Rapid and precise analysis of rare earth elements in small volumes of seawater - method and intercomparison

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Abstract

Rare earth elements (REEs) are used as tracers for oceanic trace element cycling. However, the low (picomolar level) dissolved REE concentrations and time-consuming methods have so far hindered their extensive use in marine studies. This study reports the first application of the automated seaFAST-pico system (Elemental Scientific Inc.) in offline mode and using multi-element isotope dilution inductively coupled plasma-mass spectrometry (ID ICP-MS) for the robust and rapid pre-concentration, purification, and analysis of dissolved REEs from small volumes of seawater (11-12 mL). Accuracy of our new method is checked with replicates of GEOTRACES intercalibration seawater from BATS (Bermuda Atlantic Time Series, North Atlantic) at 15 m and 2000 m water depths. Our results show excellent agreement (within the analytical uncertainty, 2σ SD) with the published intercalibrated values from the GEOTRACES intercalibration study. Replicates of GEOTRACES intercalibration seawater from SAFe at 3000 m water depth (Sampling and Analysis of Iron, North Pacific) indicate a procedural long-term error of $\leq 3.9\%$ 2σ RSD for all REEs, except for Ce and Gd. An international intercomparison from 4 labs using SAFe 3000 m seawater aliquots, 2 of which also use the seaFAST-pico system in offline mode, and different pre-concentration, purification, and analytical methods shows excellent agreement between REE concentrations

within 7% (2σ RSD) (except for Ce 71%, Gd 14%, Lu 12%). This is comparable to the agreement obtained for the BATS 15 m and 2000 m samples by six different labs for the international GEOTRACES intercalibration study (van de Flierdt et al., 2012). The REE intercomparison values of SAFe 3000 m (i.e., the average of the values from the 4 labs) in this study agree within the analytical uncertainties (2σ SD) with published REE values of deep seawater from nearby stations. Our international intercomparison provides the first REE intercomparison values for the GEOTRACES intercalibration station SAFe at 3000 m, and establishes the first reference seawater REE values for quality control of future REE studies in the Pacific Ocean as SAFe will remain a GEOTRACES baseline, and hence intercalibration station, for cruises in the North Pacific. Our method is easy to adopt and enables the extensive use of REEs, thereby opening the way to build a global seawater REE data set.

1. Introduction

Rare earth elements exist predominantly in the trivalent oxidation state. Only Eu and Ce can be reduced to Eu(II) and oxidized to Ce(IV) depending on the redox conditions. A systematic chemical property of REEs is the decrease in ionic radii with increasing atomic number, which leads to an increase in the strength of complexation by carbonate ions from light (LREEs) to heavy (HREEs) REEs in seawater that makes heavies more soluble. Light REEs are therefore preferentially scavenged by particles, resulting in a characteristic shale-normalized fractionation pattern in seawater with a HREE over LREE enrichment (e.g., Cantrell and Byrne, 1987; Elderfield, 1988; Byrne and Kim, 1990; Quinn et al., 2006; Schijf et al., 2015). Differences and changes in shale-normalized REE patterns in seawater have been used as diagnostic tool to trace and characterize 1) marine geochemical processes (e.g. scavenging, re-mineralization, redox changes), 2) sources of trace elements to the ocean, 3) anthropogenic pollution, and 4) different water masses (e.g., Alibo and Nozaki, 1999; Elderfield, 1988; Hongo et al., 2007; Jeandel et al., 2013; Kim and Kim, 2011; Kulaksiz and Bau, 2011; Lacan and Jeandel, 2001; Shaw et al., 2003; Sholkovitz et al., 1994; Zhang and Nozaki, 1996).

The wide potential for the application of REEs in marine, coastal, and estuarine environments as well as the lack of understanding of oceanic trace element cycling has led to increased interest in applying seawater REE analyses. As a result, REEs are part of the international GEOTRACES Program (e.g., Grenier et al., 2013; Hathorne et al., 2015; Jeandel et al., 2013). However, extensive use of REEs as tracers in the ocean has been hindered by major difficulties: 1) the low (picomolar level) concentration of REEs in seawater that requires sample pre-concentration, 2) the high salt matrix interferences that require sample purification, 3) the potential fractionation of REEs during the chemical procedures, 4) the high analytical precision required to resolve small changes in the fractionation among REEs, and 5) the oxide interferences (Ba on Eu, and LREEs on HREEs).

In previous approaches, dissolved REEs have been pre-concentrated and purified using liquid-phase or solid-phase extractions (e.g., magnesium or iron co-precipitation, chelating and ion-exchange resins) and analyzed by either instrumental neutron activation, thermal ionization mass spectrometry, inductively coupled plasma-atomic emission spectrometry, or inductively coupled plasma-mass spectrometry (Hatje et al., 2014; Shaw et al., 2003; Zheng et al., 2015 and references therein). However, these methods have important limitations due either the requirement of large sample volumes (up to ~20 L), the inability to analyze mono-isotopic REEs, low precision, or time-consuming procedures (e.g., de Baar et al., 1985; Greaves et al., 1989). Recently, Hathorne et al. (2012, 2015) presented a method using the commercially available seaFAST system (Elemental Scientific Inc. Omaha, Nebraska, USA)

that allows automated, rapid pre-concentration and purification of all REEs directly from small volumes of seawater (7 mL and 11 mL, respectively). In both cases, the authors used the online pre-concentration system directly connected to an ICP-MS. This allows for the immediate determination of REE concentrations yielding average precisions of 12% (2 σ RSD) for a 7 mL seawater sample (South Atlantic, 59°N, 0°E, 2000 m) (Hathorne et al., 2012) and 8.4%, 12%, and 5.0% (2 σ RSD) for an 11 mL seawater sample (BATS, 31°40'N, 64°10'W, 15 m and 2000 m; Station 113, 52°59.80'S, 0°02.00'E, 1000 m), respectively (Hathorne et al., 2015).

In this study, we present the method at ICBM (Institute for Chemistry and Biology of the Marine Environment), University of Oldenburg, that uses the seaFAST-pico system in offline pre-concentration mode, that is, the pre-concentrated REE fractions are collected into sample vials prior to analysis. We choose the offline operation for the following reasons: 1) the automated pre-concentration can be run over night independent of an ICP-MS, saving argon gas and operator time, and 2) the samples can be analyzed with a constant signal instead of an elution peak signal, allowing several measurement passes and, if required, re-analyses, thereby increasing analytical precision significantly. The disadvantages are the lack of immediate assessment of the elemental concentrations, lower signal intensities for the same sample volume compared to time-resolved analysis at the highest elution peak signal (e.g., Hathorne et al., 2012), and the potential of slightly higher total procedural blanks due to an additional dilution step.

In the first part of this manuscript, we outline the details of our procedure using the seaFAST system in offline mode and provide a robust and rapid method for the pre-concentration and purification of REEs from small sample volumes (11-12 mL). For analyses, we use the advantages of both multi-element ID ICP-MS and a desolvating sample introduction system for precise and accurate analysis of REE concentrations (presented as pmol/kg). In the second part of this manuscript, we provide an international intercomparison by four labs of dissolved REE concentrations on sample aliquots from North Pacific station SAFe from 3000 m water depth. Lab 1 is ICBM, Lab 2 is LDEO (Lamont Doherty Earth Observatory), Columbia University, Lab 3 is CEOAS (College of Earth, Ocean and Atmospheric Sciences), Oregon State University, and Lab 4 is LEGOS (Laboratoire d'Etudes en Géophysique et Océanographie Spatiale), University of Toulouse. Both LDEO and CEOAS also use the seaFAST-pico system in offline mode, and we outline the small differences in procedure. These results further validate our new method and provide the first REE intercomparison values for a GEOTRACES intercalibration station in the North Pacific, based on averaging the average values from the 4 labs. So far, there is no widely available GEOTRACES seawater standard for REE concentrations from the Pacific. The GEOTRACES intercalibration samples BATS 15 m and 2000 m from the North Atlantic are nearly depleted already, and the SAFe sample is a possible alternative.

2. Materials and procedures

2.1. Sample locations and onboard procedure

We used seawater collected during two GEOTRACES intercalibration cruises at stations BATS (31°40'N, 64°10'W, 15 m, 2000 m water depth) in the North Atlantic (R/V *Knorr*, KN193-6, June-July 2008) and SAFe (30°N, 140°W, 3000 m water depth) in the North Pacific (R/V *Knorr*, KN195-8, May 2009). The shipboard sampling procedures are described in detail in Pahnke et al. (2012) and van de Flierdt et al. (2012). Briefly, the surface water was sampled using a trace-metal clean towed sampling system (GeoFish) (Bruland et al., 2005), while deep waters were collected from multiple casts using trace-metal clean GO-FLO

bottles (General Oceanics) (Cutter and Bruland, 2012; van de Flierdt et al., 2012). Seawater samples were filtered through 0.2 μm pore size Osmonics (Memtrex) cartridge filters, transferred into large tanks through Teflon tubing, acidified to $\text{pH} \leq 2$, mixed overnight, and subsampled into acid-cleaned HDPE or LDPE bottles. The participants of this intercomparison study received aliquots directly from the intercalibration cruise in 2009 (e.g., van de Flierdt et al., 2012) or we provided them with an aliquot from our subsample in acid-cleaned HDPE bottles.

2.2. Lab 1: Offline seaFAST pre-concentration of REEs and multi-element ID ICP-MS

2.2.1. Pre-concentration of REEs from seawater

The pre-concentration method of this study (Lab 1, ICBM) is described in detail in the following and summarized in Table 1. Dilutions were prepared with high purity water (18.2 $\text{M}\Omega\text{ cm}$). Chemicals used were of high purity (ammonium hydroxide, ultra-quality Carl Roth) and ultra-high purity (nitric acid, glacial acetic acid, optima quality Fisher Chemical). The required buffer solution was prepared using 157 mL high purity water, 140 mL glacial acetic acid, and 203 mL 20% ammonium hydroxide. The pH of the buffer solution (6.0 ± 0.2) was adjusted by adding small amounts of either glacial acetic acid or ammonium hydroxide. A 1.5 N HNO_3 was used as eluting acid, and a 2% HNO_3 was used as rinse solution for the autosampler probe.

The seaFAST-pico system used here for the automated pre-concentration of REEs from seawater consists of an autosampler with 120 positions for sample and elution vials each, clean enclosure, and ultra-low particulate air filter, a pre-concentration and clean-up column with PFA (perfluoroalkoxy) housing and PTFE (polytetrafluoroethylene) frits, and triple 6-port valves with PFA rotors and CTFE (chlorotrifluoroethylene) stators that regulate the pre-concentration process. All solutions were pumped through PFA tubing using one 12 mL CTFE/PTFE and three 3 mL quartz/PFA SYRIX syringe pumps (S400V syringe pump module). The pre-concentration and clean-up columns were packed with 200 μL of a chelating resin consisting of ethylenediaminetriacetic acid and iminodiacetic acid functional groups to pre-concentrate trace elements from seawater while anions and alkali and alkaline earth cations pass through the resin (<http://www.icpms.com/pdf/seaFAST-seawater-analysis.pdf>). For our purposes, a 10 mL PFA sample loop was used that required an initial sample volume of 11-12 mL. The offline pre-concentration and elution of REEs on the seaFAST for 11-12 mL of seawater took ~ 15 min per sample and the separations were run automatically overnight.

Prior to pre-concentration on the seaFAST, we weighed 11-12 mL of each seawater sample ($\text{pH} \leq 2$) into 13 mL Teflon tubes and spiked it with a multi-element REE spike to obtain a value of $^{145}\text{Nd}/^{143}\text{Nd}$ of 6 (Table 2). The spike was diluted from a pre-mixed REE spike stock solution (prepared by Gilbert N. Hanson of SUNY Stony Brook and called DKM) by 1:24,130 (DKM3) to a concentration of 3.7 pmol/g for ^{145}Nd , and recalibrated by ICP-MS against the AMES Nd standard using reverse isotope dilution. Details on the spike solution (DKM3) including the isotope concentrations and the natural isotope abundances are reported in Table 2. The volume of spike that was added to a seawater sample was optimized for each sample aiming at a low error magnification factor while not compromising the counting statistics and thus analytical precision.

We allowed equilibration of the sample-spike mixture for at least 48 hours. The spiked samples were arranged in the seaFAST autosampler for automated pre-concentration. The seaFAST procedure was as follows: Prior to each sample pre-concentration, the buffer solution was passed through the clean-up column to reduce possible trace metal impurities in

the buffer, and used to precondition the pre-concentration column for 60 s at 0.2 mL/min. The sample was vacuum-loaded into a 10 mL PFA sample loop, then cleaned buffer (at 0.7 mL/min) and high purity water (at 2.5 mL/min) were added to ensure a pH of 6, before the mixture was passed through the pre-concentration column (at 0.5 mL/min). The column was then rinsed with 4.8 mL of the buffer solution-high purity water mix to wash out the seawater matrix (at 0.5 mL/min buffer, 2.5 mL/min water). The REEs were eluted with 200 μ L and 300 μ L of 1.5 N HNO₃ in reverse direction at a flow rate of 0.2 mL/min and 0.5 mL/min, respectively, and collected in pre-cleaned PFA micro vials.

Following each sample processing, the pre-concentration column was cleaned with 4.5 mL of the elution acid (1.5 N HNO₃) and conditioned with a buffer solution-high purity water mix in preparation for the next sample. During each session, at least three total procedural blanks of 2% HNO₃ were processed and subsequently spiked with a diluted multi-element REE spike (1:1,518,843, DKM2) for quantification. The samples were diluted to 1.2 mL with high purity water manually in preparation for analysis by ICP-MS.

BATS seawater from 15 m (11 and 22 mL) and 2000 m (11 mL) were processed as described above, except for sample volumes of 22 mL, which were loaded into a 10 mL PFA sample loop (11 mL were loaded twice). Each sample was then manually diluted with high purity water to ~0.7-0.9 mL.

In order to analyze all samples at similar final REE concentrations, we targeted a concentration range of 280-380 pmol/kg for Nd and adjusted the initial loaded sample volume or manually diluted the final sample volume accordingly.

The small differences in the seaFAST offline pre-concentration method of Lab 1 compared to those of Labs 2 and 3 (LDEO and CEOAS; see online supplementary data) are due to the different quantification methods applied by the labs (e.g., external standard calibration, isotope dilution) and the required final sample volume. Lab 2 eluted the REEs in three steps each of 100 μ L of 1.6 N HNO₃ and Lab 3 used a sample volume of ~20 mL (instead of 10 mL) that was loaded in two steps using a 10 mL PFA sample loop and REEs were eluted with 200 μ L of 1.5 N HNO₃. Other than Labs 1 and 2, Lab 3 (CEOAS) used five external calibration standards of increasing concentrations (instead of a multi-element spike) for quantification. These external calibration standards were adjusted to a pH of ~1.6 by adding ammonium hydroxide in order to increase column buffering and passed through the seaFAST column the same way as the samples.

2.2.2. REE determination by ID ICP-MS

Lab 1 (ICBM) used a Thermo Finnigan ELEMENT 2 ICP-MS for REE concentration measurements at the ICBM, University of Oldenburg. The instrument was coupled to an autosampler (CETAC ASX-100) and a desolvation introduction system (CETAC Aridus 2) that was used with a nitrogen-argon gas mixture to enhance sensitivity and to minimize oxide formation to a negligible level (e.g., Grenier et al., 2013; Rousseau et al., 2013). The ICP-MS was operated at low resolution in counting mode and the guard electrode was switched off. We optimized the instrument for sensitivity daily while aspirating a 100 ng/L tune solution of Ba, Ce, and Lu. Two mixed REE standard solutions (solution 1: Ba, La, Ce, Pr, Tb, Er, and Yb, and solution 2: Nd, Sm, Eu, Gd, and Dy) were measured to assess the formation of LREE oxides that interfere with HREEs, and of Ba oxides that interfere with Eu. We found negligible oxide interferences and monitored the long-term stability of the oxide formation with the above mentioned 100 ng/L tune solution. Typical count rates for 100 ng/L ¹⁴⁰Ce were 500 000. As analyzed samples rarely contain Ba due to the above described purification procedure, and given the low oxide formation rates for Ba and LREEs (always 0.01-0.03% for Ce and Ba), no oxide interference corrections of any element had to be applied. All

necessary masses between 137 and 177 were scanned in ESCAN (electro scan) mode that required a single magnet jump at mass 158 in order to scan the entire mass range. The sample time for every mass was 0.02 s, except for isotopes with lower signal intensities: ^{159}Tb , ^{165}Ho , ^{166}Er , ^{167}Er , ^{169}Tm , ^{175}Lu (0.04 s) and ^{147}Sm , ^{151}Eu , ^{153}Eu (0.06 s). The longer sampling time improved the precision significantly. The total measurement time of 2 min 39 s consisted of 3 runs of 4 passes and allowed for low sample volume and hence higher concentrated samples providing higher signal intensities thereby optimizing the precision. The instrument operating conditions are reported in Table 3.

We used a standard solution with seawater-like relative REE concentrations in 2% HNO_3 (REE Coral Sea standard, Zheng et al., 2015, provided by Gideon Henderson, University of Oxford) as an external standard. We analyzed the standard both unspiked and spiked at each session at similar signal intensities as the pre-concentrated samples, except for Ce (~5 times higher in the standard). The unspiked REE Coral Sea standard was analyzed after every third sample and used for sensitivity correction of the mono-isotopic elements as well as for monitoring and correction of instrumental mass bias. The results of the spiked REE Coral Sea standard were used to assess the overall analytical long-term precision (see results and discussion section).

The GEOTRACES intercalibration seawater samples from BATS at 15 m and 2000 m that were characterized previously with respect to their REE concentrations (van de Flierdt et al., 2012), were used as external standards and to check the accuracy of our method. Seawater samples from BATS were measured at similar signal intensities as the samples.

Details on the analyzed isotopes in our ID ICP-MS method that was modified from Jones (2010) and Pahnke et al. (2012) are presented in Table 4.

We measured a 2% nitric acid instrumental blank before each sample and standard. Raw count rates of each measured mass for samples and standards were first corrected for these instrumental blanks. The ID element concentrations of the samples were calculated by using ID equations as illustrated by equation (1) using Nd as an example:

$$[\text{Nd}]_{\text{smpl}} = \left(\frac{RI_{\text{sp}} - RI_{\text{mix}}}{RI_{\text{mix}} - RI_{\text{true}}} \right) \times [\text{Nd}]_{\text{sp}} \times \frac{m_{\text{sp}}}{m_{\text{smpl}}} \times \frac{M_{\text{Nd}}}{A_{\text{Nd}}} \quad (1)$$

Abbreviations sp and smpl stand for spike and sample, respectively.

RI_{sp} : isotope ratio of $^{143}\text{Nd}/^{145}\text{Nd}$ in the spike

RI_{mix} : isotope ratio of $^{143}\text{Nd}/^{145}\text{Nd}$ in the sample/spike mixture

RI_{true} : natural isotope ratio of $^{143}\text{Nd}/^{145}\text{Nd}$

$[\text{Nd}]_{\text{sp}}$: concentration of ^{145}Nd in the spike (mol/g)

m_{sp} and m_{smpl} : weighted masses of spike and sample (g)

M_{Nd} : natural atomic mass of Nd (g/mol)

A_{Nd} : natural relative abundance of ^{145}Nd

Cerium and ytterbium, both required for ID calculations (^{142}Ce and ^{174}Yb), have isobaric interferences from ^{142}Nd and ^{174}Hf , respectively. Before applying the ID equation (1) to Ce, ^{142}Ce was corrected for isobaric interference of ^{142}Nd in the sample and the spike:

$$^{142}\text{Ce} = (^{142}\text{Ce} + ^{142}\text{Nd})_{\text{M}} - \left(\frac{^{143}\text{Nd}_{\text{M-sp}}}{R2_{\text{true}}} + \frac{^{143}\text{Nd}_{\text{sp}}}{R2_{\text{sp}}} \right) \quad (2)$$

Abbreviation M stands for measured counts.

$(^{142}\text{Ce} + ^{142}\text{Nd})_{\text{M}}$: total measured counts on mass 142

$^{143}\text{Nd}_{\text{M-sp}}$: measured spike-subtracted counts on mass 143

$R2_{\text{true}}$: natural isotope ratio of $^{143}\text{Nd}/^{142}\text{Nd}$

$^{143}\text{Nd}_{\text{sp}}$: measured counts on ^{143}Nd in the spike

$R2_{\text{sp}}$: isotope ratio of $^{143}\text{Nd}/^{142}\text{Nd}$ in the spike (0.5968)

Spike-subtraction from measured counts on ^{143}Nd was done following equation (3):

$$^{143}\text{Nd}_{\text{M-sp}} = ^{143}\text{Nd}_{\text{M}} - \left(\frac{RI_{\text{true}} \times ^{145}\text{Nd}_{\text{M}} - ^{143}\text{Nd}_{\text{M}}}{\left(\frac{RI_{\text{true}}}{RI_{\text{sp}}} - 1 \right)} \right) \quad (3)$$

$^{143}\text{Nd}_{\text{M}}$: total measured counts on mass 143

$^{145}\text{Nd}_{\text{M}}$: total measured counts on mass 145

RI_{true} : natural isotope ratio of $^{143}\text{Nd}/^{145}\text{Nd}$

RI_{sp} : isotope ratio of $^{143}\text{Nd}/^{145}\text{Nd}$ in the spike

Measured counts on ^{143}Nd in the spike were calculated by subtracting the measured spike-subtracted counts on mass 143 from the total measured counts on mass 143.

No isobaric interference correction was necessary for ^{174}Yb , as ^{174}Hf (monitored by ^{177}Hf) was negligible in our samples.

Instrumental mass bias was determined on the unspiked REE Coral Sea standard and was typically $\leq 1\%$ per amu for REEs, except for Gd. Instrumental mass bias corrections for Gd used the exponential law on the measured $^{155}\text{Gd}/^{157}\text{Gd}$ ratio, assuming a natural ratio of $^{155}\text{Gd}/^{157}\text{Gd} = 0.9394$ before the application of the ID equation.

A reference isotope (^{147}Sm) was used as an internal standard to quantify the mono-isotopic elements (^{141}Pr , ^{159}Tb , ^{165}Ho , ^{169}Tm) based on the instrument's sensitivity response for these elements in the unspiked REE Coral Sea standard, defined as the number of counts per concentration in the standard. The concentration of the mono-isotopic elements was then calculated using the internal standard concentration of ^{147}Sm and multiplying with the ratio of the sensitivity of ^{147}Sm to that of the respective mono-isotopic element and vice versa for the measured sample counts.

Lanthanum and lutetium, both ID elements (^{138}La , ^{176}Lu), have isobaric interferences with ^{138}Ba and ^{138}Ce , and with ^{176}Yb and ^{176}Hf , respectively. Due to these interferences and the low abundance of ^{138}La (0.09%) and ^{176}Lu (2.59%), quantification used ^{139}La and ^{175}Lu that were spike-subtracted and treated as mono-isotopic elements.

2.3. Pre-concentration methods and mass spectrometry of labs participating in the intercomparison

Each lab used its own preferred method for pre-concentration of REEs from seawater and mass spectrometric analysis. These methods, including that of Lab 1 (ICBM) are summarized in Table 1. The methods of Labs 2-4 are described in the online supplementary data.

3. Results and discussion

3.1. Lab 1: Offline seaFAST pre-concentration of REEs and multi-element ID ICP-MS

3.1.1. Blanks and detection limit

Lab 1 measured and subtracted instrumental blank solutions of 2% nitric acid that accounted for $\leq 0.8\%$ of the measured sample and standard intensities for REEs, except for two standards with a blank signal of 1.1-1.2% for Nd and three standards with a blank signal of 1.1% for Tb (see Materials and procedures section). The average total procedural blank of 2% nitric acid (n=25) was $\leq 0.2\%$ of each REE concentration of the SAFe 3000 m analyses, except for Ce, which varied significantly and ranged from 1.6% up to 18% (Table 5).

The detection limit of our analytical method for REEs, based on three times the standard deviation of the total procedural blanks (n=25) following Zheng et al. (2015), ranged between

0.002 pmol/kg for Tm and 0.4 pmol/kg for Ce (Table 5), and was similar to those reported by Zheng et al. (2015).

3.1.2. Accuracy and precision

The accuracy of our method was checked with repeated processing and analysis of GEOTRACES intercalibration seawater from BATS 15 m (n=5) and 2000 m (n=5) and SAFe 3000 m (n=16, Nd only) and comparison to the intercalibration values, published by van de Flierdt et al. (2012) for BATS 15 m and 2000 m (n=12-26) and Pahnke et al. (2012) for SAFe 3000 m (n=2, Nd only). Our results for BATS 15 m and 2000 m together with the published intercalibration values are reported in Table 6. The precision of our REE concentration measurements for BATS 15 m was $\leq 8.8\%$ for LREEs and $\leq 3.9\%$ for HREEs, except for Ce (11.3%) and Gd (5.1%) (2σ RSD, n=5, Table 6, average precision excluding Ce: 3.5%). The precision of BATS 2000 m analyses was $\leq 4.6\%$ for LREEs and $\leq 3.7\%$ for HREEs, except for Ce (26%) and Gd (6.8%) (2σ RSD, n=5) (Table 6, average precision excluding Ce: 3.5%). The internal errors of BATS 15 m and 2000 m analyses were lower than the reported precisions for LREEs and HREEs, except for two samples (4.7% and 12.4% for Nd, 2σ RSD). Our mean REE concentrations from BATS (15 m, 2000 m) (n=5 for each depth) are well within the confidence interval (15% and 12%, respectively, 2σ RSD) of the published intercalibration values (van de Flierdt et al., 2012), with maximum relative deviations of 6.6% for all REEs (Table 6, Figs. 1a, b). Moreover, our results are close to the published data of Rousseau et al. (2013) deviating by $\leq 6.2\%$ for all REEs except for La (9.4%, BATS 15 m) and Tb (7.6%, BATS 2000 m).

The long-term precision of our method is demonstrated by multiple runs of the spiked REE Coral Sea standard (n=18) and replicates of SAFe 3000 m (n=16), respectively. The analytical long-term precision of the spiked REE Coral Sea standard that was measured at similar signal intensities as the pre-concentrated samples (except for Ce: ~5 times higher in standard), was $\leq 5.7\%$ for all REEs, except for Gd with 7.7% (2σ RSD, n=18, average precision: 4.4%). The internal errors (counting errors) of the spiked REE Coral Sea standard analyses were $\leq 7.0\%$ for all REEs, except for three samples (7.2-11%, 2σ RSD). The long-term precision of SAFe 3000 m measurements was $\leq 3.9\%$ for all REEs, except for Ce (39%) and Gd (6.2%) (2σ RSD, n=16, Table 7, average precision excluding Ce: 3.4%). The internal errors of SAFe 3000 m analyses were lower than or in the range of the reported long-term precision, except for some REEs in six samples (6.2-11%, 2σ RSD, Supplementary Table S1). Our measured Nd concentration of SAFe 3000 m (46.4 ± 1.1 pmol/kg, 2σ SD, a relative deviation of 4.5%) is in good agreement with published Nd concentrations from samples taken on the same cruise at the same station and depth (44.4 ± 1.0 pmol/kg, 2σ SD, and 44.4 ± 2.5 pmol/kg, 2σ SE) analyzed so far only for Nd concentrations by two other labs (Pahnke et al., 2012). Our long-term precision of $\leq 3.9\%$ (2σ RSD, n=16) is similar to that of Zheng et al. (2015) (~6%, 2σ RSD, n=37) for an in-house seawater standard (SWC-2). However, we used a sample volume of 11-12 mL, while Zheng et al. (2015) used 100 mL of seawater, indicating a major advancement in sample volume required for the analysis of REEs in seawater.

Our precision of Ce obtained from SAFe 3000 m (39% 2σ RSD, 4.5 pmol/kg Ce) is much lower than the one we obtained using the higher concentrated seawater standards BATS 15 m (11.3% 2σ RSD, 11.9 pmol/kg Ce) and BATS 2000 m (26% 2σ RSD, 5.0 pmol/kg Ce). The internal precision of Ce measurements of SAFe 3000 m (typically $\leq 5.3\%$ 2σ RSD) suggests that Ce can be measured with high precision even in low concentration samples. Therefore, given the highly variable blank levels for Ce and the strongly depleted Ce concentration in the deep Pacific relative to average continental material, we suggest that variable Ce

contamination during sample processing is likely contributing to the low precision of Ce in this study. We can exclude acid impurities, insufficiently cleaned vials, and preferential retention of Ce on the seaFAST column, as all these possibilities were tested and found to have negligible blank concentrations.

3.2. Blanks and precision of participating labs

All the labs (except Lab 3, CEOAS) corrected the sample raw counts for instrumental blanks of 1-3% nitric acid that were usually <1% of the signal intensities of the sample. Total procedural blanks of 1% or 2% nitric acid represented $\leq 0.9\%$ (n=5, Lab 2, LDEO) or $\leq 1.1\%$ (n=2, Lab 3) or $\leq 0.06\%$ (n=12, Lab 4, LEGOS) of the measured sample intensities for REEs, except for Ce. Total procedural blanks for Ce were higher and/or more variable than for other REEs (Lab 2: $\leq 1.7\%$, Lab 3: $\leq 1.1\%$ and 11.6%, Lab 4: 3%). Labs 2 and 4 subtracted the total procedural blanks for REEs.

Long-term precision data reported for REE concentrations in Table 7 are based on replicates of BATS 2000 m (Lab 2, n=14), an in-house deep seawater standard (Lab 3, NBP195 1097 m, n=12), and a combination of standard solutions, replicates of SAFe 3000 m, and other in-house seawater samples (Lab 4, n=30). For Lab 2, the seaFAST system has recently come online and these are the first published analyses using it.

For SAFe 3000 m, precision of Ce (Lab 2: 9.9%, Lab 3: 86%, and Lab 4: 5.9%) was worse than average precision of the other REEs (Lab 2: 2.5%, Lab 3: 6.3%, and Lab 4: 2.0%, 2σ RSD, n=5-6, Table 7).

Similar to the results from our new method discussed above, all participating labs measured higher and/or more variable blanks for Ce, and observed much lower precision for the low Ce concentrations of SAFe 3000 m. This supports the suggestion that variable Ce contamination during sample processing of low concentrated samples is likely contributing to the precision of the Ce analyses, as the effect on Ce is significant, but negligible for other REEs. As Lab 3 reported no Ce oxide formation rates for this study (only typical oxide formation rates, without correcting for it, see online supplementary data), the low precision of Ce (86%) might be also related to this issue. Further details on the analytical methods and results of each individual lab are provided in the online supplementary data.

3.3. Dissolved REE concentrations at SAFe 3000 m (North Pacific): intercomparison

Detailed results of REE concentrations of SAFe 3000 m from this study (Lab 1, n=16) and the participating labs (Labs 2-4, n=5-6) are presented in the Supplementary Tables S1 and S2, respectively. The average REE concentrations and precision reported by each lab, and the average values for SAFe 3000 m from the 4 labs (the “REE intercomparison values”) are presented in Table 7. Figures 2a and 2b show the average REE patterns of SAFe 3000 m from each lab normalized to hypothetical seawater (van de Flierdt et al., 2012) and Post-Archean Australian Shale (PAAS) (Taylor and McLennan, 1985), respectively. The plotted errors are the long-term precision of each lab as reported in Table 7. The long-term and internal precisions are typically 2-3 times higher for labs using ID ICP-MS methods (Labs 1, 2, and 4) compared to the one using an external standard calibration method (Lab 3) (Figs. 2 c, d). The REE concentrations all agree within 7%, except for Ce with 71%, Gd with 14% and Lu with 12% (2σ RSD, Table 7). This overall agreement between the 4 labs for SAFe 3000 m is comparable to the agreement reported for BATS 15 m (15%, for all REEs, except for Ce with 23%) and BATS 2000 m (12% for all REEs, except for Ce with 44%) by six different labs for the international GEOTRACES intercalibration study (van de Flierdt et al., 2012). In both studies, Ce presents the biggest challenge. Given the lower Ce concentration at SAFe 3000 m

(3.8 pmol/kg Ce) compared to BATS 15 m and 2000 m (12 pmol/kg and 5.1 pmol/kg Ce, respectively), it is not surprising that the precision of the Ce intercomparison value from SAFe 3000 m is lowest. The large spread of measured Ce concentrations is probably partly due to the higher and more variable blanks for Ce compared to the other REEs (≤ 1.1 -18% this study, 4-10% van de Flierdt et al., 2012) in combination with low Ce concentrations. In our study, the slightly lower precisions of Gd (14%) and Lu (12%) compared to the other REE results mainly from the lower concentrations of these elements measured by Lab 2. The precision of the shale-normalized REE patterns of the labs is better than that of the absolute concentrations for most REEs, which is shown by normalizing the REE results to the same Nd concentration (46.4 pmol/kg Nd of Lab 1, Table 7) and comparing the deviations (Figs. 3 a-d). This may result from slight errors in the spike concentrations (e.g., due to evaporation). Published data for SAFe 3000 m are so far only available from two other labs for Nd (44.4 ± 1.0 pmol/kg, 2σ SD, and 44.4 ± 2.5 pmol/kg, 2σ SE, Pahnke et al., 2012). These results agree well with the Nd intercomparison value of this study (45.9 ± 2.9 pmol/kg, 2σ SD, relative deviation of 3.4%).

Compared to REE analyses using the seaFAST method in online mode with reported average precisions of 8.4%, 12%, and 5% (2σ RSD) for BATS 15 m, 2000 m, and Station 113 1000 m, respectively (Hathorne et al., 2015), our offline method achieved slightly higher average precisions for REEs (3.5% for BATS 15 m and 2000 m, respectively, 3.4% for SAFe 3000 m, excluding Ce, 2σ RSD). Similarly, Labs 2 and 3 that also used the seaFAST in offline mode, reported average precisions of 4.1% and 7.4% (2σ RSD) for REEs based on BATS 2000 m and in-house seawater NBP95 1097 m, respectively. A possible reason for the slightly lower average precisions reported by Lab 3 and Hathorne et al. (2015) compared to those of Labs 1 and 2 is the use of different quantification methods using external standard calibration and ID ICP-MS, respectively.

The REE intercomparison concentrations of station SAFe (30°N, 140°W) at 3000 m reported for this study agree within the uncertainties (2σ SD) with published REE concentrations of deep water at nearby stations VERTEX II (18°N, 108°W, 3000 m, de Baar et al., 1985) and TPS24-76-1 (24°15.0'N, 159°15.6'W, 4621 m, Piepgras and Jacobsen, 1992) and show similar PAAS-normalized REE patterns (Figs. 4a, b). The consistency of REE data between stations SAFe and TPS24-76-1 demonstrates the ability of our method to provide reliable marine REE concentrations and further validates the results from the intercomparison.

4. Conclusions

This study presents a rapid and robust pre-concentration and purification method for REEs from small volumes of seawater (11-12 mL) by applying the seaFAST-pico system (Elemental Scientific Inc.) in offline mode for the first time. We provide an accurate and precise multi-element ID ICP-MS method for routine REE analyses. The accuracy of our method was assessed by repeated processing and analysis of GEOTRACES intercalibration seawater from BATS at 15 m and 2000 m. Our average REE concentrations are within the 2σ RSD confidence interval of published intercalibration values for these samples (15% and 12%, van de Flierdt et al., 2012), deviating by only 6.6% from those values.

In addition, an international intercomparison using seawater from SAFe at 3000 m (North Pacific) with three other labs applying different sample volumes and methods demonstrates the applicability of our method for high-precision measurements of dissolved REE concentrations. Overall, the REE concentrations of SAFe 3000 m are in very good agreement between all labs, reproducing (2σ RSD) within 7% for all REEs (4.1-0.1 pmol/kg, 2σ SD), except for Ce (71%, 2.7 pmol/kg, 2σ SD), Gd (14%, 1.7 pmol/kg, 2σ SD), and Lu (12%, 0.3 pmol/kg, 2σ SD). The lower precision of Ce compared to the other REEs is most likely due to

more variable and higher blank contributions to the low Ce concentration in the deep Pacific sample. The described method can be easily adopted by other labs as the seaFAST system is commercially available, and enables the extensive use of REEs in high-resolution sampling and measurement campaigns such as the GEOTRACES Program. In addition, our international intercomparison exercise provides the first intercomparison values for dissolved REE concentrations in the North Pacific from the GEOTRACES intercalibration station SAFe from 3000 m water depth, and establishes this station and depth as a seawater reference for REE concentrations in the Pacific as SAFe will remain a baseline, and hence intercalibration station, for cruises in the North Pacific. Supplementary data of this article can be found online at <http://xxxxx>.

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Figure captions

Fig. 1: Average dissolved REE concentrations of seawater at BATS 15 m and 2000 m measured in this study in comparison with published GEOTRACES mean REE intercalibration values (van de Flierdt et al., 2012) and published mean REE values from Rousseau et al. (2013). (a) REE concentrations normalized to hypothetical seawater after van de Flierdt et al. (2012). (b) REE concentrations normalized to PAAS (Taylor and McLennan, 1985). Error bars denote $\pm 2\sigma$ SD. Rousseau et al. (2013) reported no error bars for BATS 15 m and for La and Ce at BATS 2000 m.

Fig. 2: Average dissolved REE concentrations of SAFe 3000 m along with long-term and internal precisions (2σ RSD%) reported for this study (Labs 1-4). (a) REE concentrations normalized to hypothetical seawater (La: 4.1 pmol/kg, Ce: 5.0 pmol/kg, Pr: 0.78 pmol/kg, Nd: 3.54 pmol/kg, Sm: 0.67 pmol/kg, Eu: 0.20 pmol/kg, Gd: 1.08 pmol/kg, Tb: 0.19 pmol/kg, Dy: 1.60 pmol/kg, Ho: 0.42 pmol/kg, Er: 1.43 pmol/kg, Tm: 0.18 pmol/kg, Yb: 1.04 pmol/kg, Lu: 0.17 pmol/kg) after van de Flierdt et al. (2012). (b) REE concentrations normalized to PAAS (Taylor and McLennan, 1985). (a-b) Error bars denote $\pm 2\sigma$ SD calculated from the long-term precision of each lab as reported in Table 7. (c) Long-term precision (precision of Ce is omitted for Lab 1) and (d) internal precision (precision of Ce is omitted for Labs 1 and 3) of each lab as reported in Table 7.

Fig. 3: (a) REE concentrations normalized to PAAS (Taylor and McLennan, 1985). (b) PAAS-normalized REE concentrations normalized to the same Nd concentration (46.4 pmol/kg Nd of Lab 1, Table 7). (c) Absolute (ABS) deviations (%) from average values (omitting Ce). (d) Absolute deviations (%) from average values normalized to same Nd concentration (omitting Ce).

Fig. 4: (a) Map showing location of deep water sampling stations SAFe 3000 m (this study), VERTEX II 3000 m (de Baar et al., 1985) and TPS24-76-1 4621 m (Piepgras and Jacobsen, 1992). (b) REE concentrations of SAFe 3000 m (intercomparison values, this study) compared to published REE values of nearby stations VERTEX II 3000 m and TPS24-76-1 4621 m (de Baar et al., 1985; Piepgras and Jacobsen, 1992), normalized to PAAS (Taylor and McLennan, 1985). Error bars denote $\pm 2\sigma$ SD. Map produced with Ocean Data View (Schlitzer, 2014).

Tables

Table 1: Summary of methodologies used in this study (Lab 1) and by the three participating labs

Lab	Sample Volume	Spike	Pre-concentration Method	Quantification Method	Instrument
1	11-12 mL	multi-element REE spike	offline seaFAST-pico system	isotope dilution	Thermo Finnigan ELEMENT 2 ICP-MS
2	10 mL	multi-element REE spike	offline seaFAST-pico system	isotope dilution	VG PQ ExCell ICP-MS
3	20 mL		offline seaFAST-pico system	external standards	Thermo Xseries-II ICP-MS
4	500 mL	¹⁵⁰ Nd, ¹⁷² Yb, Indium, Rhenium	Fe co-precipitation with 0.5 g Fe; 2 mL of Biorad AG1X8 anion exchange resin, 100-200 µm mesh-size	isotope dilution coupled with internal and external standards	Agilent 7500 ICP-MS

Lab 1: Institute for Chemistry and Biology of the Marine Environment (ICBM), University of Oldenburg

Lab 2: Lamont-Doherty Earth Observatory (LDEO), Columbia University

Lab 3: College of Earth, Ocean and Atmospheric Sciences (CEOAS), Oregon State University

Lab 4: Laboratoire d'Etudes en Géophysique et Océanographie Spatiale (LEGOS), University of Toulouse

Table 2: Isotope concentrations and natural isotope abundances of the diluted spike solution (DKM3) together with isotope ratios of spike-sample mix and error magnification factor (EMF) used for SAFe 3000 m in this study (Lab 1)

Element	Isotope 1	Isotope 2	[Isotope 1] _{sp} (pmol/g)	[Isotope 2] _{sp} (pmol/g)	[Isotope 1] _{nat}	[Isotope 2] _{nat}	Ideal ratio*	EMF of ideal ratio	Range of measured ratio	EMF of measured ratio
La	139	138	0.322	0.023	0.9991	0.0009				
Ce	142	140	6.016	0.526	0.1107	0.8848	1.2	1.23	5.3-7.3	1.89-2.78
Nd	145	143	3.700	0.031	0.0830	0.1218	9.0	1.16	6.0-7.6	1.16-1.18
Sm	149	147	1.992	0.008	0.1380	0.1500	15.6	1.13	12.9-16.4	1.13
Eu	153	151	0.575	0.033	0.5223	0.4777	4.4	1.67	4.3-5.2	1.67-1.69
Gd	155	157	1.125	0.015	0.1473	0.1568	8.3	1.26	5.2-6.5	1.27-1.30
Dy	161	163	1.179	0.019	0.1888	0.2497	6.9	1.25	3.3-4.0	1.30-1.35
Er	167	166	0.570	0.018	0.2294	0.3341	4.6	1.35	1.8-2.1	1.56-1.68
Yb	171	174	0.628	0.006	0.1431	0.3184	6.6	1.15	1.7-2.0	1.31-1.38
Lu	176	175	0.013	0.005	0.0259	0.9741				

[Isotope 1]_{sp} and [Isotope 2]_{sp}: concentrations of isotopes 1 and 2 in the diluted spike

[Isotope 1]_{nat} and [Isotope 2]_{nat}: natural fractional abundances of isotopes 1 and 2

Note that La and Lu were treated as mono-isotopic elements (see text)

*ideal isotope ratio of spike-sample mix: $\sqrt{\frac{[\text{Isotope 1}]_{\text{sp}} \times [\text{Isotope 1}]_{\text{nat}}}{[\text{Isotope 2}]_{\text{sp}} \times [\text{Isotope 2}]_{\text{nat}}}}$

Table 3: Instrument operating conditions for the Thermo Finnigan ELEMENT 2 ICP-MS at the ICBM

Instrument	Operating Conditions
equipment	
nebulizer	PFA micro-flow pumped at 0.1 mL/ min
CETAC Aridus 2	sweep gas: 2-6 L/min, nitrogen gas: 3-6 mL/min
spray chamber	heated PFA spray chamber
sample and skimmer cones	Nickel
parameters	
nebulizer/auxiliary/cooling gas flows (L min ⁻¹)	~0.80 ^a /1.40/13
RF power (W)	1250
detection mode	counting
sample time (s)	0.02s, except: ¹⁴⁷ Sm, ¹⁵¹ Eu, ¹⁵³ Eu = 0.06s, ¹⁵⁹ Tb, ¹⁶⁵ Ho, ¹⁶⁶ Er, ¹⁶⁷ Er, ¹⁶⁹ Tm, ¹⁷⁵ Lu = 0.04s
mass window	40
samples/peak	40
resolution	low

^aoptimized for each measurement session

Table 4: Isotopes analyzed at the ICBM

Element	Isotope 1	Isotope 2	Comments
Ba	137		to monitor Ba-oxide formation (interference with ^{153}Eu)
La	139		ID element treated as mono-isotopic element
Ce	140	142	ID element; isobaric interference correction of ^{142}Nd on ^{142}Ce
Pr	141		mono-isotopic element
Nd	143	145	ID element
Sm	147	149	ID element
Eu	151	153	ID element
Gd	155	157	for instrumental mass bias correction of $^{155}\text{Gd}/^{157}\text{Gd}$
Gd	158		magnet jump
Tb	159		mono-isotopic element
Dy	161	163	ID element
Ho	165		mono-isotopic element
Er	166	167	ID element
Tm	169		mono-isotopic element
Yb	171	174	ID element
Lu	175		ID element treated as mono-isotopic element
Hf	177		to monitor any isobaric interference of ^{174}Hf on ^{174}Yb

Table 5: Average total procedural blank (n=25) and detection limit for all REEs (Lab 1)

Element	Average Blank (pmol/kg)	Detection Limit (pmol/kg) ^a
La	0.1	0.2
Ce ^b	0.2	0.4
Pr	0.02	0.04
Nd	0.06	0.1
Sm	0.01	0.03
Eu	0.002	0.008
Gd	0.01	0.03
Tb	0.001	0.003
Dy	0.01	0.02
Ho	0.001	0.01
Er	0.002	0.02
Tm	0.0004	0.002
Yb	0.002	0.01
Lu	0.0002	0.01

^athree times the standard deviation of the total procedural blanks

^bmax blank: 0.6 pmol/kg, min blank: 0.1 pmol/kg

Table 6: Dissolved REE concentrations (pmol/kg) of this study (Lab 1) compared to GEOTRACES intercalibration samples at BATS 15 m and 2000 m

	sample ID	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
BATS, 15 m															
average of this study (n=5)	KN193-6-Nd-601	14.1	11.9	3.30	13.98	3.20	0.86	4.84	0.81	5.91	1.45	4.83	0.69	4.24	0.69
2σ SD (pmol/kg)		1.2	1.3	0.25	0.44	0.07	0.02	0.25	0.01	0.23	0.04	0.11	0.02	0.11	0.01
2σ RSD%		8.8	11.3	7.6	3.1	2.1	2.3	5.1	1.1	3.9	2.7	2.3	2.4	2.5	1.2
GEOTRACES intercalibration value (van de Flierdt et al., 2012)		14.7	12.0	3.12	14.1	3.21	0.89	4.83	0.79	5.90	1.49	4.80	0.70	4.16	0.67
2σ SD (pmol/kg)		2.2	2.7	0.37	1.2	0.36	0.10	0.55	0.08	0.53	0.13	0.43	0.06	0.51	0.09
2σ RSD%		15.0	23	11.8	8.8	11.2	11.8	11.4	10.7	8.9	9.0	8.9	9.0	12.3	13.8
BATS, 2000 m															
average of this study (n=5)	KN193-6-Nd-401	22.9	5.0	4.15	17.26	3.38	0.85	4.71	0.79	5.80	1.46	5.00	0.74	4.83	0.84
2σ SD (pmol/kg)		1.0	1.3	0.04	0.80	0.10	0.03	0.32	0.03	0.19	0.05	0.17	0.02	0.09	0.02
2σ RSD%		4.3	26	0.9	4.6	2.9	4.1	6.8	3.7	3.3	3.6	3.3	2.7	1.8	2.8
GEOTRACES intercalibration value (van de Flierdt et al., 2012)		23.6	5.1	4.03	17.3	3.45	0.91	4.84	0.79	5.80	1.52	5.04	0.75	4.76	0.81
2σ SD (pmol/kg)		2.8	2.3	0.36	1.2	0.34	0.10	0.53	0.07	0.38	0.09	0.25	0.05	0.25	0.04
2σ RSD%		11.8	44	8.9	7.0	9.8	11.2	10.9	9.5	6.5	5.9	5.0	6.4	5.3	4.6

Table 7: Intercomparison of dissolved REE concentrations (pmol/kg) of SAFe 3000 m

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
SAFe, 3000 m														
Lab 1 (ICBM)														
KNR 195-8-Nd 2191														
average (n=16)	64.2	4.5	10.83	46.4	9.12	2.41	13.40	2.02	14.91	3.74	12.76	1.97	13.80	2.53
2 σ SD (pmol/kg)	2.5	1.7	0.39	1.1	0.21	0.06	0.83	0.06	0.53	0.15	0.41	0.07	0.39	0.10
long-term 2 σ RSD% (n=16) ^a	3.9	39	3.6	2.4	2.3	2.4	6.2	2.8	3.6	3.9	3.2	3.5	2.9	3.8
Lab 2 (LDEO)														
KN 195-8-Th 2210														
average (n=5)	63.2	2.35	10.07	43.9	8.72	2.28	11.49	1.90	14.29	3.69	12.51	1.87	13.37	2.25
2 σ SD (pmol/kg)	1.8	0.23	0.14	0.68	0.20	0.10	0.61	0.04	0.48	0.05	0.39	0.03	0.27	0.02
2 σ RSD%	2.9	9.9	1.4	1.5	2.3	4.3	5.3	1.9	3.4	1.4	3.1	1.8	2.0	1.0
long-term 2 σ RSD% (n=14) ^b	5.1	3.4	1.7	2.8	4.0	5.5	5.9	4.7	4.4	2.3	4.8	3.3	4.6	4.3
Lab 3 (CEOAS)														
KNR 195-8-Nd 2191														
average (n=6)	67.7	5.4	10.16	46.0	8.97	2.36	12.50	1.94	14.70	3.79	12.70	1.95	13.20	2.52
2 σ SD (pmol/kg)	4.1	4.6	0.74	3.1	0.56	0.16	0.82	0.10	0.80	0.29	0.71	0.14	0.72	0.15
2 σ RSD%	6.0	86	7.3	6.8	6.3	6.9	6.6	5.2	5.5	7.7	5.6	7.3	5.4	5.8
long-term 2 σ RSD% (n=12) ^c	6.8	6.7	6.7	6.2	6.6	8.4	7.9	4.9	8.2	8.3	7.5	8.8	8.6	7.6
Lab 4 (LEGOS)														
KNR195-8-REE-2183														
average (n=6)	66.3	3.06	10.25	47.30	9.08	2.40	13.25	1.96	14.71	3.75	12.87	1.92	13.38	2.34
2 σ SD (pmol/kg)	1.6	0.18	0.23	0.68	0.21	0.06	0.22	0.04	0.26	0.06	0.30	0.02	0.31	0.06
2 σ RSD%	2.4	5.9	2.2	1.4	2.3	2.6	1.7	2.0	1.7	1.6	2.3	1.2	2.3	2.5
long-term 2 σ RSD% (n=30) ^d	3.0	5.0	3.5	2.0	3.5	4.0	3.5	3.0	2.0	3.0	3.0	6.0	2.5	3.0
Intercomparison value (n=4)	65.3	3.8	10.3	45.9	9.0	2.4	12.7	2.0	14.7	3.7	12.7	1.9	13.4	2.4
2σ SD (pmol/kg)	4.1	2.7	0.7	2.9	0.4	0.1	1.7	0.1	0.5	0.1	0.3	0.1	0.5	0.3
2σ RSD%	6.2	71	6.7	6.3	4.1	5.1	14	5.2	3.6	2.1	2.4	4.7	3.8	12

^aprecision based on replicates of SAFe 3000 m.^bprecision based on replicates of BATS 2000 m.^cprecision based on in-house deep seawater sample NBP95 (1097 m, Bransfield Strait).^dprecision based on multiple runs of standard solutions, replicates of SAFe 3000 m, and other in-house seawater samples.

Figure 1 **b**

Figure 2

Figure 3

a Figure 4

b