

# Depth profiles of seawater dissolved $^{232}\text{Th}$ , $^{230}\text{Th}$ , and $^{231}\text{Pa}$ , 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  \$^{230}\text{Th}\$ ,  \$^{232}\text{Th}\$  and  \$^{231}\text{Pa}\$  in the NW Pacific](#) (Sources-Sinks Th-Pa)

## Program

» [Innovative North Pacific Experiment](#) (INoPEX)

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## Dataset Description

Depth profiles of seawater dissolved  $^{232}\text{Th}$ ,  $^{230}\text{Th}$ , and  $^{231}\text{Pa}$  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 Tygon<sup>TM</sup> tubing and filtered through Pall Acropak<sup>TM</sup> 500 filters on deck (gravity filtration, 0.8/0.45  $\mu\text{m}$  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  $^{229}\text{Th}$  (20 pg) and  $^{233}\text{Pa}$  (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  $\text{NH}_4\text{OH}$  (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  $\text{H}_2\text{O}$  (>18 MO) to remove the major seawater ions. The precipitate was then dissolved in 16 M  $\text{HNO}_3$  (Fisher Scientific OPTIMA grade) and transferred to a Teflon beaker for a high-temperature (180-200°C) digestion with  $\text{HClO}_4$  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  $\text{H}_2\text{O}$ , 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  $\mu\text{m}$  porous polyethylene frit. The final column elutions were dried down at 180°C in the presence of 2 drops of  $\text{HClO}_4$  and taken up in approximately 1 mL of 0.16 M  $\text{HNO}_3$ /0.026 M HF for mass spectrometric analysis.

Concentrations of  $^{232}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  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  $^{232}\text{Th}$  into the minor Th and Pa isotopes, beam intensities were measured at the half masses above and below each mass for  $^{230}\text{Th}$ ,  $^{231}\text{Pa}$ , and  $^{233}\text{Pa}$ . 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  $^{232}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{231}\text{Pa}$ , 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  $^{232}\text{Th}$ ,  $^{230}\text{Th}$ , and  $^{231}\text{Pa}$  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  $^{232}\text{Th}$  blank of 140 pg (with  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  in the reported range). Application of this blank correction to the analyzed SW STD caused an anomalously low estimate of its  $^{232}\text{Th}$  concentration (approximately  $990 \pm 15$  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  $^{232}\text{Th}$ , 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  $^{229}\text{Th}$  or  $^{233}\text{Pa}$  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  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  due to the decay of the natural  $^{234}\text{U}$  and  $^{235}\text{U}$  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  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  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),  $[\text{U}] = (0.1115 \cdot \text{S} - 0.6356) \text{ ng U (g seawater)}^{-1}$ . We used seawater U-isotopic compositions of  $^{234}\text{U}/^{238}\text{U} = 1.1468$  activity ratio (Andersen et al., 2010), and  $^{238}\text{U}/^{235}\text{U} = 137.824$  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<sup>-3</sup>) 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 10<sup>8</sup> 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
<b>INOPEX_ThPa.csv</b> (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 centigrade (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 (	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. (	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. (	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

<b>Dataset-specific Instrument Name</b>	CTD Sea-Bird
<b>Generic Instrument Name</b>	CTD Sea-Bird
<b>Generic Instrument Description</b>	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.

<b>Dataset-specific Instrument Name</b>	Mass Spectrometer
<b>Generic Instrument Name</b>	Mass Spectrometer
<b>Dataset-specific Description</b>	VG Elemental AXIOM Single Collector Magnetic Sector ICP-MS with a Resolving Power of ~400 to ensure the highest sensitivity
<b>Generic Instrument Description</b>	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.

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

<b>Website</b>	<a href="https://www.bco-dmo.org/deployment/58930">https://www.bco-dmo.org/deployment/58930</a>
<b>Platform</b>	R/V Sonne
<b>Report</b>	<a href="http://epic.awi.de/30138/">http://epic.awi.de/30138/</a>
<b>Start Date</b>	2009-07-08
<b>End Date</b>	2009-08-28
<b>Description</b>	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 $^{230}\text{Th}$ , $^{232}\text{Th}$ and $^{231}\text{Pa}$ 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  $^{231}\text{Pa}/^{230}\text{Th}$  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  $^{230}\text{Th}$ ,  $^{232}\text{Th}$  and  $^{231}\text{Pa}$  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  $^{231}\text{Pa}/^{230}\text{Th}$  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
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1029211</a>

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