

## GEOTRACES Intercalibration Document

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Investigator: Alan M. Shiller; [alan.shiller@usm.edu](mailto:alan.shiller@usm.edu); 1-228-688-1178  
Dept. of Marine Science, University of Southern Mississippi, 1020 Balch Blvd. Stennis Space Center, MS 39529 USA

Element(s): Dissolved rare earth elements, including yttrium, reported in pmol/kg-sw.

Cruise(s): GA03 (US North Atlantic section) also called USGT-10 & USGT-11

### Analytical Methodology:

Water column samples were taken from the GEOTRACES carousel and filtered through pre-cleaned, 0.2 µm Pall Acropak Supor filter capsules as described elsewhere (e.g., Cutter et al., 2012; Hatta et al., 2015). Near surface water samples were collected using an underway towed-fish pumped seawater system (Bruland et al., 2005) with samples filtered through sequential 0.45 µm Osmonics and 0.2 µm Polycarbonate (PCTE) cartridge filters. 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). Samples were acidified in a laminar flow bench aboard ship using 0.5 mL of ultrapure HCl per 125 mL sample.

For analysis of dissolved rare earth elements (including Y), 14 mL of sample was spiked with a mixture of isotopically-enriched Nd-145, Sm-149, Eu-153, Gd-155, Dy-161, Er-167, and Yb-171 (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 similar online SeaFAST extraction procedure is described by Hawthorn et al., 2012. 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.). The instrument was operated in low resolution. The enriched isotope spikes also served to provide counts/sec. calibration factors for elements that were not spiked with enriched isotopes. This calibration was also examined with a standard made in dilute nitric acid. Precision and recovery were 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. A Ba standard was also run to check for BaO<sup>+</sup> interference on several isotopes and Ba in the extracted samples was also monitored. Because the extraction resin in the SeaFAST system (Nobias PA-1) discriminates against Ba, plus the reduction of the BaO<sup>+</sup> interference by the desolvation system, BaO<sup>+</sup> was less than 0.1% of the counts in Eu-151, Eu-153, Gd-155, and Gd-157. Tests also revealed no significant low REE oxide interference on mid-/high-REEs.

Table 1 lists precision and recovery for each element determined by this method as well as the estimated detection limit. Detection limits were estimated from the standard deviation of the counts/sec. obtained when the SeaFAST was run using air as the sample.

#### Intercalibration:

We have compared our data with several published works including:

1. van de Flierdt et al., 2012. GEOTRACES REE intercalibration at BATS
2. Pahnke et al., 2012. GEOTRACES REE intercalibration at BATS
3. Middag et al., 2015 GEOTRACES multielement (including Y and La) intercalibration at BATS
4. Lambelet et al., 2015. GEOTRACES Nd at BATS.
5. Stichel et al., 2015. Nd at GA03, Stn 22.
6. Zhang & Nozaki, 1996; Nozaki et al., 1997; and, Alibo et al., 1999. Y concentration.

Our REE profiles at BATS are from GA03, Station 10 (2011 cruise). To compare with concentrations obtained by others at different depths, we used a polynomial interpolation of our data over ~1000 m intervals.

We compared our interpolated dissolved REE concentrations with the 2000 m BATS sample concentrations reported by van de Flierdt et al., 2012. Differences reported in Table 2 are such that negative numbers mean that our lab's results were lower than the others. The comparison shows generally good agreement, though some of our results for the heavy monoisotopic REEs (Tb, Ho, Tm, Lu) are more than 10% lower than van de Flierdt et al. Because our blank correction was quite small, this is unlikely to be due to an over-corrected blank.

We compared our interpolated dissolved REE concentrations at 1000, 2000, 3000, 3750, and 4500 m at BATS with those of Pahnke et al., 2012. Average differences are shown in Table 2 and show generally good agreement. Note that in a number of cases where we were lower than van de Fliert et al., we are higher than Pahnke et al. Tb and Ho, for which we were 13% lower in the van de Fliert et al. comparison, agree quite well in the Pahnke et al. comparison.

We compared our interpolated Nd data from 500 m and deeper with the data at BATS published by Lambelet et al., 2015. The 7-point linear regression was:  $USM = 0.969 \times \text{Lambelet} + 0.938$  with  $r^2 = 0.984$ . If the regression is forced through zero, the relationship is  $USM = 1.01 \times \text{Lambelet}$  with  $r^2 = 0.982$ . Our results were typically 2% higher than Lambelet et al.'s.

Stichel et al. collected water during GA03 as did we, though their samples came from the standard Niskin rosette during a separate cast from the GEOTRACES carousel where our samples came from. We had 18 samples from equivalent depths. The 18-point linear regression was:  $USM = 1.062 \times \text{Stichel} - 0.958$  with  $r^2 = 0.987$ . If the regression is forced through zero, the relationship is  $USM = 1.016 \times \text{Stichel}$  with  $r^2 = 0.985$ . Our results were typically 1% higher than Stichel et al.'s.

Middag et al. collected water at BATS during GA03 (when we did) and GA02. They provide results for Y and La collected using different sampling systems and analyzed by the same (standard additions/extraction) method in different labs. Their GA02 and GA03 results for Y and La agree well with each other. Our La results agree well with theirs. For instance, for the GA03 results:  $USM = 1.08 \times \text{Middag} - 1.3$  with  $r^2 = 0.993$ . If the regression is forced through zero, the relationship is  $USM = 1.026 \times \text{Middag}$  with  $r^2 = 0.990$ . For Y, the intercalibration is not as good, with the GA03 comparison resulting in  $USM = 1.28 \times \text{Middag} - 47$  with  $r^2 = 0.936$ . Typically, our results are ~6% lower than theirs, with greatest differences in the upper water column (>9% difference in the upper 500 m). Note that our profiles look very similar (Fig. 1). Due to the agreement between the GA02 and GA03 results in Middag et al., it is tempting to view their results as “better.” We note, however, that for the Pacific and Indian Oceans, the data of Zhang and Nozaki (1996) and Nozaki et al. (1997) for the chemically-similar Y and Ho, show a Y-Ho slope of 88.6, not unlike our Y-Ho slope of 82.2. Middag et al. did not determine Ho, but using our Ho data with their GA03 Y data yields a significantly lower slope of 61.2. Unfortunately, we know of no other independent Y-Ho data for the Atlantic Ocean. Indeed, the only other North Atlantic Y data are those of Alibo et al. (1999) who provide limited data down to 2000 m in the general vicinity of our Stn 18 (for GA03). Unfortunately, their concentrations, while similar to ours in shallow waters, are over 30% greater than ours at 2000 m. Despite this extended discussion of Y, it should still be remembered that the differences between our data and those reported in Middag et al. are not extreme.

In summary, we observe that our YREE results are comparable to those produced by several other labs. In general, YREE differences between our lab and others are similar to the interlaboratory differences found by van de Flierdt et al. (2012).

#### References:

D.S. Alibo, Y. Nozaki, and C. Jeandel, 1999. Indium and yttrium in North Atlantic and Mediterranean waters: Comparison to the Pacific data. *Geochimica et Cosmochimica Acta* 63: 1991–1999.

K.W. Bruland, E.L. Rue, G.J. Smith, and G.R. DiTullio, 2005. Iron, macronutrients and diatom blooms in the Peru upwelling regime: brown and blue waters of Peru. *Marine Chemistry* 93: 81–103.

G. Cutter, K.W. Bruland, 2012. Rapid and noncontaminating sampling system for trace elements in global ocean surveys. *Limnol. Oceanogr.: Methods* 10: 425–436.  
<http://dx.doi.org/10.4319/lom.2012.10.425>

- M. Hatta, 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
- E.C. Hawthorne, 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
- M. Lambelet, T. van de Flierdt, K. Crocket, M. Rehkämper, K. Kreissig, B. Coles, M.J.A. Rijkensberg, L.J.A. Gerringa, H.J.W. de Baar, and R. Steinfeldt, 2015. Neodymium isotopic composition and concentration in the western North Atlantic Ocean: Results from the GEOTRACES GA02 section. *Geochimica et Cosmochimica Acta* 177: 1-29. doi:10.1016/j.gca.2015.12.019
- R. Middag, R. Seferian, T.M. Conway, S.G. John, K.W. Bruland, and H.J.W. de Baar, 2015. Intercomparison of dissolved trace elements at the Bermuda Atlantic Time Series station. *Marine Chemistry* 177: 476-489. doi: 10.1016/j.marchem.2015.06.014
- Y. Nozaki, J. Zhang, and H. Amakawa, 1997. The fractionation between yttrium and holmium in the marine environment. *Earth Planet. Sci. Lett.* 148, 329–340.
- K. Pahnke, T. van de Flierdt, K. Jones, S. R. Hemming, and S.L. Goldstein, 2012. GEOTRACES intercalibration of neodymium isotopes and rare earth element concentrations in seawater and particles—Part 2: systematic tests and baseline profiles. *Limnol Oceanogr. Methods* 10: 252-269. doi:10.4319/lom.2012.10.252
- A.M. Shiller, 2003. Syringe Filtration Methods for Examining Dissolved and Colloidal Trace Element Distributions in Remote Field Locations. *Environ. Sci. Technol.* 37: 3953-3957. doi: 10.1021/es0341182
- T. Stichel, A.E. Hartman, B. Duggan, S.L. Goldstein, H. Scher, and K. Pahnke, 2015. Separating biogeochemical cycling of neodymium from water mass mixing in the Eastern North Atlantic. *Earth Planet. Sci. Lett.* 412: 245-260. doi:10.1016/j.epsl.2014.12.008
- T. van de Flierdt, and others, 2012. GEOTRACES intercalibration of neodymium isotopes and rare earth elements in seawater and marine particulates. Part 1: international intercomparison. *Limnol. Oceanogr. Methods* 10: 234-251. doi:10.4319/lom.2012.10.234
- J. Zhang and Y. Nozaki, 1996. Rare earth elements and yttrium in seawater: ICP-MS determinations in the East Caroline, Coral Sea, and South Fiji basins of the western South Pacific Ocean. *Geochim. Cosmochim. Acta* 60, 4631–4644.

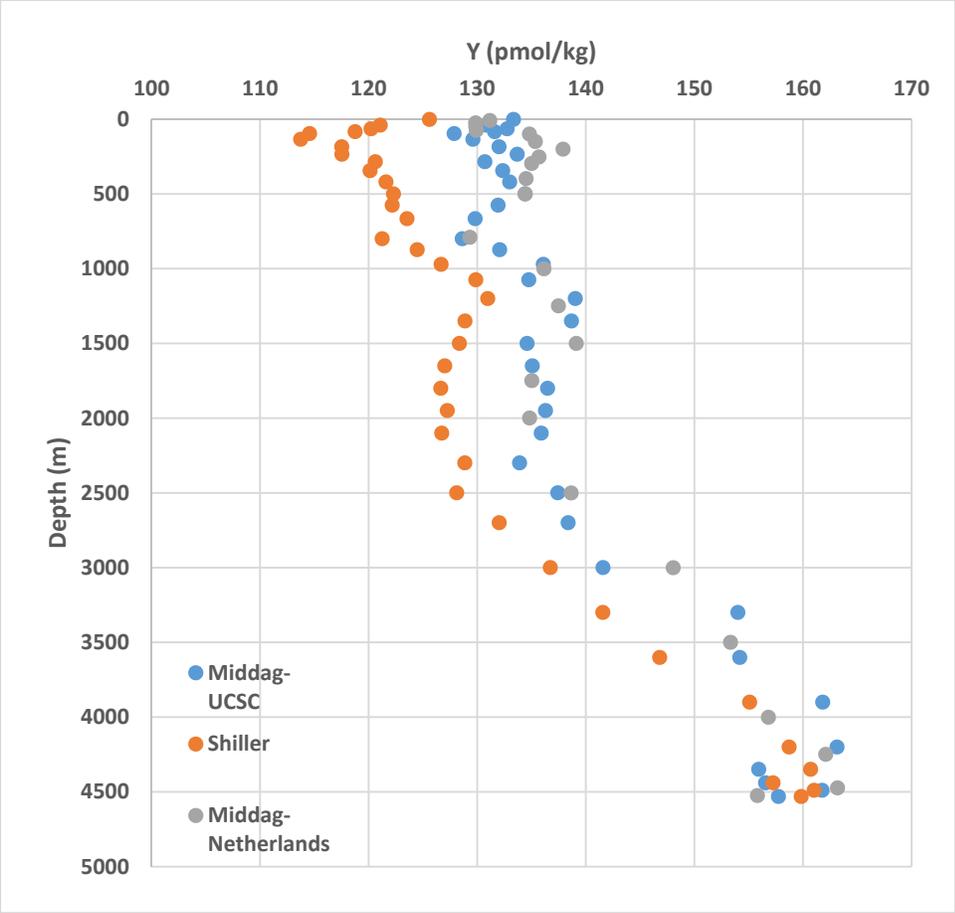


Figure 1. Comparison of Y profiles at BATS.

**Table 1. RSD's for repeated (n=40) analysis of un-spiked (NAZT) and spiked (NAZTS) large volume composite sample and recovery from difference between the two samples. Note: for Gd and Yb, concentrations were determined using isotope ratio measurements of the enriched isotope (Gd-155, Yb-171) and the two unenriched isotopes shown.**

	Y	La	Ce	Pr	Nd	Sm	Eu	Gd-157	Gd-158	Tb	Dy	Ho	Er	Tm	Yb-172	Yb-173	Lu
<b>NAZT RSD</b>	3.7%	2.9%	4.5%	1.7%	1.1%	1.4%	2.4%	1.5%	1.4%	1.5%	1.4%	1.2%	1.4%	1.4%	1.6%	1.6%	3.3%
<b>NAZTS RSD</b>	3.1%	2.5%	4.5%	2.0%	1.0%	1.2%	2.0%	2.1%	2.0%	1.4%	1.1%	1.1%	1.3%	1.3%	1.5%	1.5%	3.6%
<b>Recovery %</b>	101.9%	99.4%	112.7%	102.1%	101.4%	100.7%	101.6%	99.0%	105.9%	101.7%	101.6%	102.3%	100.2%	101.8%	101.0%	101.7%	101.8%
<b>Detn Limit (pM)</b>	0.3	0.1	0.2	0.02	0.07	0.02	0.02	0.05	0.02	0.004	0.02	0.004	0.007	0.002	0.006	0.007	0.002
<b>van de Fliert et al., 2012</b>																	
<b>Pct difference</b>	na	-7.3%	-13.4%	-10.7%	0.8%	-4.7%	-5.4%	-0.7%	-0.7%	-13.6%	-2.7%	-13.4%	-3.1%	-15.8%	-2.7%	-2.7%	-13.8%
<b>Pahnke et al., 2012</b>																	
<b>Pct difference</b>	na	1.4%	6.2%	0.5%	10.5%	6.5%	5.4%	6.6%	6.6%	0.5%	3.5%	-2.4%	2.4%	-7.9%	2.9%	2.9%	-8.8%

**Table 2. Comparison with van de Fliert et al., 2012**

	<b>La</b>	<b>Ce</b>	<b>Pr</b>	<b>Nd</b>	<b>Sm</b>	<b>Eu</b>	<b>Gd</b>	<b>Tb</b>	<b>Dy</b>	<b>Ho</b>	<b>Er</b>	<b>Tm</b>	<b>Yb</b>	<b>Lu</b>
<b>Van de Fliert data, BATS 2000 m</b>														
Conc. in ppt	3.279	0.717	0.568	2.499	0.519	0.138	0.761	0.125	0.943	0.251	0.843	0.126	0.824	0.141
Conc. in pmol/kg-sw	23.61	5.12	4.03	17.33	3.45	0.91	4.84	0.79	5.80	1.52	5.04	0.75	4.76	0.81
Uncertainty	11.8%	44.4%	8.8%	7.0%	9.8%	10.9%	10.9%	9.6%	6.6%	6.0%	5.0%	6.3%	5.2%	5.0%
<b>Shiller-USM BATS (USGT-11-10) 2000 m interpolated data</b>														
pmol/kg	21.89	4.43	3.60	17.47	3.29	0.86	4.80	0.68	5.65	1.32	4.89	0.63	4.63	0.69
<b>Percentage difference</b>	-7.3%	-13.4%	-10.7%	0.8%	-4.7%	-5.4%	-0.7%	-13.6%	-2.7%	-13.4%	-3.1%	-15.8%	-2.7%	-13.8%