



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



Melanie K. Behrens<sup>a,\*</sup>, Jesse Muratli<sup>b</sup>, Catherine Pradoux<sup>c</sup>, Yingzhe Wu<sup>d</sup>, Philipp Böning<sup>a</sup>, Hans-Jürgen Brumsack<sup>e</sup>, Steven L. Goldstein<sup>d</sup>, Brian Haley<sup>b</sup>, Catherine Jeandel<sup>c</sup>, Ronja Paffrath<sup>a</sup>, Leopoldo D. Pena<sup>f</sup>, Bernhard Schnetger<sup>e</sup>, Katharina Pahnke<sup>a</sup>

<sup>a</sup> Max Planck Research Group for Marine Isotope Geochemistry, Institute for Chemistry and Biology of the Marine Environment (ICBM), University of Oldenburg, Carl-von-Ossietzky-Str. 9-11, 26129 Oldenburg, Germany

<sup>b</sup> College of Earth, Ocean and Atmospheric Sciences, Oregon State University, 104 CEOAS Administration Building, Corvallis, OR, USA

<sup>c</sup> Laboratoire d'Etudes en Géophysique et Océanographie Spatiale (LEGOS), Université de Toulouse (CNRS/CNES/UPS/IRD), Observatoire Midi-Pyrénées, 14 Avenue Edouard Belin, 31400 Toulouse, France

<sup>d</sup> Lamont-Doherty Earth Observatory and Department of Earth and Environmental Sciences, Columbia University, 61 Rt. 9W, Palisades, NY 10964, USA

<sup>e</sup> Institute for Chemistry and Biology of the Marine Environment (ICBM), University of Oldenburg, Carl-von-Ossietzky-Str. 9-11, 26129 Oldenburg, Germany

<sup>f</sup> Department of Earth and Ocean Dynamics, University of Barcelona, Martí Franquès s/n, 08028 Barcelona, Spain

### ARTICLE INFO

#### Article history:

Received 20 April 2016

Received in revised form 5 August 2016

Accepted 24 August 2016

Available online 05 September 2016

#### Keywords:

Rare earth elements in seawater

Isotope dilution mass spectrometry

GEOTRACES intercalibration station SAFE

Intercomparison

### 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,  $2\sigma$  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  $\leq 3.9\%$   $2\sigma$  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% ( $2\sigma$  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 Fliedert 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 ( $2\sigma$  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.

© 2016 Elsevier B.V. All rights reserved.

### 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

\* Corresponding author.

E-mail addresses: [mbehrens@mpi-bremen.de](mailto:mbehrens@mpi-bremen.de) (M.K. Behrens), [jmuratli@coas.oregonstate.edu](mailto:jmuratli@coas.oregonstate.edu) (J. Muratli), [catherine.pradoux@legos.obs-mip.fr](mailto:catherine.pradoux@legos.obs-mip.fr) (C. Pradoux), [yingzhe@ldeo.columbia.edu](mailto:yingzhe@ldeo.columbia.edu) (Y. Wu), [p.boening@icbm.de](mailto:p.boening@icbm.de) (P. Böning), [brumsack@icbm.de](mailto:brumsack@icbm.de) (H.-J. Brumsack), [steveg@ldeo.columbia.edu](mailto:steveg@ldeo.columbia.edu) (S.L. Goldstein), [bhaley@coas.oregonstate.edu](mailto:bhaley@coas.oregonstate.edu) (B. Haley), [catherine.jeandel@legos.obs-mip.fr](mailto:catherine.jeandel@legos.obs-mip.fr) (C. Jeandel), [rpaffrat@mpi-bremen.de](mailto:rpaffrat@mpi-bremen.de) (R. Paffrath), [lpena@ub.edu](mailto:lpena@ub.edu) (L.D. Pena), [b.schnetger@icbm.de](mailto:b.schnetger@icbm.de) (B. Schnetger), [kpahnke@mpi-bremen.de](mailto:kpahnke@mpi-bremen.de) (K. Pahnke).

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 $\sigma$  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 $\sigma$  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 Fliedert 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 Fliedert et al., 2012). Seawater samples were filtered through 0.2  $\mu$ m pore size Osmonics (Memtrex) cartridge filters, transferred into large tanks through Teflon tubing, acidified to 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 Fliedert 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 M $\Omega$  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  $\pm$  0.2) was adjusted by adding small amounts of either glacial acetic acid or ammonium hydroxide. A1.5 N HNO<sub>3</sub> was used as eluting acid, and a 2% HNO<sub>3</sub> 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

Download English Version:

<https://daneshyari.com/en/article/7699078>

Download Persian Version:

<https://daneshyari.com/article/7699078>

[Daneshyari.com](https://daneshyari.com)