Depth profiles of seawater dissolved 232Th, 230Th, and 231Pa, NW Pacific from R/V Sonne SO202 in the North Pacific and the Bering Sea from July 2009 (Sources-Sinks Th-Pa project)

Website: https://www.bco-dmo.org/dataset/3856
Version:
Version Date: 2013-01-16

Project
» Boundary Sources and Sinks of 230Th, 232Th and 231Pa in the NW Pacific (Sources-Sinks Th-Pa)

Program
» Innovative North Pacific Experiment (INoPEx)

Contributors	Affiliation	Role
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Dataset Description

Depth profiles of seawater dissolved 232Th, 230Th, and 231Pa at seven sites in the NW Pacific.

This dataset is published:
Hayes, C.T., Anderson, R.F., Jaccard, S.L., François, R., Fleisher, M.Q., Soon, M., Gersonde, R., 2013. A new perspective on boundary scavenging in the North Pacific Ocean. Earth Planet. Sci. Lett. 369-370, 86-97.
http://dx.doi.org/10.1016/j.epsl.2013.03.008
http://www.sciencedirect.com/science/article/pii/S0012821X13001295

These data are also available through PANGAEA: http://doi.pangaea.de/10.1594/PANGAEA.811760

Methods & Sampling

Sampling and Analytical Methodology:
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 caps were held together with rubber tubing. 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 µm pore size) into Fisher I-Chem series 300 LDPE cubitainers. 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 HCl (Fisher Scientific Trace Metal Grade) for 4-5 days. Once

filtered, samples were adjusted to a pH ~2 with ultra-clean 6 M HCl (Tama Chemicals, TAMAPURE-AA-100 grade), double-bagged and stored at room temperature as packaged 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. Four to five liters of the original sample was used for Th/Pa analysis, the remaining sample kept as archive. 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 by adding ~10 mL of 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 HClO4 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 a 1 mL bed of Bio-rad resin (AG1-X8, 100-200 mesh size) and a 45 µm porous polyethylene frit. 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. 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 5 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 7.1-24.3 pg, 0.8-1.6 fg, and 0.02-0.2 fg respectively. One batch had an anomalously high 232Th blank of 140 pg (with 230Th and 231Pa in the reported range). Application of this blank correction to the analyzed SW STD caused an anomalously low estimate of its 232Th concentration (approximately 990 ± 15 pg/g). From this we concluded the blank was due to random contamination of the procedural blank and it should not be used to blank-correct samples. Instead, we determined what magnitude of blank correction would be necessary for the analyzed SW STD to achieve the intercalibrated concentration. This was 12 pg 232Th, which is close to the average blank value measured throughout the course of this project.

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 submitted manuscript (Hayes et al., submitted) 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).

Related files and references:

Anderson, R.F., Fleisher, M.Q., Robinson, L.F., Edwards, R.L., Hoff, J., Moran, S.B., Rutgers van der Loeff, M.M., Thomas, A.L., Roy-Barman, M., François, R., 2012. GEOTRACES intercalibration of 230Th, 232Th, 231Pa, and prospects for 10Be. Limnol. Oceanogr. Methods 10, 179-213.

Chen, J.H., Lawrence Edwards, R., Wasserburg, G.J., 1986. 238U, 234U and 232Th in seawater. Earth Planet. Sci. Lett. 80, 241-251.

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. Chem. Geol. 169, 17-33.

Hayes, C.T., Anderson, R.F., Jaccard, S.L., Fleisher, M.Q., Soon, M., Gersonde, R., submitted. The nature of boundary scavenging in the North Pacific Ocean. Earth Planet. Sci. Lett.

Jaffey, A.H., Flynn, K.F., Glendenin, L.E., Bentley, W.C., Essling, A.M., 1971. Precision Measurement of Half-Lives and Specific Activities of 235U and 238U. Physical Review C 4, 1889-1906.

Robert, J., Miranda, C.F., Muxart, R., 1969. Mesure de la periode du protactinium-231 par microcalorimetrie. Radiochim. Acta 11, 104-108.

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Data Files

File
INOPEX_ThPa.csv (Comma Separated Values (.csv), 11.12 KB) MD5:2f7792f59b8e6525e34b3470cc06c98a Primary data file for dataset ID 3856

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Parameters

Parameter	Description	Units
cruise_id	cruise ID number	text
sta	station number within cruise	integer
lat	station latitude; North is positive	decimal degrees
lon	station longitude; East is positive. Added by Data Mgmt.Office.	decimal degrees
depth	sample depth	meters
press	hydrostatic pressure	decibars

O2	Dissolved oxygen concentration	milliliters O2/liter seawater
sal	Practical salinity	dimensionless (PSS-78 scale)
temp	Temperature	degrees centrigrade (ITS-90 scale)
date_collected	date sample was collected, UTC	yyyymmdd
date_U_separation	date Uranium was separated from Th/Pa, UTC	yyyymmdd
Th232	Dissolved 232Thorium concentration (<0.45um)	picograms 232Th/kilogram seawater
Th232_err	1 sigma uncertainty in dissolved 232Th	picograms 232Th/kilogram seawater
Th232_flag	Data quality flag for dissolved 232Th	1 = good; 2 = questionable; 3 = bad
Th230	Dissolved 230Thorium conc. (<0.45um)	femtograms 230Th/kilogram seawater
Th230_err	1 sigma uncertainty in dissolved 230Th	femtograms 230Th/kilogram seawater
Th230_flag	Data quality flag for dissolved 230Th	1 = good; 2 = questionable; 3 = bad
Pa231	Dissolved 231Protactinium conc. (<0.45um)	femtograms 231Pa/kilogram seawater
Pa231_err	1 sigma uncertainty in dissolved 231Pa	femtograms 231Pa/kilogram seawater
Pa231_flag	Data quality flag for dissolved 231Pa	1 = good; 2 = questionable; 3 = bad
lon_360	longitude ranging from 0 to 360 degrees; especially useful for data collected during sampling transects that cross the dateline	decimal degrees

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Instruments

Dataset-specific Instrument Name	CTD Sea-Bird
Generic Instrument Name	CTD Sea-Bird
Generic Instrument Description	A Conductivity, Temperature, Depth (CTD) sensor package from SeaBird Electronics. This instrument designation is used when specific make and model are not known or when a more specific term is not available in the BCO-DMO vocabulary. Refer to the dataset-specific metadata for more information about the specific CTD used. More information from: http://www.seabird.com/

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 ~400 to ensure the highest sensitivity
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.

Dataset-specific Instrument Name	Niskin bottle
Generic Instrument Name	Niskin bottle
Dataset-specific Description	Sea-Bird Electronics CTD carousel fitted with 24 10-liter PVC Niskin bottles.
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.

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Deployments

SO202

Website	https://www.bco-dmo.org/deployment/58930
Platform	R/V Sonne
Report	http://epic.awi.de/30138/
Start Date	2009-07-08
End Date	2009-08-28
Description	Expedition of the research vessel "Sonne" to the subpolar North Pacific and the Bering Sea in 2009 (SO202-INOPEX) around the Pacific subarctic gyre sampling seawater and ocean sediments.

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Project Information

Boundary Sources and Sinks of 230Th, 232Th and 231Pa in the NW Pacific (Sources-Sinks Th-Pa)

Website: http://epic.awi.de/30138/

Coverage: Subarctic North Pacific and Bering Sea

Abstract:

The spatial distributions of the isotopes of thorium (Th) and protactinium (Pa) have previously been used to support the notion that there is enhanced "boundary scavenging" of particle reactive substances (i.e. their preferential removal from seawater) at ocean margins. However, recent evidence suggests that spatial variability in the chemical fractionation between Th and Pa (i.e. differential partitioning between the dissolved and particulate phases) may influence sedimentary 231Pa/230Th ratios as much as, or even more than, enhanced scavenging at margins. If true, then preferential removal of particle-reactive solutes at ocean margins may be less significant than previously believed.

Further research is needed to examine these two processes, and the proposed study by researchers at the Lamont Doherty Earth Observatory at Columbia University will address this problem and related objectives by analyzing samples collected at a location in the Subarctic North Pacific Ocean for the concentration and distribution of dissolved 230Th, 232Th and 231Pa together with analysis of their concentration in surface sediments. The samples have already been collected. Additional objectives of the proposed work include assessing the boundary sources and sinks for each isotope, the near bottom gradients and testing the hypothesis that enhanced scavenging near the sediment-water interface creates a significant sink at the base of the pelagic water column. Additionally, the potential regeneration and flux from settling labile biogenic particles, from the dissolution of lithogenic phases and/or mobilization of colloids will be evaluated in conjunction with an examination of the role of particulate phase composition in controlling chemical fractionation. The results will be used in modeling efforts aimed at examining the importance of the various processes outlined above. The proposed work will improve understanding of the enhancement of chemical scavenging and removal of particle-reactive substances at ocean margins.

The research will be beneficial to investigators in a variety of fields besides chemical oceanography, notably paleoceanography. The results will inform the debate concerning the applicability of sedimentary 231Pa/230Th ratios as a proxy for deep ocean circulation, and the validity and importance of various conclusions derived from prior research. The research will provide further information on aspects of sediment-water exchange of reactive substances. The results may also inform the research that will be conducted in the Pacific Ocean in the future as part of the GEOTRACES Program.

Broader Impacts: The scientific aspects of the research focus on improving the understanding the importance of boundary margin scavenging. Such knowledge is necessary for understanding the ocean biogeochemistry of many elements, not just the isotopes that are the focus of this study. The educational aspects of the proposal relate to graduate student education and related activities.

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Program Information

Innovative North Pacific Experiment (INoPEx)

Website: http://www.ldeo.columbia.edu/~cth/inopex.htm

Coverage: Subarctic North Pacific and Bering Sea

Expedition of the research vessel "Sonne" to the subpolar North Pacific and the Bering Sea in 2009 (SO202-INOPEX) around the Pacific subarctic gyre sampling seawater and ocean sediments.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1029211

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