Dissolved Lead and Lead Isotope Ratios from the GEOTRACES GI04 cruise on R/V Hakuho Maru (KH-09-5) in the Indian Ocean and the Antarctic Sea from November to December 2009

Website: https://www.bco-dmo.org/dataset/831202 Data Type: Cruise Results Version: 1 Version Date: 2020-11-23

Project

» <u>Dissolved Pb and Pb Isotopes in the Indian Ocean, GEOTRACES Japan (GI04)</u> (GEOTRACES Japan Pb)

Program

» U.S. GEOTRACES (U.S. GEOTRACES)

Contributors	Affiliation	Role
Boyle, Edward A.	Massachusetts Institute of Technology (MIT-EAPS)	Principal Investigator
Rauch, Shannon	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

Abstract

Dissolved Lead and Lead Isotope Ratios from the GEOTRACES GI04 cruise on R/V Hakuho Maru (KH-09-5) in the Indian Ocean and the Antarctic Sea from November to December 2009.

Table of Contents

- <u>Coverage</u>
- Dataset Description
 - Methods & Sampling
 - Data Processing Description
- Data Files
- <u>Related Publications</u>
- Parameters
- Instruments
- **Deployments**
- <u>Project Information</u>
- Program Information

Coverage

Spatial Extent: N:16.75 **E**:86.0333 **S**:-62 **W**:40.0833 **Temporal Extent**: 2009-11-02 - 2009-12-31

Methods & Sampling

A CTD carousel multi-sampling system (CTD-CMS) was used for collection of water samples during the KH-09-5 cruise of R/V Hakuho-Maru. The system was composed of a carousel (Sea-Bird, SBE-32), a CTD fish (Sea-Bird, Model SBE-9-plus) with a DO sensor, an Epoxy-coated Al frame, and 24 Teflon-coated Niskin-X bottles (General Oceanics, 12-liter type). A pinger (Benthos, Model BFP-312) and/or altimeter (Benthos, Model PSA-916) were installed on the frame to monitor the distance above the sea bottom. A turbidity meter (SeaPoint) was used during Legs 1 and 2. The fluorometer used was Aquatracka Mk III (Chelsea). Zn anodes except those on the CTD housing had been removed in order to avoid Zn contamination and replaced by Al anodes before the cruise.

All the Niskin-X bottles were filled with 1.5% aqueous solution of Extran MA01 for 1 day, 0.1 M HCl for 1 day, and ultra-high purity water for more than 2 days, successively. Teflon spigots of the bottles were soaked in 1% Extran solution and 1M HCl for 1 day. They were then soaked in a mixed solution of HClO4, H2SO4 and HNO3

(1:1:1 mixture) at 120 °C for 3 hrs, 6 M HCl at 120 °C for 3 hrs, and ultra-high purity water at 100 °C for 3 hrs, successively. Viton O-rings were soaked in 1% Extran (1 day), 0.1 M HCl (1 day), 0.1 M HCl at 60 °C (12hrs), and ultra-high purity water at 68 °C (12 hrs).

The CTD-CMS system was attached at the end of a Ti-armored cable (8 mm o.d.) from the No. 2 winch of the vessel and controlled by a CTD deck unit (Sea-Bird, Model 11plus) connected with a computer. During the hydrocasts, the system was lowered down to a depth of ~10 m above the bottom, and water samples were collected at appropriate depths while the system was coming up to the surface. The vessel steered so that surface water came from starboard during the sampling in order to minimize contamination from the ship. Upon retrieved, Niskin-X bottles were transferred into a clean space called "Bubble" and hold vertically on a wooden frame in the Bubble. The Bubble space has a volume of about 10 m3 (2.5 m x 2 m x 2 m), to which filtered clean air was always introduced through two HEPA filter units. A 0.2 um nominal pore size capsule type cartridge filter (Pall Scientific, AcroPak 200) was connected to the spigot of the Niskin-X bottle and water inside the bottle was pressurized with compressed clean air supplied through the top air vent of each bottle. Filtered water samples were obtained after flushing for 30 sec. Transfer of the bottle and sub-sampling inside the clean space follow the GEOTRACES Cookbook recommendations.

Pb concentration analysis: Total Pb concentration was analyzed by the NTA ID-ICPMS method described by Lee et al. (2011). Acid-leached 1.5 mL vials were used. The acidified seawater sample was poured into the vial and 1.3 mL of the sample was pipetted out using a clean pipette tip. The 1.3 mL sample in the pipette tip was pipetted back into the same vial after quickly emptying the vial. Then, the sample was spiked with 25 uL of stable ²⁰⁴Pb isotope spike and left for a few minutes to establish equilibrium between added isotope spikes with their natural isotopes in the samples. Then, the pH of the sample was adjusted to pH=5.3 using ammonium acetate buffer solution (pH= 7.9-8.0). Finally, 150 uL of an NTA resin suspension (2400 beads) were added to the vial and it was shaken on an orbital table at 2000 rpm for 4 days to allow the Pb and resin to bind. After 4 days, the sample vial was centrifuged (for 45 seconds at 14,500 rpm) and the overlying seawater was siphoned off carefully, leaving the resin beads at the bottom. The resin beads were then rinsed three times with high purity H₂O to remove seasalt. In each rinse, the vial was filled with high purity water, centrifuged down, and the supernatant was siphoned off. After rinsing, 150 uL of 0.5 M HNO₃ were added to the vial, and then two days allowed for Pb to be released into solution. The final solution was then brought to the ICPMS for measurement of the isotope ratio (²⁰⁸Pb/²⁰⁴Pb) of this solution (after on-peak zero acid blank correction) which is used to calculate the Pb concentration.

Pb isotopes were analyzed in the same laboratory from another aliquot of the same seawater samples. First, samples were concentrated and purified for Pb isotope analysis by the double Mg(OH)₂ precipitation method described by Reuer et al. (2003) as modified by Boyle et al. (2012). Depending on the Pb concentration in each sample, 270-550 ml of sample was poured into a clean 1-L polyethylene separatory funnel. A small amount of vapor-distilled ammonia solution was added to form Mg(OH)₂ precipitate, and the next day, the settled precipitate was drawn off into clean 50 mL polypropylene centrifuge tubes, centrifuged, and the supernatant siphoned off. The precipitate was then re-dissolved in high-purity 6M HCl, and a few drops of ammonia solution added again to repeat the Mg(OH)₂ precipitation. The amount of ammonia added to the samples for the first and second precipitation was determined empirically to produce Mg(OH)₂ precipitate that scavenges Pb nearly quantitatively (Wu and Boyle, 1997b), but minimizes the amount of precipitate so as to allow for a single final anion purification step. The final wet Mg(OH)₂ precipitate was usually less than 100 ul in volume. It was dissolved in high-purity 1.1M HBr for the HCl-HBr anion exchange column separation.

As described in Boyle et al. (2012), Si(OH)₄ scavenged during Mg(OH)₂ precipitation tends to precipitate as a thick gel if the amount of HBr added to the final precipitate is insufficient, and this gel clogs the anion columns during the purification procedure. This problem occurred for high-Si samples, e.g. deep samples and the samples from station 14. For most of the samples, this problem was resolved by adjusting the volume of 1.1M HBr (0.8 to 2.8 ml) added to the samples to avoid precipitation. However, for some samples, the silica gel was not dissolved completely even after increasing the volume of HBr. In that case, we centrifuged the vials to settle the silica gel to the bottom and carefully loaded the supernatant HBr solution onto the columns. This may lower the recovery efficiency of the procedure as some Pb is trapped in the silica gel. However, the loss of Pb does not seem to affect the resulting Pb isotope ratios (i.e., little fractionation occurs by Pb entrapment in the silica gel) given that 1) duplicates of a few samples processed with different amount of HBr (different amount of silica gel) gave identical results, and 2) the Pb isotope ratios of the samples processed with silica gel were consistent with samples from immediately above and below in the water column that were processed without silica gel formation.

Samples purified by passing through HCI-HBr anion exchange columns were dried on a hotplate in a clean recirculating fume hood, and then re-dissolved in 0.2M HNO₃ on the day of ICP-MS (Inductively Coupled Plasma Mass Spectrometry) analysis. The samples were spiked with TI for exponential "beta" mass fractionation

correction based on ²⁰⁵Tl/²⁰³Tl normalization. Pb isotopes (²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb) of the samples were measured using a GV/Micromass Isoprobe multiple collector ICP-MS, with ²⁰⁴Pb detection on an ion-counting Daly-style detector with WARP (Wide Aperture Retarding Potential) filter. Data processing and corrections were performed as in Boyle et al. (2012), which is the method modified from Reuer et al. (2003).

Data Processing Description

Blank Values and Detection Limits: Exactly 0.3 mL of low-Pb seawater was used to determine the Pb concentration procedure blank. At least three replicates of each sample were measured. The average blank over 24 analytical sessions was 5.9 pmol/kg. The detection limit (3 times the std. dev. of low concentration samples) is about 1.5 pmol/Kg.

Isotope Blanks: There are two main sources of blanks in this isotope analysis. One is due to the AG1-x8 ion exchange resin and the acids used to elute the Pb. A significant but contribution comes from the ICPMS hardware from Pb retained from previous analyses. The latter blank is determined by an "On Peak Zero" measurement on high purity 0.2M HNO₃. Because the AG1-x8 blank is so low, we cannot make an accurate measurement of its Pb isotope ratios. So we measure the most intense signal (²⁰⁸Pb) and then estimate the blanks for the other isotopes assuming an isotope composition for "typical U.S. Pb" assumed as the ratio of our U.S.-purchased laboratory Pb standard (diluted from Ultra Scientific Catalog Number ICP-082, Lot Number D00198). These blanks have been subtracted from the reported isotope ratios.

All of the signals from our large-volume samples were well above Pb concentration detection limits, but the precision of the measurement degrades relative to the Faraday cup Johnson noise (and Daly ion counter statistics) as the signal becomes weaker. We think that our isotope ratio measurements for ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb are good to the second decimal place for samples with 1-2 pmol/kg Pb.

Quality Flags:

The standard Ocean Data View flags were used (reference all flags at

https://www.bodc.ac.uk/data/codes_and_formats/odv_format/):

1: Good Value: Good quality data value that is not part of any identified malfunction and has been verified as consistent with real phenomena during the quality control process.

2: Probably Good Value: Data value that is probably consistent with real phenomena but this is unconfirmed or data value forming part of a malfunction that is considered too small to affect the overall quality of the data object of which it is a part. [Used when only one replicate confirmed the reported value.]

3: Probably Bad Value: Data value recognized as unusual during quality control that forms part of a feature that is probably inconsistent with real phenomena.

4: Bad Value: An obviously erroneous data value.

BCO-DMO Processing:

- modified parameter names;
- added station latitudes and longitudes from the cruise report;
- corrected years to 2009 where they were incrementally increasing by one;
- added ISO8601 date-time fields;
- removed unnecessary columns.

[table of contents | back to top]

Data Files

File
Pb.csv(Comma Separated Values (.csv), 29.15 KB) MD5:3c11bb9838891905bbb1246c131479b7
Primary data file for dataset ID 831202

[table of contents | back to top]

Related Publications

Boyle, E. A., John, S., Abouchami, W., Adkins, J. F., Echegoyen-Sanz, Y., Ellwood, M., ... Zhao, Y. (2012). GEOTRACES IC1 (BATS) contamination-prone trace element isotopes Cd. Fe. Pb. Zn. Cu. and Mo. intercalibration. Limnology and Oceanography: Methods, 10(9), 653–665. doi:10.4319/lom.2012.10.653 Methods

Cutter, G., Andersson, P., Codispoti, L., Croot, P., François, R., Lohan, M. C., Obata, H. and Rutgers v. d. Loeff, M. (2010). Sampling and Sample-handling Protocols for GEOTRACES Cruises, [Miscellaneous] Version 1. http://www.geotraces.org/libraries/documents/Intercalibration/Cookbook.pdf Methods

Lee, J.-M., Boyle, E. A., Echegoven-Sanz, Y., Fitzsimmons, J. N., Zhang, R., & Kayser, R. A. (2011). Analysis of trace metals (Cu. Cd. Pb. and Fe) in seawater using single batch nitrilotriacetate resin extraction and isotope dilution inductively coupled plasma mass spectrometry. Analytica Chimica Acta, 686(1-2), 93-101. doi:<u>10.1016/j.aca.2010</u>.11.052 Methods

Lee, J.-M., Boyle, E. A., Gamo, T., Obata, H., Norisuye, K., & Echegoyen, Y. (2015). Impact of anthropogenic Pb and ocean circulation on the recent distribution of Pb isotopes in the Indian Ocean. Geochimica et Cosmochimica Acta, 170, 126–144. doi:<u>10.1016/j.gca.2015.08.013</u> Results

Reuer, M. K., Boyle, E. A., & Grant, B. C. (2003). Lead isotope analysis of marine carbonates and seawater by multiple collector ICP-MS. Chemical Geology, 200(1-2), 137-153. doi:10.1016/s0009-2541(03)00186-4 https://doi.org/10.1016/S0009-2541(03)00186-4 Methods

[table of contents | back to top]

Parameters

Parameter	Description	Units
Station_ID	Station identifier	unitless
Station_Lat	Station latitude; from cruise report	degrees North
Station_Lon	Station longitude; from cruise report	degrees East
Start_Date_UTC	Start date; format: DD/MM/YYYY	unitless
Start_Time_UTC	Start time (UTC); format: hh:mm	unitless
Start_ISO_DateTime_UTC	Start date and time (UTC) formatted to ISO8601 standard: YYYY-MM-DDThh:mmZ	unitless
End_Date_UTC	End date; format: DD/MM/YYYY	unitless
End_Time_UTC	End time (UTC); format: hh:mm	unitless
End_ISO_DateTime_UTC	End date and time (UTC) formatted to ISO8601 standard: YYYY-MM-DDThh:mmZ	unitless

Start_Latitude	Latitude at start of sample collection; not known (all 'nd')	unitless
Start_Longitude	Longitude at start of sample collection; not known (all 'nd')	unitless
End_Latitude	Latitude at end of sample collection; not known (all 'nd')	unitless
End_Longitude	Longitude at end of sample collection; not known (all 'nd')	unitless
Event_ID	Event identifier; not known (all 'nd')	unitless
Sample_ID	Sample identifier	unitless
Sample_Depth	Sample depth	meters (m)
Pb_D_CONC_BOTTLE_46ivyo	Concentration of dissolved Pb	picomoles per kilogram (pmol/kg)
SD1_Pb_D_CONC_BOTTLE_46ivyo	One standard deviation of Pb_D_CONC_BOTTLE_46ivyo	picomoles per kilogram (pmol/kg)
Flag_Pb_D_CONC_BOTTLE_46ivyo	Quality flag for Pb_D_CONC_BOTTLE_46ivyo	unitless
Pb_206_207_D_RATIO_BOTTLE_gbbqcx	Atom ratio of given isotopes for dissolved Pb referenced to {NBS981}	unitless
SD2_Pb_206_207_D_RATIO_BOTTLE_gbbqcx	Two standard deviations of Pb_206_207_D_RATIO_BOTTLE_gbbqcx	unitless
Flag_Pb_206_207_D_RATIO_BOTTLE_gbbqcx	Quality flag for Pb_206_207_D_RATIO_BOTTLE_gbbqcx	unitless
Pb_208_207_D_RATIO_BOTTLE_aonnnn	Atom ratio of given isotopes for dissolved Pb referenced to {NBS981}	unitless
SD2_Pb_208_207_D_RATIO_BOTTLE_aonnnn	Two standard deviations of Pb_208_207_D_RATIO_BOTTLE_aonnnn	unitless
	1	

Flag_Pb_208_207_D_RATIO_BOTTLE_aonnnn	Quality flag for Pb_208_207_D_RATIO_BOTTLE_aonnnn	unitless

[table of contents | back to top]

Instruments

Dataset- specific Instrument Name	CTD carousel multi sampling system (CTD-CMS)
Generic Instrument Name	CTD Sea-Bird
Dataset- specific Description	The system was composed of a carousel (Sea-Bird, SBE-32), a CTD fish (Sea-Bird, Model SBE-9- plus) with a DO sensor, an Epoxy-coated Al frame, and 24 Teflon-coated Niskin-X bottles (General Oceanics, 12-liter type).
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	ion-counting Daly-style detector
Generic Instrument Name	Daly detector
Dataset- specific Description	Pb isotopes of the samples were measured using a GV/Micromass Isoprobe multiple collector ICP-MS, with ²⁰⁴ Pb detection on an ion-counting Daly-style detector with WARP (Wide Aperture Retarding Potential) filter.
Generic Instrument Description	The Daly detector was designed by N.R Daly in the 1960's. The design uses a conversion dynode to convert incident ions into electrons. It also separates the multiplication electronics away from the ion beam preventing secondary ion production on the multiplication dynodes.

Dataset- specific Instrument Name	ICPMS
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Generic Instrument Description	An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer.

Dataset- specific Instrument Name	Teflon-coated Niskin-X bottles (General Oceanics, 12-liter type)
Generic Instrument Name	Niskin bottle
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.

[table of contents | back to top]

Deployments

KH-09-5

Website	https://www.bco-dmo.org/deployment/831165
Platform	R/V Hakuho Maru
Report	https://datadocs.bco-dmo.org/docs/302/geotraces/KH-09-5/data_docs/hakuhomaru_kh-09- 5.pdf
Start Date	2009-11-06
End Date	2010-01-09
Description	The first three legs of the R/V Hakuho Maru KH-09-5 cruise, whose schedules are shown below, were successfully conducted by Ocean Research Institute, the University of Tokyo, and Japan Agency for Marine-Earth Science and Technology (JAMSTEC), from 6 November 2009 to 10 January 2010 (66 days in total) in the north and western Indian Ocean including the Antarctic Sea. The three legs of this cruise were nicknamed "ERIDANUS Expedition". Leg-1: Tokyo, Japan (6 Nov. 2009) to Cochin, India (24 Nov. 2009) Leg-2: Cochin, India (27 Nov. 2009) to Port Louis, Mauritius (16 Dec. 2009) Leg-3: Port Louis, Mauritius (16 Dec. 2009) to Cape Town, South Africa (10 Jan. 2010) In the original plan, this cruise should have been completed a year earlier (from Nov. 2008 to Jan. 2009), but the cruise was postponed as above due to the rapid increase of oil price at the beginning of FY2008. This cruise was internationally authorized as the first GEOTRACES meridional study in the Indian Ocean.

[table of contents | back to top]

Project Information

Dissolved Pb and Pb Isotopes in the Indian Ocean, GEOTRACES Japan (GI04) (GEOTRACES Japan Pb)

Coverage: Indian Ocean and the Antarctic Sea

This study presents the Pb and Pb isotopic composition (206Pb/207Pb, 208Pb/207Pb) of 11 deep stations from the Indian Ocean Japanese GEOTRACES cruise (KH-09-5), from the Bay of Bengal and Arabian Sea to the Southern Ocean (62°S). For more information, see Lee et al. (2015), doi: <u>10.1016/j.gca.2015.08.013</u>

This research was supported by a number of funding awards to the Boyle lab. Due to the ship's breakdown during the 2010 GEOTRACES North Atlantic Transect cruise on R/V Knorr, remaining funds combined with support from the Spanish Ministry of Science and Innovation and the Singapore National Research

Foundation supported the analysis of samples collected on the 2009-10 GEOTRACES Japan cruise KH-09-5 aboard the R/V Hakuho Maru. Sample collection was supported by grants from the Steel Foundation for Environmental Protection Technology and from Grant-in-Aid of Scientific Research, the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

[table of contents | back to top]

Program Information

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

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

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.

[table of contents | back to top]