors were below 5%. For the low-volume (i.e. 4L) total Th-234 samples, all filters were beta counted twice for a minimum of 12 h at sea. As long as the calculated gross counts per minute from these 2 measurements were within 10%, they were averaged for the at-sea Th-234 value. Instances where the replicates were different by more than 10% were individually evaluated (i.e. the raw counting data) and re-counted as needed. The few instances where the 10% difference was noticed occurred where the activities were lowest and the Th-234 deficits relative to U-238 activities the largest (i.e. over the Arctic shelves). Depths were sometimes occupied twice on different casts at the same station, such as with Station 30 (see crossover evaluation). The 225 m depth was sampled in this way and the independent replicates (i.e. two separate bottles at two separate times) are well within uncertainties (see blue dots in 3-paneled figure in Question 7). Good agreement and consistency between overlapping depths on subsequent casts at a given station were found.

In addition, to assess 'within bottle' variability and replication, we took 4, 4L samples from a Niskin bottle deployed at 2019 m at station 48. The average value was 38.4 mBq per kg (2.36 dpm per L) with a standard deviation of 1.3 (0.08) and RSD of 3.4%. A single salinity sample was taken from this bottle, but we recommend taking 4 in the future for comparison, each one after a 4L sample is taken.

Particulate Thorium-228:
For the small particle QMA filters (142 mm), 34 blanks were assessed and for the large particle Ag filters (25 mm), 30 blanks were assessed. Most of these were dipped blanks collected for each particle size using extra filter heads deployed with the McLane pumps, but without a connection to the pumping systems. A few failed pumping effort filters were also counted and assessed (volume < 2 L). Unlike with the shorter-lived Th-234 measurements, which are not generally volume- or activity-limited when counted and which are measured multiple times (subtracting out the influence of the filter itself), Th-228 particulate sample counts per minute (cpm) often drop to cpm similar to those from dipped blanks. We therefore assess the ‘below detection limit’ designation (flag 6) with respect to the cpm of the corrected Rn-220 (Th-228 daughter) RaDeCC measurement for samples and blanks.

Blank QMA counts averaged 0.012 cpm ± 0.007 cpm (1 standard deviation) and blank Ag filter counts averaged 0.009 cpm ± 0.004 cpm. Empty chambers produced similar results (e.g. the 25 mm chambers for Ag filters averaged 0.008 cpm ± 0.005 cpm), suggesting sorption of Th-228 was not a significant issue. We have blank-corrected all of the measurements reported here to account for the influence of the blank filter cpm on the (usually) single RaDeCC measurements. If the blank-corrected sample cpm (initial cpm – blank average) was within the blank standard deviation of zero cpm, the sample was flagged as (6), non-detect. The resulting sample activities were reported here to show that a sample measurement was made, however, the results are negative and should not be used. If the blank-corrected sample cpm was more than the blank standard deviation from zero cpm, the sample activity was reported as (2) or (3). The (3) flag designation is explained above.

Three internal fiber cartridge standards were measured bi-weekly during the time when the large and small particle filters were measured in the counting facility at Woods Hole Oceanographic Institution. The standards were counted on all detectors and used to monitor any potential changes in detector efficiency.

As a part of the calibration process and method development, 8 large particle Th-228 samples were measured at least once on every detector. A few of these samples were measured 3-4 times on a single detector over a few months. These 8 samples were then digested and processed with anion exchange columns to prepare them for traditional alpha spectrometry measurements in the Buesseler lab at Woods Hole Oceanographic. The results from the RaDeCC and traditional counting methods were compared and detector-to-detector consistency (replicability) was assessed.

Since this is a new method, there no certified reference materials for particulate Th-228. However, details can be found in the Charette dataset for HLY1502 radium analyses on how samples of Ra-228, the parent of Th-228, have been intercalibrated using the same instrumentation (RaDeCCs).

Intercalibration and Crossovers: For more on intercalibration and stations, refer to the two attached Intercalibration Reports, under "Supplemental Files".

Data Processing Description

Data processing: Excel and Matlab were used for basic calculations

Quality flags and missing data identifiers:
When there was no sample planned or taken (e.g. there are no subice samples for station 1 where there was no ice), we have put in a 'nd' as a placeholder. The only other time 'nd' is used is when a (9) flag is in the Flag column to indicate that there is missing or non-reportable data. All other data is reported as is with their appropriate flag, even if the numbers are below detection limits, flagged (6) and negative. This indicates that a sample was taken, but the below detection value should not be used.

The data flags used follow SeaDataNet as suggested at www.geotraces.org/geotraces-quality-flag-policy/. Most values were flagged as 'probably good' (2), per the suggestion on this website. The (1) flag was not used at all. The missing values (9) flag most commonly resulted from a successful deployment of sampling equipment followed by pump failures (i.e. head not connected to the pump or pumps only functioning for a short period and pumping a low volume) or Niskin failures (i.e. non-closure of bottles with messenger deployment).

Particulate Th-234 and Th-228 samples flagged with (9) had such low pumping volumes (e.g. 0.1 L) that a Th-234 or Th-228 value was not reportable and in many cases, the sample value was indistinguishable from a dipped blank. Particulate samples that had a reportable value with a pumping volume of $\leq$20 L were automatically flagged as a bad value (4). Particulate samples that had a reportable value with a pumping volume between 20 L and 40 L were evaluated on a sample by sample basis as (3) or (4). Probably bad values (3) corresponded to samples that still fit oceanographic trends and were consistent with the values from depths above and below. Bad values were obviously erroneous (i.e. extremely high or low). There were three particulate Th-234 samples that had pumping volumes >40 L (i.e. 43.6 L, 50.2 L, and 1050 L), but the data was obviously erroneous and flagged as (4). The two deepest particulate samples from Station 43, where it is though the pump(s) hit the ocean floor, were flagged as (3) for both Th isotopes.

Two total Th-234 samples that were flagged with (9) indicate that niskin bottles had not tripped and closed (i.e. no water available for sampling). Four samples that had a yield monitor (230Th added in primary processing step) recovery of less than 40% were flagged as (3), because with these lower yields the results are less reliable. However, we note that the flagged (3) total Th-234 results looked oceanographically consistent. There was a failure of the autopipette at station 34 during the dispensing of the yield monitor. As a result, the average recovery for the surrounding stations at the same depth range was used for these 8 samples and the recovery uncertainty (usually 5% or less) was increased to 10%. These data were kept as (2) because the results were oceanographically consistent. With the short-lived nature of Th-234, it is often difficult to evaluate whether something is a 'probably bad' value when there is a slight increase or decrease of total Th-234 at a single depth, but there is no issue with the sample processing, yield monitor recovery, or replicate analysis. For instance, at station 38 depth ~1668 m there is a rather low value compared to the surrounding water column (14% difference). We have kept these values as (2) because there is no indication besides this difference that suggests this is anything but a good value. The difference is likely real, and we do not expect that the Th-234 profiles will look as smooth as the more conservative parent U-238. Those using this data should note that all abnormal deviations from the surrounding data points were meticulously checked for any possible errors/issues from collection through reporting here. There was once instance at station 43 where a surface value was flagged as (3) because it was almost half the value of the surrounding datapoints. Surface values at the ice-covered stations, like this one, were consistently at equilibrium with parent U-238 and the lone decrease at 75 m at this station seemed suspect.

BCO-DMO Processing:
- replaced 'NaN' with 'nd' as missing data identifier;
- renamed fields to conform with BCO-DMO naming conventions;
- added date/time fields in ISO8601 format;
- 2020-10-12: made corrections to Sample_ID numbers in Event_ID 6234.

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Data Files

File
Th234_Th228.csv (Comma Separated Values (.csv), 90.33 KB) MD5:a9ece893e9b462a3a2c5f5be78935495 Primary data file for dataset ID 814857

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Supplemental Files

File
Th-228 SPT, LPT GEOTRACES HLY1502 Intercalibration Report filename: 0000-0001-7362-8796-HLY1502-multiple-param-intercal-report_228Th.pdf (Portable Document Format (.pdf), 514.26 KB) MD5:8a4a30a1217a8a7ea5646d76cb91ef17 GEOTRACES Intercalibration Report for parameters reported by Ken Buesseler (WHOI) from the HLY1502 (GN01; GEOTRACES Arctic) cruise. Parameters reported: Th_228_SPT_CONC_PUMP::efscqw, Th_228_LPT_CONC_PUMP::civqb1 uBq/kg.
Th-234 Total, SPT, LPT GEOTRACES HLY1502 Intercalibration Report filename: 0000-0001-7362-8796-HLY1502-multiple-param-intercal-report_234Th.pdf (Portable Document Format (.pdf), 370.80 KB) MD5:61702888cdd430c83b7baf9faa36b403 GEOTRACES Intercalibration Report for parameters reported by Ken Buesseler (WHOI) from the HLY1502 (GN01; GEOTRACES Arctic) cruise. Parameters reported: Th_234_T_CONC_SUBICE_PUMP::vakpla, Th_234_T_CONC_PUMP::t8ngm8, Th_234_T_CONC_BOTTLE::uap32e, Th_234_T_CONC_UWAY::eta8ui, Th_234_SPT_CONC_PUMP::bxe0xx, Th_234_LPT_CONC_PUMP::qbhjxe mBq/kg.

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Related Publications

Black, E. E., Buesseler, K. O., Pike, S. M., & Lam, P. J. (2018). 234Th as a tracer of particulate export and remineralization in the southeastern tropical Pacific. Marine Chemistry, 201, 35–50. doi:10.1016/j.marchem.2017.06.009
Methods

Buesseler, K. O., Benitez-Nelson, C., Rutgers van der Loeff, M., Andrews, J., Ball, L., Crossin, G., & Charette, M. A. (2001). An intercomparison of small- and large-volume techniques for thorium-234 in seawater. Marine Chemistry, 74(1), 15–28. doi:10.1016/s0304-4203(00)00092-x https://doi.org/10.1016/S0304-4203(00)00092-X
Methods

Charette, M. A., Dulaiova, H., Gonneea, M. E., Henderson, P. B., Moore, W. S., Scholten, J. C., & Pham, M. K. (2012). GEOTRACES radium isotopes interlaboratory comparison experiment. Limnology and Oceanography: Methods, 10(6), 451–463. doi:10.4319/lom.2012.10.451
Results

Giffin, C., Kaufman, A., & Broecker, W. (1963). Delayed coincidence counter for the assay of actinon and thoron. Journal of Geophysical Research, 68(6), 1749–1757. doi:10.1029/jz068i006p01749

https://doi.org/10.1029/JZ068i006p01749
Methods

Maiti, K., Buesseler, K. O., Pike, S. M., Benitez-Nelson, C., Cai, P., Chen, W., … Xu, C. (2012). Intercalibration studies of short-lived thorium-234 in the water column and marine particles. Limnology and Oceanography: Methods, 10(9), 631–644. doi:10.4319/lom.2012.10.631
Results

Maiti, K., Charette, M. A., Buesseler, K. O., Zhou, K., Henderson, P., Moore, W. S., … Kipp, L. (2015). Determination of particulate and dissolved 228Th in seawater using a delayed coincidence counter. Marine Chemistry, 177, 196–202. doi:10.1016/j.marchem.2014.12.001
Methods

Moore, W. S., & Arnold, R. (1996). Measurement of 223Ra and224Ra in coastal waters using a delayed coincidence counter. Journal of Geophysical Research: Oceans, 101(C1), 1321–1329. doi:10.1029/95jc03139 https://doi.org/10.1029/95JC03139
Methods

Not, C., Brown, K., Ghaleb, B., & Hillaire-Marcel, C. (2012). Conservative behavior of uranium vs. salinity in Arctic sea ice and brine. Marine Chemistry, 130-131, 33–39. doi:10.1016/j.marchem.2011.12.005
Related Research

Owens, S. A., Buesseler, K. O., & Sims, K. W. W. (2011). Re-evaluating the 238U-salinity relationship in seawater: Implications for the 238U–234Th disequilibrium method. Marine Chemistry, 127(1-4), 31–39. doi:10.1016/j.marchem.2011.07.005
Methods

Owens, S. A., Pike, S., & Buesseler, K. O. (2015). Thorium-234 as a tracer of particle dynamics and upper ocean export in the Atlantic Ocean. Deep Sea Research Part II: Topical Studies in Oceanography, 116, 42–59. doi:10.1016/j.dsr2.2014.11.010
Related Research

Pike, S. M., Buesseler, K. O., Andrews, J., & Savoye, N. (2005). Quantification of 234Th recovery in small volume sea water samples by inductively coupled plasma-mass spectrometry. Journal of Radioanalytical and Nuclear Chemistry, 263(2), 355–360. doi:10.1007/s10967-005-0062-9 https://doi.org/10.1007/s10967-005-0594-z
Methods

Rutgers van der Loeff, M., Kipp, L., Charette, M. A., Moore, W. S., Black, E., Stimac, I., … Rember, R. (2018). Radium Isotopes Across the Arctic Ocean Show Time Scales of Water Mass Ventilation and Increasing Shelf Inputs. Journal of Geophysical Research: Oceans, 123(7), 4853–4873. doi:10.1029/2018jc013888 https://doi.org/10.1029/2018JC013888
Results

Tesán Onrubia, J. A., Petrova, M. V., Puigcorbé, V., Black, E. E., Valk, O., Dufour, A., … Heimbürger-Boavida, L.-E. (2020). Mercury Export Flux in the Arctic Ocean Estimated from 234Th/238U Disequilibria. ACS Earth and Space Chemistry, 4(5), 795–801. doi:10.1021/acsearthspacechem.0c00055
Results

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Parameters

Parameter	Description	Units
Station_ID	GEOTRACES station number	None
Start_Date_UTC	All starting dates were recorded; format: DD/MM/YYYY (UTC)	None
Start_Time_UTC	All starting times were recorded; format: hh:mm (UTC)	None
Start_ISO_DateTime_UTC	Starting date and time (UTC) formatted to ISO8601 standard: YYYY-MM-DDThh:mmZ	None
End_Date_UTC	Some ending dates were recorded; format: DD/MM/YYYY (UTC)	None

End_Time_UTC	Some ending times were recorded; format: hh:mm (UTC)	None
End_ISO_DateTime_UTC	Ending date and time (UTC) formatted to ISO8601 standard: YYYY-MM-DDThh:mmZ	None
Start_Latitude	All starting latitudes were recorded	decimal degrees North
Start_Longitude	All starting longitudes were recorded	decimal degrees East
End_Latitude	No ending latitudes were recorded	decimal degrees North
End_Longitude	No ending longitudes were recorded	decimal degrees East
Event_ID	GEOTRACES event number	None
Sample_ID	GEOTRACES sample number	None
Sample_Depth	Sampling depth	meters (m)
Th_234_T_CONC_BOTTLE_uap32e	Activity of total thorium-234 from ODF rosette Niskins or above-McLane pump Niskins	mBq/kg
SD1_Th_234_T_CONC_BOTTLE_uap32e	Uncertainty of Th_234_T_CONC_BOTTLE_uap32e. Derived from counting statistics and error propagation for mass/volume measurements and ICP-MS recovery analysis. See report for additional details.	mBq/kg
Flag_Th_234_T_CONC_BOTTLE_uap32e	Data quality flag for Th_234_T_CONC_BOTTLE_uap32e. (2) probably good, (3) probably bad, (4) bad, (6) below detection, (9) missing data	None
Th_234_LPT_CONC_PUMP_qbhjxe	Activity of large particle (>51 µm) thorium-234 from high volume McLane pumping	mBq/kg
SD1_Th_234_LPT_CONC_PUMP_qbhjxe	Uncertainty of Th_234_LPT_CONC_PUMP_qbhjxe. Derived from counting statistics and error propagation for sample processing.	mBq/kg
Flag_Th_234_LPT_CONC_PUMP_qbhjxe	Data quality flag for Th_234_LPT_CONC_PUMP_qbhjxe: (2) probably good, (3) probably bad, (4) bad, (6) below detection, (9) missing data	None
Th_234_SPT_CONC_PUMP_bxe0xx	Activity of small particle (1-51 µm) thorium-234 from high volume McLane pumping	mBq/kg
SD1_Th_234_SPT_CONC_PUMP_bxe0xx	Uncertainty of Th_234_SPT_CONC_PUMP_bxe0xx. Derived from counting statistics and error propagation for sample processing.	mBq/kg
Flag_Th_234_SPT_CONC_PUMP_bxe0xx	Data quality flag for Th_234_SPT_CONC_PUMP_bxe0xx: (2) probably good, (3) probably bad, (4) bad, (6) below detection, (9) missing data	None
Th_234_T_CONC_SUBICE_PUMP_vakpla	Activity of total thorium-234 from the Beryllium-7 submersible pumping system under ice	mBq/kg

SD1_Th_234_T_CONC_SUBICE_PUMP_vakpla	Uncertainty of Th_234_T_CONC_SUBICE_PUMP_vakpla. Derived from counting statistics and error propagation for mass/volume measurements and ICP-MS recovery analysis. See report for additional details.	mBq/kg
Flag_Th_234_T_CONC_SUBICE_PUMP_vakpla	Data quality flag for Th_234_T_CONC_SUBICE_PUMP_vakpla: (2) probably good, (3) probably bad, (4) bad, (6) below detection, (9) missing data	None
Th_228_LPT_CONC_PUMP_civqb1	Activity of large particle (>51 µm) thorium-228 from high volume McLane pumping	uBq/kg
SD1_Th_228_LPT_CONC_PUMP_civqb1	Uncertainty of Th_228_LPT_CONC_PUMP_civqb1. Derived from counting statistics and error propagation for sample processing.	uBq/kg
Flag_Th_228_LPT_CONC_PUMP_civqb1	Data quality flag for Th_228_LPT_CONC_PUMP_civqb1: (2) probably good, (3) probably bad, (4) bad, (6) below detection, (9) missing data	None
Th_228_SPT_CONC_PUMP_efscqw	Activity of small particle (1-51 µm) thorium-228 from high volume McLane pumping	uBq/kg
SD1_Th_228_SPT_CONC_PUMP_efscqw	Uncertainty of Th_228_SPT_CONC_PUMP_efscqw. Derived from counting statistics and error propagation for sample processing.	uBq/kg
Flag_Th_228_SPT_CONC_PUMP_efscqw	Data quality flag for Th_228_SPT_CONC_PUMP_efscqw: (2) probably good, (3) probably bad, (4) bad, (6) below detection, (9) missing data	None
Th_234_T_CONC_PUMP_t8ngm8	Activity of total thorium-234 from the Beryllium-7 submersible pumping system. Note units of measurement are mBq/kg (changed from µBq/kg to keep consistent with other thorium-234 parameters).	mBq/kg
SD1_Th_234_T_CONC_PUMP_t8ngm8	Uncertainty of Th_234_T_CONC_PUMP_t8ngm8. Derived from counting statistics and error propagation for mass/volume measurements and ICP-MS recovery analysis. See report for additional details. Note units of measurement are mBq/kg (changed from µBq/kg to keep consistent with other thorium-234 parameters).	mBq/kg
Flag_Th_234_T_CONC_PUMP_t8ngm8	Data quality flag for Th_234_T_CONC_PUMP_t8ngm8: (2) probably good, (3) probably bad, (4) bad, (6) below detection, (9) missing data	None
Th_234_T_CONC_UWAY_eta8ui	Activity of total thorium-234 from the ship's underway system. Note units of measurement are mBq/kg (changed from µBq/kg to keep consistent with other thorium-234 parameters).	mBq/kg
SD1_Th_234_T_CONC_UWAY_eta8ui	Uncertainty of Th_234_T_CONC_UWAY_eta8ui. Derived from counting statistics and error propagation for mass/volume measurements and ICP-MS recovery analysis. See report for additional details. Note units of measurement are mBq/kg (changed from µBq/kg to keep consistent with other thorium-234 parameters).	mBq/kg
Flag_Th_234_T_CONC_UWAY_eta8ui	Data quality flag for Th_234_T_CONC_UWAY_eta8ui: (2) probably good, (3) probably bad, (4) bad, (6) below detection, (9) missing data	None

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Instruments

Dataset-specific Instrument Name	McLane pumping systems
Generic Instrument Name	McLane Pump
Dataset-specific Description	Large and small particle particulates were collected using dual-filter head in situ McLane pumping systems.
Generic Instrument Description	McLane pumps sample large volumes of seawater at depth. They are attached to a wire and lowered to different depths in the ocean. As the water is pumped through the filter, particles suspended in the ocean are collected on the filters. The pumps are then retrieved and the contents of the filters are analyzed in a lab.

Dataset-specific Instrument Name	Niskin bottle
Generic Instrument Name	Niskin bottle
Dataset-specific Description	Generally, shallow total 234Th samples (1000 m) were collected from Niskin bottles hung above the in situ pumps. However, on occasions where pump associated Niskins did not close prior to recovery, the ODF Rosette was used to obtain deep water for total 234Th.
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	Radium Delayed Coincidence Counter (RaDeCC)
Generic Instrument Name	Radium Delayed Coincidence Counter
Generic Instrument Description	The RaDeCC is an alpha scintillation counter that distinguishes decay events of short-lived radium daughter products based on their contrasting half-lives. This system was pioneered by Giffin et al. (1963) and adapted for radium measurements by Moore and Arnold (1996). References: Giffin, C., A. Kaufman, W.S. Broecker (1963). Delayed coincidence counter for the assay of actinon and thoron. J. Geophys. Res., 68, pp. 1749-1757. Moore, W.S., R. Arnold (1996). Measurement of 223Ra and 224Ra in coastal waters using a delayed coincidence counter. J. Geophys. Res., 101 (1996), pp. 1321-1329. Charette, Matthew A.; Dulaiova, Henrieta; Gonneea, Meagan E.; Henderson, Paul B.; Moore, Willard S.; Scholten, Jan C.; Pham, M. K. (2012). GEOTRACES radium isotopes interlaboratory comparison experiment. Limnology and Oceanography - Methods, vol 10, pg 451.

Dataset-specific Instrument Name	Riso Anti-coincidence Beta Counter
Generic Instrument Name	Riso Laboratory Anti-coincidence Beta Counters
Dataset-specific Description	Samples were analyzed using a Riso Anti-coincidence Beta Counter.
Generic Instrument Description	Low-level beta detectors manufactured by Riso (now Nutech) in Denmark. These instruments accept samples that can be mounted on a 25mm filter holder. These detectors have very low backgrounds, 0.17 counts per minute, and can have counting efficiencies as high as 55%.

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Deployments

HLY1502

Website	https://www.bco-dmo.org/deployment/638807
Platform	USCGC Healy
Report	https://datadocs.bco-dmo.org/docs/302/geotraces/GEOTRACES_ARCTIC/data_docs/cruise_reports/healy1502.pdf
Start Date	2015-08-09
End Date	2015-10-12
Description	Arctic transect encompassing Bering and Chukchi Shelves and the Canadian, Makarov and Amundsen sub-basins of the Arctic Ocean. The transect started in the Bering Sea (60°N) and traveled northward across the Bering Shelf, through the Bering Strait and across the Chukchi shelf, then traversing along 170-180°W across the Alpha-Mendeleev and Lomonosov Ridges to the North Pole (Amundsen basin, 90°N), and then back southward along ~150°W to terminate on the Chukchi Shelf (72°N). Additional cruise information is available in the GO-SHIP Cruise Report (PDF) and from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/HLY1502

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Project Information

U.S. Arctic GEOTRACES Study (GN01) (U.S. GEOTRACES Arctic)

Website: https://www.geotraces.org/

Coverage: Arctic Ocean; Sailing from Dutch Harbor to Dutch Harbor (GN01)

Description from NSF award abstract:
In pursuit of its goal "to identify processes and quantify fluxes that control the distributions of key trace elements and isotopes in the ocean, and to establish the sensitivity of these distributions to changing environmental conditions", in 2015 the International GEOTRACES Program will embark on several years of research in the Arctic Ocean. In a region where climate warming and general environmental change are occurring at amazing speed, research such as this is important for understanding the current state of Arctic Ocean geochemistry and for developing predictive capability as the regional ecosystem continues to warm and influence global oceanic and climatic conditions. The three investigators funded on this award, will manage a

large team of U.S.scientists who will compete through the regular NSF proposal process to contribute their own unique expertise in marine trace metal, isotopic, and carbon cycle geochemistry to the U.S. effort. The three managers will be responsible for arranging and overseeing at-sea technical services such as hydrographic measurements, nutrient analyses, and around-the-clock management of on-deck sampling activites upon which all participants depend, and for organizing all pre- and post-cruise technical support and scientific meetings. The management team will also lead educational outreach activities for the general public in Nome and Barrow, Alaska, to explain the significance of the study to these communities and to learn from residents' insights on observed changes in the marine system. The project itself will provide for the support and training of a number of pre-doctoral students and post-doctoral researchers. Inasmuch as the Arctic Ocean is an epicenter of global climate change, findings of this study are expected to advance present capability to forecast changes in regional and globlal ecosystem and climate system functioning.

As the United States' contribution to the International GEOTRACES Arctic Ocean initiative, this project will be part of an ongoing multi-national effort to further scientific knowledge about trace elements and isotopes in the world ocean. This U.S. expedition will focus on the western Arctic Ocean in the boreal summer of 2015. The scientific team will consist of the management team funded through this award plus a team of scientists from U.S. academic institutions who will have successfully competed for and received NSF funds for specific science projects in time to participate in the final stages of cruise planning. The cruise track segments will include the Bering Strait, Chukchi shelf, and the deep Canada Basin. Several stations will be designated as so-called super stations for intense study of atmospheric aerosols, sea ice, and sediment chemistry as well as water-column processes. In total, the set of coordinated international expeditions will involve the deployment of ice-capable research ships from 6 nations (US, Canada, Germany, Sweden, UK, and Russia) across different parts of the Arctic Ocean, and application of state-of-the-art methods to unravel the complex dynamics of trace metals and isotopes that are important as oceanographic and biogeochemical tracers in the sea.

Collaborative Research: GEOTRACES Arctic Section: Radium and Thorium Isotopes as Natural Geochemical Tracers in the Arctic Ocean (Arctic GEOTRACES Ra Th)

Coverage: Western Arctic Ocean

NSF Award Abstract:
In this project, investigators participating in the 2015 U.S. GEOTRACES Arctic expedition will measure radium and thorium isotopes in the western Arctic Ocean. In common with other national initiatives in the International GEOTRACES Program, the goals of the U.S. Arctic expedition are to identify processes and quantify fluxes that control the distributions of key trace elements and isotopes in the ocean, and to establish the sensitivity of these distributions to changing environmental conditions. Some trace elements are essential to life, others are known biological toxins, and still others are important because they can be used as tracers of a variety of physical, chemical, and biological processes in the sea. The radionuclides to be measured as part of this project are important because they are oceanographic tracers that provide information on rates of cycling of other trace elements. The project will involve training opportunities for graduate student researchers and for undergraduate students from under-represented groups. Results from the study will be shared publicly through the Woods Hole Oceanographic Institution's Center for Marine and Environmental Radioactivity.

While other GEOTRACES projects will map the distribution of numerous trace elements and their isotopes (TEIs), their distribution cannot be properly interpreted without concurrent measurement of tracers capable of providing rates of internal TEI cycling processes and fluxes at boundaries and across interfaces. The isotopes to be measured in this project include a suite of uranium/thorium series radionuclides, including the shorter-lived 234-Th and 228-Th as well as the radium quartet (224-Ra, 223-Ra, 228-Ra, 226-Ra). These tracers have the appropriate half-lives and reactivities to allow for study of horizontal and vertical transport and mixing, as well as removal at ocean boundaries, supply via rivers and submarine groundwater discharge, surface scavenging and export and subsurface remineralization. The researchers have considerable experience developing and implementing the most efficient methods to sample and quantify this suite of tracers, which includes use of battery powered in-situ pumps for large volume sampling. Hence, in addition to the proposed work on uranium/thorium series radionuclides, the team will also provide a service to other GEOTRACES researchers by coordinating pump use and sampling for many essential particulate TEIs.

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Program Information

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

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

Coverage: Global

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

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)	OCE-1458305

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