Seawater dissolved 232Thorium, 230Thorium and 231Protactinium from R/V Knorr KN193-06 and KN195-08 in the eastern N. Pacific and Sargasso Sea from 2008-2009 (GEOTRACES IC project)

Website: https://www.bco-dmo.org/dataset/3828 Version: Version Date: 2012-12-31

Project

» <u>GEOTRACES InterCalibration</u> (GEOTRACES IC)

Program

» U.S. GEOTRACES (U.S. GEOTRACES)

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Dataset Description

GEOTRACES Baseline profiles of seawater dissolved thorium and protactinium in the forms 232Th, 230Th, and 231Pa at SAFe in the SAFe station in the subtropical N. Pacific and the BATS station in the subtropical N.Atlantic.

BCO-DMO Note: "Trace Metal Pump - Towed" removed as an instrument. Was inadvertently included. 20Oct2014/srg

Methods & Sampling

Sampling and Analytical Methodology - BATS station:

Water samples were collected with a Sea-Bird Electronics CTD carousel fitted with

24 10-liter PVC Niskin bottles. The carousel was lowered from the ship with steel wire. Niskin bottles were equipped with nylon-coated closure springs and Viton O-rings. After collection seawater was filtered by in-line filtration (47 mm 0.45 µm pore diameter Supor polysulfone membranes in acid cleaned Teflon filter holders) from pressurized Niskin bottles. Bottles were pressurized at 8-10 psi (54-70 kPa) with a system that distributed filtered air from a compressor via a manifold to each bottle through a fitting placed in its air vent. Each distribution line from the manifold was fitted with a valve so that each bottle could be pressurized or vented independently, while still allowing for the possibility to simultaneously filter all the bottles. Pressurized

bottles were held closed with Irwin Quick-Grip bar clamps spanning the endcaps. No attempt was made to evaluate the blank contributed by the pressurization scheme. Filtered water was collected in low-density polyethylene cubitainers (10 liter volume; Hedwin Corp.). Approximately 9-10 L was collected per desired depth. Prior to the cruise, the tubing, filters and cubitainers were cleaned by immersion in 1.2 M HCI (Fisher Scientific Trace Metal Grade) for 4-5 days. Once filtered, samples were adjusted to a pH ~2 with ultra-clean 6 M HCI (Fisher Scientific OPTIMA grade) and were double bagged for storage at room temperature until analysis.

In the on-shore laboratory, samples were weighed to determine sample size, taking into account the weight of the cubitainer and of the acid added at sea. Then weighed aliquots of the artificial isotope yield monitors 229Th (20 pg) and 233Pa (0.5 pg) and 15 mg dissolved Fe were added to each sample. After allowing 1 day for spike equilibration, the pH of each sample was raised to 8-8.5 (checked with pH paper) by adding concentrated NH4OH (Fisher Scientific OPTIMA grade) which caused iron (oxy)hydroxide precipitates to form. This precipitate was allowed to settle for 1-2 days before the overlaying seawater was siphoned off. The Fe precipitate was transferred to centrifuge tubes for centrifugation and rinsing with Milli-Q H2O (>18 MO) to remove the major seawater ions. The precipitate was then dissolved in 16 M HNO3 (Fisher Scientific OPTIMA grade) and transferred to a Teflon beaker for a high-temperature (180-200°C) digestion with HCIO4 and HF (Fisher Scientific OPTIMA grade) on a hotplate in a HEPA-filtered laminar flow hood. After total dissolution of the sample, another precipitation of iron (oxy)hydroxide followed and the precipitate was washed with Mill-Q H2O, centrifuged, and dissolved in 12 M HCl for a series of anion-exchange chromatography using 6 mL polypropylene columns each containing Bio-rad resin (AG1-X8, 100-200 mesh size) and a 45 µm porous polyethylene frit (for details see Anderson et al., 2012). The final column elutions were dried down at 180°C in the presence of 2 drops of HClO4 and taken up in approximately 1 mL of 0.16 M HNO3/0.026 M HF for mass spectrometric analysis.

Concentrations of 232Th, 230Th and 231Pa were calculated by isotope dilution using nuclide ratios determined on a VG Elemental AXIOM Single Collector Magnetic Sector ICP-MS with a Resolving Power of ~400 to ensure the highest sensitivity. All measurements were done using a peak jumping routine in ion counting mode. A solution of SRM129, a natural U standard, 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,

used to correct for the instrument background count rates on the masses measured.

To correct for potential tailing of 232Th into the minor Th and Pa isotopes, beam intensities were measured at the half masses above and below each mass for 230Th, 231Pa, and 233Pa. Tailing under each minor isotope was estimated as the log mean intensity of the half masses on either side of each minor isotope.

Water samples were analyzed in batches of 10-12. Procedural blanks were determined by processing 4-5 L of Milli-Q water in an acid-cleaned cubitainer acidified to pH ~2 with 6 M HCl as a sample in each batch. Total procedural blanks for 232Th, 230Th, and 231Pa ranged from 63-93 pg, 12.1-12.4 fg, and 1.9-2.4 fg respectively.

Sampling and Analytical Methodology - SAFe station:

Water samples were collected with a Sea-Bird Electronics CTD carousel fitted with 24 10-liter PVC Niskin bottles. The carousel was lowered from the ship with steel wire. Niskin bottles were equipped with nylon-coated closure springs and Viton O-rings. After collection seawater was drained with Teflon-lined TygonTM tubing and filtered through Pall AcropakTM 500 filters on deck (gravity filtration, 0.8/0.45 μ m pore size) into low-density polyethylene cubitainers (1 gallon volume; Hedwin Corp.). Approximately 4 L was collected per desired depth. Prior to the cruise, the tubing, filters and cubitainers were cleaned by immersion in 1.2 M HCI (Fisher Scientific Trace Metal Grade) for 4-5 days. Once filtered, samples were adjusted to a pH ~2 with ultra-clean 6 M HCI (Fisher Scientific OPTIMA grade) and were double bagged for storage at room temperature until analysis.

In the on-shore laboratory, samples were weighed to determine sample size, taking into account the weight of the cubitainer and of the acid added at sea. Then weighed aliquots of the artificial isotope yield monitors 229Th (20 pg) and 233Pa (0.5 pg) and 15 mg dissolved Fe were added to each sample. After allowing 1 day for spike equilibration, the pH of each sample was raised to 8-8.5 (checked with pH paper) by adding concentrated NH4OH (Fisher Scientific OPTIMA grade) which caused iron (oxy)hydroxide precipitates to form. This precipitate was allowed to settle for 1-2 days before the overlaying seawater was siphoned off. The Fe precipitate was transferred to centrifuge tubes for centrifugation and rinsing with Milli-Q H2O (>18 MO) to remove the major seawater ions. The precipitate was then dissolved in 16 M HNO3 (Fisher Scientific OPTIMA grade) on a hotplate in a HEPA-filtered laminar flow hood. After total dissolution of the sample, another precipitation of iron (oxy)hydroxide followed and the precipitate was washed with Mill-Q H2O,

centrifuged, and dissolved in 12 M HCl for a series of anion-exchange chromatography using 6 mL polypropylene columns each containing a bed of Bio-rad resin (AG1-X8, 100-200 mesh size) and a 45 μ m porous polyethylene frit (for details see Anderson et al., 2012). The final column elutions were dried down at 180°C in the presence of 2 drops of HClO4 and taken up in approximately 1 mL of 0.16 M HNO3/0.026 M HF for mass spectrometric analysis.

Concentrations of 232Th, 230Th and 231Pa were calculated by isotope dilution using nuclide ratios determined on a VG Elemental AXIOM Single Collector Magnetic Sector ICP-MS with a Resolving Power of ~400 to ensure the highest sensitivity. All measurements were done using a peak jumping routine in ion counting mode. A solution of SRM129, a natural U standard, 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,

used to correct for the instrument background count rates on the masses measured.

To correct for potential tailing of 232Th into the minor Th and Pa isotopes, beam intensities were measured at the half masses above and below each mass for 230Th, 231Pa, and 233Pa. Tailing under each minor isotope was estimated as the log mean intensity of the half masses on either side of each minor isotope.

Water samples were analyzed in batches of 10-12. Procedural blanks were determined by processing 3-4 L of Milli-Q water in an acid-cleaned cubitainer acidified to pH ~2 with 6 M HCl as a sample in each batch. An aliquot of an intercalibrated working standard solution of 232Th, 230Th and 231Pa, SW STD 2010-1 referred to by Anderson et al. (2012), was added to a separate cubitainer with 4 L of Milli-Q water (acidified to pH 2) and also processed like a sample in each batch. Total procedural blanks for 232Th, 230Th, and 231Pa ranged from 19-24 pg, 1.4-2.8 fg, and 0.4 fg respectively.

To test the overall method, an aliquot of an intercalibrated working standard solution of 232Th, 230Th and 231Pa, SW STD 2010-1 referred to by Anderson et al. (2012), was added to a separate cubitainer with 3 L of Milli-Q water (acidified to pH 2) and also processed like a sample.

Further details on sampling and analysis are given by Anderson et al. (2012).

Data Processing Description

Data Processing:

The reported errors for radionuclide concentrations represent the propagation of one sigma errors based on the standard deviation of five sequences of isotope ratios collected by ICP-MS, estimated error in the 229Th or 233Pa spike concentration, and the blank correction of the individual isotopes for each sample batch.

Analysis of all samples was completed over the course of 2 years. A correction was made to account for the ingrowth of 230Th and 231Pa due to the decay of the natural 234U and 235U 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 230Th and 231Pa 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 of North Pacific seawater (Chen et al., 1986), [U] = (0.1115*S - 0.6356) ng U (g seawater)-1. We used seawater U-isotopic compositions of 234U/238 U = 1.1468 activity ratio (Andersen et al., 2010), and 238U/235U = 137.824 mole ratio (Weyer et al., 2008), to calculate [234U] and [235U] respectively based on [U]. In our manuscript (Anderson et al., 2012) we converted gravimetric concentration (fg/kg) into volumetric activities (dpm m-3) for easier comparison to historical data. The half-lives used were 75,690 yrs for 230Th (Cheng et al., 2000), 32,760 yrs for 231Pa (Robert et al., 1969), 245,250 yrs for 234U (Cheng et al., 2000), and 7.0381 x 108 yrs for 235U (Jaffey et al. 1971).

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Data Files

File

GT_IntCal_ThPa.csv(Comma Separated Values (.csv), 4.54 KB) MD5:8b5621e4633120fb75fd38cba41930e9

Primary data file for dataset ID 3828

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Parameters

Parameter	Description	Units
cruise_id	cruise ID number	dimensionless
station	station number within cruise	dimensionless
lat	station latitude; North is positive	decimal degrees
lon	station longitude; East is positive	decimal degrees
depth_max	station water depth	meters
depth	water depth at which bottle tripped	meters
event	event number from event log	dimensionless
date_collected	date sample was collected	mm/dd/yy
year	year sample was collected	уууу
month	month sample was collected	1 to 12
day	day of month sample was collected	1 to 31
yrday_gmt	year day sample was collected; 1 is Jan. 1 and 365 is Dec. 31	1 t 365
bottle	Niskin bottle of 24-bottle sequence	dimensionless
sample	GEOTRACES sample identification number	integer
date_U_separation	date Uranium was separated from Th/Pa	mm/dd/yy
Th232	Dissolved 232Thorium concentration (picograms 232Th per kilogram seawater
Th232_err	1 sigma uncertainty in dissolved 232Th	picograms 232Th per kilogram seawater
Th232_flag	Data quality flag for dissolved 232Th	1 = good; $2 = questionable$; $3 = rejected$; $4 = blanks toolarge to obtain data; 5 = 232Th tail too large to obtain data$
Th230	Dissolved 230Thorium conc. (femtograms 230Th per kilogram seawater
Th230_err	1 sigma uncertainty in dissolved 230Th	femtograms 230Th per kilogram seawater
Th230_flag	Data quality flag for dissolved 230Th	1 = good; $2 = questionable$; $3 = rejected$; $4 = blanks toolarge to obtain data; 5 = 232Th tail too large to obtain data$
Pa231	Dissolved 231Protactinium conc. (femtograms 231Pa per kilogram seawater
Pa231_err	1 sigma uncertainty in dissolved 231Pa	femtograms 231Pa per kilogram seawater
Pa231_flag	Data quality flag for dissolved 231Pa	1 = good; 2 = questionable; 3 = rejected; 4=blanks too large to obtain data; 5=232Th tail too large to obtain data

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Instruments

Dataset- specific Instrument Name	CTD Sea-Bird
Generic Instrument Name	CTD Sea-Bird
Dataset- specific Description	The carousel was fitted with 24-liter Niskin bottles. The carousel was lowered from the ship with steel wire. Niskin bottles were equipped with nylon-coated closure springs and Viton O-rings.
Generic Instrument Description	Conductivity, Temperature, Depth (CTD) sensor package from SeaBird Electronics, no specific unit identified. This instrument designation is used when specific make and model are not known. See also other SeaBird instruments listed under CTD. More information from Sea-Bird Electronics.

Dataset- specific Instrument Name	Mass Spectrometer
Generic Instrument Name	Mass Spectrometer
Dataset- specific Description	VG Elemental AXIOM Single Collector Magnetic Sector ICP-MS with a Resolving Power of ${\sim}400$
Generic Instrument Description	General term for instruments used to measure the mass-to-charge ratio of ions; generally used to find the composition of a sample by generating a mass spectrum representing the masses of sample components.

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Deployments

KN195-08

Website	https://www.bco-dmo.org/deployment/57842
Platform	R/V Knorr
Start Date	2009-05-06
End Date	2009-05-29
Description	GEOTRACES intercalibration cruise 2 (May 2009) GEOTRACES completed the first Intercalibration cruise from June 8 to July 12, 2008, collecting water and particle samples for analysis and intercalibration. The second intercalibration cruise is planned for May 2009 in the eastern North Pacific and will include sampling near the North Pacific SAFe Station at 30°N 140°W, and the Santa Barbara Basin, 34.25°N 120°W. This International GEOTRACES intercalibration exercise aims to provide reference materials that could be distributed to the international community and reference profiles of Trace Elements and their Isotopes to ensure compatibility and consistency of GEOTRACES data. Sampling Activities: for full details see cruise synopsis or cruise report when available Pre-cruise Sampling Activity Summary: This is a 'trace metal clean' cruise, during which the researchers plan to use the following sampling devices and gear: ship's standard CTD with 24x10L Niskin bottle rosette Ken Buesseler's McLane in situ pumps and MITESS vane samplers a trace metal-clean GEOTRACES carousel with GO-Flo bottles (like the one used during IC 1 in 2008. This will be deployed using the newly developed method described by Glosten Associates. The plan is to use this system for up to 10 casts per day. a towed/stationary fish (depressor and weighted torpedo) for pumping trace metal clean water to the MLML sampling and GEOTRACES clean vans, deployed using our aluminum pivoting boom just like in 2008. We will be testing several different towed fish during the transits. Jim Bishop's MULFVS pumping system (http://www-ocean.lbl.gov/MULVFSops.html) An EOS paper (Johnson, 2007) describes the SAFe station and efforts to establish the SAFe dissolved Fe in seawater standards.K.S. Johnson et al. 2007. Developing standards for dissolved iron in seawater, EOS 88 (11), pp. 131-132 (http://boyle.mit.edu/~ed/PDFs/Johnson(2007)EOS88_131.pdf) Cruise information and original data are available from the NSF R2R data catalog.

KN193-06

Website	https://www.bco-dmo.org/deployment/58676	
Platform	R/V Knorr	
Start Date	2008-06-29	
End Date	2008-07-12	

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Project Information

GEOTRACES InterCalibration (GEOTRACES IC)

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

Coverage: Sargasso Sea, eastern North Pacific

An international intercalibration effort has been assigned a high priority during the initial phase of GEOTRACES to ensure that results from different cruises, and from different labs, can be compared in a meaningful way.

While the original data from the Intercalibration cruises are not available online, consensus values for the SAFe and North Atlantic GEOTRACES Reference Seawater Samples are available from the GEOTRACES Program Office: <u>Standards and Reference Materials</u>

The ultimate goal for the intercalibration component of the international GEOTRACES program is to achieve the best accuracy possible (lowest random and systematic errors) for the suite of GEOTRACES' Trace Elements and Isotopes (TEI) as a prelude to the sampling program, and continuing effort throughout the sampling and analysis program. To achieve this goal, there will be two primary efforts:

(1) Evaluate and develop GEOTRACES sample acquisition, handling, and storage protocols during initial Intercalibration Cruises;

(2) Identify existing GEOTRACES primary standards and certified reference materials (CRMs) for the TEI suite (and where needed, producing reference materials or primary standards), including the establishment of GEOTRACES Baseline Stations that can be used to evaluate accuracy from sampling to analysis (to facilitate intercalibration for TEIs that do not have CRMs).

Tentative schedule of Intercalibration events:

• June - July 2008. 1st Intercalibration cruise (Sargasso Sea): evaluate sampling apparati and handling methods (diss and part), collect and distribute intercalibration samples, sample storage experiments, establish Baseline Station at BATS

• Dec. 2008. Second Intercalibration workshop (AGU): evaluate and interpret intercalibration results, planning for 2nd cruise

• Spring 2009. 2nd Intercalibration cruise (eastern North Pacific): final testing of complete sampling system and procedures, intercalibrate with other (non-US) sampling systems, speciation + total TEI intercalibration, determine the time to occupy one GEOTRACES station (for cruise planning purposes)

• Jan.-Feb 2010. Third Intercalibration workshop: finalize complete intercalibration results, begin assembling GEOTRACES User Manuals

GEOTRACES intercalibration cruise 1 June 2008

GEOTRACES completed the first Intercalibration cruise from June 8 to July 12, 2008 to collect intercalibration water and particle samples. This intercalibration exercise aimed to provide reference materials that could be distributed to the international community and reference profiles of Trace Elements and their Isotopes to ensure compatibility and consistency of GEOTRACES data.

GEOTRACES intercalibration cruise 2 May 2009

The second intercalibration cruise is planned for May 2009 in the eastern North Pacific and will include sampling near the North Pacific SAFe Station at 30°N, 140°W.

If you are interested in participating in this exercise, note that selected samples for intercalibration will also be available after the cruise. For general information about the intercalibration effort please contact Greg Cutter.

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Program Information

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

Website: <u>http://www.geotraces.org/</u>

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-0752402</u>

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