GEOTRACES intercalibration of neodymium isotopes and rare earth element concentrations in seawater and suspended particles. Part 2: Systematic tests and baseline profiles

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Abstract

The large-scale collection of seawater samples and analysis of trace elements and isotopes by the GEOTRACES program call for careful comparison and examination of different methods for sample collection, treatment, and processing. Here we report results for different filter types, sampling bottles, and preconcentration methods for Nd from seawater. Neodymium isotope ratios and concentrations of unfiltered and filtered seawater using five different filter types agree within 43-56 ppm (2σ standard deviation, SD) and 10% (relative 2σ standard deviation), respectively. The filter choice therefore has no effect on the measured parameters at the studied locations in the western North Atlantic. This could well be different, however, in areas of high particle concentrations. We therefore strongly recommend filtration of seawater for Nd isotope and rare earth element concentration measurements. Dissolved $^{143}Nd/^{144}Nd$ ratios of seawater collected with Niskin bottles with internal nylon-coated stainless steel springs and trace metal-clean GO-FLO bottles were the same within 43 ppm (2σ SD). The Niskin bottles used here are therefore suitable for the collection of seawater samples for the analysis of $^{143}Nd/^{144}Nd$ ratios. Iron coprecipitation and complexation with HDEHP/H$_2$MEHP using C18 cartridges for the preconcentration of Nd from seawater yielded the same $^{143}Nd/^{144}Nd$ ratios within 37 ppm (2σ SD). Both methods are therefore appropriate. Water column profiles of $^{143}Nd/^{144}Nd$ ratios and Nd concentrations are reported for the North Atlantic (BATS) and North Pacific (SAFe), and profiles of all rare earth elements are reported for BATS. These baseline profiles are recommended for continued quality control and intercalibration by future GEOTRACES cruises.

The GEOTRACES program is aimed at characterizing the sources, sinks, and internal cycling of trace elements and isotopes in the global ocean to further our understanding of the processes that determine their distributions. This extensive effort requires the participation and collaboration of laboratories worldwide and makes it necessary to ensure that all data collected are precise and internally consistent, and that accuracy is carefully assessed.

The main goals of the international GEOTRACES intercalibration effort were therefore 1) to intercalibrate all participating laboratories using their individual methods for sample processing and analysis, and 2) to establish whether different shipboard sampling and sample processing procedures affect the concentration and isotopic composition of the analyzed parameters. For Nd isotope ratios ($^{143}Nd/^{144}Nd$) and rare earth element (REE) concentrations, goal 1 is addressed in van de Flierdt et al. (2012). Goal 2 is addressed here, together with the presentation of seawater profiles of Nd isotope ratios and REE concentrations

at two baseline stations in the western North Atlantic at BATS (Bermuda Atlantic Time-Series Study station) and the eastern North Pacific at SAFe (Sampling and Analysis of Iron station).

Most previously published seawater Nd isotopic compositions and Nd concentrations are reported for unfiltered seawater (e.g., Piepgras et al. 1979; Piepgras and Wasserburg 1980, 1987; Jeandel 1993; Jeandel et al. 1998; Amakawa et al. 2004; Lacan and Jeandel 2004a, 2004b, 2005; Rickli et al. 2009). Alibo and Nozaki (1999) observed that concentrations of REE in unfiltered seawater from the western North Pacific only deviate from truly dissolved concentrations (e.g., filtered at 0.04 μm) by 2% to 5% except for Ce (31%). This implies that the acid-soluble particulate fraction in seawater from the western North Pacific is relatively small, suggesting that filtration is not required for the analysis of REE. However, until now, no systematic tests have been carried out to verify whether unfiltered and filtered samples, in different oceanic settings (e.g., open ocean, continental margin, surface water, deep water) yield the same Nd isotope composition and concentration. Similarly, it has not been established whether different filter materials and pore sizes, or different sampling bottles (standard Niskin versus trace metal-clean GO-FLO bottles) affect the Nd isotopic composition and concentration of seawater.

Here, we report results on the Nd isotopic composition and Nd concentration of seawater from several sampling, filtration, and preconcentration tests carried out at BATS and a station on the Virginia continental slope (Virginia slope station). Moreover, we present water column profiles of $^{143}Nd/^{144}Nd$ ratios and REE concentrations at BATS, and of $^{143}Nd/^{144}Nd$ ratios and Nd concentrations at SAFe. The results obtained on filtered seawater are compared with previously published results, hydrography at the stations, and particle compositions. We recommend the use of these profiles as 'baseline profiles' for reoccupation and continuous intercalibration in the future, in particular of the deeper samples for which a stronger temporal stability can be expected.

Materials and procedures

Sample locations

Samples for this study were collected during two GEOTRACES intercalibration cruises on R/V *Knorr*. During cruise KN193-6 (Bermuda-Norfolk, June-July 2008), we collected seawater samples at the Bermuda Atlantic Time-Series Study station (BATS, 31°40′ N, 64°10′ W) from 20 m and 2000 m water depth and a full water column profile, as well as seawater from a station on the Virginia continental slope (Virginia slope station, 37°2′ N, 74°24′ W) from 36 m water depth (Fig. 1a). During cruise KN195-8 (Honolulu-San Diego, May 2009), we collected a seawater profile at the North Pacific Sampling and Analysis of Iron station (SAFe, 30°N, 140°W) from 20 to 4500 m water depth (Table 1). The samples from BATS and the Virginia slope station were used to test the effect of (i) different filter types and pore sizes, (ii) different sampling bottles, and (iii) different REE preconcentration methods on the dissolved Nd isotopic com-

position and REE concentration of seawater. The full water column profiles at BATS and SAFe will serve as 'baseline profiles' and provide the basis for continuous intercalibration when reoccupied during GEOTRACES section cruises in the future.

The hydrography at the baseline stations BATS and SAFe is depicted in the potential temperature-salinity diagrams in Fig. 1b. The water masses found at BATS are Subtropical Mode Water (STMW), marked by constant temperature and salinity, and North Atlantic Deep Water (NADW). The salinity minimum of Antarctic Intermediate Water (AAIW) is only weakly developed. At SAFe, North Pacific Intermediate Water (NPIW) is underlain by North Pacific Deep Water (NPDW).

Sample collection and tests

The CTD rosette of R/V *Knorr* (WHOI) that was used on both cruises is a standard rosette on a steel hydrowire with 24 × 10 L Niskin bottles. The Niskin bottles from General Oceanics were equipped with internal stainless steel springs with a 0.25 mm thick nylon coating, Viton O-rings at the end caps and spigots, and mounted on a powder-coated stainless-steel rosette frame. The Seabird sensors had stainless steel and anodized aluminum housings. To facilitate filtration through filter membranes directly from the Niskin bottles in reasonable time, the bottles were pressurized with compressed (8-10 psi) HEPA-filtered air. The air was distributed to the bottles from a compressor using a manifold that was attached to the air vent of each bottle. The endcaps of the bottles were kept closed using large Quick-Grip bar clamps. For AcroPak500 filter cartridges with paired 0.45 and 0.8 μm membranes used at SAFe, pressurizing the Niskin bottles was not necessary.

At BATS 2000 m and 20 m, 10 L seawater each were filtered through the following filters: Nuclepore polycarbonate track-etched 0.4 μm membranes, Nuclepore 1 μm membranes, QMA quartz fiber filters with 1 μm pore size, Supor filters with paired 0.8 μm and 0.45 μm polyethersulfone membranes (500 cm² filtration surface area), Osmonics (Memtrex) filter cartridge with a 0.2 μm polycarbonate, track-etched (PCTE) filter membrane (1.6 m² filtration surface area), and Pall AcroPak200 cartridge filters with paired 0.8 μm and 0.2 μm Supor polyethersulfone membranes (200 cm² filtration surface area). Before use, the filter membranes (47 mm and 90 mm diameter) and cartridges were leached in ~1N ultra-clean, double-distilled (Nd < 1ppt) hydrochloric acid for 2 d and thoroughly rinsed with ultra-clean water until the pH of the ultra-clean water was reached. For the membranes, this was done by dripping copious amounts of water on a stack of filter membranes placed on a filter holder to wash out the acid.

In preparation for seawater filtration, the filter membranes were placed into single-stage 47 mm or 90 mm diameter all PFA filter holders (Savillex Corp.) and attached to the Niskin bottles using acid-cleaned Teflon-lined Tygon tubing. The filter holders were placed directly above the sampling containers (10 L cubitainer). Filtration durations varied depending on the filter material, pore size and membrane diameter used and were shortest at all stations for QMA 1 μm and Supor 0.8 μm (Fig. 2).
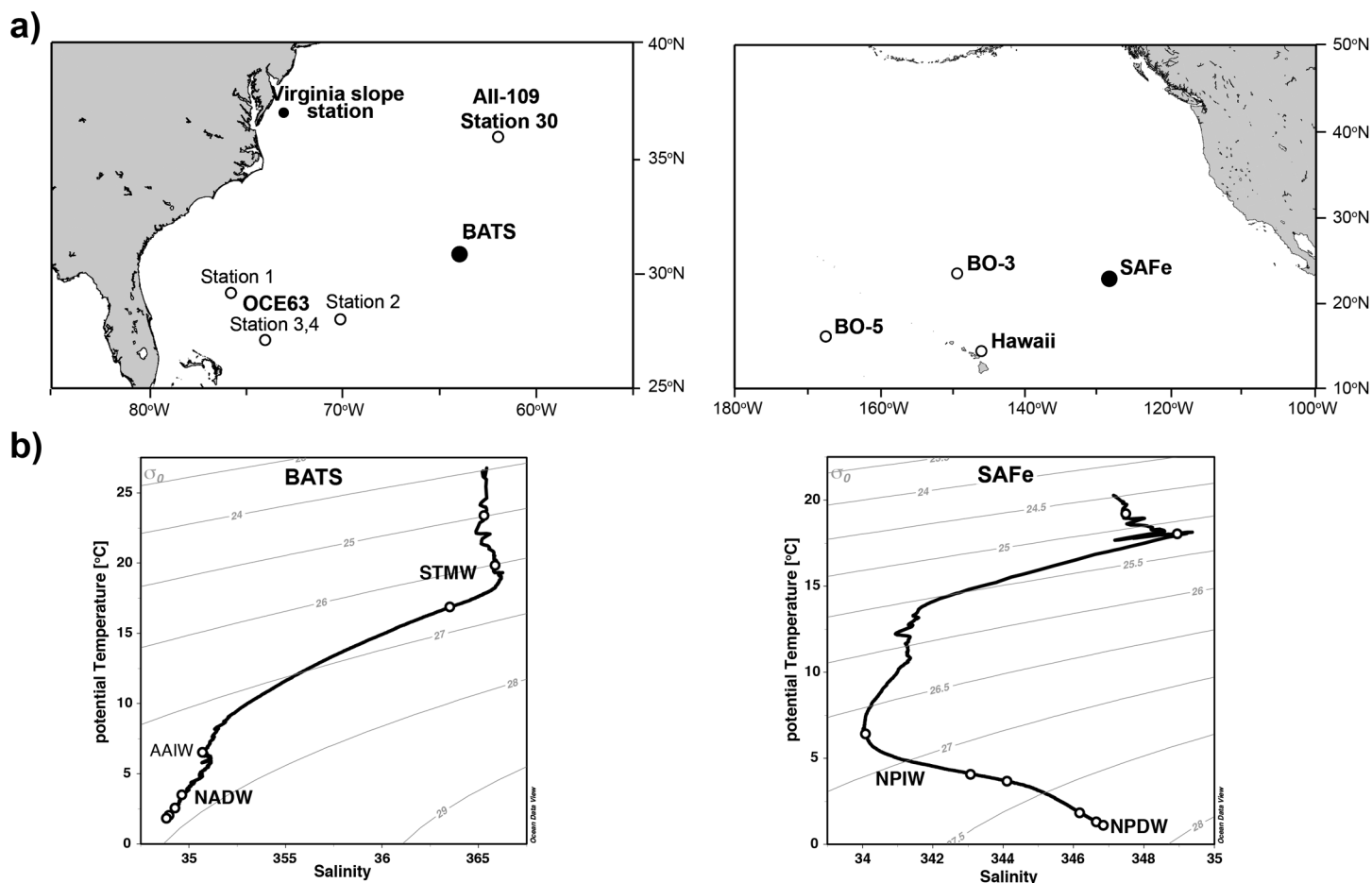
a)

b)

Fig. 1. a) Maps of sampling locations in the North Atlantic: BATS (Bermuda Time Series Station) and Virginia slope station, and in the North Pacific: SAFe (Sampling and Analysis of Iron). Stations of published Nd isotope profiles are also shown (open symbols). In the North Atlantic: All-109-Station 30 (Piepgras and Wasserburg 1987), OCE63-Stations 1-4, combined profile (Piepgras and Wasserburg 1980). In the North Pacific: BO-3 and BO-5 (Amakawa et al. 2009), combined stations around Hawaii (Vance et al. 2004). b) Potential temperature-salinity diagrams for BATS and SAFe. Samples for Nd isotope analyses are indicated by circles. STMW = Subtropical Mode Water, AAIW = Antarctic Intermediate Water, NADW = North Atlantic Deep Water, NPIW = North Pacific Intermediate Water, NPDW = North Pacific Deep Water. Potential density (σ_θ) lines are shown in gray.

Table 1: Station locations, sample depths, and tests carried out

Cruise	Station	Latitude	Longitude	Water depth [m]	Sampling device	Tests
KN193-6	BATS	31° 45' N	64° 06' W	15	tow-fish	pre-concentration
				20	Niskin	filter, sampling bottles
				2000	GO-FLO	pre-concentration, sampling bottles
				2000	Niskin	filter, sampling bottles
				20-4500		baseline profile (Supor 0.45mm)
KN193-6	Slope	37° 02' N	74° 24' W	36	Niskin	filter
KN195-8	SAFe	30° 00' N	140° 00' W	20-4500	Niskin	baseline profile (AcroPak 0.8/0.45mm)

The filtered samples were collected directly into precleaned low-density polyethylene collapsible containers (cubitainers) and acidified to pH ~2 with ultra-clean 6N hydrochloric acid (Nd ≤ 1 ppt) within a few hours of collection.

Additionally, samples were collected from the trace metal-clean, interconnected 2 × 500 L tanks (made of fluorinated low density polyethylene, UCSC SAFe tanks) that were filled with seawater collected using trace metal-clean GO-FLO bottles
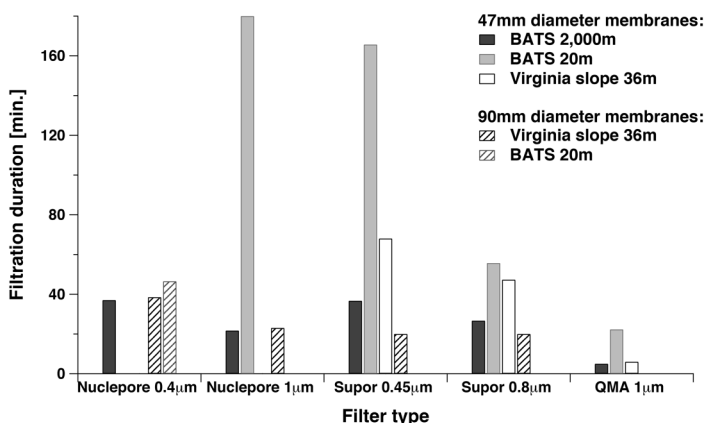
Fig. 2. Filtration duration for 10 L seawater from BATS and Virginia slope station filtered through different filter membranes and pressurizing the Niskin bottles using filtered, compressed air.

(Measures et al. 2008) for seawater from 2000 m water depth, and a trace metal-clean tow-fish (Geoffrey Smith, UCSC) for seawater from 15 m water depth, and filtered through an Osmonics cartridge filter with polycarbonate track-etched 0.2 μm membrane. The water in the tanks was acidified to pH ~2 with ultra-clean 6N hydrochloric acid (Nd ≤ 1ppt) and homogenized for several hours using an all PFA Teflon diaphragm pump. These samples were used to compare Niskin and GO-FLO bottles and to test the effect of two different preconcentration methods on dissolved Nd isotopic composition and REE concentrations in seawater. The preconcentration methods that we tested are iron hydroxide coprecipitation and complexation with HDEHP/H$_2$MEHP using C18 cartridges (see below).

The samples collected for the baseline profiles (8 depths) were obtained from Niskin bottles and were filtered through Supor 0.45 μm membrane filters (diameters 47 mm and 90 mm) at BATS (10 L per sample), and AcroPak500 0.8/0.45 μm cartridges at SAFe (5 L per sample).

Before sampling, all sample containers, tubing, and filter holders were leached with ultra-clean or trace metal-clean 0.5-1 N hydrochloric acid for 2 d and thoroughly rinsed with ultra-pure water. Between sampling, the sample holders were rinsed with water, leached in trace-metal clean ~1N hydrochloric acid for at least a few hours, and rinsed with Milli-Q water. The tubing to connect the filter holders to the Niskin bottles was thoroughly rinsed with Milli-Q water between sampling.

Preconcentration and isolation of Nd from seawater

Using 10 L seawater samples from BATS 20 m and 2000 m onboard R/V *Knorr*, we performed two commonly used procedures to preconcentrate REEs from seawater: 1) iron hydroxide co-precipitation (e.g., Piepgras and Wasserburg 1980; Amakawa et al. 2004; Andersson et al. 2008), and 2) complexation with HDEHP/H$_2$MEHP using C18 cartridges ('C18 cartridge tests' hereafter) (Shabani et al. 1992; Jeandel et al. 1998; Lacan and Jeandel 2004a). Iron used for the Fe-hydroxide coprecipitation

was cleaned by dissolving FeCl$_3$ in 6N hydrochloric acid and performing isopropyl ether back extraction (Dodson et al. 1936). We added ~5 mg cleaned Fe per liter of seawater to the samples that were previously acidified to pH ~2. Following vigorous shaking of the samples and equilibration for at least 24 h, ammonium hydroxide (Optima grade, Nd ≤ 0.1 ppt) was added to raise the pH to 8.2-8.5. The samples were left for at least 48 h to allow the Fe-hydroxide precipitate to settle. All but 250-500 mL of the supernatant was then carefully siphoned off and discarded. To further separate the precipitate from the remaining supernatant and remove the salt, samples were centrifuged and washed three times with ultra-pure water, which was adjusted to a pH of ~8 with ammonium hydroxide (Optima grade, Nd ≤ 1 ppt). This pH adjustment is important, as ultra-pure water has a slightly acidic pH and would hence redissolve some of the previously formed Fe-hydroxides. Back in the shore-based ultra-clean laboratory, the washed precipitate was dissolved in 2 mL of 1.5N ultra-pure nitric acid. The iron was reduced by the addition of 1 mL of 0.9N ascorbic acid, and the sample was passed through columns filled with Eichrom RE-Spec resin to remove the iron and the remaining sample matrix (Jones 2010). For REE analysis by multi- (MC) or single-collector inductively coupled plasma mass spectrometry (ICP-MS), no further purification was necessary. For Nd isotope analysis by thermal ionization mass spectrometry (TIMS), Nd was further isolated using α-hydroxyisobutyric acid (α-HIBA) chemistry (Choppin and Silva 1956).

For preconcentration of Nd from seawater using C18 cartridges, a method initially proposed by Shabani et al. (1992), we followed the method of Jeandel et al. (1998) and Lacan and Jeandel (2004a). Briefly, C18 cartridges (Waters Corp., Sep-Pak™ classic C18 cartridge 360 mg 55-105 μm) were loaded with 300 μL phosphoric acid 2-ethylhexyl ester (HDEHP/ H$_2$MEHP) to three-quarters of the cartridge volume. For 10 L seawater, two cartridges that were connected in sequence using Kynar (polyvinylidene fluoride) barbed connectors, were used per sample. Seawater pH was adjusted to ~3.5 using ultra-clean ammonia hydroxide, and samples were pumped over the cartridges at 20 mL/min using a peristaltic pump and Tygon tubing. In the shore-based ultra-clean laboratory, cartridges were washed with 5 mL 0.01N hydrochloric acid to remove barium, and REEs were subsequently eluted with 35 mL 6N hydrochloric acid. After taking the samples to dryness, the REEs were further purified using Eichrom TRU-Spec resin, and Nd was isolated using α-HIBA chemistry. SAFe profile samples processed at Imperial College London were separated using Ln-Spec resin instead of α-HIBA (e.g., Pin and Zalduegui 1997).

Analysis of Nd isotopes

Purified samples for Nd isotope analyses were loaded on single rhenium filaments with silica gel and analyzed as NdO$^+$ on a VG Sector 54 thermal ionization mass spectrometer (TIMS) at Lamont-Doherty Earth Observatory of Columbia University (LDEO) and on a VG Sector TIMS at the University of Hawaii (UH). The total procedural blank for Nd using this

procedure at LDEO/UH is 3 pg. At Imperial College London, purified samples were loaded on single tungsten filaments with $TaCl_5$ activator and analyzed as NdO^+ on a Thermo Scientific Triton TIMS. The total procedural blank using this procedure is 20 pg (column chemistry and mass spectrometry blank: <7 pg).

All Nd isotope ratios were normalized to $^{146}Nd/^{144}Nd = 0.7219$ and are reported relative to a La Jolla of $^{143}Nd/^{144}Nd = 0.511858$ (Lugmair et al. 1983) or a JNd_i of 0.512115 (Tanaka et al. 2000). By convention, the $^{143}Nd/^{144}Nd$ ratios are expressed in ε_{Nd} notation: $\varepsilon_{Nd} = [(^{143}Nd/^{144}Nd_{sample}/^{143}Nd/^{144}Nd_{CHUR}) - 1] \times 10{,}000$, with a CHUR value of $^{143}Nd/^{144}Nd_{CHUR} = 0.512638$ (Jacobsen and Wasserburg 1980). The average La Jolla or JNd_i $^{143}Nd/^{144}Nd$ ratio for each analytical session is listed as footnote under the data tables.

Analysis of REE concentrations

For the analysis of REE concentrations at eight water depths at BATS, 50-100 mL aliquots of 10 L seawater samples were weighed and spiked with an REE spike that contains the isotopes ^{142}Ce, ^{145}Nd, ^{149}Sm, ^{153}Eu, ^{155}Gd, ^{161}Dy, ^{167}Er, and ^{171}Yb. The solution used was diluted from a mixed and calibrated spike provided by Prof. Gil Hanson of Stony Brook University. The samples were left to equilibrate with the spike for at least 24 h before addition of ~600 µg Fe. Ultra-clean ammonium hydroxide was used to raise the pH to 8-8.5, and the samples were allowed to settle for 2 d. The supernatant was then decanted and discarded and the Fe-hydroxide precipitate was concentrated by centrifugation and washed with pH-adjusted ultra-clean water.

The REEs were subsequently isolated following the method of Jones (2010). Briefly, after reacting the samples with nitric acid and hydrofluoric acid to remove any hydrated silica, the samples were dissolved in 6N nitric acid and 0.9M ascorbic acid and loaded onto 100 µL columns containing 50-100 µm Eichrom RE-spec resin. Iron and major elements were washed with 4N nitric acid and the REEs were eluted with 4N hydrochloric acid. The samples were dissolved in 1-2 mL of 2% nitric acid in preparation for analysis.

The REE samples were analyzed on a VG Axiom multi-collector ICP-MS, using peak jumping on the axial multiplier in ion counting mode at LDEO. The MC-ICP-MS was equipped with a Cetac Aridus desolvating nebulizer that was used with a nitrogen-argon gas mixture to minimize oxide formation. The formation of oxides was monitored several times per day and the Ce oxide peaks were always between 0.015-0.008% of the primary peak. Nine procedural blanks were measured and yielded a maximum blank of less than 1.2% for all elements except for Ce (blank of 4.6%). Blank corrections were carried out for all REE by subtracting the procedural blank from each sample.

The typical internal error was better than 2% and often better than 1%, which includes the error magnification factors inherent to all isotope dilution measurements. External reproducibility for the isotope ratios measured for all the spike-enriched REEs was monitored with a spiked standard solution and was better than 3% for all elements except Ce, which had an external error of 3.8%.

For the analysis of Nd concentrations at BATS 20 m and Virginia slope station 36 m, and eight depths at SAFe, 250 mL aliquots of 10 L (5 L at SAFe) seawater samples were weighed and spiked with a solution enriched in ^{146}Nd. The spike was diluted and calibrated from a spike solution provided by Prof. John Mahoney (University of Hawaii at Manoa). The subsequent sample processing followed that described above. Neodymium concentrations were analyzed on a ThermoFinnigan Element 2 ICP-MS at UH. Procedural blanks had an Nd concentration of less than 0.6%. The internal 2σ standard error was better than 3% (with one exception of 4%) and typically less than 2%. For the SAFe profile analyzed at Imperial College London (ICL), 5 L samples were spiked with ^{150}Nd, pre-concentrated using C18 cartridges loaded with HDEHP/H_2MEHP, separated using TRU Spec and Ln Spec chemistry, and analyzed for Nd isotope ratios and concentrations on a Thermo Scientific Triton TIMS.

Assessment and discussion of filtration, sampling and preconcentration tests and GEOTRACES ε_{Nd} and REE baseline profiles at BATS and SAFe

Filter tests

The Nd isotopic compositions obtained on seawater samples from BATS 20 m, BATS 2000 m, and Virginia slope station 36 m filtered using the different filter types and pore sizes described above, show good agreement for each station with 2σ standard deviations of 56 ppm (BATS 20 m, $n = 12$), 43 ppm (BATS 2000m, $n = 13$), and 53 ppm (Virginia slope station 36 m, $n = 11$) (Table 2a, 2b, 2c, Fig. 3). Comparison of the individual ε_{Nd} results from the different stations reveals no systematic offsets among the different filter types and pore sizes. Furthermore, the obtained average Nd isotopic compositions at BATS (20m: $\varepsilon_{Nd} = -9.8 \pm 0.56$, 2000 m: $\varepsilon_{Nd} = -13.3 \pm 0.43$) agree well with the average values and precision achieved by the international intercalibration at BATS 15 m ($\varepsilon_{Nd} = -9.2 \pm 0.60$, 13 labs) and BATS 2000 m ($\varepsilon_{Nd} = -13.1 \pm 0.59$, 13 labs) (van de Flierdt et al. 2012). The additional analysis of an 'unknown' Nd standard by participating labs also resulted in a similar 2σ standard deviation of 56 ppm (13 labs, van de Flierdt et al. 2012). The close similarity between the precision of seawater samples that included extensive sample processing by the individual labs, using different preconcentration and ion chromatography methods, and the 'unknown' Nd standard that did not require any processing, led us to conclude that an inter-laboratory precision of around ± 0.6 ε_{Nd} units is the best that can be achieved on samples of 5-15 ng Nd, and that the observed differences are due to analytical uncertainty rather than sample processing or matrix effects (van de Flierdt et al. 2012). The precision of our filter tests of ± 0.43-0.56 ε_{Nd} units is therefore within the expected analytical uncertainty.

Similarly, the concentration of dissolved Nd measured on the same seawater samples at BATS 20 m and Virginia slope

Table 2a: Filter tests at BATS 20m water depth (31°40'N, 64°10'W)

filter type	filter pore size [μm]	sample ID	sample volume[a]	^{143}Nd/^{144}Nd measured	internal 2σ SE	^{143}Nd/^{144}Nd normalized[b]	ε_{Nd}[c]	internal 2σ SE	external 2σ SD[d]	Nd [ppt]	internal % 2σ SE
BATS, 20m											
Nuclepore	0.4	KN193-6-Nd-801	10L, 0.25L	0.512091	± 0.000013	0.512130	-9.9 ± 0.3		0.3	2.0 ± 2.5	
Nuclepore	0.4	KN193-6-Nd-802	10L	0.512088	± 0.000014	0.512127	-10.0 ± 0.3		0.3		
Nuclepore	1	KN193-6-Nd-805	10L, 0.25L	0.512070	± 0.000027	0.512109	-10.3 ± 0.5		0.3	2.0 ± 2.9	
Nuclepore	1	KN193-6-Nd-806	10L	0.512082	± 0.000018	0.512121	-10.1 ± 0.4		0.3		
Supor	0.8	KN193-6-Nd-811	10L, 0.25L	0.512107	± 0.000011	0.512147	-9.6 ± 0.2		0.3	2.1 ± 0.7	
Supor	0.8	KN193-6-Nd-812	10L	0.512105	± 0.000010	0.512144	-9.6 ± 0.2		0.3		
QMA	1	KN193-6-Nd-813	10L, 0.25L	0.512103	± 0.000012	0.512142	-9.7 ± 0.2		0.3	2.1 ± 4.1	
QMA	1	KN193-6-Nd-814	10L	0.512119	± 0.000011	0.512158	-9.4 ± 0.2		0.3		
Osmonics	0.2	KN193-6-Nd-817	10L, 0.25L	0.512116	± 0.000010	0.512155	-9.4 ± 0.2		0.3	1.9 ± 0.3	
Osmonics	0.2	KN193-6-Nd-818	10L	0.512101	± 0.000011	0.512140	-9.7 ± 0.2		0.3		
none	N/A	KN193-6-Nd-823	10L, 0.25L	0.512097	± 0.000015	0.512136	-9.8 ± 0.3		0.3	2.1 ± 1.7	
none	N/A	KN193-6-Nd-824	10L	0.512085	± 0.000013	0.512124	-10.0 ± 0.3		0.3		
						average BATS 20m	**-9.8**			**2.0**	
						2σ SD	**0.6**			**0.1**	

all samples analyzed at LDEO (VG Sector 54 TIMS).

[a] samples for isotope analyzes = 10L, for Nd concentrations ~250mL.

[b] normalized to repeat analyses of La Jolla of ^{143}Nd/^{144}Nd=0.511820 ± 0.000013 (n=9), relative to a La Jolla value of 0.511858 (Lugmair et al., 1983).

[c] ε_{Nd} values were calculated relative to a CHUR of 0.512638 (Jacobsen and Wasserburg, 1980).

[d] external errors are derived from repeat standard analyses over the period of sample measurements;

if internal errors are larger than external errors, these are plotted in Figure 3.

Table 2b: Filter tests at BATS 2,000m water depth (31°40'N, 64°10'W)

filter type	filter pore size [μm]	sample ID	sample volume	^{143}Nd/^{144}Nd measured	internal 2σ SE	^{143}Nd/^{144}Nd normalized[a]	ε_{Nd}[b]	internal 2σ SE	external 2σ SD[c]
BATS, 2000m									
Nuclepore	0.4	KN193-6-Nd-701	10L	0.511956	± 0.000030	0.511963	-13.2 ± 0.6		0.2
Nuclepore	0.4	KN193-6-Nd-702	10L	0.511948	± 0.000018	0.511955	-13.3 ± 0.4		0.2
Nuclepore	1	KN193-6-Nd-704	10L	0.511951	± 0.000014	0.511958	-13.3 ± 0.3		0.2
Nuclepore	1	KN193-6-Nd-706*	10L	0.511937	± 0.000012	0.511958	-13.3 ± 0.2		0.3
Supor	0.45	KN193-6-Nd-707	10L	0.511939	± 0.000016	0.511947	-13.5 ± 0.3		0.2
Supor	0.45	KN193-6-Nd-708	10L	0.511953	± 0.000012	0.511961	-13.2 ± 0.2		0.2
Supor	0.8	KN193-6-Nd-710	10L	0.511958	± 0.000012	0.511965	-13.1 ± 0.2		0.2
Supor	0.8	KN193-6-Nd-711*	10L	0.511941	± 0.000007	0.511962	-13.2 ± 0.1		0.3
QMA	1	KN193-6-Nd-713	10L	0.511947	± 0.000014	0.511954	-13.3 ± 0.3		0.2
Osmonics	0.2	KN193-6-Nd-719	10L	0.511919	± 0.000018	0.511926	-13.9 ± 0.4		0.2
Osmonics	0.2	KN193-6-Nd-720	10L	0.511953	± 0.000020	0.511961	-13.2 ± 0.4		0.2
none	N/A	KN193-6-Nd-716	10L	0.511955	± 0.000012	0.511963	-13.2 ± 0.2		0.2
none	N/A	KN193-6-Nd-717	10L	0.511934	± 0.000015	0.511941	-13.6 ± 0.3		0.2
						average BATS 2000m	**-13.3**		
						2σ SD	**0.4**		

all samples analyzed at LDEO (VG Sector 54 TIMS), except those marked with * that were analyzed at UH (VG Sector TIMS).

[a] normalized to repeat analyses of La Jolla of ^{143}Nd/^{144}Nd=0.511850 ± 0.000011 (n=13), relative to a La Jolla value of 0.511858.

For samples analyzed at UH (KN193-6-Nd-706, -711): La Jolla ^{143}Nd/^{144}Nd=0.511838 ± 0.000015 (n=5)

[b] ε_{Nd} values were calculated relative to a CHUR of 0.512638 (Jacobsen and Wasserburg, 1980).

[c] external errors are derived from repeat standard analyses over the period of sample measurements.

if internal errors are larger than external errors, these are plotted in Figure 3.

station 36 m shows agreement within 10% (2σ RSD) (Fig. 4). This is again similar to the uncertainty of the results achieved by the international intercalibration of REE concentrations for Nd of 9% 2σ RSD (11 labs) for BATS 15 m. Together with the lack of any systematic differences in Nd isotopic composition or Nd concentration between filters when comparing the results from all three sampling locations, this suggests that the filter type and pore size of the most commonly used filters

Table 2c: Filter tests at Virginia slope station 36m water depth (37°2'N, 47°24'W)

filter type	filter pore size [µm]	sample ID	sample volume[a]	^{143}Nd/^{144}Nd measured	internal 2σ SE	^{143}Nd/^{144}Nd normalized[b]	ε$_{Nd}$[c]	internal 2σ SE	external 2σ SD[d]	Nd [ppt]	internal % 2σ SE
Slope, 36m											
Nuclepore	0.4	KN193-6-Nd-902,1	10L, 0.25L	0.512042	± 0.000008	0.512063	-11.2 ± 0.2		0.3	2.4 ± 2.0	
Nuclepore	1	KN193-6-Nd-904,3	10L, 0.25L	0.512046	± 0.000007	0.512067	-11.1 ± 0.1		0.3	2.3 ± 1.3	
Supor	0.45	KN193-6-Nd-905	10L, 0.25L	0.512049	± 0.000009	0.512070	-11.1 ± 0.2		0.3	2.2 ± 0.2	
Supor	0.45	KN193-6-Nd-906	10L	0.512051	± 0.000009	0.512072	-11.0 ± 0.2		0.3		
Supor	0.8	KN193-6-Nd-907	10L, 0.25L	0.512073	± 0.000005	0.512094	-10.6 ± 0.1		0.3	2.3 ± 1.2	
Supor	0.8	KN193-6-Nd-908	10L	0.512060	± 0.000006	0.512081	-10.9 ± 0.1		0.3		
QMA	1	KN193-6-Nd-913	10L, 0.25L	0.512076	± 0.000006	0.512097	-10.6 ± 0.1		0.3	2.3 ± 2.0	
QMA	1	KN193-6-Nd-914	10L	0.512075	± 0.000010	0.512096	-10.6 ± 0.2		0.3		
none	N/A	KN193-6-Nd-915	10L, 0.25L	0.512078	± 0.000007	0.512099	-10.5 ± 0.1		0.3	2.5 ± 1.3	
none	N/A	KN193-6-Nd-916	10L	0.512073	± 0.000007	0.512094	-10.6 ± 0.1		0.3		
AcroPak	0.8/0.2	KN193-6-Nd-917	10L, 0.25L	0.512063	± 0.000009	0.512084	-10.8 ± 0.2		0.3	2.3 ± 1.2	
						average Slope 36m	**-10.8**			**2.3**	
						2σ SD	**0.5**			**0.2**	

all samples analyzed at UH (VG Sector TIMS).

[a] samples for isotope analyzes = 10L, for Nd concentrations ~250mL.

[b] normalized to repeat analyses of La Jolla of ^{143}Nd/^{144}Nd=0.511837 ± 0.000013 (n=5), relative to a La Jolla value of 0.511858.

[c] ε$_{Nd}$ values were calculated relative to a CHUR of 0.512638 (Jacobsen and Wasserburg, 1980).

[d] external errors are derived from repeat standard analyses over the period of sample measurements.

if internal errors are larger than external errors, these are plotted in Figure 3.

tested here do not affect the Nd isotopic composition or Nd concentration of seawater. Moreover, we did not observe a significant difference in Nd isotopic composition or concentration between filtered and unfiltered seawater (Figs. 3 and 4) either in the deep samples from BATS or the surface samples from BATS and the Virginia slope station, which have higher particle concentrations than deep water. We note, however, that suspended particles at the studied locations have a very similar Nd isotopic composition to ambient seawater (see below), making it difficult to rigorously assess the necessity of filtration and required filter type and pore-size on the dissolved Nd isotope ratios based on the results from the studied sites. We are aware of at least one sample from the near-bottom North Pacific, where the Nd isotopic composition of filtered seawater shows the influence of resuspended particles from the seafloor with a very different isotopic composition than would be realistically expected from bottom waters at that site (Amakawa et al. 2009). Therefore, despite the lack of evidence from this study that filtration of seawater for the analysis of dissolved Nd isotope ratios and concentrations is required, we strongly recommend filtration of seawater using filters of ≤ 0.45 µm pore size in particular in areas where suspended particles are expected to have a different isotopic composition from local seawater and at stations and water depths with high particle concentrations, such as bottom or detached nepheloid layers, coastal regions, or areas of high aeolian or river input of particles.

Preconcentration tests

The comparison of two commonly used methods to preconcentrate REEs from seawater clearly shows that the use of iron hydroxide coprecipitation, and C18 cartridges loaded with HDEHP/H$_2$MEHP yield the same ε$_{Nd}$ values with a 2σ_standard deviation of 37 ppm (BATS 2000 m and 20 m, *n* = 11) (Table 3, Fig. 5). Similarly, for the intercalibration of Nd isotopes (van de Flierdt et al. 2012), results from labs that used C18 cartridges for preconcentration compared well with those of labs that used iron hydroxide coprecipitation (Table 1 and Fig. 1 of van de Flierdt et al. 2012). As discussed by van de Flierdt et al. (2012), the only problem that may arise when using the Fe coprecipitation method is a high blank level of the Fe solution, which can, however, be addressed by thoroughly cleaning the Fe beforehand, using isopropyl ether back extraction (Dodson et al. 1936), as demonstrated by our total procedural blank of 3 pg (see above).

Standard Niskin versus trace metal-clean GO-FLO sampling bottles

Comparison of ε$_{Nd}$ values measured on water collected with two different water bottles, standard Niskin bottles and trace metal-clean GO-FLO bottles, yields the same values with an overall (BATS 2000 m and 20 m) uncertainty of 43 ppm (2σ_SD, *n* = 11) (Table 3, Fig. 5). Neodymium concentrations measured on water collected with Niskin bottles (filter tests at BATS 20 m) of 2.0 ± 0.13 ppt (*n* = 6) (Table 2) also show good agreement with Nd concentrations of seawater collected with GO-FLO bottles from BATS 15 m that were measured as part of the international intercalibration of Nd isotopes and REE concentrations (2.0 ± 0.19 ppt, mean of results from 11 different labs; van de Flierdt et al. 2012). All other REE concentrations measured on seawater collected with standard Niskin bottles (BATS profile samples) and trace metal-clean GO-FLO bottles (intercalibration samples measured by LDEO, van de Flierdt et al. 2012) also show agreement within 8% and 9% 2σ RSD for BATS 20 m and
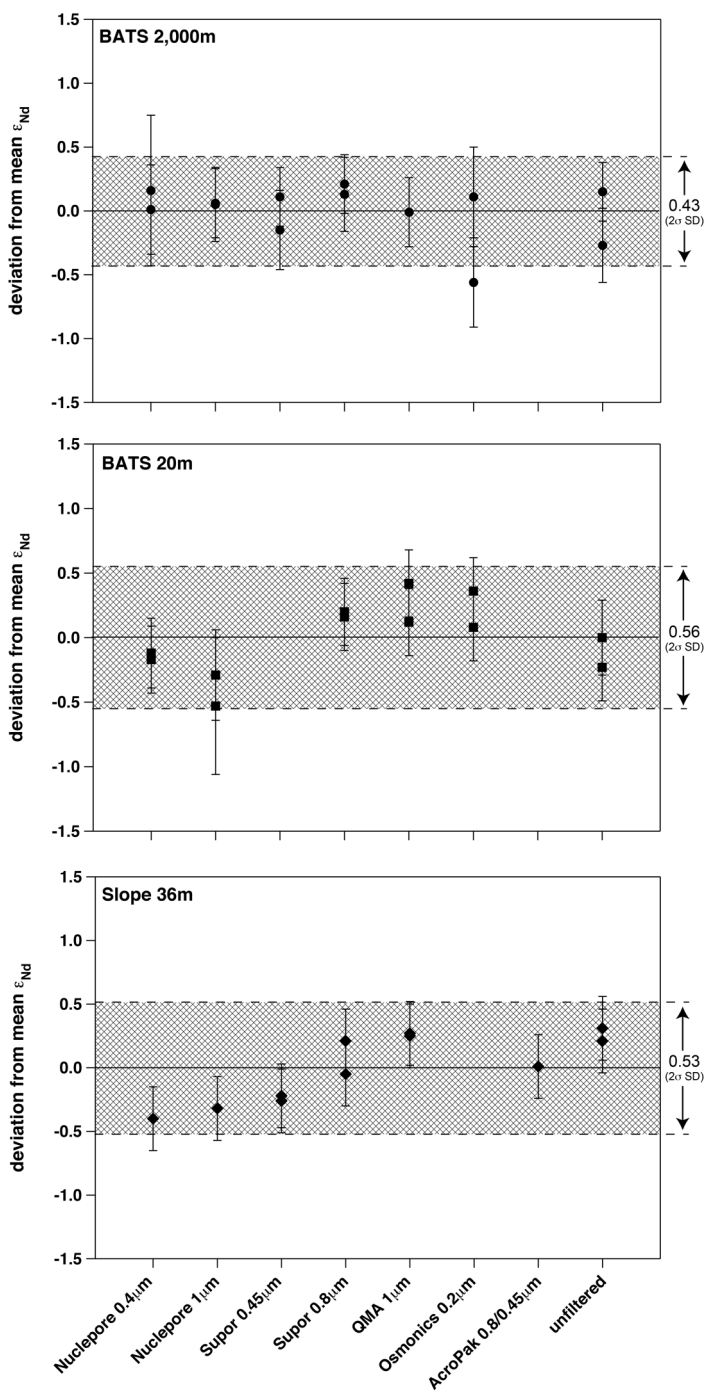
Fig. 3. Nd isotope ratios in ε_{Nd} notation plotted as deviations from the mean for the filter tests at BATS 2000 m (mean ε_{Nd} = –13.3 ± 0.4), BATS 20 m (mean ε_{Nd} = –9.8 ± 0.6), and Virginia slope station (mean ε_{Nd} = –10.8 ± 0.5). Errors plotted are external two sigma standard deviations. In cases where the internal two sigma standard error of an individual analysis was larger, this error was plotted.

2000 m, respectively. Cerium concentrations show slightly higher deviations of 13% and 14% 2σ RSD at BATS 20 m and 2000 m, respectively. This is within the uncertainty observed in the international intercalibration of dissolved REE concentra-
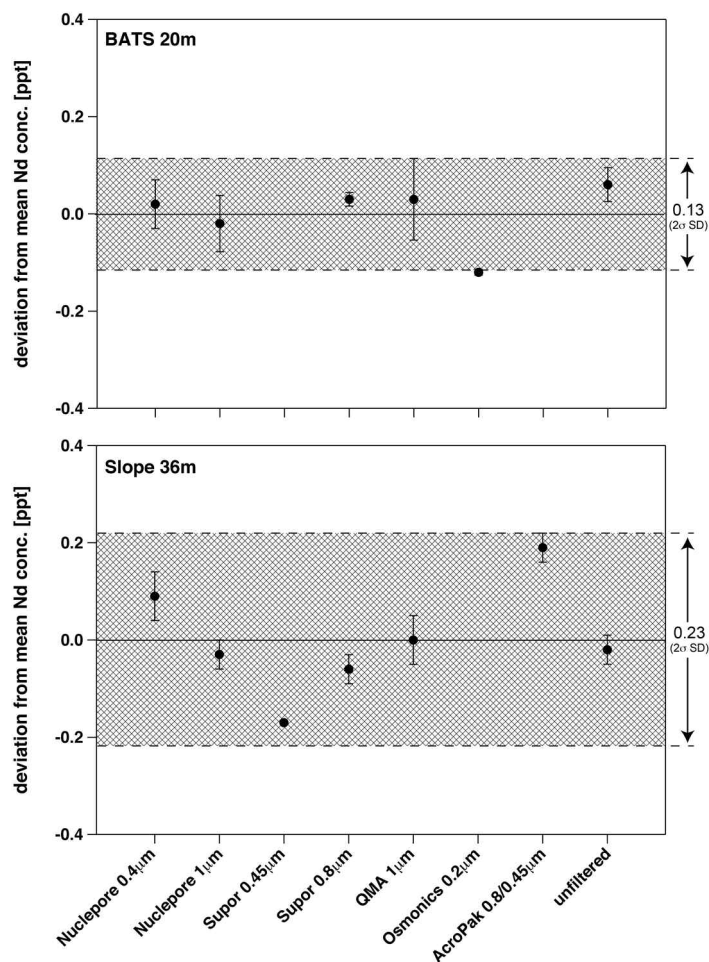

Fig. 4. Nd concentrations for filter tests at BATS 20 m (mean = 2.0 ± 0.1 ppt Nd) and Virginia slope station 36 m (mean = 2.3 ± 0.2 ppt Nd), plotted as deviations from the mean. Errors plotted are 2 sigma standard errors.

tions between six different laboratories (van de Flierdt et al. 2012) and confirms the assumption by investigators who have measured dissolved Nd isotopes and REE concentrations in the past that trace metal-clean bottles are not required for the collection of seawater samples for accurate and precise analyses of dissolved Nd isotopes and REE concentrations.

BATS baseline profiles and particles

Full water column profiles of dissolved Nd isotope ratios and REE concentrations at BATS are shown in Figs. 6-9 and documented in Tables 4 and 5. The Nd isotopic composition at BATS is highest at the surface with an ε_{Nd} value of –9.3 at 20 m (Fig. 6), similar to that reported by Piepgras and Wasserburg (1980) from a station southwest of BATS (OCE63 Station 1, 27°N, 74° 20′ W, Fig. 7). The depth interval 75-500 m at BATS shows a constant isotopic composition of ε_{Nd} = –10.1. Values below that depth decrease to ε_{Nd} = –13.3 at 1000 m water depth, followed by a small gradual increase to –12.5 at 3000 m, and a constant ε_{Nd} of –12.5 to –12.6 from 3000 m to 4500 m water depth (Fig. 6).

Table 3: Sampling and preconcentration tests at BATS

Preconcentration tests: C18 cartridge vs. Fe co-precipitation

preconc. method	filter type[a]	sample ID	sample volume	^{143}Nd/^{144}Nd measured		internal 2σ SE	^{143}Nd/^{144}Nd normalized[b]	$ε_{Nd}$[c]		internal 2σ SE	external 2σ SD[d]
BATS, 20m											
Fe co-precip.	Osmonics 0.2μm	KN193-6-Nd-609	10L	0.512108	±	0.000014	0.512147	-9.6	±	0.3	0.3
Fe co-precip.	Osmonics 0.2μm	KN193-6-Nd-526	10L	0.512149	±	0.000008	0.512162	-9.3	±	0.2	0.4
Fe co-precip.	Osmonics 0.2μm	KN193-6-Nd-527	10L	0.512132	±	0.000011	0.512145	-9.6	±	0.2	0.4
C18 cartridge	Osmonics 0.2μm	KN193-6-Nd-612	10L	0.512119	±	0.000010	0.512158	-9.4	±	0.2	0.4
C18 cartridge	Osmonics 0.2μm	KN193-6-Nd-613	10L	0.512146	±	0.000015	0.512152	-9.5	±	0.3	0.3
						average BATS 20m		**-9.5**			
						2σ SD		**0.3**			
BATS, 2000m											
Fe co-precip.	Osmonics 0.2μm	KN193-6-Nd-412	10L	0.511905	±	0.000010	0.511944	-13.5	±	0.2	0.3
Fe co-precip.	Osmonics 0.2μm	KN193-6-Nd-413	10L	0.511922	±	0.000010	0.511961	-13.2	±	0.2	0.3
Fe co-precip.	Osmonics 0.2μm	KN193-6-Nd-323	10L	0.511941	±	0.000008	0.511954	-13.3	±	0.2	0.4
Fe co-precip.	Osmonics 0.2μm	KN193-6-Nd-324	10L	0.511943	±	0.000015	0.511956	-13.3	±	0.3	0.4
C18 cartridge	Osmonics 0.2μm	KN193-6-Nd-414	10L	0.511963	±	0.000019	0.511969	-13.0	±	0.4	0.3
C18 cartridge*	Osmonics 0.2μm	KN193-6-Nd-415	10L	0.511856	±	0.000011	0.511895	-14.5	±	0.2	0.4
C18 cartridge	Osmonics 0.2μm	KN193-6-Nd-416	10L	0.511938	±	0.000009	0.511977	-12.9	±	0.2	0.4
						average BATS 2000m		**-13.2**			
						2σ SD		**0.5**			

Sampling tests: Niskin vs. GO-GLO bottles

preconc. method	filter type[a]	sample ID	sample volume	^{143}Nd/^{144}Nd measured		internal 2σ SE	^{143}Nd/^{144}Nd normalized[b]	$ε_{Nd}$[c]		internal 2σ SE	external 2σ SD[d]
BATS, 20m											
Niskin	Osmonics 0.2μm	KN193-6-Nd-817	10L	0.512116	±	0.000010	0.512157	-9.4	±	0.2	0.3
Niskin	Osmonics 0.2μm	KN193-6-Nd-818	10L	0.512101	±	0.000011	0.512143	-9.7	±	0.2	0.3
GO-FLO	Osmonics 0.2μm	KN193-6-Nd-609	10L	0.512108	±	0.000014	0.512147	-9.6	±	0.3	0.3
GO-FLO	Osmonics 0.2μm	KN193-6-Nd-526	10L	0.512149	±	0.000008	0.512162	-9.3	±	0.2	0.4
GO-FLO	Osmonics 0.2μm	KN193-6-Nd-527	10L	0.512132	±	0.000011	0.512145	-9.6	±	0.2	0.4
						average BATS 20m		**-9.5**			
						2σ SD		**0.3**			
BATS, 2000m											
Niskin	Osmonics 0.2μm	KN193-6-Nd-719	10L	0.511919	±	0.000018	0.511926	-13.9	±	0.4	0.2
Niskin	Osmonics 0.2μm	KN193-6-Nd-720	10L	0.511953	±	0.000020	0.511961	-13.2	±	0.4	0.2
GO-FLO	Osmonics 0.2μm	KN193-6-Nd-412	10L	0.511905	±	0.000010	0.511944	-13.5	±	0.2	0.3
GO-FLO	Osmonics 0.2μm	KN193-6-Nd-413	10L	0.511922	±	0.000010	0.511961	-13.2	±	0.2	0.3
GO-FLO	Osmonics 0.2μm	KN193-6-Nd-323	10L	0.511941	±	0.000008	0.511954	-13.3	±	0.2	0.4
GO-FLO	Osmonics 0.2μm	KN193-6-Nd-324	10L	0.511943	±	0.000015	0.511956	-13.3	±	0.3	0.4
						average BATS 2000m		**-13.4**			
						2σ SD		**0.5**			

all analyzed at LDEO (VG Sector 54 TIMS).

[a] collected from trace metal-clean 2 x 500L tanks.

[b] KN193-6-415, 416, 612: normalized to repeat analyses of JNdi of ^{143}Nd/^{144}Nd=0.51208 ±0.000021 (n=6)
   relatice to a JNd$_i$ value of 0.512115 (Tanaka et al., 2000).
   KN193-6-323, 324, 526, 527: normalized to repeat analyses of La Jolla of ^{143}Nd/^{144}Nd=0.511845 ±0.000021 (n=10),
   relative to a La Jolla value of 0.511858 (Lugmair et al, 1983).
   all other samples: normalized to repeat analyses of La Jolla of ^{143}Nd/^{144}Nd=0.51185 ±0.000011 (n=13),
   relative to a La Jolla value of 0.511858 (Lugmair et al, 1983).

[c] $ε_{Nd}$ values were calculated relative to a CHUR of 0.512638 (Jacobsen and Wasserburg, 1980).

[d] external errors are derived from repeat standard analyses over the period of sample measurements;
   if internal errors are larger than external errors, these are plotted

* excluded from calculation of mean and 2σ standard deviation

  The hydrography at BATS shows a similar profile with constant salinity of 36.5-36.6 psu and potential temperature of 17-20°C in the upper ~70-500 m, and a rapid salinity and temperature decrease toward 1000 m water depth (Fig. 6) (KN193-
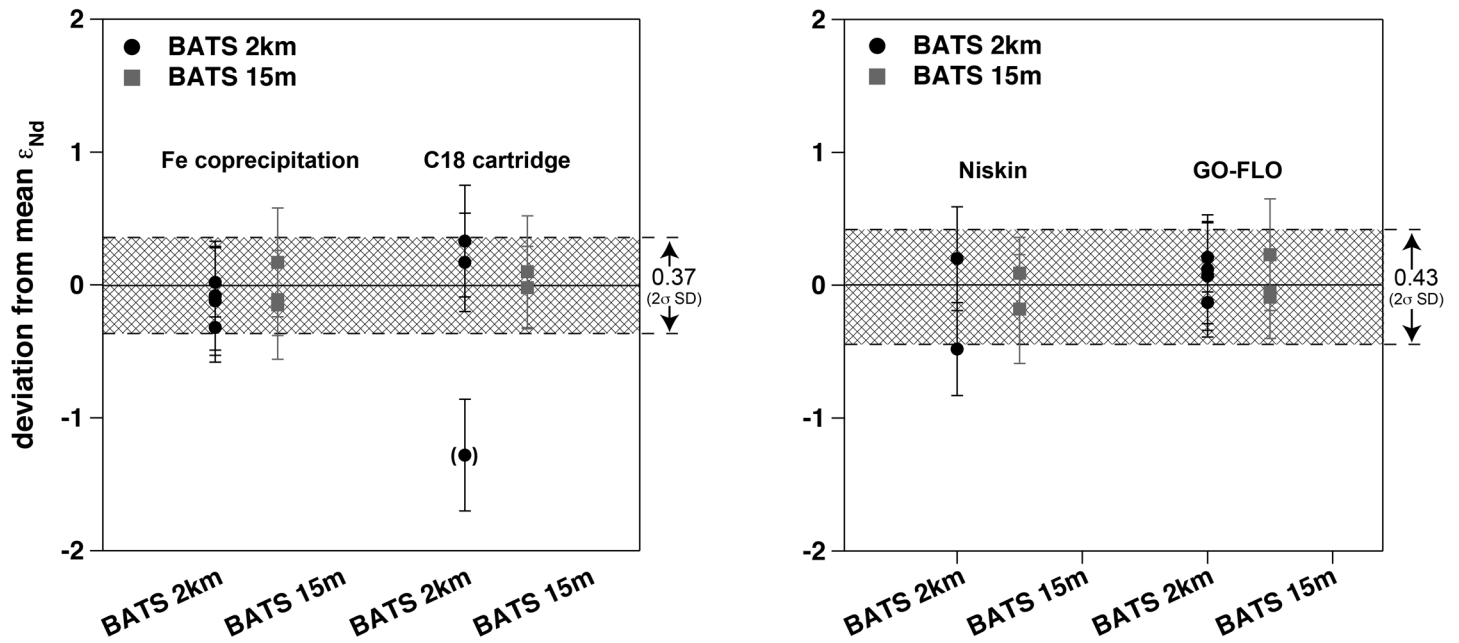
Fig. 5. Nd isotope ratios in ε_{Nd} notation at BATS 15 m and 2000 m plotted as deviations from the mean for the preconcentration tests (Fe coprecipitation compared with C18 cartridges; BATS 2000 m: mean ε_{Nd} = –13.2 ± 0.5, BATS 15 m: mean ε_{Nd} = –9.5 ± 0.3), and sampling bottle tests (standard Niskin bottles compared to trace metal-clean GO-FLO bottles; BATS 2000 m: mean ε_{Nd} = –13.4 ± 0.5, BATS 15 m: mean ε_{Nd} = –9.5 ± 0.3). One value from the C18 cartridge test was excluded from the calculation of the mean and standard deviation. Errors plotted are external two sigma standard deviations. In cases where the internal two sigma standard error of an individual analysis was larger, this error was plotted.

Table 4: Nd isotope ratio and concentration baseline profiles at BATS (31°45.62'N, 64°6.02'W)

sample ID	water depth [m]	sigma-t [kg/m³]	pot. Temp. [°C]	Salinity	filter type	filter diameter [mm]	sample volume	$^{143}Nd/^{144}Nd$ normalized[a]	±	internal 2σ SE	ε_{Nd}[b]	±	internal 2σ SE	external 2σ SD[c]
KN193-6-Nd-Th-022	20	24.980	23.366	36.518	Supor 0.45μm	90	10L	0.512165	±	0.000010	-9.2	±	0.2	0.2
KN193-6-Nd-Th-019	75	26.013	19.848	36.586	Supor 0.45μm	90	10L	0.512120	±	0.000012	-10.1	±	0.2	0.3
KN193-6-Nd-Th-016	500	26.588	16.855	36.353	Supor 0.45μm	47	10L	0.512118	±	0.000011	-10.1	±	0.2	0.2
KN193-6-Nd-Th-013	1000	27.550	6.414	35.065	Supor 0.45μm	47	10L	0.511957	±	0.000009	-13.3	±	0.2	0.3
KN193-6-Nd-Th-010	2000	27.810	3.493	34.964	Supor 0.45μm	47	10L	0.511967	±	0.000010	-13.1	±	0.2	0.3
KN193-6-Nd-Th-007	3000	27.872	2.506	34.927	Supor 0.45μm	47	10L	0.511999	±	0.000011	-12.5	±	0.2	0.3
KN193-6-Nd-Th-004	3750	27.891	1.949	34.894	Supor 0.45μm	47	10L	0.511994	±	0.000012	-12.6	±	0.2	0.3
KN193-6-Nd-Th-001	4500	27.891	1.815	34.881	Supor 0.45μm	47	10L	0.511994	±	0.000013	-12.6	±	0.3	0.3

[a] normalized to repeat analyses of La Jolla, relative to a La Jolla value of 0.51186.
[b] ε_{Nd} values were calculated relative to a CHUR of 0.512638 (Jacobsen and Wasserburg, 1980).
[c] external errors are derived from repeat standard analyses over the period of sample measurements;
   if internal errors are larger than external errors, these are plotted in Figure 6

6 CTD data: Table 4). Below 1000 m, salinity and temperature gradually decrease toward the bottom. The constant temperature-salinity properties in the upper ~70-500 m (Figs. 1b and 6) mark the position of Subtropical Mode Water (STMW, 'Eighteen-Degree Water' of Worthington 1959) that is formed south of the Gulf Stream extension at ~65°N (Worthington 1959; McCartney 1982; Hanawa and Talley 2001). The constant Nd isotopic composition of ε_{Nd} = –10.1 over the depth range of STMW is consistent with the characteristic vertical homogeneity of STMW properties and supports the validity of ε_{Nd} as a water mass tracer even at shallow water depth. The same

constant Nd isotope ratios of STMW have been reported by Piepgras and Wasserburg (1987) from a station further north of BATS (ε_{Nd} = –10.5; AII-109-1-Station 30, 36°15'_N, 61°58' W; Fig. 7).

The water below the STMW layer at BATS shows a small but well-defined silicate maximum that marks the depth of AAIW (e.g., Tsuchiya 1989), which is underlain by NADW (Figs. 1b and 6). The Nd isotope ratio at 1000 m water depth of ε_{Nd} = –13.3 shows no influence of the typical ε_{Nd} signature of AAIW in the South Atlantic (ε_{Nd} = –9 to –8, Jeandel 1993). Other intermediate water ε_{Nd} data available from the West Atlantic

Table 5: Rare earth element baseline profiles at BATS (31°45.62′N, 64°6.02′W)

Depth [m]	sample ID	La [ppt]	%2σ SE	Ce [ppt]	%2σ SE	Pr [ppt]	%2σ SE	Nd [ppt]	%2σ SE	Sm [ppt]	%2σ SE	Eu [ppt]	%2σ SE	Gd [ppt]	%2σ SE	Tb [ppt]	%2σ SE	Dy [ppt]	%2σ SE	Ho [ppt]	%2σ SE	Er [ppt]	%2σ SE	Tm [ppt]	%2σ SE	Yb [ppt]	%2σ SE	Lu [ppt]	%2σ SE
20	KN193-6-Nd-022a	2.02	±0.56	1.38	±0.55	0.43	±0.68	2.02	±1.06	0.47	±1.83	0.13	±2.56	0.76	±1.13	0.12	±1.27	0.98	±1.38	0.24	±1.28	0.80	±2.2	0.12	±1.27	0.73	±1.66	0.11	±1.25
20	KN193-6-Nd-022b	2.02	±0.71	1.38	±0.56	0.43	±0.66	2.02	±1.09	0.47	±1.46	0.13	±3.49	0.76	±1.33	0.12	±1.44	0.98	±1.98	0.24	±1.43	0.81	±1.81	0.12	±1.65	0.73	±1.81	0.11	±1.98
75	KN193-6-Nd-019	1.93	±0.73	1.29	±0.69	0.42	±0.67	1.96	±1.04	0.46	±1.75	0.13	±2.63	0.74	±1.12	0.12	±1.18	0.96	±1.29	0.24	±1.04	0.82	±1.81	0.11	±0.95	0.72	±1.29	0.12	±1.27
1000	KN193-6-Nd-013a	3.35	±0.83	0.55	±0.84	0.58	±0.63	2.58	±1.04	0.53	±1.60	0.14	±2.61	0.76	±1.14	0.12	±1.11	0.94	±1.29	0.23	±1.25	0.84	±1.40	0.12	±1.06	0.80	±1.11	0.14	±0.97
1000	KN193-6-Nd-013b	3.39	±0.65	0.59	±0.92	0.58	±0.67	2.58	±1.10	0.52	±1.46	0.14	±2.72	0.77	±1.21	0.12	±1.18	0.93	±1.41	0.24	±1.13	0.81	±1.29	0.12	±1.43	0.81	±1.62	0.14	±1.35
2000	KN193-6-Nd-010	3.21	±0.53	0.61	±0.88	0.54	±0.81	2.42	±0.89	0.49	±2.04	0.13	±2.06	0.74	±0.97	0.11	±1.32	0.92	±1.41	0.24	±1.13	0.82	±1.55	0.12	±0.98	0.82	±1.02	0.14	±1.37
3000	KN193-6-Nd-007a	3.58	±0.62	0.57	±0.80	0.60	±0.74	2.66	±0.85	0.54	±1.54	0.14	±2.88	0.79	±1.16	0.12	±1.06	0.98	±1.49	0.24	±1.36	0.86	±1.84	0.13	±1.41	0.85	±1.30	0.15	±1.26
3000	KN193-6-Nd-007b	3.62	±0.50	0.60	±0.81	0.61	±0.61	2.70	±0.76	0.54	±1.41	0.14	±2.51	0.79	±0.99	0.12	±1.08	0.97	±1.15	0.24	±0.68	0.84	±1.65	0.13	±1.15	0.85	±1.23	0.15	±1.26
3750	KN193-6-Nd-004	4.51	±0.69	0.85	±0.63	0.80	±0.53	3.47	±1.20	0.69	±1.29	0.17	±2.02	0.94	±0.87	0.14	±1.06	1.12	±1.07	0.28	±1.06	0.98	±1.31	0.14	±1.55	0.96	±1.23	0.16	±1.12
4500	KN193-6-Nd-001	5.24	±0.58	0.95	±0.78	0.92	±0.53	3.99	±1.00	0.77	±1.38	0.19	±1.95	1.04	±1.19	0.16	±1.05	1.21	±1.17	0.30	±1.06	1.04	±1.76	0.15	±1.07	1.03	±1.19	0.17	±1.48

all samples and elements blank-corrected
analyzed at LDEO (Axiom ICP-MS)
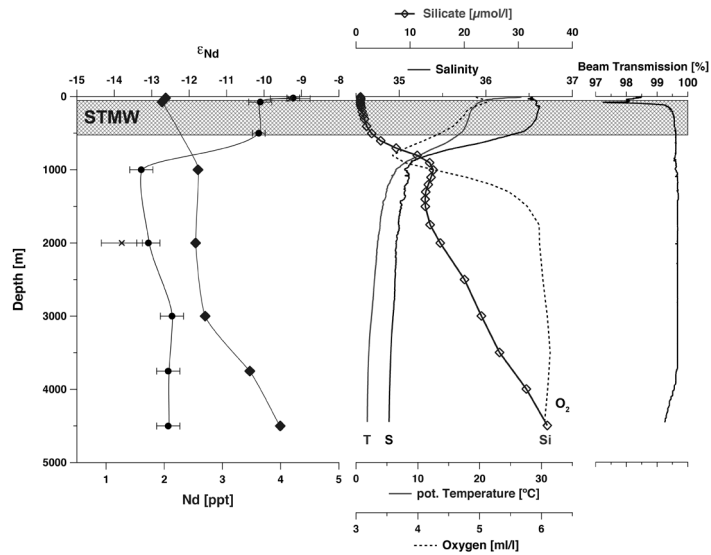errors are internal 2σ standard errors

Fig. 6. Seawater Nd isotope ratios (in ε_Nd notation) and Nd concentration baseline profiles compared with hydrographic data at BATS. Suspended particle ε_Nd values (gray crosses) from the intercalibration effort (average values from 5 labs (30 m), and 4 labs (2000 m), van de Flierdt et al. 2012) are also shown. Epsilon Nd errors plotted are external two sigma standard deviations. Two sigma standard errors of Nd concentrations are smaller than the symbols for Nd concentrations in the plot. Potential temperature, salinity, beam transmission (KN193-6 CTD data), silicate (Garcia et al. 2006), and dissolved oxygen (Levitus and Boyer 1994) are shown for comparison. The depth of Subtropical Mode Water (STMW) is marked by a gray bar.
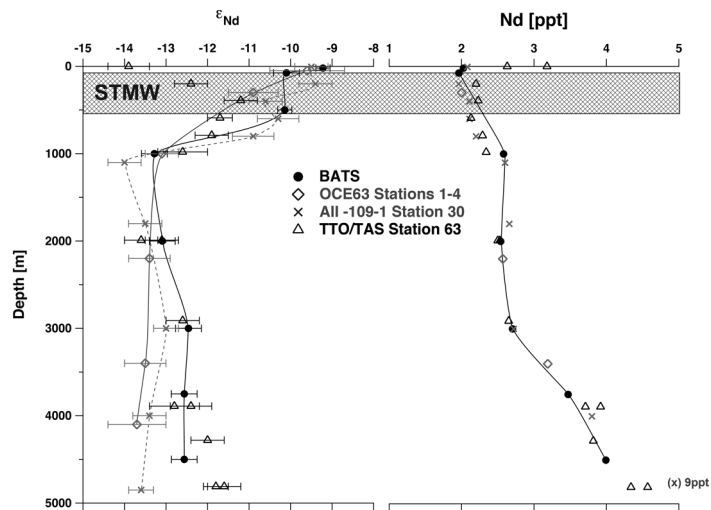

Fig. 7. Seawater Nd isotope ratios (in ε_Nd notation) and Nd concentrations at BATS (31°40′N, 64°10′W, this study), OCE63-Stations 1-4 (27°N, 74° 20′W, Piepgras and Wasserburg 1980), AII-109-1-Station 30 (36° 15′N, 61° 58′W, Piepgras and Wasserburg 1987), and TTO/TAS Station 63 (7° 43.8′N, 40° 42′W, Piepgras and Wasserburg 1987). Errors plotted are external two sigma standard deviations. The depth of Subtropical Mode Water (STMW) is marked by a gray bar.

(36°N: ε_{Nd} = –14; 7°N: ε_{Nd} = –12.6, Piepgras and Wasserburg 1987), however, indicate a slight trend from higher values in the south to lower values in the north (Fig. 7). This could suggest that the more radiogenic ε_{Nd} signature of AAIW, similar to its characteristic salinity minimum, is degraded or lost at this latitude through mixing with less radiogenic North Atlantic water masses (Fig. 6). The rapid change to lower ε_{Nd} at 1000 m water depth clearly marks the transition to underlying Upper-NADW (ε_{Nd} ~ –13.5, Lacan and Jeandel 2005). The change to higher ε_{Nd} near 3000 m water depth (ε_{Nd} = –12.5) is consistent with a change to Middle and Lower NADW (Lacan and Jeandel 2005), and the increasing influence of more radiogenic Antarctic Bottom Water (AABW) below 3000 m, as suggested by increasing phosphate and silicate concentrations (Fig. 6).

Neodymium isotope ratios of suspended particles from the sub-surface at BATS (30 m, QMA 1 μm double filters) and 2000 m water depth (Supor 0.45 μm filters) were measured as part of the international intercalibration effort (van de Flierdt et al. 2012). The surface particles were leached from the filter with 0.6N hydrochloric acid at 60°C for 20 h following the method of Jeandel et al. (1995), and the deep particles were subjected to a total digest by three laboratories following the method of Cullen and Sherrell (1999), while one lab leached the deep particles as described for the surface particles above. The Nd isotopic composition of particles from both depths [ε_{Nd} = –9.3 ± 0.5 BATS 30 m (5 labs); ε_{Nd} = –13.8 ± 0.6 BATS 2000m (4 labs)] is within the uncertainty of ambient seawater ε_{Nd} (Fig. 6), and no difference in isotopic composition is observed between the leached and digested samples from 2000 m water depth (van de Flierdt et al. 2012). This is in line with previous studies of particulate and ambient dissolved Nd isotope ratios in the North Atlantic and the Mediterranean Sea that show isotopic equilibrium between particulate and dissolved ε_{Nd} (Henry et al. 1994; Jeandel et al. 1995; Tachikawa et al. 1999).

Potential sources of particles to the Sargasso Sea are aerosols and dust, river runoff from the North American continent, and laterally advected particles. North American aerosols have lower ε_{Nd} values (ε_{Nd} = –14.1, Jeandel et al. 1995) than Saharan dust collected on Bermuda (ε_{Nd} = –13.2, Jeandel et al. 1995). The Nd isotopic composition of suspended particles from rivers draining the northeastern United States ranges from ε_{Nd} = –11.3 (Hudson River, Goldstein et al. 1984) to ε_{Nd} = –12.9 and –13.6 (Goldstein and Jacobsen 1988). The Nd isotopic composition of particles from 30 m and 2000 m at BATS of ε_{Nd} = –9.3 ± 0.5 and ε_{Nd} = –13.8 ± 0.6, respectively, is close to previously published particle ε_{Nd} values from the Sargasso Sea (Jeandel et al. 1995). Their close correspondence with ambient seawater ε_{Nd} of –9.3 ± 0.2 (20 m) and –13.1 ± 0.2 (2000 m) suggests that particulate and dissolved Nd are in isotopic equilibrium. These findings are consistent with the observations by Sholkovitz et al. (1994) that the largest fraction of particulate REE is contained in the easily leachable (with acetic acid) ferromanganese oxide coatings of marine particles.

It is, therefore, not surprising that the leached and digested samples from BATS have similar Nd isotopic compositions and are consistent with the dissolved ε_{Nd} of ambient seawater. This suggests that if the provenance of the suspended particles is of interest, Fe-Mn oxide coatings have to be thoroughly removed before analysis of the silicate fraction.

The concentration profiles of the light REE (LREE) (except Ce) and heavy REE (HREE) at BATS show an increase to 1000 m water depth, followed by relatively constant or slightly lower concentrations between 2000 m and 3000 m (Table 5, Fig. 8). The middle REE (MREE) vary little from the surface to 3000 m water depth. All REE concentrations rapidly increase below 3000 m to the bottom at 4500 m water depth. Cerium concentrations are highest near the surface (20 m, 75 m), lowest between 1000 m and 3000 m water depth, and increase again toward the bottom. This behavior is typical for Ce and reflects the oxidation of Ce from dissolved trivalent Ce to particulate tetravalent Ce within the upper water column, and remineralization at depth (Sholkovitz and Schneider 1991). Over the entire depth profile, the LREE reveal a stronger increase with depth than the HREE, e.g., La shows a 163% increase with depth compared with a 42% increase of Yb.

The sharp increase in concentrations across all REEs below 3000 m is coincident with a decrease in beam transmission measured by a transmissometer attached to the conductivity-temperature-depth (CTD) rosette on cruise KN193-6 (Fig. 6). The KN193-6 samples are located within or near the southern edge of the deep nepheloid layer, where sediments on the seafloor are resuspended by vigorous bottom currents (Biscaye and Eittreim 1977). Because dissolved and particulate REE concentrations are closely related (e.g., Jeandel et al. 1995; Siddall et al. 2008), the increase in REE concentrations at this depth (>3000 m) may be due to REE release from resuspended sediments in the bottom nepheloid layer. However, the observed Nd concentrations and isotope compositions of samples from this depth range are consistent with those from all nearby profiles including open ocean locations (Fig. 7), suggesting that the increase in REE concentrations is dominated by remineralization of sinking particles at depth and water mass advection rather than REE release from resuspended particles. Siddall et al. (2008) noted that downward transport of ε_{Nd} signatures through reversible scavenging does not overprint the advected ε_{Nd} signal in areas of strong lateral transport, such as the Atlantic, suggesting that remineralization at depth can increase Nd concentrations without significantly changing the deep water Nd isotopic composition. If surface particles at BATS were isolated from exchange with seawater through binding in biologically formed aggregates that only decompose at the seafloor, as suggested by Jeandel et al. (1995), this would not be inconsistent with the isotopic composition of bottom waters at BATS of ε_{Nd} = –12.6, because particles entering the Sargasso Sea through rivers, dust, or as aerosols have ε_{Nd} values of –11 to –14 (Goldstein et al. 1984; Goldstein and Jacobsen 1988; Jeandel et al. 1995). Additionally, northward advection and mixing of relatively Nd- and Si-
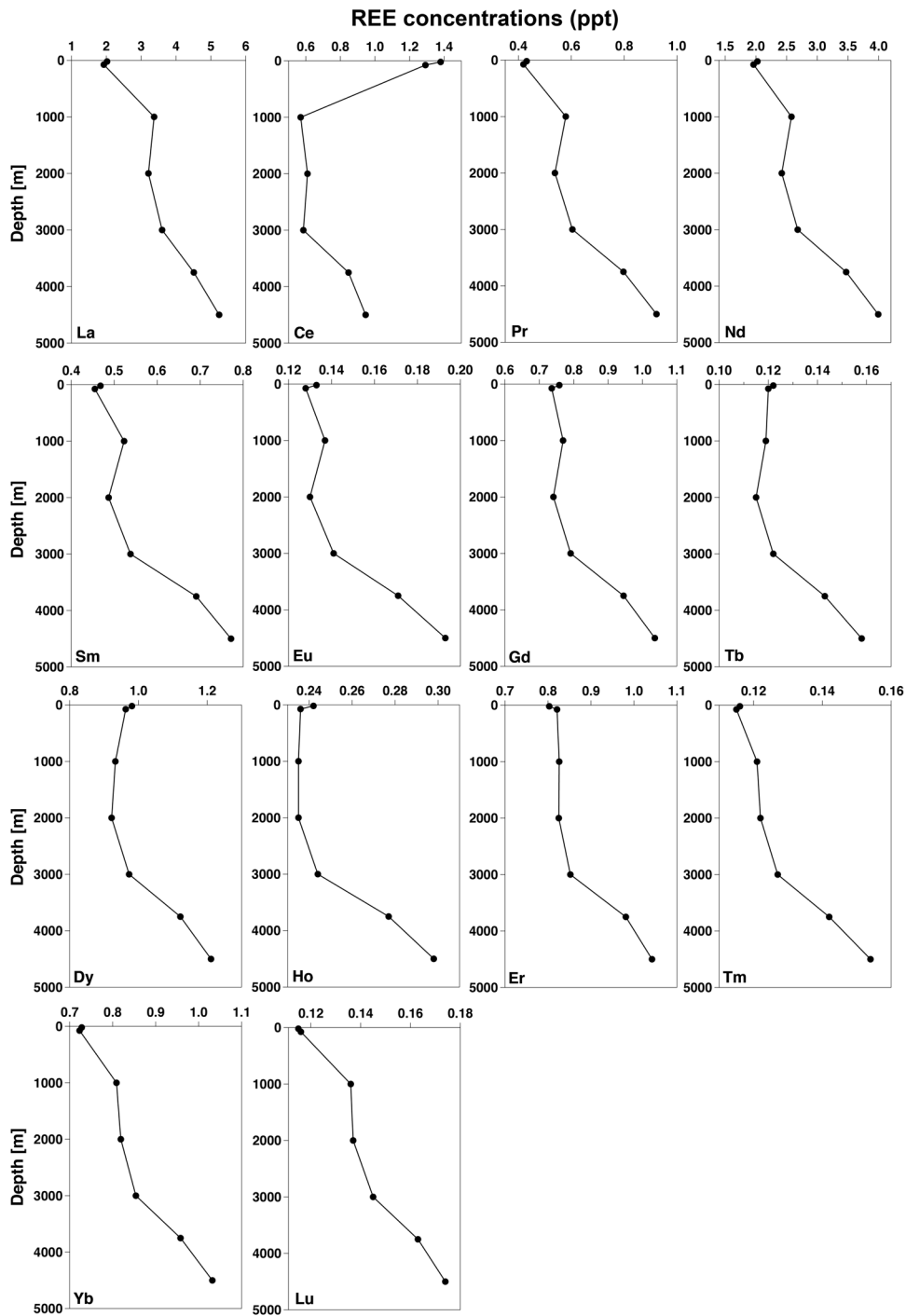
Fig. 8. Rare earth element baseline profiles at BATS.

rich, more radiogenic Antarctic Bottom Water (AABW) with southward flowing Nd- and Si-poor, less radiogenic NADW at depth could contribute to the Nd and Si increases and the small ε_{Nd} shift to higher values below 3000 m (Fig. 6).

Normalized to Post-Archean Australian Shale REE concentrations (PAAS, McLennan 1989), the REE patterns at all depths show a typical seawater pattern with an increase from LREE to HREE, and a negative Ce anomaly (Fig. 9). Previously published REE profiles from BATS (Sholkovitz and Schneider 1991; Sholkovitz et al. 1994) show different REE/PAAS patterns. Absolute values differ from the data reported here for all but the surface samples (15 m, 30 m). In detail, at 1000 m and 2000 m water depth analyzed by both studies, previously published concentrations are higher by 0.5 pg/g (1000 m) and 0.4 pg/g
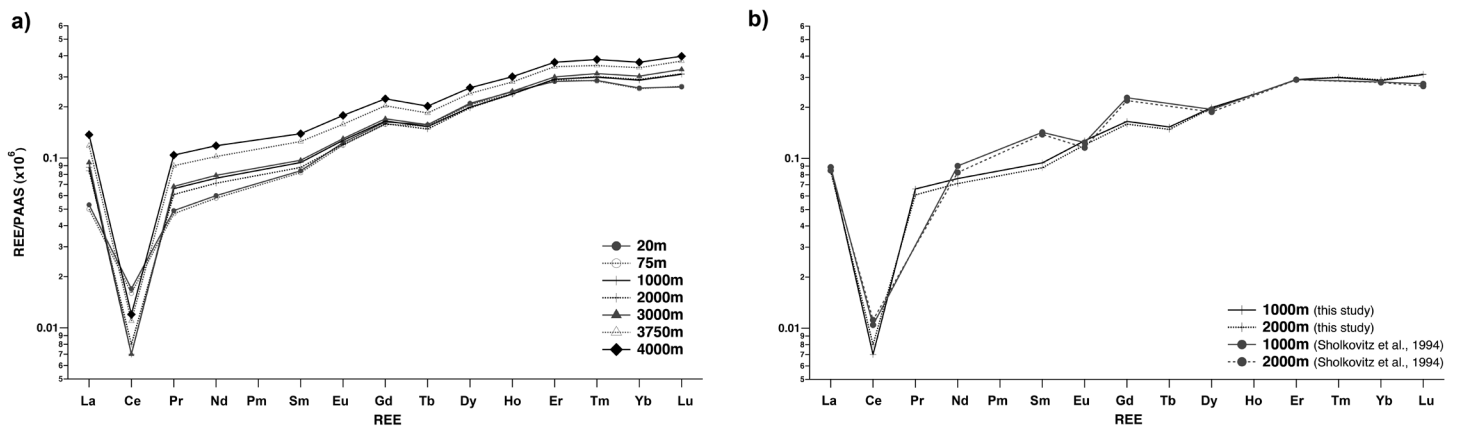
Fig. 9. Rare earth element concentrations at BATS normalized to average shale (Post Archean Australian Shale, PAAS, McLennan 1989). a) REE patterns from this study and b) comparison of REE patterns from 1000 m and 2000 m from this study and Sholkovitz et al. (1994).

(2000 m) for Nd, 0.3 pg/g (1000 m and 2000 m) for Sm, and 0.3 pg/g (1000 m and 2000 m) for Gd, and a decrease from Yb to Lu, while our data show an increase from Yb to Lu (Fig. 9). The trends and absolute concentrations of our data are supported by the REE intercalibration results from 15 m and 2000 m water depth at BATS (6 participating laboratories) that were collected at the same location and on the same cruise as our samples and that only differed by 9% (Nd), 10% (Sm), and 11% (Gd) (van de Flierdt et al. 2012). The differences between our data and those of Sholkovitz et al. (1994), therefore, have to be attributed to either the different season and year the samples were collected in (this study: May-June 2008, Sholkovitz: April 1989), or to analytical uncertainties or spike calibration.

SAFe baseline profile

The water column profiles of Nd isotope ratios and concentrations at the northeast Pacific SAFe station were analyzed at the University of Hawaii (UH) and Imperial College London (ICL) and are shown in Table 6 and Fig. 10. The ε_{Nd} profiles show an average ε_{Nd} of –3.6 at 4500 m water depth and a gradual increase to ε_{Nd} = –2.6 at 2000 m and ε_{Nd} = –2.9 at 1000 m water depth. The two shallowest samples analyzed at UH (500 m and 100 m) deviate significantly from those analyzed at ICL: while the ICL ε_{Nd} values range between ε_{Nd} = –3.2 and –3.4, the UH ε_{Nd} values show a decrease to ε_{Nd} = –4.2 at 500 m and ε_{Nd} = –5.4 at 100 m water depth. Both laboratories adhere to routine quality control through analysis of standards and blanks, and their measurements of Nd isotope ratios and concentrations on seawater as part of the international intercalibration exercise (BATS 20 m and 2000 m, SAFe 2000 m, and an unknown standard) agreed well with those of other laboratories (see van de Flierdt et al. 2012). We find no reason to discount any of the Nd isotope measurements of the upper water column profiles at SAFe. Possible reasons for the disagreement are either contamination during sampling on the ship or during chemical separation of Nd in the laboratory, or unknown complications during the analysis. We compare both profiles to the few available Nd isotope measurements in the North

Pacific but refrain from an in-depth discussion of the upper water column ε_{Nd} profile at SAFe until future analyses have confirmed the isotopic composition.

Published water column ε_{Nd} profiles from the North Pacific (Station BO-3, 30°N 160°W; and Station BO-5 20°N, 175°W, Amakawa et al. 2009) to the west and southwest of SAFe, respectively, show similar (BO-3) to slightly lower (BO-5) ε_{Nd} values below 1000 m water depths than those at SAFe and a minimum of ε_{Nd} = –3.3 (BO-3) and –2.7 (BO-5) at 1000 m water depth (Figs. 1 and 11). This relatively homogenous vertical isotopic composition suggests no significant influence of more unradiogenic Antarctic Bottom Water (AABW) at depth, in contrast to the central and western North Pacific, where bottom water ε_{Nd} values decrease to ε_{Nd} = –4.5 and –5.8 (Piepgras and Jacobsen 1988; Amakawa et al. 2004; Amakawa et al. 2009) (Fig. 11).

The higher ε_{Nd} values between 500 m and 850 m water depth at SAFe (ε_{Nd} = –3.0 to –4.2) coincide with the depth range of North Pacific Intermediate Water (NPIW, core layer density σ(= 26.9, You 2003) at this location, that is associated with a salinity minimum (Yasuda 2004). NPIW is formed in the western North Pacific through mixing of subpolar water and older subtropical water of the same density and is incorporated into the North Pacific subtropical gyre (Talley 1997). The ε_{Nd} values of NPIW at SAFe of both profiles are similar with Nd isotope ratios that have previously been reported for NPIW near its formation region (ε_{Nd} = –3.2; 40°N, 160°E, Amakawa et al. 2004), and near the Hawaiian Islands (ε_{Nd} = –3.7, Vance et al. 2004).

The shift to lower values of ε_{Nd} = –4.2 (500 m) and ε_{Nd} = –5.4 (200 m) in the profile analyzed at UH is consistent with the gradual ε_{Nd} decrease at BO-3 (ε_{Nd} = –5.6, 200 m) and BO-5 (ε_{Nd} = –4.9, 200 m) (Fig. 11). The upper water column ε_{Nd} values analyzed at ICL (ε_{Nd} = –3.2 to –3.4), on the other hand, agree with the isotopic composition of subsurface waters (300-600 m) around Hawaii (20-22.8°N, 156-158°W) of ε_{Nd} = –3.3 to –3.7 (Fig. 11).

Table 6: Nd isotope ratio and concentration baseline profiles at SAFe (30°N, 140°E)

analyzed at the University of Hawaii

water depth [m]	sigma-t [kg/m³]	pot. Temp. [°C]	Salinity	filter type	sample ID	sample volume[a]	^{143}Nd/^{144}Nd measured		internal 2σ SE	^{143}Nd/^{144}Nd normalized[b]	ε_{Nd}[c]		internal 2σ SE	external 2σ SD[d]	Nd [ppt]		internal % 2σ SE
20	24.769	19.23	34.75	AcroPak 0.8/0.45μm	KN195-8-Nd-2323	0.25L									0.9	±	1.4
100	25.172	18.06	34.89	AcroPak 0.8/0.45μm	KN195-8-Nd-2321	5L, 0.25L	0.512343	±	0.000014	0.512362	-5.4	±	0.3	0.3	1.1	±	1.8
500	26.707	6.43	34.01	AcroPak 0.8/0.45μm	KN195-8-Nd-2318	5L, 0.25L	0.512406	±	0.000006	0.512425	-4.2	±	0.1	0.3	2.2	±	0.7
850	27.215	4.11	34.31	AcroPak 0.8/0.45μm	KN195-8-Nd-2314	5L, 0.25L	0.512454	±	0.000009	0.512473	-3.2	±	0.2	0.3	2.8	±	1.0
1000	27.340	3.69	34.41	AcroPak 0.8/0.45μm	KN195-8-Nd-2311	5L, 0.25L	0.512468	±	0.000005	0.512487	-2.9	±	0.1	0.3	2.8	±	1.1
2000	27.663	1.88	34.62	AcroPak 0.8/0.45μm	KN195-8-Nd-2308	0.25L									4.3	±	1.8
3000	27.736	1.33	34.66	AcroPak 0.8/0.45μm	KN195-8-Nd-2305	5L, 0.25L	0.512456	±	0.000004	0.512475	-3.2	±	0.1	0.3	6.4	±	1.4
4500	27.753	1.14	34.68	AcroPak 0.8/0.45μm	KN195-8-Nd-2302	5L, 0.25L	0.512427	±	0.000004	0.512446	-3.7	±	0.1	0.3	7.8	±	0.6

analyzed at Imperial College London

water depth [m]	sigma-t [kg/m³]	pot. Temp. [°C]	Salinity	filter type	sample ID	sample volume	^{143}Nd/^{144}Nd measured		internal 2σ SE	^{143}Nd/^{144}Nd normalized[e]	ε_{Nd}[c]		internal 2σ SE	external 2σ SD[d]	Nd [ppt]		internal % 2σ SE
20	24.769	19.23	34.75	AcroPak 0.8/0.45μm	KN195-8-Nd-2324	5L	0.512450	±	0.000019	0.512463	-3.4	±	0.4	0.2	0.8	±	0.01
100	25.172	18.06	34.89	AcroPak 0.8/0.45μm	KN195-8-Nd-2320	5L	0.512463	±	0.000011	0.512475	-3.2	±	0.2	0.2	1.0	±	0.01
500	26.707	6.43	34.01	AcroPak 0.8/0.45μm	KN195-8-Nd-2317	5L	0.512458	±	0.000016	0.512471	-3.3	±	0.3	0.2	2.1	±	0.01
850	27.215	4.11	34.31	AcroPak 0.8/0.45μm	KN195-8-Nd-2315	5L	0.512470	±	0.000021	0.512483	-3.0	±	0.4	0.2	2.8	±	0.02
1000	27.340	3.69	34.41	AcroPak 0.8/0.45μm	KN195-8-Nd-2312	5L	0.512481	±	0.000018	0.512494	-2.8	±	0.3	0.2	2.9	±	0.02
2000	27.663	1.88	34.62	AcroPak 0.8/0.45μm	KN195-8-Nd-2309	5L	0.512490	±	0.000008	0.512503	-2.6	±	0.2	0.2	4.3	±	0.01
3000	27.736	1.33	34.66	AcroPak 0.8/0.45μm	KN195-8-Nd-2306	5L	0.512467	±	0.000008	0.512479	-3.1	±	0.2	0.2	6.4	±	0.01
4500	27.753	1.14	34.68	AcroPak 0.8/0.45μm	KN195-8-Nd-2303	5L	0.512447	±	0.000005	0.512460	-3.5	±	0.1	0.2	7.8	±	0.00

[a] sample volume for isotope analyses = 5L, for Nd concentrations ~250mL.

[b] UH: normalized to repeat analyses of La Jolla of ^{143}Nd/^{144}Nd=0.511839 ±0.000014 (n=5), relative to a La Jolla value of 0.511858 (Lugmair et al., 1983).

[c] ε_{Nd} values were calculated relative to a CHUR of 0.512638 (Jacobsen and Wasserburg, 1980).

[d] external errors are derived from repeat standard analyses over the period of sample measurements (10ng at UH, 5ng at ICL);
if internal errors are larger than external errors, these are plotted.

[e] ICL: normalized to repeat analyses of JNd$_i$ of ^{143}Nd/^{144}Nd= 0.512102 ±0.000003 (n=5), relative to a JNd$_i$ value of 0.512115 (Tanaka et al., 2000).
UH: reports an external reproducibility of 0.14ppt based on n=7 aliquots of a seawater sample
ICL: reports an external reproducibility of 5.6% (2σ SE) based on n=5 repeat analyses of rock standard BCR
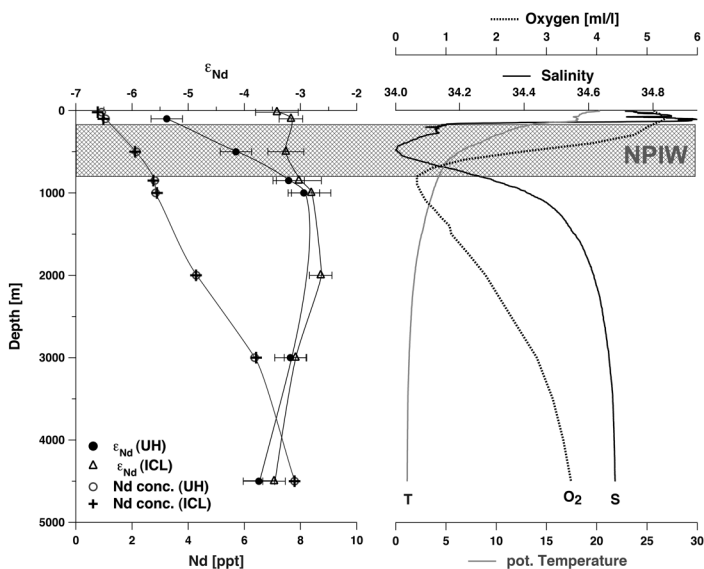

Fig. 10. Seawater Nd isotope ratio (in ε_{Nd} notation) and Nd concentration baseline profiles at SAFe analyzed at UH (circles) and ICL (triangles and crosses). Epsilon Nd errors plotted are external two sigma standard deviations. Two sigma standard errors of Nd concentrations are smaller than the symbols for Nd concentrations in the plot. Potential temperature, salinity (KN195-8 CTD data), and dissolved oxygen (Levitus and Boyer 1994) are shown for comparison. NPIW = North Pacific Intermediate Water.

The Nd concentration profiles at SAFe of both laboratories agree well (maximum difference of 0.1 ppt Nd) and show a gradual increase from an average surface Nd concentration of 0.85 ppt to a bottom water Nd concentration of 7.8 ppt (Fig. 8), reflecting the typical behavior of Nd in the ocean of scavenging in the upper water column and remineralization at depth.

Conclusions and recommendations

The nature of the GEOTRACES program requires careful testing and evaluation of the techniques and materials to be used to collect, process, and analyze the seawater samples. In an effort to provide this basis for the analysis of Nd isotope ratios and concentrations in seawater, we have tested different filter materials and pore sizes, two widely used sampling bottles, and two methods for the preconcentration of REEs from seawater at three different locations.

The comparison of five different filter types and pore sizes with unfiltered seawater suggests that dissolved Nd isotope ratios and Nd concentrations of seawater are not affected by the choice of the filter (Nuclepore, Supor, QMA), filter type (membrane, cartridge), or pore size (0.2, 0.45, 0.8, 1.0 μm). At all locations chosen for this study, Bermuda Atlantic Time-Series Study (BATS) station (20 m and 2000 m water depth) and the depth of the chlorophyll maximum at a site on the Virginia continental slope, the Nd isotope ratios and Nd con-
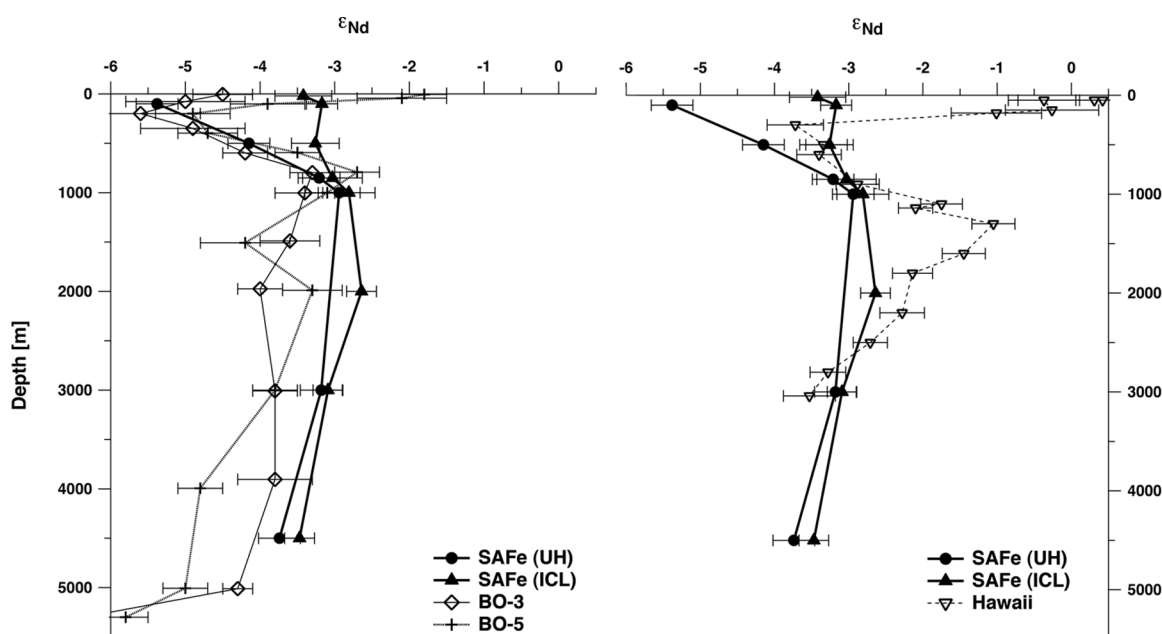
Fig. 11. Seawater Nd isotope ratio profiles (in ε_{Nd} notation) at SAFe compared with other North Pacific ε_{Nd} water column profiles. a) ε_{Nd} profiles at SAFe analyzed at the University of Hawaii (UH) and Imperial College London (ICL) (filled symbols) compared to ε_{Nd} profiles at BO-3 (30°N 160°W, Amakawa et al. 2009) and BO-5 (20°N, 175°W, Amakawa et al. 2009) (open symbols). b) Same as in a) but in comparison with water column ε_{Nd} from stations around Hawaii combined to one profile (20-22.8°N, 156-158°W) (Vance et al. 2004).

centrations of filtered and unfiltered seawater were the same within the uncertainty of the analysis: ≤ 56 ppm (2σ standard deviation) for $^{143}Nd/^{144}Nd$ ratios, and ≤ 10% (2σ RSD) for Nd concentrations. The international GEOTRACES intercalibration of Nd isotopes and REE concentrations achieved very similar reproducibilities of ≤ 60ppm and ≤ 9% (van de Flierdt et al. 2012), suggesting that the results from our filter tests are within the analytical uncertainty for sample sizes of 5-15 ng Nd. Therefore, the assumption made in previous studies that at most locations filtration is not required may be justified. However, the sites studied here may not be representative of all possible scenarios in the global ocean in terms of particle flux and isotopic composition of suspended particles relative to ambient seawater. We therefore highly recommend routine filtration of seawater samples using any of the filter material tested here with a pore size of 0.45 µm or less, particularly in high-particle environments such as areas of high dust flux, river discharge, and/or within bottom or detached nepheloid layers. This applies especially to areas where suspended particles are expected to have a different isotopic composition than local seawater.

Our tests of two different sampling bottles, standard Niskin versus trace metal-clean GO-FLO bottles, confirm the general notion that trace metal-clean sampling equipment is not necessary for obtaining accurate Nd isotope and concentration data from seawater samples. Moreover, we observed no difference in dissolved Nd isotope ratios between two commonly used methods for the preconcentration of REEs from seawater, Fe coprecipitation, and C18 cartridges. Both methods are

therefore applicable and suited for the purposes of the GEOT-RACES program.

Neodymium isotope ratios of suspended particles at 30 m and 2000 m water depth at BATS indicate isotopic equilibrium with ambient seawater, suggesting thorough removal of Fe-Mn-oxide coatings is required if the provenance of suspended particles is of interest.

The baseline profiles for BATS in the western North Atlantic (ε_{Nd} and REE) and SAFe in the eastern North Pacific (ε_{Nd}; results > 800 m water depths), are recommended for inclusion in future cruises for continued quality control, intercalibration, and method validation. The Nd isotopic composition at shallow water depths at SAFe needs to be further constrained on future expeditions.

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