Lead isotope data collected from the R/V Pourquoi pas (GEOVIDE) in the North Atlantic, Labrador Sea (section GA01) during 2014

Website: https://www.bco-dmo.org/dataset/652127
Data Type: Cruise Results
Version: 1
Version Date: 2017-10-03

Project
» Filling Gaps in the Atlantic and Pacific Pb and Pb Isotope Spatial and Temporal Evolution (GA01) (GEOVIDE_Pb)

Program
» U.S. GEOTRACES (U.S. GEOTRACES)

Contributors	Affiliation	Role
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Abstract
Lead isotope data collected from the R/V Pourquoi pas (GEOVIDE) in the North Atlantic, Labrador Sea (section GA01) during 2014

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Dataset Description

These data are the isotope ratios of Pb passing through a 0.2um filter (SARTOBRAN 300, Sartorius) or a 0.45um filter (Pall Gelman Supor, polystersulfone).

Methods & Sampling

Sample storage bottle lids and threads were soaked overnight in 2N reagent grade HCl, then filled with 1N reagent grade HCl to be heated in an oven at 60 degrees Celsius overnight, inverted, heated for a second day, and rinsed 5X with pure distilled water. The bottles were then filled with trace metal clean dilute HCl (0.01N HCl) and again heated in the oven for one day on either end. Clean sample bottles were emptied, and double-bagged prior to rinsing and filling with sample.

As stated in the cruise report, trace metal clean seawater samples were collected using the French GEOTRACES clean rosette (General Oceanics Inc. Model 1018 Intelligent Rosette), equipped with twenty-two new 12L GO-FLO bottles (two bottles were leaking and were never deployed during the cruise). The 22 new GO-FLO bottles were initially cleaned in LEMAR laboratory following the GEOTRACES procedures (Cutter and Bruland, 2012). The rosette was deployed on a 6mm Kevlar cable with a dedicated custom designed clean winch. Immediately after recovery, GO-FLO bottles were individually covered at each end with plastic bags to minimize contamination. They were then transferred into a clean container (class-100) for sampling. On each trace metal cast, nutrient and/or salinity samples were taken to check potential leakage of the Go-Flo bottles. Prior to filtration, GO-FLO bottles were mixed manually three times. GO-FLO bottles were pressurized to less than 8 psi with 0.2-um filtered N2 (Air Liquide). For Stations 1, 11, 15, 17, 19, 21, 25, 26, 29, 32 GO-FLO spigots were fitted with an acid-cleaned piece of Bev-a-Line tubing that fed into a 0.2 um capsule filters (SARTOBRAN 300, Sartorius). For all other stations (13, 34, 36, 38, 40, 42, 44, 49, 60, 64, 68, 69, 71, 77) seawater was filtered directly through paired filters (Pall Gelman Supor 0.45um polystersulfone, and Millipore mixed ester cellulose MF 5 um) mounted in Swinnex polypropylene filter holders, following the Planquette and Sherrell (2012) method. Filters were cleaned following the protocol described in Planquette and Sherrell (2012) and kept in acid-cleaned 1L LDPE bottles (Nalgene) filled with ultrapure water (Milli-Q, 18.2 megaohm/cm) until use. Subsamples were taken into acid-cleaned (see above) Nalgene HDPE bottles after a triple rinse with the sample. All samples were acidified back in the Boyle laboratory at 2mL per liter seawater (pH 2) with trace metal clean 6N HCl.

On this cruise, only the particulate samples were assigned GEOTRACES numbers. In this dataset, the dissolved Pb samples collected at the same depth (sometimes on a different cast) as the particulate samples have been assigned identifiers as “SAMPNO” which corresponds to the particulate GEOTRACES number. In cases where there were no corresponding particulate samples, a number was generated as “PI_SAMPNO”.

Upon examining the data, we observed that the sample taken from rosette position 1 (usually the near-bottom sample) was always higher in [Pb] than the sample taken immediately above that, and that the excess decreased as the cruise proceeded. The Pb isotope ratio of these samples were higher than the comparison bottles as well. A similar situation was seen for the sample taken from rosette positions 5, 20 and 21 when compared to the depth-interpolated [Pb] from the samples immediately above and below. Also, at two stations where our near-bottom sample was taken from rosette position 2, there was no [Pb] excess over the samples immediately above. We believe that this evidence points to sampler-induced contamination that was being slowly washed out during the cruise, but never completely. So we have flagged all of these analyses with a “3” indicating that we do not believe that these samples should be trusted as reflecting the true ocean [Pb].

In addition, we observed high [Pb] in the samples at Station 1 and very scattered Pb isotope ratios. The majority of these concentrations were far in excess of those values observed at nearby Station 11, and also the nearby USGT10-01. Discussion among other cruise participants revealed similarly anomalous data for other trace metals (e.g., Hg species). After discussion at the 2016 GEOVIDE Workshop, we came to the conclusion that this is*- evidence of GoFlo bottles not having sufficient time to “clean up” prior to use, and that most or all bottles from Station 1 were contaminated. We flagged all Station 1 data with a “3” indicating that we do not believe these values reflect the true ocean [Pb].

Samples were analyzed at least 1 month after acidification over 11 mass spectrometry sessions by the method of Reuer et al. (2003) as modified by Boyle et al. (2012) and further slightly modified as noted in the following:

Double magnesium hydroxide co-precipitation followed by anion exchange purification: This method is a slight adaptation of the isotope ratio method of Reuer *et al.,* 2003, which was further modified as described by Boyle et al. (2012) and as slightly revised as described below. The method includes low-blank pre-concentration by $Mg(OH)_2$ co-precipitation and isotope ratio analysis on a GV/Micromass IsoProbe multicollector ICPMS using a 50 uL/min nebulizer aspirated into an APEX/SPIRO desolvator, using post-desolvator trace N_2 addition to boost sensitivity.

Nalgene polypropylene separatory funnels (1000mL) and Corning 50 ml conical centrifuge vials were cleaned by heated submersion for 2 days at 60 degrees Celsius in 1N reagent grade HCl, followed by a bulk rinse and 4X individual rinse of each vial with pure distilled water. Each vial was then filled with trace metal clean dilute HCl (0.01N HCl) and heated in the oven at 60 degrees Celsius for one day on either end. Centrifuge vials were kept filled until just before usage.

The separatory funnels were rinsed with distilled water after each use and then filled with high-purity distilled water spiked with high-purity HCl (final concentration 0.01N) between uses.

1000mL polypropylene separatory funnels (Nalgene) were weighed and rinsed one time with seawater sample, then filled with 500ml of sample. $Mg(OH)_2$ coprecipitation was induced by minimal addition of high-purity ammonia solution and mixing (typically 8uL ammonia per 1mL seawater sample). The separatory funnels were left to settle overnight, then agitated to move the precipitate down the funnel walls. After complete settling, the precipitate was drawn from the bottom of the funnels into a 50mL conical centrifuge tubes. The solution/precipitate mix was centrifuged and the solution siphoned off, and then the precipitate was dissolved in a minimal amount of high-purity 6N HCl before undergoing another ammonia addition and $Mg(OH)_2$ coprecipitation. The mixture was centrifuged and the overlying solution was siphoned.

Eichrom AG-1x8 resin was cleaned by three batch rinses with 6N trace metal clean HCl for a 12 hours on a shaker table, followed by multiple washes with distilled water until the pH of the solution was above 4.5. Resin was stored at room temperature in the dark until use.

The precipitate was dissolved in 1 ml of high purity 1.1M HBr. The amount of solution was adjusted depending on the Si concentration of the seawater sample; if too little solution is used, the Si precipitates as a gel, impeding the column separation. The resin in the column was first cleaned with 6M HCl, equilibrated with 1.1M HBr, and then sample was loaded onto the column. The column was then washed with 1.1M HBr followed by 2M HCl and then eluted with 6M HCl. The samples in a 5 ml Savillex PTFE vial were then taken to dryness on a hotplate in a recirculating filtered air fume hood, and stored sealed until analysis.

Just before analysis, samples were dissolved for several minutes in 10µl concentrated ultrapure HNO_3. Then, an appropriate volume of ultrapure water was added (typically 400ul) and spiked with an appropriate amount of Tl for mass fractionation correction. IsoProbe multicollector ICPMS Faraday cups were used to collect on $_{202}$Hg, $_{203}$Tl, $_{205}$Tl, $_{206}$Pb, $_{207}$Pb, and $_{208}$Pb. An Isotopx Daly detector with a WARP filter was used to collect on $_{204}$Pb+$_{204}$Hg. This Daly detector is a revised version that eliminates a reflection problem with the electronic circuitry of the previous version. We do not report $_{206}$Pb/$_{204}$Pb data for samples run on the old Daly detector. Because the deadtime of the Daly detector varied from day to day, we calibrated deadtime on each day by running a standard with known $_{206}$Pb/$_{204}$Pb at a high 204 count rate. The counter efficiency drifts during the course of a day, so we established that drift by running a standard with known $_{206}$Pb/$_{204}$Pb (and a 204 count rate comparable to the samples) every five samples. Tailing from one Faraday cup to the next was corrected by the $_{209}$Bi half-mass method as described by Thirlwall (2000).

On each analytical date, we calibrated the instrument by running NBS981 and normalized measured sample isotope ratios to our measured raw NBS981 isotope ratios to those established by Baker et al. (2004). Using this method for 22 determinations of an in-house standard ("BAB") shows that for samples near the upper range of the Pb signals shown for samples (~1V), $_{206}$Pb/$_{207}$Pb and $_{208}$Pb/$_{207}$Pb can be reproduced to 200ppm. Low-level samples will be worse than that, but generally better than 1000ppm in this data set. Because of the drift uncertainty in the Daly detector, $_{206}$Pb/$_{204}$Pb for samples in the mid-to-upper range of sample concentrations will be at best reproducible to 500ppm.

We have intercalibrated Pb isotope analyses with two labs as reported in Boyle et al. (2012). Since that report, two more labs have added intercalibration data. The outcome of that intercalibration suggests that the accuracy of our measurements approaches the analytical reproducibility we note above.

Data Processing Description

During the isotope ratio analysis, the data were collected in 20 cycles. The isotope ratios were edited for outliers, and averaged with standard errors estimated from the multiple cycles. 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.

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.

In this data set, we encounter any samples that did not yield acceptably reproducible results upon repeated analysis. However, there were a few points that fall off of the depth profiles based on adjacent samples and for which an obvious hydrographic argument could not be made for the anomaly. These samples may be contaminated, and they are given the quality control flag of 3 (probably bad value).

BCO-DMO Processing Notes:

- Column names changed to conform with GEOTRACES conventions
- Originally, data were submitted without GEOTRACES sample numbers. After requesting them from PI, sample numbers were submitted, but they were not GEOTRACES issued. A few of these sample numbers were missing, and so an arbitrary sample number was issued by the PI.
- Two columns were created to accomodate the sample numbers sent by the PI. One was SAMPNO (those not created by PI) and PI_SAMPNO (those created by the PI) in order to distinguish between the two numbers more easily.
- nd was added to blank fields in SAMPNO and PI_SAMPNO

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Data Files

File
Pb_isotopes.csv(Comma Separated Values (.csv), 26.35 KB) MD5:878799481abaec134e7fb435e2cbd6a0 Primary data file for dataset ID 652127

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Related Publications

Baker, J., Peate, D., Waight, T., & Meyzen, C. (2004). Pb isotopic analysis of standards and samples using a 207Pb–204Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS. Chemical Geology, 211(3-4), 275–303. doi:10.1016/j.chemgeo.2004.06.030
Methods

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
Results

Cutter, G. A., & Bruland, K. W. (2012). Rapid and noncontaminating sampling system for trace elements in global ocean surveys. Limnology and Oceanography: Methods, 10(6), 425–436. doi:10.4319/lom.2012.10.425
Methods

Planquette, H., & Sherrell, R. M. (2012). Sampling for particulate trace element determination using water sampling bottles: methodology and comparison to in situ pumps. Limnology and Oceanography: Methods, 10(5), 367–388. doi:10.4319/lom.2012.10.367
Methods

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

Thirlwall, M. (2001). Inappropriate tail corrections can cause large inaccuracy in isotope ratio determination by MC-ICP-MS. Journal of Analytical Atomic Spectrometry, 16(10), 1121–1125. doi:10.1039/b103828c
https://doi.org/10.1039/B103828C
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Parameters

Parameter	Description	Units

cruise_id	Cruise identification	unitless
SECT_ID	Cruise section identifier	unitless
CASTNO	Cast number	unitless
STNNBR	Station number	unitless
BTLNBR	Bottle number; typically 1-24	unitless
CTDPRS	CTD pressure	decibars
SAMPNO	Sequential sample number within the cast (usually corresponds to the bottle number)	unitless
PI_SAMPNO	PI issued sample number for when a standard SAMPNO was not appropriate.	unitless
Pb_206_207_D_RATIO_BOTTLE	Dissolved Pb isotope ratios Pb 206/Pb 207 for Pb passing through a 0.2um SARTOBRAN or 0.45um Supor filter.	dimensionless
Pb_208_207_D_RATIO_BOTTLE	Dissolved Pb isotope ratios Pb 208/Pb 207 for Pb passing through a 0.2um SARTOBRAN or 0.45um Supor filter.	dimensionless
Pb_206_204_D_RATIO_BOTTLE	Dissolved Pb isotope ratios Pb 206/Pb 204 for Pb passing through a 0.2um SARTOBRAN or 0.45um Supor filter.	dimensionless
Pb_206_207_D_RATIO_BOTTLE_FLAG	Quality flag for parameter Pb_206_207_D_RATIO_BOTTLE; follows the convention: 1 = good; 3 = questionable; 4 = bad	unitless
BTL_DATE	Date (yyyymmdd) when the bottle was fired according to the bottle file.	unitless
BTL_LAT	Latitude of bottle firing; north is positive.	decimal degrees
BTL_LON	Lonitude of bottle firing; east is positive.	decimal degrees

Pb_208_207_D_RATIO_BOTTLE_FLAG	Quality flag for parameter Pb_208_207_D_RATIO_BOTTLE; follows the convention: 1 = good; 3 = questionable; 4 = bad	unitless
Pb_206_204_D_RATIO_BOTTLE_FLAG	Quality flag for parameter Pb_206_204_D_RATIO_BOTTLE; follows the convention: 1 = good; 3 = questionable; 4 = bad	unitless

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Instruments

Dataset-specific Instrument Name	12L GO-FLO
Generic Instrument Name	Bottle
Dataset-specific Description	The General Oceanics Inc Model 1018 Intelligent Rosette was equipped with 22 new 12L GO-FLO bottles.
Generic Instrument Description	A container, typically made of glass or plastic and with a narrow neck, used for storing drinks or other liquids.

Dataset-specific Instrument Name	Isotopx Daly detector
Generic Instrument Name	Daly detector
Dataset-specific Description	Revised version that eliminates a reflection problem with the electronic circuitry of the previous version.
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	IsoProbe multicollector ICPMS Faraday Cup
Generic Instrument Name	Faraday cup
Dataset-specific Description	Metal (conductive) cup designed to catch charged particles in a vacuum.
Generic Instrument Description	A Faraday cup is a metal (conductive) cup designed to catch charged particles in a vacuum. The resulting current can be measured and used to determine the number of ions or electrons hitting the cup.

Dataset-specific Instrument Name	APEX/SPIRO Desolvator
Generic Instrument Name	Heated Membrane Desolvator
Dataset-specific Description	Reduces solvent derived polyatomic interferences in the ICPMS mass spectrum
Generic Instrument Description	Membrane desolvation module that reduces solvent derived polyatomic interferences in the ICPMS mass spectrum. Both aqueous and organic solutions can be desolvated.

Dataset-specific Instrument Name	ICP-MS
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Dataset-specific Description	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.

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Deployments

GEOVIDE

Website	https://www.bco-dmo.org/deployment/651998
Platform	R/V Pourquoi pas
Start Date	2014-05-19
End Date	2014-06-25
Description	This is a French GEOTRACES cruise.

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Project Information

Filling Gaps in the Atlantic and Pacific Pb and Pb Isotope Spatial and Temporal Evolution (GA01) (GEOVIDE_Pb)

Website: http://www.geovide.obs-vlfr.fr/

Coverage: Subpolar North Atlantic; Labrador Sea; Greenland

Lead is a trace metal that has historically been emitted into the atmosphere through human activities such as coal burning and the use of leaded gasoline followed by deposition into the ocean. Once introduced into the marine environment, lead is dispersed via currents and removed by biota and other sinking particles. This century-scale growth of lead emissions followed by a decline upon the phase-out of leaded gasoline is one of the great global geochemical experiments. In this study, researchers at the Massachusetts Institute of

Technology will analyze archived seawater samples to improve our knowledge on the spatial and temporal variability of lead concentrations and lead isotope ratios. This data will yield new insights into the sources and transport of lead and other metals, document the time-evolving human footprint on the ocean, and assist with validating models.

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Program Information

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

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

Coverage: Global

GEOTRACES is a SCOR sponsored program; and funding for program infrastructure development is provided by the U.S. National Science Foundation.

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.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1357224

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