

GEOTRACES Intercalibration Report

Cruise ID*: RR1814

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Parameters to be intercalibrated*:

- Ga_D_CONC_FISH::ucndh3 pmol/kg
- Ba_D_CONC_BOTTLE::hndhco nmol/kg
- Mn_D_CONC_FISH::0k2rmu nmol/kg
- Cu_D_CONC_BOTTLE::l8pofx nmol/kg
- Mn_D_CONC_BOTTLE::s3mevt nmol/kg
- Cd_D_CONC_FISH::rysl9e nmol/kg
- Cd_D_CONC_BOTTLE::3qngnv nmol/kg
- Ni_D_CONC_FISH::yj7vul nmol/kg
- Ni_D_CONC_BOTTLE::9xta6d nmol/kg
- Nd_D_CONC_BOTTLE::cfkxfb pmol/kg
- Cu_D_CONC_FISH::lkwnfb nmol/kg
- Nd_D_CONC_FISH::xs9ega pmol/kg
- Pb_D_CONC_BOTTLE::xtsjbw pmol/kg
- Ga_D_CONC_BOTTLE::wbt8su pmol/kg
- Ba_D_CONC_FISH::nwzpgf nmol/kg
- Pb_D_CONC_FISH::ugbi36 pmol/kg

***Once generated, these headings must not be changed or altered.**

Important note for CTD-sensor data submitters: it is not necessary for you to fill in and submit an intercalibration report for these parameters through D0oR (you can skip step 4). Please proceed to send the data registered in D0oR to your appropriate data centre using the data template downloaded from D0oR in step 3 as soon as possible.

Please fill in as many sections as possible.

1. Did your lab participate in an intercalibration exercise

Our lab participated in a previously published dissolved Cd/Pb intercalibration exercise (Zurbrick et al., 2012; <https://doi.org/10.4319/lom.2012.10.270>). Where possible, our GEOTRACES publications have also included comparisons to published literature values or reference waters. This includes comparisons for dissolved Ga

(Whitmore et al., 2020, <https://doi.org/10.1029/2019JC015842>; Ho et al., 2019, <https://doi.org/10.1016/j.dsr.2019.04.009>), dissolved V (Whitmore et al., 2019, <https://doi.org/10.1016/j.marchem.2019.103701>; Ho et al., 2018, <https://doi.org/10.1016/j.marchem.2017.12.003>), dissolved Mo (Ho et al., 2018, <https://doi.org/10.1016/j.marchem.2017.12.003>), and dissolved Ba (Whitmore et al., to be submitted). *Additionally, in the sections below we present results of ongoing intercalibration efforts using GEOTRACES reference waters and crossover stations.*

2. Did your sampling method at sea follow the GEOTRACES cookbook

Yes, we followed the GEOTRACES cookbook. Clean seawater samples were collected using a GEOTRACES CTD referred to as GT-C/12L GoFlo, and also from the Super-GeoFISH towed surface vehicle. For more information, see the cruise report.

Water samples were filtered through pre-cleaned, 0.2 μm Pall Acropak Supor filter capsules as described elsewhere (e.g., Cutter et al., 2014; Hatta et al., 2015). Filtered water was collected in 125 mL HDPE bottles (Nalgene) that had been pre-cleaned by soaking in hot 1.2 M HCl (reagent grade) for at least 8 h with subsequent thorough rinsing with ultrapure distilled deionized water (Barnstead E-pure).

3. Briefly outline the analytical methodology used in your laboratory, and provide associated metadata and references, as appropriate.

Dissolved Ga was determined by isotope dilution ICP-MS using a ThermoFisher Element XR operated in low resolution. Samples (20-30 mL) were concentrated using a SeaFAST system; a dilute HF rinse was used for column cleaning between samples. An enriched isotope spike of known concentration was prepared using purified enriched ^{71}Ga (99.8%), obtained from Oak Ridge National Laboratories. The substantial sample pre-concentration of this method allows for ICP-MS analysis using medium resolution which eliminates isobaric interferences including doubly charged ^{138}Ba with ^{69}Ga .

The reagent blank contribution to the dissolved Ga analysis is typically 0.6 pmol/kg and the detection limit (based on 3 times the standard deviation of the blank) is 0.3 pmol/kg. Repeated runs of US GEOTRACES intercalibration samples (GS and GD), in-house reference solutions, and cast overlap samples suggest a precision of $\pm 4\%$; the limit of detection for Ga was 1.5 pmol/kg. Recovery of the method, as determined by repeated analysis of a spiked and unspiked seawater sample was $100 \pm 7\%$. See Table 1 for data.

Dissolved Ba was measured using a ThermoFisher Element XR Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and the isotope dilution method as described by Jacquet et al. (2005). Aliquots (50 μL) of each sample were spiked with 25 μL of a ^{135}Ba -enriched solution (~ 170 nM) and then diluted 30-fold with 0.2 μm ultrapure

filtered water. A sample of ~93% enriched ^{135}Ba was obtained from Oak Ridge National Laboratories for use as the enriched isotope spike. The ICP-MS was operated in low resolution and both ^{135}Ba and ^{138}Ba were determined. The samples were bracketed every 10 samples with a blank and the spike ^{135}Ba solution. The volumes of the spikes, samples and dilution water were accurately assessed by calibrating each pipette by weight. The reproducibility error of this method was estimated by comparing samples collected at the same depths on different casts at the same station. For 12 pairs of these replicate samples, the average absolute deviation of 0.7 nmol/kg or typically 1.5%. Repeated runs of runs of US GEOTRACES intercalibration samples and in-house reference solutions suggest a similar precision; the limit of detection for barium was 0.7 nmol/kg. Our precision is similar to that reported by other labs for Ba (e.g., Jacquet et al., 2005). See Table 1 for data.

Dissolved Ni, Cu, Cd, Pb, and Mn were determined using 14 mL of sample that was spiked with a mixture of isotopically-enriched Ni-62, Cu-65, Cd-111, and Pb-207 (Oak Ridge Nat'l. Labs). Each spike was >90% enriched in the listed isotopes. The sample/spike ratio was chosen so as to have the analytical isotope ratios approximately the geometric mean of the natural and enriched spike isotope ratios. Samples were then extracted/pre-concentrated using a SeaFAST system (Elemental Scientific, Inc.) operated in offline mode. A 10-mL sample loop was employed and the elution volume was 750 μL . A similar online SeaFAST extraction procedure is described by Hathorne et al. (2012) for rare earth elements. The extracted samples were subsequently analyzed using a Thermo-Fisher high resolution ICP-MS with an Apex-FAST high efficiency sample introduction system with Spiro desolvator (Elemental Scientific, Inc.). All elements were determined in medium resolution, except Cd which was determined in low resolution. For Mn-55, the Ni and Cu spikes served as internal standards. Calibration was checked by analysis of a large-volume composite North Atlantic surface seawater sample. Spiked (with a natural isotopic abundance elemental spike) and unspiked aliquots of this sample were analyzed twice in each analytical run. Mo-98 was monitored to correct for MoO^+ interference on Cd isotopes.

Dissolved Nd was determined in a separate seaFAST extraction, but with essentially the same methodology as the transition metals. The samples were spike with isotopically-enriched Nd-145. Nd was determined in low resolution.

The reproducibility error of this method was estimated by comparing samples collected at the same depths on different casts at the same station as well as by repeated measurement of GEOTRACES reference waters and an in-house standard. Recovery of the method was determined by repeated analysis of a spiked and unspiked seawater. The recoveries, precisions, and comparisons to reference waters are shown in Table 1 for the dissolved concentration data.

4. Report your blank values and detection limits, and explain how these were defined and evaluated.

The reagent blank contribution to the dissolved Ga analysis is typically 0.6 pmol/kg and the detection limit (based on 3 times the standard deviation of the blank) is 0.3 pmol/kg.

For dissolved Ba, the blank was estimated by isotopically spiking the ultrapure water used for sample dilution and averaged 0.1 ± 0.2 nmol/kg. For these blank data, the limit of detection for barium was 0.7 nmol/kg.

For dissolved Nd, Ni, Cu, Cd, Pb and Mn, detection limits were estimated based on 3x the standard deviation of repeated analyses of low analyte samples: Nd = 0.07 pmol/kg; Ni = 0.2 nmol/kg; Cu = 0.2 nmol/kg; Cd = 0.005 nmol/kg; Mn = 0.07 nmol/kg; Pb < 0.001 nmol/kg. Detection limits were estimated by repeated analysis of both the SeaFAST elution acid as well as SeaFAST 'air blanks', i.e., blanks where the extracted 'sample' was simply air. Excepting Cd, blanks were <1% of typical sample concentrations; for Cd, there appears to be an unresolved 0.007 nmol/kg blank based on comparison with reference samples and other labs.

5. Report how you monitored the internal consistency of your data (e.g., through replicate analyses of samples).

For dissolved trace element concentrations, see Table 1, below, which contains data on repeated analyses of in-house consistency standards as well as analysis of cast overlap samples (i.e., samples collected at the same depth/station but on different casts). Table also contains spike recovery data.

Table 1. Summary statistics for trace element determination, USM.								
	Ba	Cd	Cu	Ga	Mn	Nd	Ni	Pb
	nmol/kg	pmol/kg	nmol/kg	pmol/kg	nmol/kg	pmol/kg	nmol/kg	pmol/kg
Cast overlap comparison (n=12) (Note 1)								
Average concentration	94.2	847	1.9	10.8	0.35	15.6	7.8	20
Average absolute difference	1.7	21	0.08	0.6	0.02	0.6	0.10	1
Spike Recovery (Note 2)								
Percent recovery	101.6%	104.6%	103.3%	99.9%	101.6%	101.4%	98.7%	98.0%
Std. dev.	1.4%	4.3%	5.0%	7.1%	4.3%	1.1%	1.7%	3.0%
Replicates	n=3	n=12	n=12	n=13	n=12	n=40	n=12	n=27

GEOTRACES Reference Waters (Notes 3-6)								
Replicates	n=12	n=9	n=9	n=12	n=9	n=3	n=9	n=10
Sample GS (GSP for Nd)								
Concentration (USM)	44.3	11	0.88	42.5	1.50	3.96	2.20	30
Std. deviation	0.8	4	0.04	1.6	0.09	0.17	0.05	1
Consensus conc. (Std. Dev.)	43.0 (1.1)	2.1 (0.6)	0.84 (0.06)	42.5 (1.7)	1.50 (0.11)	unk.	2.08 (0.06)	28.6 (1.0)
	43.7 (1.0)							
Sample GD (GSD for Nd)								
Concentration (USM)	54.1	278	1.73	32.8	0.24	14.3 5	4.12	44
Std. deviation	0.9	6	0.04	1.4	0.02	0.34	0.07	1
Consensus conc. (Std. Dev.)	52.7 (0.5)	271 (6)	1.62 (0.07)	32.7 (1.4)	0.21 (0.03)	unk.	4.00 (0.10)	42.7 (1.5)
	54.3 (1.5)							
In-House Reference Waters								
Replicates	n=6	n=12	n=12	n=23	n=12	n=19	n=12	n=17
"NAZT"								
Concentration	42.9	864	3.45	21.2	0.18	7.5	8.98	9
Std. deviation	0.6	20	0.18	2.4	0.02	0.3	0.09	1
"NAZT-S"								
Concentration	84.8	1171	5.58	49.1	1.16	51.9	13.8 6	27
Std. deviation	1.0	24	0.17	3.3	0.04	2.0	0.10	2

Notes

1. Cast overlap shows comparison of samples collected at approx. the same depth on different casts at the same station.
2. Spike recovery shows percentage recovery based on the difference between a metal-spiked and unspiked seawater sample.
3. Consensus values for GS and GD for Cd, Cu, Mn, and Ni taken from <http://www.geotraces.org/sic/intercalibrate-a-lab/standards-and-reference-materials>
4. Consensus values for Ga from Ho et al., 2019; doi: 10.1016/j.dsr.2019.04.009.
5. Consensus values for V from Ho et al., 2018; doi: 10.1016

/j.marchem.2017.12.003.

6. Consensus values for Ba from Shiller, analyses of Ba from GEOTRACES GA03 (<http://lod.bco-dmo.org/id/dataset/3827>) and GP16 (<http://lod.bco-dmo.org/id/dataset/648753>).

6. Report the external consistency of your data (e.g., results from analyses of certified reference materials and/or consensus materials).

For dissolved trace element concentrations, see Table 1, above, which contains data on GEOTRACES reference waters.

7. If you occupied a crossover station, include a plot and a table that show relevant data and their level of agreement, and explain any significant discrepancies (e.g., where discrepancies may reflect differences in the depth of isopycnal surfaces between occupations). If possible please also include a profile of Temperature & Salinity.

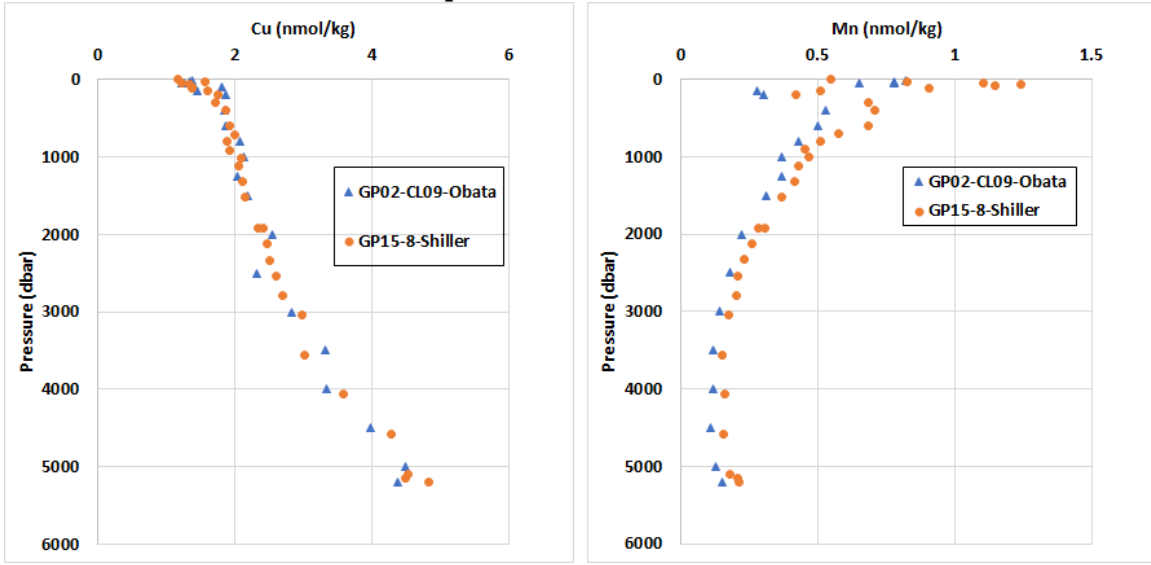
For Leg 1 of GP15, there was a crossover station between GP15-Stn 8 and the 2017 Japanese GP02-Stn CL09 (also called KH17-03 or GP02-bis). Unfortunately, for GP02, only Mn and Cu data are available (courtesy H. Obata). The comparison is quite good for these elements. There was also a 2012 Japanese cruise in the North Pacific (also called GP02 or KH12-04): their stn BD-14 is about 1400 km away from GP15-Stn 8.

For Leg 2 of GP15, there is a crossover between GP15-Stn 35 and GP16-Stn 36. Both are US cruises using the same sampling equipment.

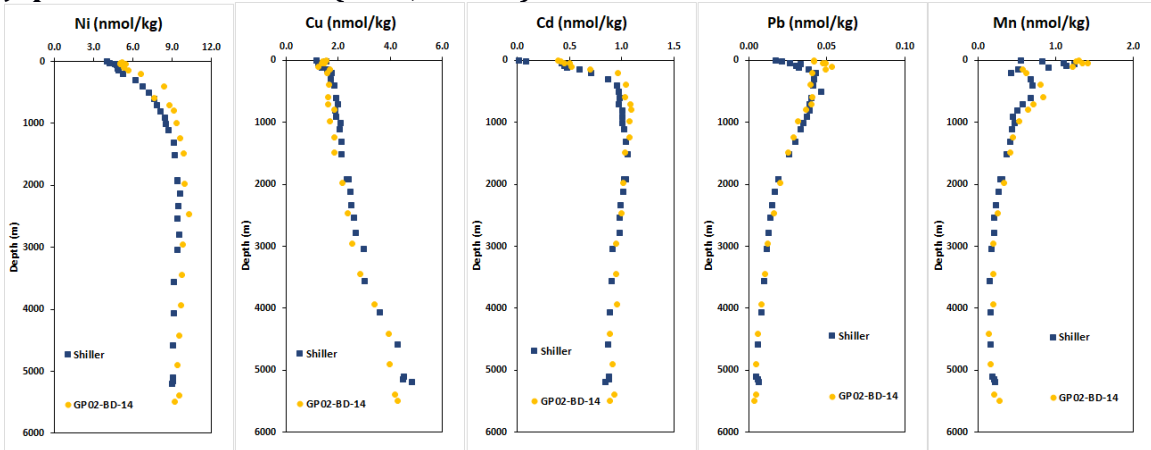
US labs involved in GP15 also made intercomparisons of their TEI determinations, where possible.

We show graphs of these various comparisons below. In general, these comparisons show that our lab's data are quite similar to the results from other labs.

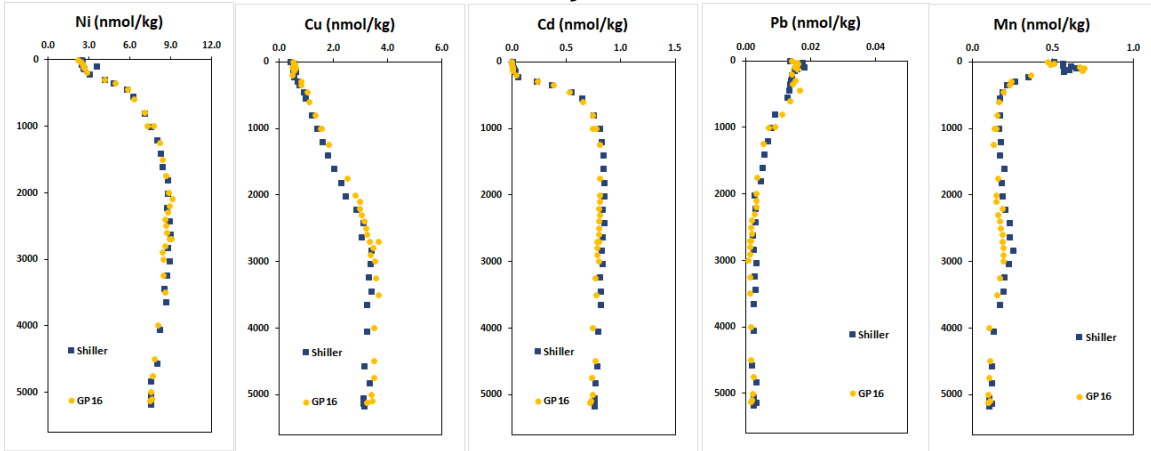
North Pacific GP15-Stn 8: Comparisons with Obata 2017 GP02 data



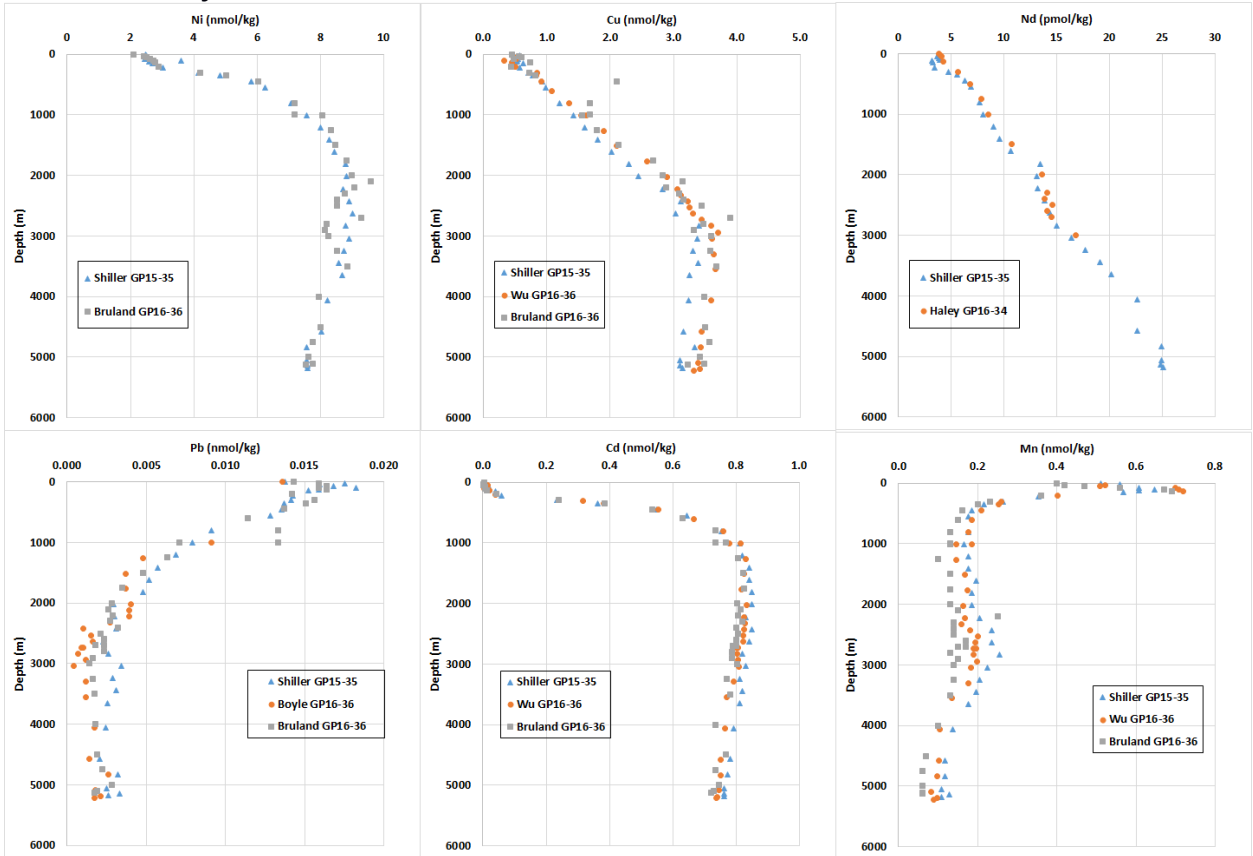
North Pacific GP15-Stn 8 (47 N, 152 W) comparison with data from 2012 Japanese GP02-BD-14 (47 N, 170 W).



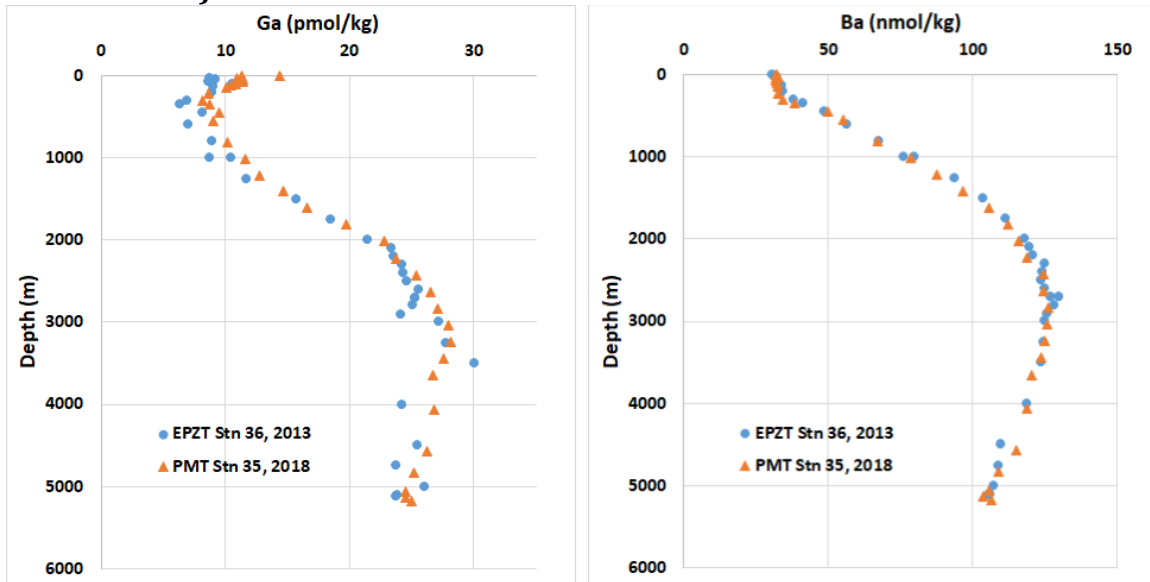
South Pacific GP15-Stn 35 comparison with GP16-Stn 36 crossover data (GP16 data are consensus results from IDP17).



Expanded comparison of Shiller GP15-35 data with individual labs doing GP16-36 analyses.



South Pacific GP15-35 and GP16-36 comparisons for Ga and Ba, two elements analyzed only by Shiller lab. (Note: for Ba and Ga papers by Whitmore et al., 2020 and Whitmore et al. in prep. show Ga and Ba intercalibrations for the Arctic Ocean.)



8. If you did not occupy a crossover station, report replicate analyses from a different laboratory, or if there were no replicate analyses (e.g., due to large volumes or short half-lives), explain how your data compare to historical data including results from nearby stations, even though they may not be true crossover stations.

See Sec. 7, above.

9. If not already included in your responses to the questions above, please provide a representative vertical profile or report the range of values, for the parameter(s) that are addressed in this intercalibration report.

For dissolved trace element concentrations, see crossover and other intercomparison profiles, above.

References

Cutter, G., Andersson, P. S., Codispoti, L. A., Croot, P., Francois, R., Lohan, M., et al. (2014). Sampling and Sample-handling Protocols for GEOTRACES Cruises, *Version 2*. <https://www.geotraces.org/methods-cookbook/>

Hathorne, E.C., B. Haley, T. Stichel, P. Grasse, M. Zieringer, and M. Frank. (2012).

Online preconcentration ICP-MS analysis of rare earth elements in seawater. *Geochemistry Geophysics Geosystems* 13: Q01020. doi: 10.1029/2011GC003907

Hatta, M., C.I. Measures, J. Wu, S. Roshan, J.N. Fitzsimmons, P. Sedwick, P. Morton. (2015). An overview of dissolved Fe and Mn distributions during the 2010–2011 U.S. GEOTRACES North Atlantic Cruises: GEOTRACES GA03. *Deep-Sea Res. II* 116: 117–129. doi:10.1016/j.dsr2.2014.07.005

Ho, P., J. Lee, M. Heller, P. Lam, and A.M. Shiller. (2018). The distribution of dissolved and particulate Mo and V along the U.S. GEOTRACES East Pacific Zonal Transect (GP16): the roles of oxides and biogenic particles in their distributions in the oxygen deficient zone and the hydrothermal plume. *Marine Chemistry* 201: 242-255; doi: 10.1016 /j.marchem.2017.12.003.

Ho, P., Resing, J. A., & Shiller, A. M. (2019). Processes controlling the distribution of dissolved Al and Ga along the U.S. GEOTRACES East Pacific Zonal Transect (GP16). *Deep Sea Research Part I: Oceanographic Research Papers*, 147, 128–145. <https://doi.org/10.1016/j.dsr.2019.04.009>

Jacquet, S.H.M., F. Dehairs, D. Cardinal, J. Naveza, B. Delille. (2005). Barium distribution across the Southern Ocean frontal system in the Crozet–Kerguelen Basin. *Marine Chemistry* 95: 149–162. doi:10.1016/j.marchem.2004.09.002.

Whitmore, L. M., Morton, P. L., Twining, B. S., & Shiller, A. M. (2019). Vanadium cycling in the Western Arctic Ocean is influenced by shelf-basin connectivity. *Marine Chemistry*, 216, 103701. <https://doi.org/10.1016/j.marchem.2019.103701>

Whitmore, L.M., A. Pasqualini, R. Newton, A.M. Shiller. (2020). Gallium: A New Tracer of Pacific Water in the Arctic Ocean. *J. Geophys. Res.: Oceans* 124, e2019JC015842. <https://doi.org/10.1029/2019JC015842>.

Whitmore, L.M., A.M. Shiller, T. Horner, Y. Xiang, D. Bauch, F. Dehairs, P. Lam, J. Li, M. Maldonado, C. Mears, R. Newton, A. Pasqualini, H. Planquette, R. Rember, H. Thomas. (To be submitted). Barium Cycling in the Arctic Ocean: A Basin-wide Perspective Reveals Strong Shelf Influences.

Zurbrick, C.M., P. Morton, C. Gallon, A. Shiller, W.M. Landing, and A.R. Flegal. (2012). Intercalibration of cadmium and lead concentration measurements in the northwest Pacific Ocean. *Limnology & Oceanography: Methods* 10: 270-277.

Once completed, please upload the report here: <https://geotraces-portal.sedoo.fr/pi/>