GEOTRACES Intercalibration Report

<u>Cruise ID*:</u> HLY1502 <u>Submitting investigator*:</u> Alan Shiller - University of Southern Mississippi alan.shiller@usm.edu <u>Parameters to be intercalibrated*:</u>

- Ga_D_CONC_BOTTLE::1mgxwx pmol/kg - Cu_D_CONC_SUBICE_PUMP::detas0 nmol/kg - Ga_D_CONC_SUBICE_PUMP::xsfaz3 pmol/kg - Cu_D_CONC_BOTTLE::tq3sck nmol/kg - Ga_D_CONC_BOAT_PUMP::yl8lnv pmol/kg - Ba_138_134_D_DELTA_SUBICE_PUMP::xjmpgx per mil - Cd_D_CONC_BOTTLE::wikkhy nmol/kg - Ni_D_CONC_SUBICE_PUMP::vmo4mu nmol/kg - Ni_D_CONC_BOAT_PUMP::jxf39e nmol/kg - Cd_D_CONC_SUBICE_PUMP::gorkxq nmol/kg - Ba_D_CONC_BOTTLE::gaggba nmol/kg - Ba_138_134_D_DELTA_BOTTLE::gorel8 per mil - V_D_CONC_SUBICE_PUMP::o0swtf nmol/kg - Cd_D_CONC_BOAT_PUMP::jz0rob nmol/kg - V_D_CONC_BOAT_PUMP::6ejtax nmol/kg - Ni_D_CONC_BOTTLE::tpaocv nmol/kg - Ba_D_CONC_BOAT_PUMP::s9e7xv nmol/kg - Cu_D_CONC_BOAT_PUMP::6crw16 nmol/kg - Ba_D_CONC_SUBICE_PUMP::d6phfd nmol/kg - Mn_D_CONC_BOTTLE::itu1qi nmol/kg - Mn_D_CONC_BOAT_PUMP::tdgkvz nmol/kg - V_D_CONC_BOTTLE::y54tnw nmol/kg - Mn_D_CONC_SUBICE_PUMP::md5sbr nmol/kg - Ba_138_134_D_DELTA_BOAT_PUMP::qgmo1e per mil

<u>*</u>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 DOoR (you can skip step 4). Please proceed to send the data registered in DOoR to your appropriate data centre using the data template downloaded from DOoR 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; <u>https://doi.org/10.4319/lom.2012.10.270</u>). 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, <u>https://doi.org/10.1029/2019JC015842</u>; Ho et al., 2019, <u>https://doi.org/10.1016/j.dsr.2019.04.009</u>), dissolved V (Whitmore et al., 2019, <u>https://doi.org/10.1016/j.marchem.2019.103701</u>; Ho et al., 2018, <u>https://doi.org/10.1016/j.marchem.2017.12.003</u>), dissolved Mo (Ho et al., 2018, <u>https://doi.org/10.1016/j.marchem.2017.12.003</u>), and dissolved Ba (Whitmore et al., 2018, <u>https://doi.org/10.1016/j.marchem.2017.12.003</u>), and dissolved Ba (Whitmore et al., to be submitted). <u>Additionally, in the sections below we present results of ongoing intercalibration efforts using GEOTRACES reference waters and crossover stations.</u>

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. For more information, see the cruise report. Additional near surface samples were collected using either a small boat or through the ice using Teflon coated Tygon tubing and a trace metal clean pump (IWAKI, model WMD-30LFY-115).

Water samples were filtered through pre-cleaned, 0.2 μ m 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 precleaned 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). Small boat and under-ice samples were first collected into large acid-washed carboys and subsampled into 125 mL bottles.

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 2 operated in low resolution. Samples were concentrated using Mg(OH)₂ co-precipitation (e.g., Shiller & Bairamadgi, 2006; Zurbrick et al., 2012). Briefly, in this technique, a small addition (~70 μ L) of clean aqueous ammonia is added to the acidified seawater sample (~7.5 mL) which precipitates a fraction of the dissolved magnesium as the hydroxide, which in turn, scavenges the gallium from solution. An enriched isotope spike of known concentration was prepared using purified enriched ⁷¹Ga (99.8%), obtained from Oak Ridge National Laboratories. See Whitmore et al., 2020 (<u>https://doi.org/10.1029/2019JC015842</u>) and Ho et al., 2019 (<u>https://doi.org/10.1016/j.dsr.2019.04.009</u>) for further details.

Because there is a significant interference of doubly charged ¹³⁸Ba with ⁶⁹Ga, the precipitate was washed three times with a solution of high purity 0.1% NH₄OH to minimize residual Ba. The precipitate was then dissolved in 550 mL ultrapure 3% HNO₃ (Seastar Chemicals, Baseline) and analyzed in low resolution using a ThermoFinnigan Element 2 High Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS). Isotopes monitored on the ICP-MS were ⁶⁹Ga, ⁷¹Ga, and ¹³⁸Ba. A slight correction for residual Ba was made based on the ratio of responses at masses 69 and 138 to a Ba standard solution. Because the residual salt content varied from sample to sample, it was not possible to matrix-match the Ba correction standard. However, typically, this correction affected the final result by < 2.5 pmol/kg; where higher Ba corrections were noted, the sample was reprecipitated and re-analyzed because of concerns about the accuracy of applying the Ba standard correction to samples of high salt content.

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), inhouse 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 2 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and the isotope dilution method as described by Jacquet et al. (2005). Aliquots (50 μ L) of each sample were spiked with 25 μ L of a ¹³⁵Ba-enriched solution (\sim 170 nM) and then diluted 30-fold with 0.2 µm ultrapure filtered water. A sample of ~93% enriched ¹³⁵Ba was obtained from Oak Ridge National Laboratories for use as the enriched isotope spike. The ICP-MS was operated in low resolution and both ¹³⁵Ba and ¹³⁸Ba were determined. The samples were bracketed every 10 samples with a blank and the spike ¹³⁵Ba 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 δ^{138} **Ba (Ba isotopes)** were measured at WHOI (Woods Hole Oceanographic Institution) using a ThermoFinnigan Neptune multicollector ICP-MS. Five mL aliquots were prepared by first spiking with a known quantity of ¹³⁵Ba– ¹³⁶Ba double spike to achieve a spike:sample ratio of between 1-2. Following equilibration with the spike, samples were co-precipitated with CaCO₃ by dropwise addition of 350 µL of 1 M Na₂CO₃ solution. The precipitate was dissolved and reconstituted in 2 M HCl for ion-exchange chromatography. Chromatography protocols are detailed in Horner et al. (2015). Following purification, samples were again reconstituted in 2 % nitric acid and analyzed for δ^{138} Ba at the WHOI Plasma Facility. Samples were aspirated at 140 µL/min, desolvated using an Aridus II, and introduced into the instrument using 1 L/min Ar carrier gas containing 2-5 mL/min admixed nitrogen. Samples are measured in low-resolution mode relative to concentration- and spike:sample-matched aliquots of NIST SRM 3108 ($\equiv 0 \%_0$), measured after every fourth sample. Samples are themselves analyzed between 2-4 times, and Ba-isotopic compositions calculated using an iterative, geometric-based deconvolution of spike-sample mixtures.

Dissolved V, Ni, Cu, Cd 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 V-50 (Oak Ridge Nat'l. Labs). Each spike was >90% enriched in the listed isotopes, except for V-50 (0.25% natural abundance) which was 44.3% enriched. 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 V, 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. Ti-47 and Cr-52 were monitored to correct for any Ti-50 or Cr-50 isobaric interference on V-50; the correction was generally <1%. Likewise, Mo-98 was monitored to correct for MoO⁺ interference on Cd isotopes. 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 δ^{138} Ba, blanks were estimated by spiking a 5 mL solution of 18.2 M Ω grade de-ionized water with 5 ng of 135 Ba $^{-136}$ Ba double spike and processing as if it were a seawater sample. Since no precipitate forms during Na₂CO₃ addition, the entire solution is evaporated and reconstituted in 2 M HCl for ion-exchange chromatography. The 135 Ba: 138 Ba on the resultant 'sample' was measured on the multicollector ICP-MS and the Ba content calculated using isotope dilution. The median Ba blank measured over the course of this study was 318 pg (n = 7), which was between 0.6–1.4 % (median 0.8 %) of the total Ba in processed samples (median = 40 ng Ba). Given that the δ^{138} Ba of the Ba blank is \approx -0.1±0.1 ‰ (Horner et al., 2015), no correction is made to our isotope data as the blank correction would not shift δ^{138} Ba outside of analytical uncertainty, which is estimated to be ±0.03– 0.05 ‰ (± 2\sigma). The range of uncertainties reflects the fact that our precision depends almost entirely on the amount of Ba in the sample, with samples containing >40 ng achieving the highest level of precision of ±0.03 ‰.

For dissolved V, Ni, Cu, Cd and Mn, detection limits were estimated based on 3x the standard deviation of repeated analyses of low analyte samples: V = 1 nmol/kg; Ni = 0.2 nmol/kg; Cu = 0.2 nmol/kg; Cd = 0.005 nmol/kg; Mn = 0.07 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).

Sample δ^{138} Ba values are calculated by normalizing individual analyses to the nearest four measurements of NIST. Final δ^{138} Ba represent the mean of between 2–4 NIST-normalized measurements. The accuracy of the NIST normalization is itself monitored using a secondary standard (AccuSPEC Ba), which is analyzed in place of every 11th sample.

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 1 also contains spike recovery data.

Table 1. Summary statistics for trace element determination, USM.Concentrations in nmol/kg

	Ga	Ва	Cd	v	Ni	Cu	Mn
Cast overlap comparison (n=12) (Note 1)							
Average concentration	25.9	44.2	0.242	29.1	3.82	1.63	0.55
Average absolute difference	0.8	0.7	0.009	0.6	0.07	0.07	0.05
Spike Recovery (Note 2)							
Percent recovery	99.9%	101.6%	104.6%	96.8%	98.7%	103.3%	101.6%
Std. dev.	7.1%	1.4%	4.3%	3.4%	1.7%	5.0%	4.3%
Replicates	n=13	n=3	n=12	n=12	n=12	n=12	n=12
GEOTRACES Reference Waters (Notes 3-6)							
Replicates	n=12	n=12	n=9	n=9	n=9	n=9	n=9
Sample GS							
Concentration	42.5	44.3	0.011	34.3	2.20	0.88	1.50
Std. deviation	1.6	0.8	0.004	0.7	0.05	0.04	0.09
	42.5	43.0	0.0021	34.5	2.08	0.84	1.50
Consensus conc. (Std. Dev.)	(1.7)	(1.1) 43.7 (1.0)	(0.0006)	(0.5)	(0.06)	(0.06)	(0.11)
Sample GD		(- <i>i</i>					
Concentration	32.8	54.1	0.278	32.5	4.12	1.59	0.24
Std. deviation	1.4	0.9	0.006	0.7	0.07	0.06	0.02
	32.7	52.7	0.271	32.9	4.00	1.62	0.21
Consensus conc. (Std. Dev.)	(1.4)	(0.5) 54.3 (1.5)	(0.006)	(0.5)	(0.10)	(0.07)	(0.03)
In-House Reference Waters							
Replicates "NAZT"	n=23	n=6	n=12	n=12	n=12	n=12	n=12
Concentration	21.2	42.9	0.864	34.6	8.98	3.45	0.18
Std. deviation	2.4	0.6	0.020	0.7	0.09	0.18	0.02
"NAZT-S"							
Concentration	49.1	84.8	1.171	68.6	13.86	5.58	1.16
Std. deviation	3.3	1.0	0.024	1.7	0.10	0.17	0.04

Notes

1. Cast overlap is comparison of samples collected at approx. the same depth (~500 m) 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.

 Consensus values for GS and GD for Cd, Cu, Mn, and Ni.
Consensus values for Ga from Ho et al., 2019; doi: 10.1016/j.dsr.2019.04.009.
Consensus values for V from Ho et al., 2018; doi: 10.1016 /j.marchem.2017.12.003.
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.

Consistency of Ba isotope data were monitored by performing sample replicates (e.g., GN01 #10557) and processing GEOTRACES consensus standards alongside samples. During the course of this study, we processed the following: GSP (aliquot #138), GSC (#161), and GEOTRACES D1 (#591). For GSP, we obtained d[Ba] = 35.7 ± 0.9 and δ^{138} Ba = $+0.60\pm0.03 \%_0$ (n = 2); for GSC d[Ba] = 42.3 ± 1.1 and δ^{138} Ba = $+0.55\pm0.03 \%_0$ (n = 3); and, for D1 d[Ba] = 102.0 ± 2.6 and δ^{138} Ba = $+0.33\pm0.03 \%_0$ (n = 2). The values for D1 compare well with published data (Table 2). Table 2. Barium isotope data comparison for WHOI, Oxford, and GEOMAR.

Material	WHOI			Oxf	ord	GEOMAR			
	d[Ba] (nmol kg ⁻¹)	δ ¹³⁸ Ba (‰)	Ref.	d[Ba] (nmol kg ⁻¹)	δ ¹³⁸ Ba (‰)	Ref.	d[Ba] (nmol kg ⁻¹)	δ ¹³⁸ Ba (‰)	Ref.
SAFe S	34.7 ± 0.9	0.63 ± 0.04	{1}	34.3	0.62 ± 0.02	{2}	34.1	0.64 ± 0.08	{3}
SAFe D1	98.7 ± 2.5	0.31 ± 0.03	{1}				99.3	0.31 ± 0.03	{3}
SAFe D2	97.2 ± 2.4	0.32 ± 0.03	{1}	99.6	0.27 ± 0.02	{2}			

Refs: **{1}** Geyman et al. (2019; doi:10.1016/j.epsl.2019.115751); **{2}** Hsieh & Henderson (2017; doi:10.1016/j.epsl.2017.06.024); **{3}** Cao et al. (2020; doi:10.1016/j.epsl.2015.11.017)

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 dissolved Ba, we have crossover station comparisons with both the Canadian (GN02/03) and European (GN04) cruises. The comparison is quite good as show in the table/figure below. Note: There are no crossover data for δ^{138} Ba.

				Approximate	Dissolv	Dissolved Ba (nmol kg ⁻¹)		
Cruise	Station	Latitude (°N)	Longitude (°E)	Distance between stations (km)	Median Offset	Min Offset	Max Offset	
GN01	32	89.99	32.54	7	0.6	0.24	1.8	
GN04	87	89.93	-120.19					
GN01	30	87.52	-179.81	3	2.0	0.20	8.1	
GN04	101	87.50	179.80					
GN01	57	73.39	-156.53	266	1.9	0.12	18.1	
GN02/3	CB4	75.00	-150.00					
GN01	52	77.50	-148.01	203	1.1	0.14	10.8	
GN02/3	CB3	76.99	-140.05					
Summary					1.4	0.12	18.1	



For dissolved Ga, we were only able to compare with the Canadian cruise (Orians lab); the Europeans have actually provided us with sample splits for Ga analysis. The comparison below (CB stations are Orians) shows that the Canadian data are about 10% lower than ours. We have reanalyzed our samples using a new isotope

dilution/SeaFAST extraction method that allows us to do the ICP-MS analysis in medium resolution. Although precision is greatly improved with the new method, the results are nearly identical. Thus, we have reproduced our results with another method and have yet to identify a calibration issue on our end. We do note, however, that our dissolved Ga data compare well with those published by McAlister & Orians (2015) for other western Arctic stations (see second figure below).

Ga	GT-12147			GT-12151			GT-12155			GT-12161		
pmol/kg	AVG	SD	п	AVG	SD	п	AVG	SD	п	AVG	SD	n
USM	28.9	-	1	26.9	-	1	7.8	-	1	6.7	-	1
UBC	25.2	1.41	3	23.6	0.53	3	6.4	0.39	3	6.1	0.21	3

Canadian/GN02-03 (blue)-US/GN01 (orange) Ga comparison....from Orians intercalibration report



Dissolved Ga comparison between McAlister & Orians (2015) and our GN01 data (figure from Whitmore et al., 2020).



For dissolved V, we have obtained splits of both the Canadian and European samples for V analysis. For the Europeans (GN04), a preliminary V analysis was made at NIOZ (Loes Gerringa, pers. comm.). They do not intend to submit their V data since they found offsets between stations. Our isotope dilution method is much less susceptible to that since changes in extraction efficiency are much less of an issue with ID methods. Nonetheless, the comparison shows a better than 5% overall agreement, though with obvious scatter. The figure below shows both our and their V analysis of their (GN04) samples as well as of the GN01 crossover station.





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.

Inter-laboratory comparisons were made among US participants at select GN01 stations. Below are comparison graphs of our data with those other labs for dissolved Cd, Cu, Ni, and Mn at station 32 (90 N; crossover with GN04) and station 57 (73 N, 157 W; near Canadian station CB4). Where only our point is visible (red circles) it is because all labs produced nearly identical values and hence the other points are hidden.



GN01-Station 32 US Interlaboratory Comparison:





As noted above, there are no crossover stations for dissolved δ^{138} Ba. However, we have compared dissolved data obtained along the UK-GEOTRACES 40 °S, which were measured at WHOI (GA10E; 2010-2011) with those obtained at Oxford (GA10; 2011-2012). The results shown in panels A-C below indicate excellent agreement at two stations spaced ~1,300 km apart. The data have been plotted against potential density anomaly to facilitate comparison. We also compared dissolved Ba isotope data for seawater measured at WHOI against that obtained by other labs and construct a global compilation (panel D in figure, below). This compilation includes only published data and does not include GN01 samples submitted here. The compilation shows that samples measured at WHOI agree with those measured elsewhere, despite different approaches to sampling and sample handling, processing protocols, and analytical methods.



Dissolved δ^{138} Ba data comparison along GA10 (Panels A–C) and a global compilation of published data (D). Data sources in compilation: GEOMAR (Cao et al., 2020), Oxford (Hsieh & Henderson, 2017; Bridgestock et al., 2018; Hemsing et al., 2018), and WHOI (Horner et al., 2015; Bates et al., 2017; Geyman et al., 2019).

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.

The figure below shows the global compilation of dissolved Ba isotope data (grey points) with the Arctic GN01 data obtained here overlain (blue). With two notable exceptions, these data overlap with the global array, presumably indicating their accuracy. (Figure courtesy of Whitmore et al., to be submitted.)



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