Neodymium isotope analyses after combined extraction of actinide and lanthanide elements from seawater and deep-sea coral aragonite

Torben Struve1,2,3, Tina van de Flierdt1, Laura F. Robinson4,5, Louisa I. Bradtmiller5,6, Sophia K. Hines7, Jess F. Adkins7, Myriam Lambelet1, Kirsty C. Crocket6, Katharina Kreissig1, Barry Coles1, and Maureen E. Auro5

1Department of Earth Science and Engineering, Imperial College London, London, UK, 2The Grantham Institute for Climate Change, Imperial College London, London, UK, 3Now at Max Planck Research Group for Marine Isotope Geochemistry, Institute for Chemistry and Biology of the Marine Environment, University of Oldenburg, Oldenburg, Germany, 4School of Earth Sciences, University of Bristol, Bristol, UK, 5Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA, 6Department of Environmental Studies, Macalester College, St. Paul, Minnesota, USA, 7Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, USA, 8SAMS, Scottish Marine Institute, Oban, Argyll, UK

Abstract Isotopes of the actinide elements protactinium (Pa), thorium (Th), and uranium (U), and the lanthanide element neodymium (Nd) are often used as complementary tracers of modern and past oceanic processes. The extraction of such elements from low abundance matrices, such as seawater and carbonate, is however labor-intensive and requires significant amounts of sample material. We here present a combined method for the extraction of Pa, Th, and Nd from 5 to 10 L seawater samples, and of U, Th, and Nd from <1 g carbonate samples. Neodymium is collected in the respective wash fractions of Pa-Th and U-Th anion exchange chromatographies. Regardless of the original sample matrix, Nd is extracted during a two-stage ion chromatography, followed by thermal ionization mass spectrometry (TIMS) analysis as NdO\(^+\). Using this combined procedure, we obtained results for Nd isotopic compositions on two GEOTRACES consensus samples from Bermuda Atlantic Time Series (BATS), which are within error identical to results for separately sampled and processed dedicated Nd samples (\(\epsilon_{Nd} = -9.20 \pm 0.21\) and \(-13.11 \pm 0.21\) for 15 and 2000 m water depths, respectively; intercalibration results from 14 laboratories: \(\epsilon_{Nd} = -9.19 \pm 0.57\) and \(-13.14 \pm 0.57\)). Furthermore, Nd isotope results for an in-house coral reference material are identical within analytical uncertainty for dedicated Nd chemistry and after collection of Nd from U-Th anion exchange chromatography. Our procedure does not require major adaptations to independently used ion exchange chromatographies for U-Pa-Th and Nd, and can hence be readily implemented for a wide range of applications.

1. Introduction

The isotopes of the radionuclides protactinium (Pa), thorium (Th), uranium (U), and of the rare earth element (REE) neodymium (Nd) are invaluable tools for studying modern ocean biogeochemistry and past ocean conditions [e.g., Goldstein and Hemming, 2003; Henderson and Anderson, 2003]. Even though our understanding of their modern biogeochemical cycles is still relatively poor, \(^{230}\)Th, \(^{232}\)Th, \(^{231}\)Pa, and Nd isotopes (\(^{143}\)Nd/\(^{144}\)Nd ratio, expressed as \(\epsilon_{Nd} = ((^{143}\text{Nd})/^{144}\text{Nd}_{\text{sample}})/(^{143}\text{Nd}_{\text{CHUR}})/^{144}\text{Nd}_{\text{CHUR}} - 1) \times 10,000; \text{CHUR: chondritic uniform reservoir}) [Jacobsen and Wasserburg, 1980] are frequently used as proxies to reconstruct past ocean chemistry and dynamics [e.g., van de Flierdt et al., 2012; Anderson et al., 2012]. This situation is currently being rectified in the context of the international GEOTRACES program [SCOR Working Group, 2007] where \(^{230}\)Th, \(^{231}\)Pa, and Nd isotopes are “key parameters,” which have to be measured on all planned and completed GEOTRACES section cruises. However, accurate and precise analysis of these nuclides in seawater requires relatively large sample volumes (5–10 L) [van de Flierdt et al., 2012; Anderson et al., 2012]. Although recent analytical advances allow some laboratories to target sample volumes of less than 5 L, shipping large volumes of water to home laboratories is nevertheless an expensive endeavor. In order to reduce shipping costs and sample processing time, a combined extraction method for \(^{231}\)Pa, \(^{230}\)Th, and Nd isotopes, which are typically analyzed by different groups, would be desirable [e.g., Jeandel et al., 2011].
Similarly, in paleoarchives such as deep-sea corals, sample material could be saved and time-consuming sample preparation could be reduced by simultaneous separation of U, Th, and Nd. The aragonite skeleton of corals allows for accurate age control by U-series dating [e.g., Cheng et al., 2000], and Nd isotopes have been shown to present a promising tracer to reconstruct past water mass properties [e.g., van de Flierdt et al., 2006, 2010; Copard et al., 2010]. Deep-sea corals are increasingly targeted as a paleoceanographic archive, as they are found in areas where other traditional archives (e.g., foraminiferal carbonate) tend to be scarce, such as the Southern Ocean, or in water depths which are undersampled by sediment cores (e.g., intermediate waters) [see Robinson et al., 2014 for a recent summary]. Moreover, such combined extraction approaches could ensure that the data obtained are from exactly the same sample thus facilitating optimal comparison between different geochemical parameters.

Here, we demonstrate accurate Nd isotope results obtained from a combined extraction scheme of Pa, Th, and Nd from seawater and U, Th, and Nd from coralline aragonite. The method is easy to adapt, as it merely requires collecting elution fractions from anion exchange columns set up for separating U-Th-Pa [e.g., Auro et al., 2012; Edwards et al., 1987], which normally would go to waste, and subsequent processing through standard ion exchange chromatography for Nd isotope analyses [e.g., van de Flierdt et al., 2006, 2012]. Our Nd isotope intercalibration results for the combined chemistries are in excellent agreement with results from seawater and coral samples processed for Nd only.

2. Methodology

2.1. Seawater Sample Preparation and Anion Exchange Chemistry: The Neodymium Fraction During Protactinium-Thorium Separation

A refined methodology to extract protactinium and thorium from large volume seawater samples was recently published by Auro et al. [2012]. We here briefly summarize the key features of the method (Figure 1). Acidified seawater samples of 10 L volume were spiked with 239Th and 233Pa and left to equilibrate. In order to remove the trace metals of interest from the sample matrix, 100 mg of purified Fe were added per sample as FeCl₃. Purification of Fe was achieved by repeated isopropyl ether extraction, and the rather high amount of Fe was chosen to quantitatively precipitate Pa [Auro et al., 2012]. The trace metals were isolated from solution by adjusting the pH to between 7.5 and 8.0 through addition of ammonium hydroxide to precipitate Fe(OH)₃. The precipitate was subsequently transferred into 50 mL Teflon® centrifuge tubes in which it was washed four times with pH-adjusted Milli-Q® H₂O (pH = 8) and then dissolved in 12 M HCl for a three stage anion exchange chromatography [Auro et al., 2012] (Figure 1). Samples were loaded onto the first column (Eichrom® prefilter resin + 1X-8, 100–200 mesh resin) in 12 M HCl, followed by Th and REE elution in 12 M HCl, and Pa elution in 12 M HCl + 0.13 M HF. The prefilter resin thereby served to remove organic compounds from the sample solution [Auro et al., 2012]. The second stage targeted a purification of the Pa fraction, by repeating the first column (Eichrom® prefilter resin + 1X-8, 100–200 mesh resin). During the third stage, Th and REE were separated from each other by loading the REE/Th elute from the first column in 8 M HNO₃, eluting the REE in the same acid, and collecting Th in 12 M HCl (resin: Eichrom® prefilter resin + 1X-8, 100–200 mesh resin; Figure 1) [Auro et al., 2012].

2.2. Carbonate Sample Preparation and Anion Exchange Chemistry: The Neodymium Fraction During Uranium-Thorium Separation

Uranium-series dating of deep-sea coral aragonite (<1 g) requires thorough removal of contaminating phases prior to ion exchange chromatography and mass spectrometry. This is typically achieved by rigorous physical cleaning with a Dremel® tool and subsequent oxidative and reductive chemical cleaning [e.g., Cheng et al., 2000; Robinson et al., 2005; van de Flierdt et al., 2010]. Sample dissolution was achieved in nitric acid to which a mixed 236U-229Th spike was added [Edwards et al., 1987; Hines et al., 2015]. The samples were evaporated, then dissolved in 2 M HCl and ~3–5 mg of purified Fe were added as FeCl₃, followed by addition of ammonium hydroxide to coprecipitate trace metals at pH = 7–9, whereas alkaline earth metals, and in particular Ca, are not precipitated [e.g., Dulski, 1996]. It should be noted that this FeCl₃ precipitation step would not be required for processing coral samples for Nd isotopes alone [e.g., Crocket et al., 2014; Wilson et al., 2014]. After a MQ rinse, samples were re-dissolved in 8 M HNO₃ for U and Th separation during two-stage anion exchange chemistry based on the recipe of Edwards et al. [1987]. In brief, samples were loaded in 8 M HNO₃ on BioRad® AG1-X8 (100–200 mesh) anion exchange resin, followed by matrix elution in
M$\text{HNO}_3$, which is the fraction containing the REE. Thorium is subsequently stripped off the column using 6 M$\text{HCl}$, evaporated to dryness and then converted to nitric form for MC-ICP-MS analyses. The U fraction was the last to be eluted from the first column using 18.2 M$\text{HNO}_3$ (hereafter: MQ; Figure 1) [Hines et al., 2015].

2.3. Two-Stage Neodymium Purification for TIMS NdO$^+$ Analyses

The method for ion chromatography in preparation for TIMS NdO$^+$ analysis as performed in the MAGIC laboratories at Imperial College London was recently published by Crocket et al. [2014]. Here, we briefly summarize the key points with a focus on amendments to the published procedure. We note that for this study all Nd cuts from U-Th and Pa-Th separation were doped with $^{150}$Nd after anion exchange chromatography to determine minimum Nd concentrations omitting Nd loss during sample preparation and U-Th and Pa-Th anion exchange chromatographies. It is however recommended for future work to add a mixed spike that contains Nd at an earlier stage (Figure 1) to obtain accurate Nd concentration measurements on all samples.

Dried Nd cuts from U-Th and Pa-Th chemistries were oxidized with aqua regia at 200°C, followed by a 1:1 mixture of concentrated HNO$_3$ and 30% H$_2$O$_2$ prior to Nd extraction to break down potential residual organics. Such residual organics may be sourced either from sample matrix or from anion exchange chromatography as observed by Auro et al. [2012] for Pa-Th separation. Subsequently, samples were converted to $8\text{ M HNO}_3$, which is the fraction containing the REE. Thorium is subsequently stripped off the column using 6 M$\text{HCl}$, evaporated to dryness and then converted to nitric form for MC-ICP-MS analyses. The U fraction was the last to be eluted from the first column using 18.2 M$\text{HNO}_3$ (hereafter: MQ; Figure 1) [Hines et al., 2015].

![Figure 1. Working scheme of combined Pa-Th-Nd and U-Th-Nd chemical procedures toward Nd isotope analyses. Purified U, Pa, and Th fractions were analyzed by MC-ICP-MS [Anderson et al., 2012; Auro et al., 2012; Hines et al., 2015]. Note that some laboratories apply a second Th purification step during U-Th separation [cf. Burke and Robinson, 2012]. It is also noted that isotopic spiking is not yet tested for the combined method in seawater and corals. It has however successfully been achieved for combined Pa-Th-Nd chemistry of marine particulate samples (Kretschmer et al., personal communication, 2013). Finally, our preferred method for REE separation after Fe coprecipitation and actinide extraction is the traditional cation exchange chemistry, as the application of strong oxidizing agents to combat leaking organics from such resins can be avoided (e.g., Lambelet et al., accepted manuscript, 2015).]
chloride form and redissolved in 1 mL 1 M HCl for cation exchange chromatography or to nitrate form for RE spec\(^{-}\) chemistry.

### 2.3.1. Step 1: Cation Exchange Chemistry or TRU spec\(^{-}\)/RE spec\(^{-}\) Chemistry: Separating Rare Earth Elements From the Sample Matrix

The procedure to isolate REE from sample matrix was designed to accommodate high Fe content of up to \(~10\) mg and was then used for REE separation from anion exchange wash fractions collected from both, Pa-Th and U-Th chemistries. In order to preconcentrate trace metals, \(~100\) mg Fe were added to each seawater sample and \(~5\) mg to each coral sample rendering REE separation from Fe a major concern. During the first step of Pa-Th separation, Fe is expected to be retained by the anion exchange resin (Figure 1). This is based on the fact that Fe\(^{2+}\) has a high distribution constant \(K_D\) with strong-base anion exchange resin in hydrochloric acid \([\text{Kraus et al.}, 1956]\), which should inhibit Fe elution with the Th/REE fraction during Pa separation (Figure 1). In praxis, small amounts of Fe are however eluted into the REE fraction. During the first step of U-Th separation on the other hand, nitric acid is used to achieve efficient separation of U and Th from Fe (no adsorption of Fe in 0.1 to 14 M HNO\(_3\) with anion exchange resin) \([\text{Faris and Buchanan, 1964}]\). Hence, the \(~5\) mg of Fe added to coral samples will be eluted together with the REE during matrix elution so that the REE fraction contains a significant Fe matrix (Figure 1). Therefore, we initially applied a modified version of the RE spec\(^{-}\) \([\text{cf. Huff and Huff, 1993}]\) chemistry published by \textit{Crocket et al.} [2014]. More specifically, we added 1 mL of 0.9 M ascorbic acid to 2 mL 1.5 M HNO\(_3\) in order to reduce Fe and obtain minimal adsorption onto the resin \(\text{e.g., Horwitz et al.}, 1993\). While efficient in removing Fe (tested for up to 50 mg of Fe), leaking organics from TRU/RE spec\(^{-}\) resins require strong sample oxidation after REE separation \(\text{e.g., Gault-Ringold and Stirling, 2012; Crocket et al., 2014; Murphy et al., 2015}\) \((\text{M. Lambelet et al., Neodymium isotopic composition and concentration in the western North Atlantic Ocean: results from the GEOTRACES GA02 section, accepted Geochimica et Cosmochimica Acta, 2015})\). We therefore substituted the RE spec\(^{-}\) chemistry by traditional cation exchange chromatography \(\text{e.g., Cohen et al., 1988}\), using 1.4 mL of pre-cleaned Biorad\(^{\text{TM}}\) AG50 W-X8 resin (200–400 mesh) in hand-packed Biorad\(^{\text{TM}}\) Poly-Prep columns. Cleaning of resin and columns was done with 10 mL 6 M HCl, followed by resin conditioning with 1 + 0.5 mL 1 M HCl. Samples were loaded in 0.5 + 0.5 mL 1 M HCl and subsequently washed in with 0.5 + 0.5 mL 1 M HCl. Sample matrix was eluted with 1 + 6 mL 3 M HCl and 0.5 mL 6 M HCl, after which the REE fraction was stripped off using 7 mL 6 M HCl. We chose 3 M HCl for Fe elution rather than \(~3.7\) M HCl \(\text{i.e., the minimum} K_D \text{of Fe on AG50W-X8 resin} [\text{Strelow, 1960; Nelson et al., 1964}]\) to avoid REE loss during Fe elution. As the resin in the columns was re-used, a final wash was carried out with 10 mL 6 M HCl, followed by 1 + 1 mL MQ for storage in 0.5 M HCl. Most elements of relevance, and in particular barium, have \(K_D\)s in 6 M HCl on AG50W-X8 \([\text{Nelson et al., 1964}]\) similar to or lower than REE so that the extensive 6 M HCl wash is considered sufficient to avoid cation build-up on negatively charged resin exchange spaces. It is however noted that a nitric acid wash may be desirable to add \([\text{cf. Strelow et al., 1965}]\).

### 2.3.2. Step 2: Ln spec\(^{-}\) Chemistry: Neodymium Purification

Separation of neodymium (Nd) from the light rare earth elements (LREE), and in particular from praseodymium (Pr) is crucial for analysis as NdO\(^{+}\). We followed the method by \textit{Crocket et al.} [2014] and packed Savillex\(^{\text{TM}}\) columns (4 cm long, 3.2 mm inner diameter, 20 \(\mu\)m frits) with \(~320\) \(\mu\)L Eichrom Ln spec\(^{-}\) resin (20–50 \(\mu\)m) \([\text{see also Pin and Zalduegui, 1997}]\). The calibration with 0.140 M HCl yielded \(>75\%\) Nd and less than 5% Pr contribution to the Nd fraction, but it is noted that Nd yields on different columns can be variable. Different to the published method \([\text{Crocket et al., 2014}]\), we left the Ln spec\(^{-}\) resin in the columns between procedural batches. Resuspension of the resin in the column was achieved in MQ water with acid cleaned 8.3 cm long Corning\(^{\text{TM}}\) gel-loading pipette tips \((1–200\) \(\mu\)L\) in order to avoid resin compaction, which could affect the precisely calibrated elution scheme, and to keep the flow rates between \(~0.55\) and 0.6 mL/h. After a washing step in 6 M HCl and addition of MQ water, the resin was preconditioned with 0.140 M HCl and samples were loaded and later on collected in the same acid \([\text{Crocket et al., 2014}]\). The resin was reused until degradation of separation efficiency of Nd and Pr was observed. In order to pool the Nd fraction in one spot during evaporation for subsequent TIMS NdO\(^{+}\) analyses, 10 \(\mu\)L 0.001 M H\(_2\)PO\(_4\) were added to the Nd fraction after Ln spec\(^{-}\) chemistry.

### 2.4. Synthesizing a TaF\(_5\) Activator for TIMS NdO\(^{+}\) Analyses

As detailed in \textit{Crocket et al.} [2014], samples were loaded in 2 \(\times\) 0.5 \(\mu\)L 2.5 M HCl between two layers of 0.5 \(\mu\)L TaF\(_5\) activator on degassed single W filaments in smallest possible increments in order to reduce domain mixing effects \(\text{e.g., Andreasen and Sharma, 2009}\). During sample loading, the current was set to
0.9 Å and afterwards increased slowly to ∼2.0 Å (over a time period of 4 min). For this study, TaF₅ was prepared from Ta₂O₅ powder, which was fluxed in 28 M HF at 80°C for 7 days in an acid clean Teflon beaker (10 mL 28 M HF for 250 mg Ta₂O₅) [Charlier et al., 2006], after which the solution was evaporated to dryness at 130°C. Per 150 mg of TaF₅, we used 0.178 mL 28 M HF, 7.98 mL MQ water, 1.025 mL 3 M HNO₃, and 0.169 mL 14.8 M H₃PO₄, which is a modified version of the recipe used by Charlier et al. [2006]. It is important to add the aliquot of 28 M HF first in order to dissolve the crystals either upon contact or leave until fully dissolved; otherwise the crystals remain undissolved once the remaining reagents are added. The combined activator and loading Nd blank was <0.2 pg. The performance of the activator was variable, similar to results reported in detail by Crocket et al. [2014] and Lambelet et al. (accepted manuscript, 2015). We found that purification of the activator solution by NH₂OH coprecipitation, described in the literature [e.g., Charlier et al., 2006] to reduce the loading blank, was not improving Nd blank levels and sometimes compromised beam intensity and stability and was hence omitted.

2.5. Thermal Ionization Mass Spectrometry

All Nd isotope analyses were carried out on a Thermo Triton TIMS at the Department of Earth Science and Engineering, Imperial College London, closely following the analytical protocol of Crocket et al. [2014]. Samples were routinely analyzed in nine blocks comprising 20 cycles using a peak integration time of 8.4 s at temperatures between 1520°C and 1580°C. Isobaric interferences on ¹⁴⁰Ce/¹⁴⁰O, ¹⁴¹Pr/¹⁴¹O, and ¹⁴⁷Sm/¹⁴⁷O were routinely monitored for correction whereas La and in particular Ba were monitored manually. Residual Ba was however negligible in all our samples. Interference and mass bias corrections were applied as outlined by Crocket et al. [2014] using ¹⁷O/¹⁶O = 0.0000390, ¹⁸O/¹⁶O = 0.002073, and ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. A slightly higher ¹⁴⁶Nd/¹⁴⁴Nd was applied to spiked samples [Crocket et al., 2014 and references therein].

Over a period of 26 months 5 and 15 ng loads of pure JNd-1 were analyzed [¹⁴³Nd/¹⁴⁴Nd = 0.512105 ± 0.000009, 2SD, n = 110] to monitor instrumental offset and normalize mass bias corrected ¹⁴³Nd/¹⁴⁴Nd ratios of samples to the reference ratio of ¹⁴³Nd/¹⁴⁴Nd = 0.512115 ± 0.000007 [Tanaka et al., 2000]. Repeated analyses of 10, 20, and 30 ng Nd loads of the USGS BCR-2 reference material yielded ¹⁴³Nd/¹⁴⁴Nd results of 0.512637 ± 0.000011 (2SD, n = 32) and 10 and 30 ng loads of our in-house coral reference material resulted in ¹⁴³Nd/¹⁴⁴Nd ratios of 0.512336 ± 0.000009 (2SD, n = 23), both of which are in excellent agreement with previously published values [Weis et al., 2006; Crocket et al., 2014]. The observed raw ratios of major interfering masses for column processed BCR-2 material and our in-house coral reference material were ¹⁴⁷Sm/¹⁴⁴Nd < 0.0012, ¹⁴⁰Ce/¹⁴⁴Nd < 0.024, and ¹⁴¹Pr/¹⁴⁴Nd < 0.46 and hence within the suggested limits presented by Crocket et al. [2014]. Blank levels of Nd chemistry alone were mostly <5 pg, regardless of the procedure used for REE isolation. The first batch of samples processed through cation exchange chemistry showed, however, slightly elevated Nd blanks of 7 and 17 pg for unresolved reasons.

Full procedural blanks of combined U, Th, and Nd separation from deep-sea corals ranged from 2 to 35 pg Nd, averaging at 11 pg (n = 31) and contributed <1% to the analyzed sample Nd. This shows that the procedural Nd blank is low in the combined method although no efforts were made to specifically reduce Nd blank during sample preparation and actinide separation (Figure 1). Full procedural Nd blanks of combined Pa, Th, and Nd separation on seawater samples reported in this study were 140 and 160 pg. The reasons for these abnormally high blanks are discussed below in more detail and are related to initial problems in the Pa-Th chemistry described by Auro et al. [2012].

3. Application: Seawater and Carbonates

3.1. Intercomparison of Results for Nd Extraction From Seawater

We tested our combined Pa, Th, and Nd separation procedure on filtered and acidified seawater samples collected at 15 and 2000 m water depth at Bermuda Atlantic Time Series (BATS) station (31°50′ N, 64°10′ W) from the GEOTRACES Pa-Th intercalibration [Anderson et al., 2012]. The Nd isotope results generated for these samples are compared to GEOTRACES Nd intercalibration results from samples collected independently from the same water depth on the same expedition (KNR193-6/2) [van de Flierdt et al., 2012] (Table 1). The GEOTRACES Nd isotope intercalibration results for seawater from 15 m water depth are $\varepsilon_{\text{Nd}} = -9.19 \pm 0.57$ and $\varepsilon_{\text{Nd}} = -13.14 \pm 0.57$ for 2000 m water depth [van de Flierdt et al., 2012] (Table 1). These values are indicated by the dashed line in Figure 2 (representing the consensus values, i.e., $\Delta\varepsilon_{\text{Nd}} = 0$).
Geochemistry, Geophysics, Geosystems

10.1002/2015GC006130

Our newly obtained Nd isotope data from the Pa-Th chemistry wash fractions are reported in Table 1 and plotted as deviation from the reported consensus values for 15 and 2000 m water depth, respectively (Figure 2). The maximum offset of \( \Delta \varepsilon_{\text{Nd}} \) is 0.06 epsilon units and demonstrates the excellent agreement between samples processed for Nd only and samples processed through the combined methodology (Figure 1).

We should however note that the Nd data presented here were generated by the ‘initial method’ reported by Auro et al. [2012]. This method suffered from procedural problems during column chemistry resulting in higher Th blanks and lower Th yields [see Auro et al., 2012 for details]. Neodymium and Th are eluted from the same column (Figure 1), and we can see this reflected in elevated Nd blanks of up to \( \sim 2\% \), paired with estimated sample loss of up to 72% (Table 1) when compared to expected seawater Nd concentrations from published Nd results [van de Flierdt et al., 2012]. As our TIMS Nd\(^{146}\) method allows for analyses of sub-nanogram levels of Nd, we were however able to isotopically constrain the Nd blank from these samples, i.e., 0.14 ng Nd with \( \varepsilon_{\text{Nd}} = -19.31 \pm 0.78 \) and 0.16 ng Nd with \( \varepsilon_{\text{Nd}} = -10.49 \pm 0.69 \). These values are used for a mixing calculation to assess the significance of blank contamination to our BATS seawater Nd results.

\[
I_{C_{\text{sample}}} = \frac{I_{C_{\text{final}}} \times (\frac{[\text{Nd}]_{\text{sample}} \times f_{\text{sample}} + [\text{Nd}]_{\text{blank}} \times f_{\text{blank}}}{[\text{Nd}]_{\text{sample}} \times f_{\text{sample}}}) - I_{C_{\text{blank}}} \times [\text{Nd}]_{\text{blank}} \times f_{\text{blank}}}{[\text{Nd}]_{\text{sample}} \times f_{\text{sample}}}
\]

\( I_{C_{\text{sample}}} \) stands for the isotopic composition, \([\text{Nd}]\) for the Nd concentration, and \( f \) for the fraction. Following above mixing equation, we can calculate that the maximum Nd blank contribution of 160 pg would shift the sample Nd isotopic composition by 0.01 epsilon units. Such blank contribution is considered negligible, supported by the accurate results we report for the Nd isotopic compositions from Pa-Th wash fractions (Table 1 and Figure 2).

### 3.2. Intercomparison of Results for Nd Extraction From Aragonitic Deep-Sea CoralSkeletons

The application of combined uranium, thorium, and neodymium extraction from aragonitic sample matrices was tested on a coral reference material created from a homogenized mixture of *Desmophyllum dianthus*...
deep-sea corals from the Southern Ocean (in-house coral reference material) [see Crocket et al., 2014 for details]. Neodymium yields for the Fe coprecipitation and U-Th anion exchange chromatography were found to be nearly quantitative at 88–90% during three individual batches of chemistry, consistent with “slight adsorption” of Nd on anion exchange resins in HNO₃ [Faris and Buchanan, 1964]. Such Nd yields are likely representative for the Pa-Th separation as well, considering that there is no adsorption of Nd on strong-base anion exchange resins in HCl minimizing Nd loss on the first column [Kraus and Nelson, 1958] (Figure 1). Hence, the matrix elution with HNO₃ on the second column of Pa-Th separation is considered to be the only place where minimal loss of Nd could occur, resulting in similar quantitative Nd yields for both anion exchange based chemistries, i.e., U-Th and Pa-Th separation [cf. Kraus and Nelson, 1958; Faris and Buchanan, 1964].

In order to test our combined U-Th-Nd separation for accuracy of Nd isotopes, we report results on 20 repeats of our in-house coral reference material (10 and 30 ng Nd aliquots) processed individually through RE specV chemistry (n = 11) and cation exchange chemistry (n = 9) (Table 1 and Figure 3). These results are compared to Nd isotope data obtained from three coral reference material aliquots (30 ng Nd each; Table 1) processed individually through Fe coprecipitation and U-Th anion exchange chromatography. The results document excellent reproducibility of coral reference material aliquots regardless of the applied procedure. In particular, results are consistent between samples collected from U-Th chemistry
Acknowledgments

We thank the team on the second leg of the first GEOTRACES intercalibration cruise for sample collection, Joanne Goudreau, Kuo Fang Huang, Jurek Goubert, Martin Fleisher and Sven Kretschmer for discussion, and Derek Vance for sharing his 106Nd spike. Torben Stichel is acknowledged for help during column calibration. All data presented in this manuscript can be found in the table included in the main body of the text. Funding that supported this work was received from the National Science Foundation (NSF 0752402), the Leverhulme Trust (RPG-398), the Natural Environmental Research Council (NE/J021636/1 and NE/N003861/1), the European Research Council (278708), and the Grantham Institute for Climate Change. We thank Marcus Gutjahr and an anonymous reviewer for constructive comments on the manuscript and acknowledge the editorial handling by Yusuke Yokoyama.

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