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One of the key activities during the initial phase of the international GEOTRACES program was an extensive international intercalibration effort, to ensure that results for a range of trace elements and isotopes (TEIs) from different cruises and from different laboratories can be compared in a meaningful way. Here we present the results from the intercalibration efforts on neodymium isotopes and rare earth elements in seawater and marine particles. Fifteen different laboratories reported results for dissolved $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in seawater at three different locations (BATS 15 m, BATS 2000 m, SAFe 3000 m), with an overall agreement within 47 to 57 ppm (2σ standard deviation of the mean). A similar agreement was found for analyses of an unknown pure Nd standard solution carried out by 13 laboratories (56 ppm), indicating that mass spectrometry is the main variable in achieving accurate and precise Nd isotope ratios. Overall, this result is very satisfactory, as the achieved precision is a factor of 40 better than the range of Nd isotopic compositions observed in the global ocean. Intercalibration for dissolved rare earth element concentrations (REEs) by six laboratories for two water depths at BATS yielded a reproducibility of 15% or better for all REE except Ce, which seems to be the most blank-sensitive REE. Neodymium concentrations from 12 laboratories show an agreement within 9%, refk¹⁷², [http://4h9z "K4f-jhlj4\]](#) [http://4h9z "K4f-jhlj4\]](#) [http://4h9z "K4f-jhlj4\]](#)

intercalibration efforts for dissolved Nd isotopes, which include a total of 15 participating laboratories, some of which have a long-standing history of seawater Nd isotope measurements, and some of which are relatively new to the field.

Although not one of the key parameters of the GEOTRACES program, the REE concentrations in seawater have been historically used by a large number of laboratories to decipher lateral and ~~and deep~~ [Nd]_{seawater} values.

lab	spike	preconcentration of Nd			mass spectrometry	blank
1	NA	Fe co-precipitation (100 mg Fe for 20L of seawater)	cation exchange	DEP column	TIMS (Nd^+)/MC-ICP-MS	<20 pg
2	mixed ^{150}Nd - ^{149}Sm	Fe co-precipitation (8 mg Fe per litre of seawater)	cation exchange	Ln Spec	MC-ICP-MS	30 pg (275 pg*)
3	NA	Fe co-precipitation (50 mg Fe for 10L of seawater)	RE Spec	!-HIBA	TIMS (NdO^+)	3 pg
4 ^a	NA	Fe co-precipitation (50 mg Fe for 10L of seawater)	cation exchange	Ln Spec	MC-ICP-MS	<2 pg
4 ^b	NA	preconcentrated 10L on C18 cartridge	NA	Ln Spec	MC-ICP-MS	ND
5	spiked samples 511 and 311 with 250 μg ^9Be	Fe co-precipitation			TIMS (Nd^+)	70 pg
6	^{150}Nd , ^{147}Sm	Fe co-precipitation (14 mg Fe for 3.6L seawater)			TIMS (Nd^+)	8-12 pg ^a 4 pg ^b
7 ^a	NA	Fe co-precipitation (60 mg Fe for 10L seawater)			MC-ICP-MS	2.5 pg
7 ^b	NA	preconcentrated 10L on C18 cartridge	NA	Ln Spec	MC-ICP-MS	2.5 pg
8	NA	preconcentrated 10L on C18 cartridge	cation exchange	Ln Spec	TIMS (Nd^+)/MC-ICP-MS	187 pg
9	NA	Fe co-precipitation			TIMS (Nd^+)	120 pg
10	NA	Fe co-precipitation (1 mg Fe per litre of seawater)	TRU Spec	Ln Spec	MC-ICP-MS	ND
11	NA	Fe co-precipitation (50 mg Fe for 10L of seawater)	RE Spec	!-HIBA	TIMS (NdO^+)	3 pg
12	NA	preconcentrated 10L on C18 cartridge	TRU Spec	Ln Spec	TIMS (NdO^+)	7 pg ^c 20 pg ^d
13	NA	preconcentrated 10L on C18 cartridge	cation exchange	Ln Spec	MC-ICP-MS	8 pg
14	NA	Fe co-precipitation (0.5 g Fe per 20L of seawater)	cation exchange	Ln Spec	MC-ICP-MS	ND
15	NA	preconcentrated 10L on C18 cartridge	cation exchange	Ln Spec	TIMS (Nd)	

ammonium hydroxide leads to the formation of iron hydroxides, which in turn, efficiently scavenge rare earth elements out of the seawater solution (e.g., Piepras and Wasserburg 1987). Depending on the laboratory, between 1 and 25 mg purified Fe are added per liter of seawater. Purification of Fe is typically carried out by isopropyl ether back-extraction (Dodon et al. 1936), or by ion exchange chromatography. Lack of careful purification has been reported as the most likely can-

didate to introduce a significant procedural blank (e.g., a few hundred picograms; see Table 1a). A few laboratories choose to concentrate Nd from the seawater matrix by liquid-liquid extraction, pumping 10 L seawater aliquots, adjusted to a pH of ~3.5, through two coupled Sep-Pack C18 cartridges, each filled with 300 mg of a mixture of 65% bis(2-ethylhexyl) hydrogen phosphate (HDEHP) and 35% 2-ethylhexyl dihydrogen phosphate (H₂MEHP), at a speed of 20 mL/min (Sha-

bani et al. 1992; see Table 1a). Barium was subsequently eluted from the cartridges using 5 mL 0.01M HCl and the REE were collected in 35 mL 6M HCl.

Following preconcentration of Nd, chemical separation of Nd from the sample matrix is required to minimize possible interferences during subsequent analyses by mass spectrometry. Dependent on the column set up, high Fe concentrations affect the final REE

54) or Multiple Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS: Nu Plasma or Neptune). While historically TIMS was the method of choice for all laboratories, the phiphim

Neodymium isotope intercalibration in seawater at BATS and SAFe

To achieve comparability of results, all measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios have been normalized relative to a JNd_i ratio of 0.512115 (Tanaka et al. 2000) or a La Jolla ratio of 0.511858 (Lugmair et al. 1983) using standard values reported by each laboratory (see caption of Table 2). For laboratories that routinely use other in-house standards than the ones listed above, their reported cross-calibration for their respective standards relative to JNd_i/La Jolla was used. Figs. 1 and 2 and Tables 2 and 3 show the results for the Nd isotopic composition of seawater at three distinct water depths at BATS and SAFe as measured by 15 different laboratories. Sub-surface water at BATS yielded an average Nd isotopic composition of -9.2 ± 0.6 , deep water at BATS a value of -13.1 ± 0.6 , and the average Nd isotopic composition of deep water at SAFe is -3.2 ± 0.5 (errors:

two sigma standard deviations of the mean). Interpretation of the results concerning comparability to published literature values can be found in the accompanying paper by Pahnke et al. (2012). Here we focus on assessing the agreement achieved between the different laboratories (i.e., reproducibility; reproducibility is defined as the standard deviation of the mean divided by the mean).

oratory environment using distilled acids only. Two different stock solutions (15 ppb Nd in 0.1M HNO₃ and 15 ppm Nd in 4M HNO₃) were prepared from a single digest of the powder, and aliquots were subsequently sent out to each laboratory (15 ppb and 15 ppm solutions dependent on the use of MC-ICP-MS or TIMS respectively). Concentrations were chosen to mimic those typical for Atlantic seawater. Data returns from 13 laboratories yielded an average Nd isotopic composition of -17.3 ± 0.6 (Table 4). The two sigma standard deviation of 56 ppm from the mean of all individual measurements is very similar to the reproducibility obtained on seawater samples (47 to 57 ppm). The two sigma standard deviation calculated for each laboratory on the unknown standard solution varies between 11 and 86 ppm (Table 4), which is similar to the range reported by individual laboratories on La Jolla, JNd_I, and other in house standard runs (Tables 2,3; 6-100 ppm). Detailed comparison shows that some laboratories may underestimate their external errors, whereas others report rather conservative errors. Hence, it crr v

important to note that not all laboratories chose to run their isotopic standards at the same concentrations as the samples (see notes in the caption of Table 2). In detail, Laboratories 7 and 9 report results on significantly higher concentrated standards. In the case of Laboratory 9, ion beam intensity however was controlled at a level similar to the one obtained during sample runs. Laboratory 13 reports a much larger reproducibility on the unknown standard than for their in-house standard [Kr] > 4 kg] 4] Krééz "Kr

Applying however the same leaching method at the slope station (same filter type, same pumping system) yielded results that do not agree within error (Laboratories 6 and 7: Fig. 4, Table 5).

Similarly, results from four laboratories for the deep water samples at BATS show excellent agreement (mean Nd isotopic composition of -13.8 ± 0.6) despite the use of different digestion/leaching methods. Two laboratories (numbers 2 and 6)

followed the prescribed method for total digestion of particles and filter material described by Cullen and Sherrell (1999). The method used by L

At the moment, we can only speculate on the reasons for the inconsistent results reported above, which go along with variable total particle Nd concentrations as well as variable calculated Nd concentrations per pumped amount of seawater (Table 5). Possible explanations include heterogeneous particle distributions on the filters, differences between the filters from individual pumps, or contamination either during sampling, drying, and cutting on the ship, or during processing in the laboratory.

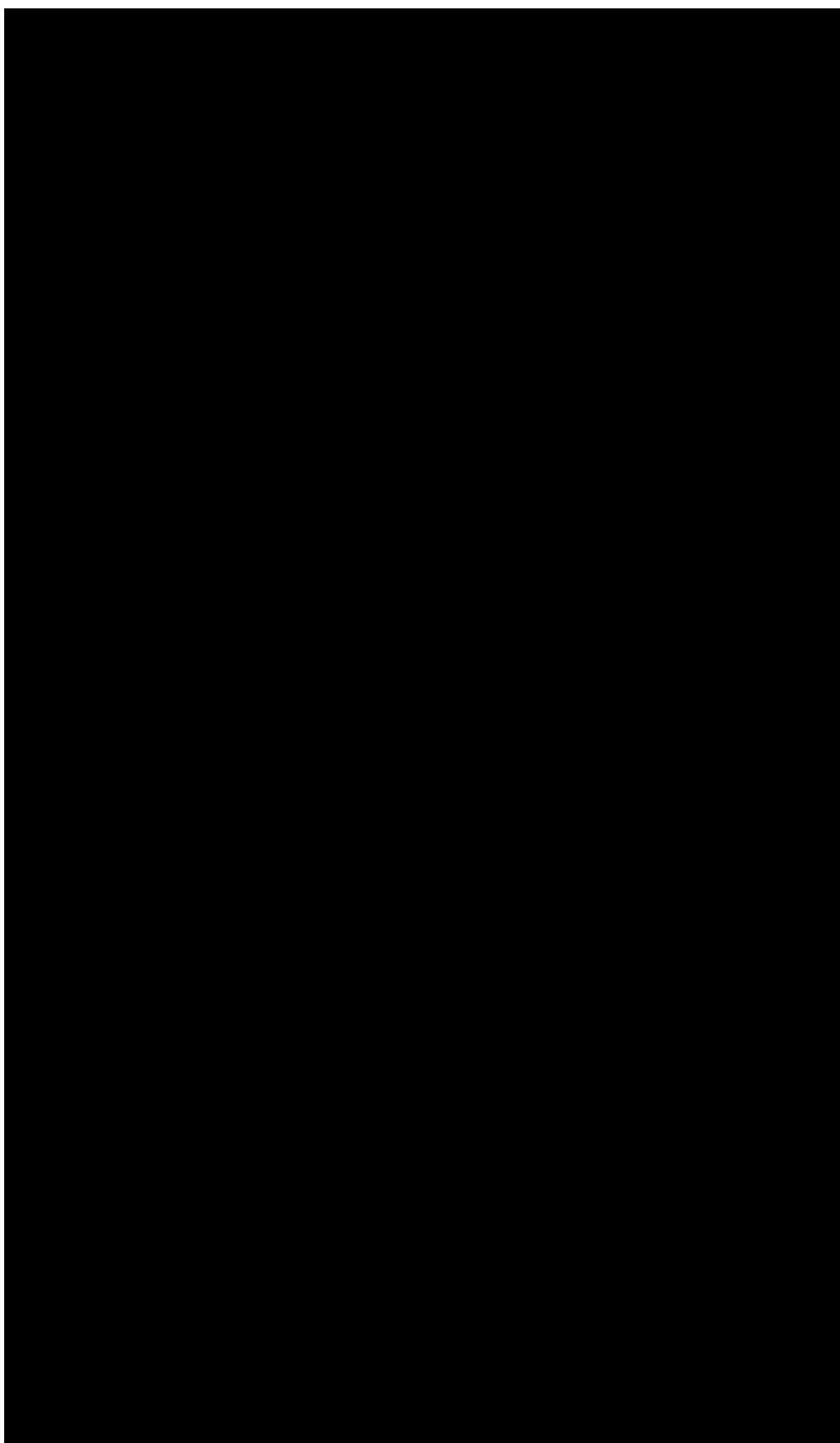
Due to the difficulties with interpreting Nd concentration and isotope data, we refrain at this point from reporting full REE patterns, which were submitted by three laboratories (Laboratories 10, 16, 17).

Rare earth element concentrations in seawater at BATS

Figures 5a and 5b and Table 6 summarize the results for seawater REE concentrations from the two intercalibration samples collected from BATS, analyzed by seven laboratories with significantly different experience levels.

Average REE patterns from all participating laboratories (1,3,5,8,10,16,17), except Laboratory 17 (see discussion below),

show agreement within 12% for deep water at BATS and 15% for shallow water at BATS (relative 2σ SD of the mean = RSD; Table 6). Overall, slightly better agreement is observed for the heavy rare earth elements (HREEs), than for the light rare earth elements (LREE), a result typical for REE measurements. The exception from this overall agreement are Ce concentrations [K4fh4gβ-]4]



all other laboratories (Table 1b). A similarly good result is however obtained by Laboratory 10, for the deep water samples where results agree within 3% RSD with the average values. Laboratories 1, 5, and 16 show deviations from the average within 6% to 8% for both water depths, and Laboratory 8 is just outside this margin with agreements within 10% to 13% (RSDs cited include all REE but Ce).

How good is the observed agreement? Taking into account that most individual laboratories quote external errors for their methodologies well below 10%, it might be expected that an agreement within 10% should be possible. The observed agreement is not far from this number, and data returns on an unknown REE standard solution sent to the individual laboratories did not yield an improved agreement over natural samples (Table 7; Fig. 6). The last statement is based on comparison of results from Laboratories 1 and 8, which show an agreement within 10% for most REE, and 16% for all REE (relative 2σ SD).

REE concentrations reported by Lab 17 (not shown in Fig. 5) are significantly lower than results obtained by other laboratories (~30% to 70%). Looking into the detail of the methodology applied by this laboratory (Table 1b), a number of factors could be responsible for this offset. First, the laboratory did not spike their concentration samples, which means that imperfect yields and fractionation of REE during preconcentration and ion chromatography cannot be corrected for. Second, the laboratory used the REE cut from their Nd isotope chemistry to determine REE concentrations, which again stresses that sample recovery up to this point is not 100%. This is a significant problem for REE analysis.

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