**iDATASET description metadata for BCO-DMO**

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**Dataset Name:**

Dissolved Pb isotope ratios [dimensionless]

**Dataset description:**

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

Project:

GEOVIDE, 2014

Funding:   
NSF-OCE-1357224

**Cruise:**

*R/V Pourquoi pas?* GA01

Deployment Synonyms:

GEOVIDE, GA01

Location:

The cruise track began in Lisbon, Portugal on 15 May 2014 and followed the OVIDE section from the Iberian upwelling system to the subpolar North Atlantic region up to the Greenland margin before continuing on to the Labrador Sea / Canadian margin, ending on 30 June 2014, in order to better constrain the deep water export.

Parameter names, definitions and units:

Dissolved Pb isotope ratios 206Pb/207Pb, 208Pb/207Pb, and 206Pb/204Pb for Pb passing through a 0.2µm SARTOBRAN or 0.45μm Supor filter, in nondimensional units.

Sampling and Analytical Methodology:

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˚C 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 <8 psi with 0.2-µm filtered N2 (Air Liquide). For Stations 1, 11, 17, 21, 26, 29, 32 GO-FLO spigots were fitted with an acid-cleaned piece of Bev-a-Line tubing that fed into a 0.2 μm capsule filters (SARTOBRAN® 300, Sartorius). For all other stations (13, 38, 40, 44, 60, 64, 69, 77) seawater was filtered directly through paired filters (Pall Gelman Supor 0.45µm polystersulfone, and Millipore mixed ester cellulose MF 5 µm) 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 MΩ·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 “SAMP\_NO” 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 composition.

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.

1. **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 N2 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˚C 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˚C 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 HNO3. Then, an appropriate volume of ultrapure water was added (typically 400μl) and spiked with an appropriate amount of Tl for mass fractionation correction. IsoProbe multicollector ICPMS Faraday cups were used to collect on 202Hg, 203Tl, 205Tl, 206Pb, 207Pb, and 208Pb. An Isotopx Daly detector with a WARP filter was used to collect on 204Pb+204Hg. This Daly detector is a revised version that eliminates a reflection problem with the electronic circuitry of the previous version. We do not report 206Pb/204Pb 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 206Pb/204Pb 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 206Pb/204Pb (and a 204 count rate comparable to the samples) every five samples. Tailing from one Faraday cup to the next was corrected by the 209Bi 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), 206Pb/207Pb and 208Pb/207Pb 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, 206Pb/204Pb 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:

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).

Access restrictions:

It is my understanding that as much as possible, access to the data will be restricted to BCO-DMO, BODC, and the GEOTRACES Data Management Committee (DMC) and Standards and Intercalibration Committee (SIC) until the IDP-2 product is publicly released in 2017.

Related files and references:

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