

GEOTRACES-EPZT

Depth profiles of seawater dissolved ^{232}Th , ^{230}Th , and ^{231}Pa
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Notes:

Radionuclide concentrations are given as micro-Becquerel (10^{-6} Bq, μBq or micro-Bq) per kg seawater for ^{230}Th and ^{231}Pa , and pmol (10^{-12} mol) per kg seawater for ^{232}Th . A Becquerel is the SI unit for radioactivity and is defined as 1 disintegration per second. These units are recommended by the GEOTRACES community.

“Dissolved” (D) here refers to that which passed through a 0.45 μm Acropak™ 500 filter capsule sampled from conventional Niskin bottles. This is true for all dissolved samples except for a select number that came from a towed pumping system designed to collect uncontaminated water at 2-3 m depth, indicated by FISH or Stn-GeoF in the sample bottle type. Surface Fish samples were filtered by a 0.2 μm Osmonics filter capsule, unlike Niskin samples.

For dissolved, seawater was weighed directly in the laboratory to determine sample size, taking into account acid added at sea. Concentrations below detection are listed as “bdl”. The abbreviation “nd” refers to no data available.

Parameter names in the form such as “Th_232_D_CONC_BOTTLE” are adopted based on a recommendation from the GEOTRACES community (http://www.geotraces.org/Parameter_Naming_Conventions.html).

This is compiled data produced by two laboratories with the following associations: Lamont-Doherty Earth Observatory of Columbia University (LDEO) and the University of Minnesota (UMN).

Parameter	Description	Units
SAMPLE INFO:		
cruise_id	Ship’s cruise designation	text
station_GEOTRC	Station number, specific to each cruise	integer
LATITUDE	Station latitude	degrees north
LONGITUDE	Station longitude	degrees east
depth_GEOTRC	Sample depth	meters
cast_GEOTRC	Cast number, within a station	integer
event_GEOTRC	GEOTRACES event number	integer
date_collected	Date sample collected	yyyymmdd
time	Time sample collected	hhmm
bottle_GEOTRC	Sample bottle designation, Niskin (NIS), In-situ Pump (PUMP) or towed fish (FISH)	text-integer
sample_GEOTRC	GEOTRACES sample number	integer
lab	Analytical lab (LDEO or UMN)	text

date_dissolved_U_separation Date when dissolved U separated from Th and Pa (used for
correcting measured dissolved Th-230 and Pa-231 for ingrowth by decay of dissolved
uranium during the time between sample collection and U separation mm/dd/yyyy

MEASURED PARAMETERS:

Th_232_D_CONC_BOTTLE	Dissolved Th-232 concentration	pmol/kg
Th_232_D_CONC_BOTTLE_ERR	1 sigma error in Dissolved Th-232	pmol/kg
Th_232_D_CONC_BOTTLE_FLAG	Flag for Dissolved Th-232	1 = good, 2 = questionable, 3 bad or no data
Th_230_D_CONC_BOTTLE	Dissolved Th-230 concentration	µBq/kg
Th_230_D_CONC_BOTTLE_ERR	1 sigma error in Dissolved Th-230	µBq/kg
Th_230_D_CONC_BOTTLE_FLAG	Flag for Dissolved Th-230	1 = good, 2 = questionable, 3 = bad or no data
Pa_231_D_CONC_BOTTLE	Dissolved Pa-231 concentration	µBq/kg
Pa_231_D_CONC_BOTTLE_ERR	1 sigma error in Dissolved Pa-231	µBq/kg
Pa_231_D_CONC_BOTTLE_FLAG	Flag for Dissolved Pa-231	1 = good, 2 = questionable, 3 = bad or no data

Definition of flags:

1 = Value is oceanographically consistent with the vertical concentration profile
2 = Value departs from an oceanographically consistent profile by more than analytical
uncertainty but by no more than a factor of two, or if the value departs from an
oceanographically consistent profile by more than a factor of two, the feature is also apparent in
a nearby station at the same depth.
3 = Value departs from an oceanographically consistent profile by more than a factor of two and
the feature is not apparent in nearby profiles.

DERIVED VARIABLES (All are based solely on measured parameters. Units and error
designations are the same as for the associated measured parameters. See derived parameter
section below for equations used to calculate derived variables):

Th_230_D_XS_CONC_BOTTLE	Dissolved Th-230 concentration corrected for the dissolution of lithogenic minerals, thereby isolating the dissolved Th-230 produced by decay of dissolved uranium
Th_230_D_XS_CONC_BOTTLE_ERR	
Th_230_D_XS_CONC_BOTTLE_FLAG	

Pa_231_D_XS_CONC_BOTTLE	Dissolved Pa-231 concentration corrected for the dissolution of lithogenic minerals (see notes for full explanation)
Pa_231_D_XS_CONC_BOTTLE_ERR	
Pa_231_D_XS_CONC_BOTTLE_FLAG	

Definition of flags:

- 1 = Both Th-232, used to correct for lithogenic dissolution, and Th-230 (Pa-231) are flagged as good.
- 2 = Either Th-232 or Th-230 (Pa-231) are flagged as questionable.
- 3 = Either Th-232 or Th-230 (Pa-231) are flagged as bad.

Notes on DERIVED PARAMETERS:

Th_230_D_XS_CONC_BOTTLE:

The dissolved excess Th-230 concentration refers to the measured dissolved Th-230 corrected for a contribution of Th-230 due to the partial dissolution of uranium-bearing minerals, or lithogenics. Thereby the dissolved excess represents solely the fraction of Th-230 produced in the water by decay of dissolved uranium-234. We estimate the lithogenic Th-230 using measuring dissolved Th-232 and a lithogenic Th-230/Th-232 ratio of 4.0e-6 (atom ratio) as determined by Roy-Barman et al. (2002) and a conversion factor to convert picomoles to micro-Becquerels.

$$\text{Th_230_D_XS_CONC_BOTTLE} = \text{Th_230_D_CONC_BOTTLE} - 4.0\text{e-}6 * 1.7473\text{e}5 * \text{Th_232_D_CONC_BOTTLE}$$

Pa_231_D_XS_CONC_BOTTLE:

The dissolved excess Pa-231 concentration refers to the measured dissolved Pa-231 corrected for a contribution of Pa-231 due to the partial dissolution of uranium-bearing minerals, or lithogenics. Thereby the dissolved excess represents solely the fraction of Pa-231 produced in the water by decay of dissolved uranium-235. We estimate the lithogenic Pa-231 using measuring dissolved Th-232 and a lithogenic Pa-231/Th-232 ratio of 8.8e-8 (atom ratio) which is derived from assuming an average upper continental crustal U/Th ratio (Taylor and McClelland, 1995) and secular equilibrium between Pa-231 and U-235 in the lithogenic material. An additional conversion factor is needed to convert picomoles to micro-Becquerels.

$$\text{Pa_231_D_XS_CONC_BOTTLE} = \text{Pa_231_D_CONC_BOTTLE} - 8.8\text{e-}8 * 4.0370\text{e}5 * \text{Th_232_D_CONC_BOTTLE}$$

Sampling Methodology:

Dissolved data:

Water samples were collected with a Sea-Bird Electronics CTD carousel fitted with 12 30-liter PVC Niskin bottles, maintained and operated by the Ocean Data Facility of Scripps Institution of Oceanography. 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 Tygon™ tubing and filtered through Pall Acropak™ 500 filters on deck (gravity filtration, 0.8/0.45 μm pore size) into Fisher I-Chem series 300 LDPE cubitainers. Approximately 4-5 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

(Fisher Scientific OPTIMA grade), double-bagged, stored in pallet boxes on-deck until the end of the cruise and then at room temperature once shipped to the participating laboratories analysis.

Analytical methods for dissolved radionuclides:

LDEO:

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 ^{229}Th (20 pg) and ^{233}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 NH_4OH (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 H_2O (>18 M Ω) to remove the major seawater ions. The precipitate was then dissolved in 16 M HNO_3 (Fisher Scientific OPTIMA grade) and transferred to a Teflon beaker for a high-temperature (180-200°C) digestion with 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 H_2O , 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 (Anderson et al. 2012). The final column elutions were dried down at 180°C in the presence of 2 drops of HClO_4 and taken up in approximately 1 mL of 0.16 M HNO_3 /0.026 M HF for mass spectrometric analysis.

Concentrations of ^{232}Th , ^{230}Th and ^{231}Pa were calculated by isotope dilution using nuclide ratios determined on a Thermo-Finnegan ELEMENT XR Single Collector Magnetic Sector ICP-MS, equipped with a high performance Interface pump (Jet Pump), and specially-designed sample (X) and skimmer (Jet) cones to ensure the highest possible sensitivity. All measurements were made in low resolution mode (resolving power ~300), peak jumping across the central 5% of the flat-topped peaks. Analyses were made in Escan mode. 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 aliquots of the run solution to gauge background count rates. To correct for potential tailing of ^{232}Th into the minor Th and Pa isotopes, beam intensities were measured at the half masses above and below each mass for ^{230}Th , ^{231}Pa , and ^{233}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 12-15. 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}Th , ^{230}Th and ^{231}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}Th , ^{230}Th , and ^{231}Pa were about 7 pg, 0.4 fg, and 0.1 fg

respectively.

UMN:

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 ^{229}Th and ^{233}Pa and several milligrams dissolved Fe were added to each sample. After allowing 3 days for spike equilibration (at a temperature of about 40°C , the pH of each sample was raised to 8-8.5 by adding concentrated NH_4OH 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 deionized H_2O ($>18\text{ M}\Omega$) to remove the major seawater ions. The precipitate was then dissolved in 14 M HNO_3 and transferred to a Teflon beaker. It was then dried down and taken up in 7N HNO_3 for anion-exchange chromatography using AG1-X8, 100-200 mesh size resin and a polyethylene frit. Initial separation was done on Teflon columns with a 0.75 ml column volume (CV). The sample was loaded in one CV of 7N HNO_3 , followed by 1.5 CV of 7N HNO_3 , 3 CV of 8N HCl (collect Th fraction), and 3 CV of 8N HCl combined with 0.015N HF (collect Pa fraction). The Pa and Th fractions were then dried down in the presence of 2 drops of HClO_4 and taken up in 7N HNO_3 . They were each passed through second and third columns (each with 0.5 ml column volumes) using similar elution schemes. The final Pa and Th fractions were then dried down in the presence of 2 drops of HClO_4 and dissolved in weak nitric acid for analysis on the mass spectrometer.

Concentrations of ^{232}Th , ^{230}Th and ^{231}Pa were calculated by isotope dilution using nuclide ratios determined on a Thermo-Finnigan Neptune mass spectrometer. All measurements were done using a peak jumping routine in ion counting mode on the discreet dynode multiplier behind the retarding potential quadrupole. A solution of ^{233}U - ^{236}U tracer 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.

Water samples were analyzed in batches of 28-56. An aliquot of an intercalibrated working standard solution of ^{232}Th , ^{230}Th and ^{231}Pa , SW STD 2010-1, was added to a separate acid-cleaned Teflon beaker along with weighed aliquots of ^{229}Th spike and ^{233}Pa spike. Spike and Standard were equilibrated for 3 days. It was then dried down and taken up in 7N HNO_3 for anion-exchange chromatography using AG1-X8, 100-200 mesh size resin and a polyethylene frit, and also processed like a sample. Procedural blanks for chemical and mass spectrometric analyses at Minnesota are about 450 fg for ^{232}Th , 11 ag for ^{230}Th , and 28 ag for ^{231}Pa .

Further details on Pa and Th analysis at the U. Minnesota laboratory are given in Shen et al. (2002, 2003, 2012), and Cheng et al. (2000, 2013).

Data Processing:

The reported errors for radionuclide concentrations represent the propagation of one sigma errors

based on the standard isotope ratios collected by ICP-MS, estimated error in the ^{229}Th or ^{233}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 several years. A correction was made to account for the ingrowth of ^{230}Th and ^{231}Pa due to the decay of the natural ^{234}U and ^{235}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}Th and ^{231}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 in seawater (Owens et al. 2011), $[\text{U}] = (0.100 \cdot \text{S} - 0.326) \text{ ng U (g seawater)}^{-1}$. 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 $[\text{U}^{234}]$ and $[\text{U}^{235}]$ respectively based on $[\text{U}]$.

Individual uncertainties for thorium were calculated to include contributions from (a) blank correction using the variance of the blanks measured over the course of the analyses, (b) standard error of the ratios of the analysis (typically close to counting statistics) and (c) spike calibration. For Pa we also included assessment of the correction from the yield correction, mass bias and machine background. In order to assess the reproducibility of the procedure, repeat analyses were performed on the GEOTRACES 2010-1 standard. For standards run alongside EPZT samples, the reproducibility for each isotope was 1.44% for ^{230}Th , 2.14% for ^{232}Th and 3.89% for ^{231}Pa .

References:

Andersen, M.B., Stirling, C.H., Zimmermann, B., Halliday, A.N. (2010) Precise determination of the open ocean $^{234}\text{U}/^{238}\text{U}$ composition. *Geochem. Geophys. Geosyst.* 11, Q12003.

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 ^{230}Th , ^{232}Th , ^{231}Pa , and prospects for ^{10}Be . *Limnol. Oceanogr. Methods* 10, 179-213.

Auro ME, LF Robinson, A Burke, LI Bradtmiller, MQ Fleisher, RF Anderson (2012) Improvements to ^{232}Th , ^{230}Th , and ^{231}Pa analysis in seawater arising from GEOTRACES intercalibration *Limnology and Oceanography, Methods* 10, 464-474

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

Cheng, H., Edwards, R.L., Hoff, J., Gallup, C.D., Richards, D.A., and Asmerom, Y. (2000) The half-lives of uranium-234 and thorium-230. *Chemical Geology* 169, 17-33.

Cheng, H., Edwards, R.L., Shen, C.-C., Polyak, V.J., Asmerom, Y., Woodhead, J., Hellstrom, J., Wang, Y.J., Kong, X.G., Spötl, C., Wang, X.F., and E. Calvin Alexander Jr. (2013) Improvements in ^{230}Th dating, ^{230}Th and ^{234}U half-life values, and U-Th isotopic measurements

by multi-collector inductively coupled plasma mass spectrometry. *Earth and Planetary Science Letters* 371-372, 82-91.

Owens, S.A., Buesseler, K.O., Sims, K.W.W. (2011) Re-evaluating the ^{238}U -salinity relationship in seawater: Implications for the ^{238}U - ^{234}Th disequilibrium method. *Marine Chemistry* 127, 31-39.
Rev. Geophys. 33 (2), 241-265.

Roy-Barman, M., Coppola, L. and Souhaut, M. (2002) Thorium isotopes in the western Mediterranean Sea: an insight into the marine particle dynamics. *Earth Planet. Sci. Lett.* 196, 161-174.

Shen, C.-C., Cheng, H., Edwards, R.L., Thomas, R.B. and Moran, S.B. (2003) Attogram-sized ^{231}Pa Analysis in Dissolved and Particulate fractions of Seawater by Thermal Ionization Mass Spectroscopy. *Analytical Chemistry* v. 75, issue 5, 1075-1079.

Shen, C.-C., Edwards, R.L., Cheng, H., Dorale, J.A., Thomas, R.B., Moran, S.B., Weinstein, S., and Edmonds, H.N. (2002) Uranium and thorium isotopic and concentration measurements by magnetic sector inductively coupled plasma mass spectrometry. *Chemical Geology* 185. no. 3-4, 165-178.

Shen, C.C., Wu, C.C., Cheng, H., Edwards, R.L., Hsieh, Y.T., Gallet, S., Chang, C.C., Li, T.Y., Lam, D.D., Kano, A, Hori, M. and Spotl, C. (2012) High-precision and high-resolution carbonate Th-230 dating by MC-ICP-MS with SEM protocols. *Geochimica Cosmochim. Acta* 99, 71-86.
DOI: 10.1016/j.gca.2012.09.018

Taylor, S.R., McLennan, S.M., (1995) *The geochemical evolution of the continental crust.*

Weyer, S., Anbar, A.D., Gerdes, A., Gordon, G.W., Algeo, T.J., Boyle, E.A., 2008. Natural fractionation of $^{238}\text{U}/^{235}\text{U}$. *Geochim. Cosmochim. Acta* 72, 345-359.