GEOTRACES Intercalibration Report

Cruise ID*: TN303
Submitting investigator*: Alan Shiller - University of Southern Mississippi - alan.shiller@usm.edu
Parameters to be intercalibrated*:

- **Ga_D_CONC_BOTTLE::qmbktp pmol/kg**
- **Ga_D_CONC_FISH::ndt0dj 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 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

Few labs analyze dissolved Ga. A comparison between our Ga analyses in the Arctic Ocean and those of McAlister & Orians (2015) can be found in Whitmore et al. (2020). Additionally, the calibration of the GP16 disssolved Ga data considered below was discussed in Ho et al. (2019).

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 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).

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 µL) 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 ^{71}Ga (99.8%), obtained from Oak Ridge National Laboratories. See Whitmore et al., 2020 (https://doi.org/10.1029/2019JC015842) and Ho et al., 2019 (https://doi.org/10.1016/j.dsr.2019.04.009) for further details.
Because there is a significant interference of doubly charged ^{138}Ba with ^{69}Ga, the precipitate was washed three times with a solution of high purity 0.1% NH_4OH to minimize residual Ba. The precipitate was then dissolved in 550 mL ultrapure 3% HNO_3 (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 ^{69}Ga, ^{71}Ga, and ^{138}Ba. 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), in-house reference solutions, and cast overlap samples suggest a precision of ± 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 ± 7%. See Table 1 (below) for data.

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

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

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.

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

See Table 1, below, which contains data on GEOTRACES reference waters.

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

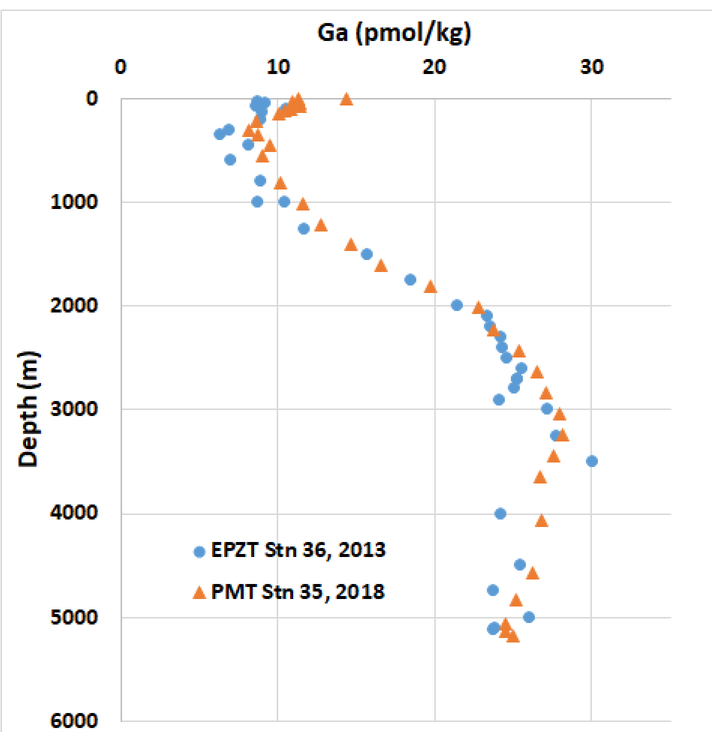
	Ga
Cast overlap comparison (n=12) (Note 1)	
Average concentration	25.9
Average absolute difference	0.8
Spike Recovery (Note 2)	
Percent recovery	99.9%
Std. dev.	7.1%
Replicates	n=13
GEOTRACES Reference Waters (Note 3)	
Replicates	n=12
Sample GS	
Concentration	42.5
Std. deviation	1.6
Consensus conc. (Std. Dev.)	42.5 (1.7)
Sample GD	
Concentration	32.8
Std. deviation	1.4
Consensus conc. (Std. Dev.)	32.7 (1.4)
In-House Reference Waters	
Replicates	n=23
"NAZT"	
Concentration	21.2
Std. deviation	2.4

"NAZT-S"	
Concentration	49.1
Std. deviation	3.3

Notes
1. Cast overlap shows comparison of samples collected at approx. the same depth on different casts at the same station; depth was typically ~500 m.
2. Spike recovery shows percentage recovery based on the difference between a metal-spiked and unspiked seawater sample.
3. Consensus values for Ga from Ho et al., 2019; doi: 10.1016/j.dsr.2019.04.009.

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.

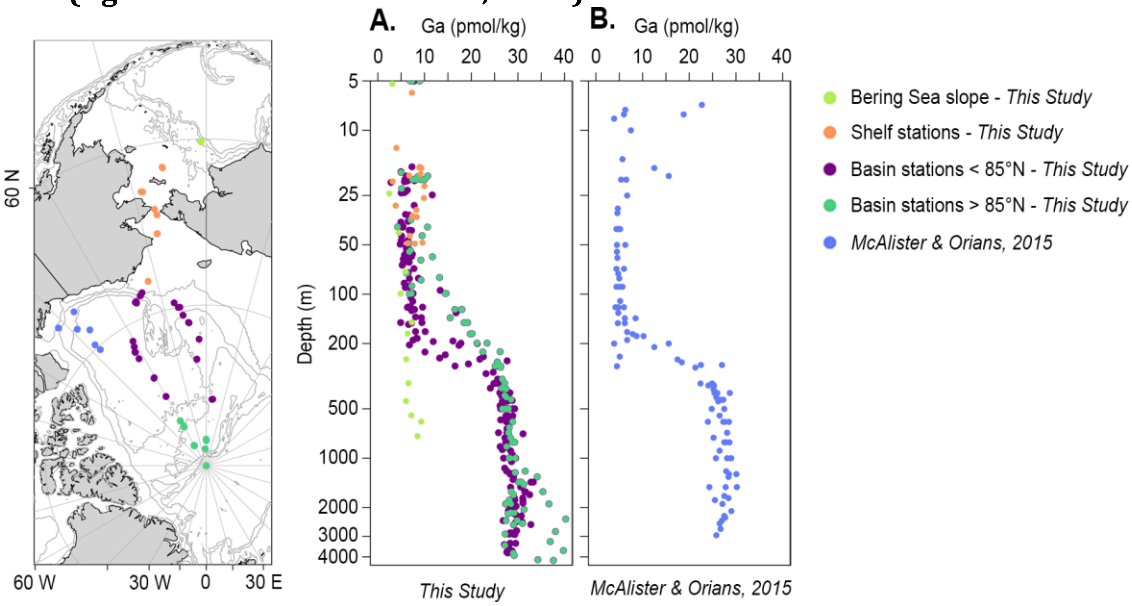
The GP16 crossover station near Tahiti (Stn 36 "EPZT") was reoccupied during GP15 (Stn 35 "PMT"). However, the only comparison we can make is with our own data for the two cruises since so few labs analyze dissolved Ga. As shown below, the agreement is excellent. (Note that a newer method having better precision was used for the later GP15 cruise.)



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.

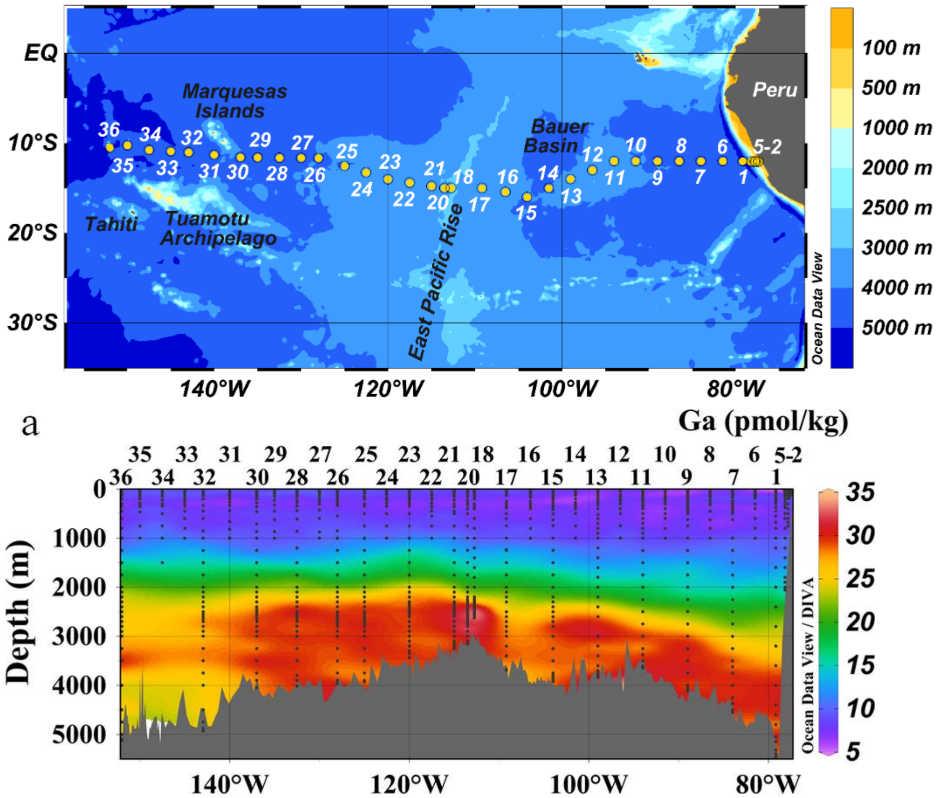
There is little oceanic dissolved Ga data, especially in the South Pacific. We show below one of the few comparisons that can be made between our data in the Arctic Ocean and similar profiles done by McAlister & Orians (2015). The comparison is very good.

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



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.

See crossover and other intercomparison profiles, above. The entire GP16 section is shown in Ho et al. (2019) and reproduced below.



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/

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., 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

McAlister, J. A., & Orians, K. J. (2015). Dissolved gallium in the Beaufort Sea of the Western Arctic Ocean: A GEOTRACES cruise in the International Polar Year. *Marine Chemistry*, *177*, 101–109. https://doi.org/10.1016/j.marchem.2015.05.007

Shiller, A. M., & Bairamadgi, G. R. (2006). Dissolved gallium in the northwest Pacific and the south and central Atlantic Oceans: Implications for aeolian Fe input and a reconsideration of profiles. *Geochemistry, Geophysics, Geosystems*, *7*, Q08M09. https://doi.org/10.1029/2005GC001118

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.

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