

## **DATASET description** [Version: June 2011]

Robert F. Anderson; Cruise SO-202; Seawater dissolved  $^{232}\text{Th}$ ,  $^{230}\text{Th}$ , and  $^{231}\text{Pa}$

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### **Dataset Name:**

SO-202 Dissolved Th/Pa

### **Literature Reference:**

Hayes, C.T., Anderson, R.F., Jaccard, S.L., Fleisher, M.Q., Soon, M., Gersonde, R., 2013. A new perspective on boundary scavenging in the North Pacific Ocean. Earth Planet. Sci. Lett.

<http://dx.doi.org/10.1016/j.epsl.2013.03.008>.

### **Dataset description:**

Depth profiles of seawater dissolved  $^{232}\text{Th}$ ,  $^{230}\text{Th}$ , and  $^{231}\text{Pa}$  at seven sites

Project: Boundary Sources and Sinks of  $^{230}\text{Th}$ ,  $^{232}\text{Th}$  and  $^{231}\text{Pa}$  in the NW Pacific

Funding: NSF-OCE 1029211

## Cruise or Deployment:

German Research Vessel *Sonne*; Cruise ID SO-202

Deployment Synonyms: The Innovative North Pacific Experiment (INOPEX)

Location: Subarctic North Pacific

### Parameter names, definitions and units:

Notes:

“Dissolved” refers to that which passed through a 0.45  $\mu\text{m}$  Acropak™ 500 filter capsule.

Radionuclide concentrations are given as the mass of radionuclide contained in a given mass of filtered seawater: fg ( $10^{-15}$  g) radionuclide per kg seawater for  $^{230}\text{Th}$  and  $^{231}\text{Pa}$ , and pg ( $10^{-12}$  g) radionuclide per kg seawater for  $^{232}\text{Th}$ . The units are written simply as fg/kg and pg/kg.

Hydrographic data (salinity, temperature, pressure, depth, and dissolved oxygen) for each radionuclide sample was collected from the Sea-Bird Electronics CTD associated with the water sampling rosette of the *Sonne* which was calibrated by the ship’s crew.

Parameter	Description	Units
Cruise	Cruise ID number	dimensionless
Station	Station number within cruise	dimensionless
Lat.	Station latitude	degrees North
Long.	Station longitude	degrees East
Depth	Sample depth	meters
O2	Dissolved oxygen concentration	milliliters O2 per liter seawater
Salinity	Practical salinity	dimensionless (PSS-78 scale)
Temp.	Temperature	degrees centigrade (ITS-90 scale)
Pres.	Hydrostatic pressure	decibars
Collected	Date sample collected	m/d/yyyy
Date U separated	Date U separated from Th/Pa	m/d/yyyy
Diss. 232Th	Dissolved 232Th conc. (<0.45 $\mu\text{m}$ )	picograms 232Th per kilogram seawater
Diss. 232Th_err	1 sigma uncertainty in Diss. 232Th	picograms 232Th per kilogram seawater
Flag_Diss. 232Th	Data quality flag for Diss. 232Th	1 = good; 2 = questionable; 3 = bad
Diss. 230Th	Dissolved 230Th conc. (<0.45 $\mu\text{m}$ )	femtograms 230Th per kilogram seawater
Diss. 230Th_err	1 sigma uncertainty in Diss. 230Th	femtograms 230Th per kilogram seawater
Flag_Diss. 230Th	Data quality flag for Diss. 230Th	1 = good; 2 = questionable; 3 = bad
Diss. 231Pa	Dissolved 231Pa conc. (<0.45 $\mu\text{m}$ )	femtograms 231Pa per kilogram seawater
Diss. 231Pa_err	1 sigma uncertainty in Diss. 231Pa	femtograms 231Pa per kilogram seawater
Flag_Diss. 231Pa	Data quality flag for Diss. 231Pa	1 = good; 2 = questionable; 3 = bad

### 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™ tubing and filtered through Pall Acropak™ 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 M $\Omega$ ) 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:

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  $[\text{U}]$  and  $[\text{U}]$  respectively based on  $[\text{U}]$ . In our submitted manuscript (Hayes et al., submitted) we converted gravimetric concentration (fg/kg) into volumetric activities (dpm  $\text{m}^{-3}$ ) for easier comparison to historical data. The half-lives used were 75,690 yrs for  $^{230}\text{Th}$  (Cheng et al., 2000), 32,760 yrs for  $^{231}\text{Pa}$  (Robert et al., 1969), 245,250 yrs for  $^{234}\text{U}$  (Cheng et al., 2000), and  $7.0381 \times 10^8$  yrs for  $^{235}\text{U}$  (Jaffey et al. 1971).

### Access restrictions:

None.

### Related files and references:

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