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

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Key points

- **Combined extraction of Pa/U-Th-Nd from seawater and coralline aragonite**
- **Successful neodymium isotope intercalibration**
- **Reduction of sample volume requirements and workload**

1 **Abstract**

2 Isotopes of the actinide elements protactinium (Pa), thorium (Th) and uranium (U), and the
3 lanthanide element neodymium (Nd) are often used as complementary tracers of modern and
4 past oceanic processes. The extraction of such elements from low abundance matrices, such
5 as seawater and carbonate, is however labor-intensive and requires significant amounts of
6 sample material. We here present a combined method for the extraction of Pa, Th and Nd
7 from 5 to 10 L seawater samples, and of U, Th and Nd from <1 g carbonate samples.
8 Neodymium is collected in the respective wash fractions of Pa-Th and U-Th anion exchange
9 chromatographies. Regardless of the original sample matrix, Nd is extracted during a two-
10 stage ion chromatography, followed by thermal ionization mass spectrometry (TIMS)
11 analysis as NdO^+ . Using this combined procedure, we obtained results for Nd isotopic
12 compositions on two GEOTRACES consensus samples from Bermuda Atlantic Time Series
13 (BATS), which are within error identical to results for separately sampled and processed
14 dedicated Nd samples ($\epsilon_{\text{Nd}} = -9.20 \pm 0.21$ and -13.11 ± 0.21 for 15 and 2000 m water depths,
15 respectively; intercalibration results from 14 laboratories: $\epsilon_{\text{Nd}} = -9.19 \pm 0.57$ and $-13.14 \pm$
16 0.57). Furthermore, Nd isotope results for an in-house coral reference material are identical
17 within analytical uncertainty for dedicated Nd chemistry and after collection of Nd from U-
18 Th anion exchange chromatography. Our procedure does not require major adaptations to
19 independently used ion exchange chromatographies for U-Pa-Th and Nd, and can hence be
20 readily implemented for a wide range of applications.

21

22

23 **Index Terms:** 1040, 1050, 4803, 4825, 4924

- 24 **Keywords:** deep-sea corals, seawater, GEOTRACES, extraction methods, neodymium
- 25 isotopes

26

27 **1. Introduction**

28 The isotopes of the radionuclides protactinium (Pa), thorium (Th), uranium (U) and of the
29 rare earth element (REE) neodymium (Nd) are invaluable tools for studying modern ocean
30 biogeochemistry and past ocean conditions [e.g., *Goldstein and Hemming, 2003; Henderson*
31 *and Anderson, 2003*]. Even though our understanding of their modern biogeochemical cycles
32 is still relatively poor ^{230}Th , ^{232}Th , ^{231}Pa , and Nd isotopes ($^{143}\text{Nd}/^{144}\text{Nd}$ ratio, expressed as ϵ_{Nd}
33 $= ((^{143}\text{Nd}/^{144}\text{Nd}_{\text{sample}})/(^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}}) - 1) \times 10,000$; CHUR: chondritic uniform reservoir;
34 *Jacobsen and Wasserburg, 1980*) are frequently used as proxies to reconstruct past ocean
35 chemistry and dynamics [e.g., *van de Flierdt et al., 2012; Anderson et al., 2012*]. This
36 situation is currently being rectified in the context of the international GEOTRACES program
37 [*SCOR Working Group, 2007*] where ^{230}Th , ^{231}Pa , and Nd isotopes are ‘key parameters’,
38 which have to be measured on all planned and completed GEOTRACES section cruises.
39 However, accurate and precise analysis of these nuclides in seawater requires relatively large
40 sample volumes (5 to 10 L) [*van de Flierdt et al., 2012; Anderson et al., 2012*]. Although
41 recent analytical advances allow some laboratories to target sample volumes of less than 5 L,
42 shipping large volumes of water to home laboratories is nevertheless an expensive endeavor.
43 In order to reduce shipping costs and sample processing time, a combined extraction method
44 for ^{231}Pa , ^{230}Th and Nd isotopes, which are typically analyzed by different groups, would be
45 desirable [e.g., *Jeandel et al., 2011*].

46

47 Similarly, in paleo-archives such as deep-sea corals, sample material could be saved and time
48 consuming sample preparation could be reduced by simultaneous separation of U, Th and Nd.
49 The aragonitic skeleton of corals allows for accurate age control by U-series dating [e.g.,
50 *Cheng et al., 2000*], and Nd isotopes have been shown to present a promising tracer to

51 reconstruct past water mass properties [e.g., *van de Flierdt et al.*, 2006, 2010; *Copard et al.*,
52 2010]. Deep-sea corals are increasingly targeted as a paleoceanographic archive, as they are
53 found in areas where other traditional archives (e.g., foraminiferal carbonate) tend to be
54 scarce, such as the Southern Ocean, or in water depths which are undersampled by sediment
55 cores (e.g., intermediate waters) [see *Robinson et al.*, 2014 for a recent summary]. Moreover,
56 such combined extraction approaches could ensure that the data obtained are from exactly the
57 same sample thus facilitating optimal comparison between different geochemical parameters.

58

59 Here, we demonstrate accurate Nd isotope results obtained from a combined extraction
60 scheme of Pa, Th and Nd from seawater and U, Th and Nd from coralline aragonite. The
61 method is easy to adapt, as it merely requires collecting elution fractions from anion
62 exchange columns set up for separating U-Th-Pa [e.g., *Auro et al.*, 2012; *Edwards et al.*,
63 1987], which normally would go to waste, and subsequent processing through standard ion
64 exchange chromatography for Nd isotope analyses [e.g., *van de Flierdt et al.*, 2006, 2012].
65 Our Nd isotope intercalibration results for the combined chemistries are in excellent
66 agreement with results from seawater and coral samples processed for Nd only.

67

68 **2. Methodology**

69 **2.1. Seawater sample preparation and anion exchange chemistry: the neodymium** 70 **fraction during protactinium – thorium separation**

71 A refined methodology to extract protactinium and thorium from large volume seawater
72 samples was recently published by *Auro et al.* [2012]. We here briefly summarize the key
73 features of the method (Fig. 1). Acidified seawater samples of 10 L volume were spiked
74 (^{229}Th and ^{233}Pa) and left to equilibrate. In order to remove the trace metals of interest from
75 the sample matrix, 100 mg of purified Fe were added per sample as FeCl_3 . Purification of Fe

76 was achieved by repeated isopropyl ether extraction, and the rather high amount of Fe was
77 chosen to quantitatively precipitate Pa [Auro *et al.*, 2012]. The trace metals were isolated
78 from solution by adjusting the pH to between 7.5 and 8.0 through addition of ammonium
79 hydroxide to precipitate Fe(OH)₃. The precipitate was subsequently transferred into 50 ml
80 Teflon[®] centrifuge tubes in which it was washed four times with pH-adjusted Milli-Q[®] H₂O
81 (pH = 8) and then dissolved in 12 M HCl for a three stage anion exchange chromatography
82 [Auro *et al.*, 2012; Fig. 1]. Samples were loaded onto the first column (Eichrom[®] prefilter
83 resin + 1X-8, 100-200 µm mesh resin) in 12 M HCl, followed by Th and REE elution in 12
84 M HCl, and Pa elution in 12 M HCl + 0.13 M HF. The prefilter resin hereby served to
85 remove organic compounds from the sample solution [Auro *et al.*, 2012]. The second stage
86 targeted a purification of the Pa fraction, by repeating the first column (Eichrom[®] prefilter
87 resin + 1X-8, 100-200 µm mesh). During the third stage Th and REE were separated from
88 each other by loading the REE/Th elute from the first column in 8 M HNO₃, eluting the REE
89 in the same acid, and collecting Th in 12 M HCl (resin: Eichrom[®] prefilter resin + 1X-8, 100-
90 200 µm mesh; Fig. 1) [Auro *et al.*, 2012].

91

92 **2.2. Carbonate sample preparation and anion exchange chemistry: the neodymium** 93 **fraction during uranium – thorium separation**

94 Uranium-series dating of deep-sea coral aragonite (<1 g) requires thorough removal of
95 contaminating phases prior to ion exchange chromatography and mass spectrometry. This is
96 typically achieved by rigorous physical cleaning with a Dremel[®] tool and subsequent
97 oxidative and reductive chemical cleaning [e.g., Cheng *et al.*, 2000; Robinson *et al.*, 2005;
98 van de Flierdt *et al.*, 2010]. Sample dissolution was achieved in nitric acid to which a mixed
99 ²³⁶U-²²⁹Th spike was added [Edwards *et al.*, 1987; Hines *et al.*, 2015]. The samples were
100 evaporated, then dissolved in 2 M HCl and ~3-5 mg of purified Fe were added as FeCl₃,

101 followed by addition of ammonium hydroxide to co-precipitate trace metals at pH = 7-9,
102 whereas alkaline earth metals, and in particular Ca, are not precipitated [e.g., *Dulski*, 1996]. It
103 should be noted that this FeCl₃ precipitation step would not be required for processing coral
104 samples for Nd isotopes alone [e.g., *Crocket et al.*, 2014; *Wilson et al.*, 2014]. After a MQ
105 rinse, samples were re-dissolved in 8 M HNO₃ for U and Th separation during two-stage
106 anion exchange chemistry based on the recipe of *Edwards et al.* [1987]. In brief, samples
107 were loaded in 8 M HNO₃ on Biorad[®] AG1-X8 (100-200 mesh) anion exchange resin,
108 followed by matrix elution in 8 M HNO₃, which is the fraction containing the REE. Thorium
109 is subsequently stripped off the column using 6 M HCl, evaporated to dryness and then
110 converted to nitric form for MC-ICP-MS analyses. The U fraction was the last to be eluted
111 from the first column using 18.2 MΩ Milli-Q[®] (hereafter: MQ; Fig. 1) [*Hines et al.*, 2015].

112

113 **2.3. Two-stage neodymium purification for TIMS NdO⁺ analyses**

114 The method for ion chromatography in preparation for TIMS NdO⁺ analysis as performed in
115 the MAGIC laboratories at Imperial College London was recently published by *Crocket et al.*
116 [2014]. Here, we briefly summarize the key points with a focus on amendments to the
117 published procedure. We note that for this study all Nd cuts from U-Th and Pa-Th separation
118 were doped with ¹⁵⁰Nd after anion exchange chromatography to determine minimum Nd
119 concentrations omitting Nd loss during sample preparation and U-Th and Pa-Th anion
120 exchange chromatographies. It is however recommended for future work to add a mixed
121 spike that contains Nd at an earlier stage (Fig. 1) to obtain accurate Nd concentration
122 measurements on all samples.

123

124 Dried Nd cuts from U-Th and Pa-Th chemistries were oxidized with aqua regia at 200°C,
125 followed by a 1:1 mixture of concentrated HNO₃ and 30% H₂O₂ prior to Nd extraction to

126 break down potential residual organics. Such residual organics may be sourced either from
127 sample matrix or from anion exchange chromatography as observed by *Auro et al.* [2012] for
128 Pa-Th separation. Subsequently, samples were converted to chloride form and redissolved in
129 1 ml 1 M HCl for cation exchange chromatography or to nitrate form for RE spec[®] chemistry.

130

131 **2.3.1. Step 1 - Cation exchange chemistry or TRU spec[®]/RE spec[®] chemistry: separating**
132 **rare earth elements from the sample matrix**

133 The procedure to isolate REE from sample matrix was designed to accommodate high Fe
134 content of up to ~10 mg, and was then used for REE separation from anion exchange wash
135 fractions collected from both, Pa-Th and U-Th chemistries. In order to pre-concentrate trace
136 metals ~100 mg Fe were added to each seawater sample and ~5 mg to each coral sample
137 rendering REE separation from Fe a major concern. During the first step of Pa-Th separation
138 Fe is expected to be retained by the anion exchange resin (Fig. 1). This is based on the fact
139 that Fe³⁺ has a high distribution constant K_D with strong-base anion exchange resin in
140 hydrochloric acid [*Kraus et al.*, 1956], which should inhibit Fe elution with the Th/REE
141 fraction during Pa separation (Fig. 1). In praxis, small amounts of Fe are however eluted into
142 the REE fraction. During the first step of U-Th separation on the other hand, nitric acid is
143 used to achieve efficient separation of U and Th from Fe (no adsorption of Fe in 0.1 to 14 M
144 HNO₃ with anion exchange resin; *Faris and Buchanan*, 1964). Hence, the ~5 mg of Fe added
145 to coral samples will be eluted together with the REE during matrix elution so that the REE
146 fraction contains a significant Fe matrix (Fig. 1). Therefore, we initially applied a modified
147 version of the RE spec[®] [cf. *Huff and Huff*, 1993] chemistry published by *Crocket et al.*
148 [2014]. More specifically, we added 1 ml of 0.9 M ascorbic acid to 2 ml 1.5 M HNO₃ in order
149 to reduce Fe and obtain minimal adsorption onto the resin [e.g., *Horwitz et al.*, 1993]. While
150 efficient in removing Fe (tested for up to 50 mg of Fe), leaking organics from TRU/RE spec[®]

151 resins require strong sample oxidation after REE separation [e.g., *Gault-Ringold and Stirling*,
152 2012; *Crocket et al.*, 2014; *Murphy et al.*, 2015; *Lambelet et al.*, submitted]. We therefore
153 substituted the RE spec[®] chemistry by traditional cation exchange chromatography [e.g.,
154 *Cohen et al.*, 1988], using 1.4 ml of pre-cleaned Biorad[®] AG50 W-X8 resin (200-400 mesh)
155 in hand-packed Biorad[®] Poly-Prep columns. Cleaning of resin and columns was done with 10
156 ml 6 M HCl, followed by resin conditioning with 1 + 0.5 ml 1 M HCl. Samples were loaded
157 in 0.5 + 0.5 ml 1 M HCl and subsequently washed in with 0.5 + 0.5 ml 1 M HCl. Sample
158 matrix was eluted with 1 + 6 ml 3 M HCl and 0.5 ml 6 M HCl, after which the REE fraction
159 was stripped off using 7 ml 6 M HCl. We chose 3 M HCl for Fe elution rather than ~3.7 M
160 HCl (i.e. the minimum K_D of Fe on AG50W-X8 resin; *Strelow*, 1960; *Nelson et al.*, 1964) to
161 avoid REE loss during Fe elution. As the resin in the columns was re-used, a final wash was
162 carried out with 10 ml 6 M HCl, followed by 1 + 1 ml MQ for storage in 0.5 M HCl. Most
163 elements of relevance, and in particular barium, have K_D s in 6 M HCl on AG50W-X8
164 [*Nelson et al.*, 1964] similar to or lower than REE so that the extensive 6 M HCl wash is
165 considered sufficient to avoid cation build-up on negatively charged resin exchange spaces. It
166 is however noted that a nitric acid wash may be desirable to add [cf. *Strelow et al.*, 1965].

167

168 **2.3.2. Step 2 - Ln spec[®] chemistry: neodymium purification**

169 Separation of neodymium (Nd) from the light rare earth elements (LREE), and in particular
170 from praseodymium (Pr) is crucial for analysis as NdO⁺. We followed the method by *Crocket*
171 *et al.* [2014] and packed Savillex[®] columns (4 cm long, 3.2 mm inner diameter, 20 μ m frits)
172 with ~320 μ l Eichrom Ln spec[®] resin (20-50 μ m) [see also *Pin and Zaldugui*, 1997]. The
173 calibration with 0.140 M HCl yielded >75 % Nd and less than 5 % Pr contribution to the Nd
174 fraction, but it is noted that Nd yields on different columns can be variable. Different to the
175 published method [*Crocket et al.*, 2014], we left the Ln spec[®] resin in the columns between

176 procedural batches. Re-suspension of the resin in the column was achieved in MQ water with
177 acid cleaned 8.3 cm long Corning[®] gel-loading pipette tips (1-200 μ L) in order to avoid resin
178 compaction, which could affect the precisely calibrated elution scheme, and to keep the flow
179 rates between \sim 0.55 and 0.6 ml/hr. After a washing step in 6 M HCl and addition of MQ
180 water, the resin was pre-conditioned with 0.140 M HCl and samples were loaded and later on
181 collected in the same acid [Crocket *et al.*, 2014]. The resin was re-used until degradation of
182 separation efficiency of Nd and Pr was observed. In order to pool the Nd fraction in one spot
183 during evaporation for subsequent TIMS NdO⁺ analyses, 10 μ l 0.001 M H₃PO₄ were added to
184 the Nd fraction after Ln spec[®] chemistry.

185

186 **2.4. Synthesizing a TaF₅ activator for TIMS NdO⁺ analyses**

187 As detailed in Crocket *et al.* [2014], samples were loaded in 2 x 0.5 μ l 2.5 M HCl between
188 two layers of 0.5 μ l TaF₅ activator on degassed single W filaments in smallest possible
189 increments in order to reduce domain mixing effects [e.g., *Andreassen and Sharma*, 2009].
190 During sample loading the current was set to 0.9 A and afterwards increased slowly to \sim 2.0 A
191 (over a time period of 4 minutes). For this study, TaF₅ was prepared from Ta₂O₅ powder,
192 which was fluxed in 28 M HF at 80 °C for 7 days in an acid clean Teflon beaker (10 ml 28 M
193 HF for 250 mg Ta₂O₅) [Charlier *et al.*, 2006], after which the solution was evaporated to
194 dryness at 130°C. Per 150 mg of TaF₅ we used 0.178 ml 28 M HF, 7.98 ml MQ water, 1.025
195 ml 3 M HNO₃ and 0.169 ml 14.8 M H₃PO₄, which is a modified version of the recipe used by
196 Charlier *et al.* [2006]. It is important to add the aliquot of 28 M HF first in order to dissolve
197 the crystals either upon contact or leave until fully dissolved; otherwise the crystals remain
198 un-dissolved once the remaining reagents are added. The combined activator and loading Nd
199 blank was $<$ 0.2 pg. The performance of the activator was variable, similar to results reported
200 in detail by Crocket *et al.* [2014] and Lambelet *et al.* [submitted]. We found that purification

201 of the activator solution by NH₄OH co-precipitation, described in the literature [e.g., *Charlier*
202 *et al.*, 2006] to reduce the loading blank, was not improving Nd blank levels and sometimes
203 compromised beam intensity and stability and was hence omitted.

204

205 **2.5. Thermal Ionization Mass Spectrometry**

206 All Nd isotope analyses were carried out on a Thermo Triton TIMS at the Department of
207 Earth Science and Engineering, Imperial College London, closely following the analytical
208 protocol of *Crocket et al.* [2014]. Samples were routinely analyzed in nine blocks comprising
209 20 cycles using a peak integration time of 8.4 s at temperatures between 1520°C and 1580°C.
210 Isobaric interferences on ¹⁴⁰Ce¹⁶O, ¹⁴¹Pr¹⁶O and ¹⁴⁷Sm¹⁶O were routinely monitored for
211 correction whereas La and in particular Ba were monitored manually. Residual Ba was
212 however negligible in all our samples. Interference and mass bias corrections were applied as
213 outlined by *Crocket et al.* [2014] using ¹⁷O/¹⁶O = 0.000390, ¹⁸O/¹⁶O = 0.002073 and
214 ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. A slightly higher ¹⁴⁶Nd/¹⁴⁴Nd was applied to spiked samples [*Crocket*
215 *et al.*, 2014 and references therein].

216 Over a period of 26 months 5 and 15 ng loads of pure JNdi-1 were analyzed (¹⁴³Nd/¹⁴⁴Nd =
217 0.512105 ± 0.000009, 2SD, n = 110) to monitor instrumental offset and normalize mass bias
218 corrected ¹⁴³Nd/¹⁴⁴Nd ratios of samples to the reference ratio of ¹⁴³Nd/¹⁴⁴Nd = 0.512115 ±
219 0.000007 [*Tanaka et al.*, 2000]. Repeated analyses of 10, 20 and 30 ng Nd loads of the USGS
220 BCR-2 reference material yielded ¹⁴³Nd/¹⁴⁴Nd results of 0.512637 ± 0.000011 (2SD, n = 32)
221 and 10 and 30 ng loads of our in-house coral reference material resulted in ¹⁴³Nd/¹⁴⁴Nd ratios
222 of 0.512336 ± 0.000009 (2SD, n = 23), both of which are in excellent agreement with
223 previously published values [*Weis et al.*, 2006; *Crocket et al.*, 2014]. The observed raw ratios
224 of major interfering masses for column processed BCR-2 material and our in-house coral
225 reference material were ¹⁴⁷Sm¹⁶O/¹⁴⁴Nd¹⁶O < 0.0012, ¹⁴⁰Ce¹⁶O/¹⁴⁴Nd¹⁶O < 0.024 and

226 $^{141}\text{Pr}^{16}\text{O}/^{144}\text{Nd}^{16}\text{O} < 0.46$ and hence within the suggested limits presented by *Crocket et al.*
227 [2014]. Blank levels of Nd chemistry alone were mostly <5 pg, regardless of the procedure
228 used for REE isolation. The first batch of samples processed through cation exchange
229 chemistry showed however slightly elevated Nd blanks of 7 and 17 pg for unresolved
230 reasons.

231

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

240

241 **3. Application: seawater and carbonates**

242 **3.1. Intercomparison of results for Nd extraction from seawater**

243 We tested our combined Pa, Th and Nd separation procedure on filtered and acidified
244 seawater samples collected at 15 and 2000 m water depth at Bermuda Atlantic Time Series
245 (BATS) station ($31^{\circ}50'$ N, $64^{\circ}10'$ W) from the GEOTRACES Pa-Th intercalibration
246 [*Anderson et al.*, 2012]. The Nd isotope results generated for these samples are compared to
247 GEOTRACES Nd intercalibration results from samples collected independently from the
248 same water depth on the same expedition (KNR193-6/2) [*van de Flierdt et al.*, 2012] (Table
249 1). The GEOTRACES Nd isotope intercalibration results for seawater from 15 m water depth
250 are $\epsilon_{\text{Nd}} = -9.19 \pm 0.57$ and $\epsilon_{\text{Nd}} = -13.14 \pm 0.57$ for 2000 m water depth [*van de Flierdt et al.*,

251 2012; Table 1]. These values are indicated by the dashed line in Figure 2 (representing the
 252 consensus values, i.e. $\Delta\epsilon_{Nd} = 0$). Our newly obtained Nd isotope data from the Pa-Th
 253 chemistry wash fractions are reported in Table 1 and plotted as deviation from the reported
 254 consensus values for 15 and 2000 m water depth, respectively (Fig. 2). The maximum offset
 255 of $\Delta\epsilon_{Nd}$ is 0.06 epsilon units and demonstrates the excellent agreement between samples
 256 processed for Nd only and samples processed through the combined methodology (Fig. 1).
 257 We should however note that the Nd data presented here were generated by the “initial
 258 method” reported by *Auro et al.* [2012]. This method suffered from procedural problems
 259 during column chemistry resulting in higher Th blanks and lower Th yields [see *Auro et al.*,
 260 2012 for details]. Neodymium and Th are eluted from the same column (Fig. 1), and we can
 261 see this reflected in elevated Nd blanks of up to ~2 %, paired with estimated sample loss of up
 262 to 72 % (Table 1) when compared to expected seawater Nd concentrations from published Nd
 263 results [*van de Flierdt et al.*, 2012]. As our TIMS NdO⁺ method allows for analyses of sub-
 264 nanogram levels of Nd, we were however able to isotopically constrain the Nd blank from
 265 these samples, i.e. 0.14 ng Nd with $\epsilon_{Nd} = -19.31 \pm 0.78$ and 0.16 ng Nd with $\epsilon_{Nd} = -10.49 \pm$
 266 0.69. These values are used for a mixing calculation to assess the significance of blank
 267 contamination to our BATS seawater Nd results.

268

$$269 \quad IC_{sample} = \frac{IC_{final} \times ([Nd]_{sample} \times f_{sample} + [Nd]_{blank} \times f_{blank}) - IC_{blank} \times [Nd]_{blank} \times f_{blank}}{([Nd]_{sample} \times f_{sample})}$$

270

271 IC stands for the isotopic composition, [Nd] for the Nd concentration, and f for the fraction.
 272 Following above mixing equation we can calculate that the maximum Nd blank contribution
 273 of 160 pg would shift the sample Nd isotopic composition by 0.01 epsilon units. Such blank
 274 contribution is considered negligible, supported by the accurate results we report for the Nd
 275 isotopic compositions from Pa-Th wash fractions (Table 1, Fig. 2).

276

277 **3.2. Intercomparison of results for Nd extraction from aragonitic deep-sea coral**
278 **skeletons**

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

292

293 In order to test our combined U-Th-Nd separation for accuracy of Nd isotopes, we report
294 results on 20 repeats of our in-house coral reference material (10 and 30 ng Nd aliquots)
295 processed individually through RE spec[®] chemistry (n = 11) and cation exchange chemistry
296 (n = 9) (Table 1; Fig. 3). These results are compared to Nd isotope data obtained from three
297 coral reference material aliquots (30 ng Nd each; Table 1) processed individually through Fe
298 co-precipitation and U-Th anion exchange chromatography. The results document excellent
299 reproducibility of coral reference material aliquots regardless of the applied procedure. In
300 particular, results are consistent between samples collected from U-Th chemistry wash

301 fractions, those loaded directly onto the respective first column of Nd extraction, and
302 previously published coral reference material Nd isotope data [*Crocket et al.*, 2012] (Fig. 3,
303 Table 1). Together with previous work [cf. *Jeandel et al.*, 2011], these results highlight the
304 benefit of combined procedures to separate different elements from the same sample, and
305 moreover, show the potential to extend the range of extracted elements.

306

307 **4. Summary and concluding remarks**

308 We here presented intercalibration Nd isotope results of combined separation procedures for
309 Pa, Th and Nd from seawater, and U, Th and Nd from aragonitic sample matrices. The
310 method was designed with minor modifications to existing protocols used in separate
311 laboratories carrying out U-Th-Pa and Nd isotope analyses as it utilizes wash fractions from
312 U-Th and Pa-Th anion exchange chemistries that are then further processed for Nd
313 separation. The method significantly reduces the workload and sample consumption for
314 common applications in low temperature geochemistry and is easy to implement between
315 different laboratories.

316 We tested the combined methodology for Nd isotope accuracy and obtained excellent results
317 compared to previously published data for Nd isotope processing alone. Future optimization
318 of our combined approach can be obtained by separation of additional elements from the
319 same samples and inclusion of a mixed Nd-Th-Pa and/or Nd-U-Th spike prior to Fe co-
320 precipitation in order to generate quantitative Nd concentration data from the same samples.

321

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5. References

- 336 Anderson, R. F., M. Q. Fleisher, L. F. Robinson, R. L. Edwards, J. A. Hoff, S. B. Moran, M.
337 R. van der Loeff, A. L. Thomas, M. Roy-Barman, and R. Francois (2012), GEOTRACES
338 intercalibration of ^{230}Th , ^{232}Th , ^{231}Pa , and prospects for ^{10}Be , *Limnol. Oceanogr.*
339 *Meth.*, **10**(4), 179–213, doi:10.4319/lom.2012.10.179.
- 340 Andreasen, R., and M. Sharma (2009), Fractionation and mixing in a thermal ionization mass
341 spectrometer source: Implications and limitations for high-precision Nd isotope analyses,
342 *Int. J. Mass Spectrom.*, **285**(1–2), 49–57, doi:10.1016/j.ijms.2009.04.004.
- 343 Auro, M. E., L. F. Robinson, A. Burke, L. I. Bradtmiller, M. Q. Fleisher, and R. F. Anderson
344 (2012), Improvements to $^{232}\text{-thorium}$, $^{230}\text{-thorium}$, and $^{231}\text{-protactinium}$ analysis in
345 seawater arising from GEOTRACES intercalibration, *Limnol. Oceanogr. Meth.*, **10**(7),
346 464–474, doi:10.4319/lom.2012.10.464.
- 347 Burke, A., and L. F. Robinson (2012), The Southern Ocean’s Role in Carbon Exchange
348 During the Last Deglaciation, *Science*, **335**(6068), 557–561,
349 doi:10.1126/science.1208163.
- 350 Charlier, B. L. A., C. Ginibre, D. Morgan, G. M. Nowell, D. G. Pearson, J. P. Davidson, and
351 C. J. Ottley (2006), Methods for the microsampling and high-precision analysis of
352 strontium and rubidium isotopes at single crystal scale for petrological and
353 geochronological applications, *Chem. Geol.*, **232**(3–4), 114–133,
354 doi:10.1016/j.chemgeo.2006.02.015.
- 355 Cheng, H., J. Adkins, R. L. Edwards, and E. A. Boyle (2000), U-Th dating of deep-sea corals,
356 *Geochim. Cosmochim. Acta*, **64**(14), 2401–2416, doi:10.1016/S0016-7037(99)00422-6.
- 357 Cohen, A. S., R. K. O’Nions, R. Siegenthaler, and W. L. Griffin (1988), Chronology of the
358 pressure-temperature history recorded by a granulite terrain, *Contr. Mineral. Petrol.*,
359 **98**(3), 303–311, doi:10.1007/BF00375181.
- 360 Copard, K., C. Colin, E. Douville, A. Freiwald, G. Gudmundsson, B. De Mol, and N. Frank
361 (2010), Nd isotopes in deep-sea corals in the North-eastern Atlantic, *Quat. Sci. Rev.*,
362 **29**(19-20), 2499–2508, doi:10.1016/j.quascirev.2010.05.025.
- 363 Crocket, K. C., M. Lambelet, T. van de Flieddt, M. Rehkämper, and L. F. Robinson (2014),
364 Measurement of fossil deep-sea coral Nd isotopic compositions and concentrations by
365 TIMS as NdO^+ , with evaluation of cleaning protocols, *Chem. Geol.*, **374–375**(0), 128–
366 140, doi:10.1016/j.chemgeo.2014.03.011.
- 367 Dulski, T. R. (1996), A Manual for the Chemical Analysis of Metals, *ASTM Manual*

368 *Series*, **25**, ASTM, West Conshohocken, PA, doi: 10.1520/MNL25-EB.

369 Edwards, R. ., J. H. Chen, and G. J. Wasserburg (1987), 238U234U230Th232Th systematics
370 and the precise measurement of time over the past 500,000 years, *Earth Planet. Sci. Lett.*,
371 **81**(2–3), 175–192, doi:10.1016/0012-821X(87)90154-3.

372 Faris, J. P., and R. F. Buchanan (1964), Anion Exchange Characteristics of the Elements in
373 Nitric Acid Medium, *Anal. Chem.*, **36**(6), 1157–1158, doi:10.1021/ac60212a067.

374 Gault-Ringold, M., and C. H. Stirling (2012), Anomalous isotopic shifts associated with
375 organic resin residues during cadmium isotopic analysis by double spike MC-ICPMS, *J.*
376 *Anal. At. Spectrom.*, **27**(3), 449–459, doi:10.1039/C2JA10360E.

377 Goldstein, S. L., and S. R. Hemming (2003), Long-lived Isotopic Tracers in Oceanography,
378 Paleooceanography, and Ice-sheet Dynamics, in *Treatise on Geochemistry*, vol. 6, edited by
379 H. Elderfield, pp. 453–489, Elsevier, Pergamon, Oxford, doi: 10.1016/B0-08-043751-
380 6/06179-X.

381 Henderson, G. M., and R. F. Anderson (2003), The U-series Toolbox for Paleooceanography,
382 *Rev. Mineral. Geochem.*, **52**(1), 493–531, doi:10.2113/0520493.

383 Hines, S. K., J. R. Southon, and J. F. Adkins (2015), A high resolution record of Southern
384 Ocean intermediate water radiocarbon over the past 30,000 years, *Earth Planet. Sci. Lett.*,
385 **432**, 46–58, doi:10.1016/j.epsl.2015.09.038.

386 Horwitz, E. P., R. Chiarizia, M. L. Dietz, H. Diamond, and D. M. Nelson (1993), Separation
387 and preconcentration of actinides from acidic media by extraction chromatography, *Anal.*
388 *Chim. Acta*, **281**(2), 361–372, doi:10.1016/0003-2670(93)85194-O.

389 Huff, E. A., and D. R. Huff (1993), TRU-Spec and RE-Spec Chromatography: Basic Studies
390 and Applications, *34th ORNL/DOE Conf. on Anal. Chem. in Energy Technology*,
391 Gatlinburg, TN.

392 Jacobsen, S. B., and G. J. Wasserburg (1980), Sm-Nd isotopic evolution of chondrites, *Earth*
393 *Planet. Sci. Lett.*, **50**(1), 139–155, doi: 10.1016/0012-821X(80)90125-9.

394 Jeandel, C., C. Venchiarutti, M. Bourquin, C. Pradoux, F. Lacan, P. van Beek, and J. Riotte
395 (2011), Single Column Sequential Extraction of Ra, Nd, Th, Pa and U from a Natural
396 Sample, *Geostand. Geoanal. Res.*, **35**(4), 449–459, doi:10.1111/j.1751-
397 908X.2010.00087.x.

398 Kraus, K. A., G. E. Moore, and F. Nelson (1956), Anion-exchange Studies. XXI. Th(IV) and
399 U(IV) in Hydrochloric Acid. Separation of Thorium, Protactinium and Uranium^{1,2}, *J. Am.*
400 *Chem. Soc.*, **78**(12), 2692–2695, doi:10.1021/ja01593a010.

401 Kraus, K. A., and F. Nelson (1958), Metal separations by anion exchange, in *Ion Exchange*
402 *and Chromatography in Analytical Chemistry*, *ASTM Special Technical Publications 195*,
403 edited by American Society for Testing and Materials, pp. 27–57, ASTM, Philadelphia.

404 Lambelet, M., T. van de Flierdt, K. Crocket, M. Rehkämper, K. Kreissig, B. Coles, M. J. A.
405 Rijkenberg, L. J. A. Gerringa, H. J. W. De Baar, and R. Steinfeldt (resubmitted after minor
406 revisions), Neodymium isotopic composition and concentration in the western North

407 Atlantic Ocean: results from the GEOTRACES GA02 section, *Geochim. Cosmochim.*
408 *Acta*.

409 Murphy, K., M. Rehkämper, K. Kreissig, B. Coles, and T. van de Flierdt (2015),
410 Improvements in Cd stable isotope analysis achieved through use of liquid-liquid
411 extraction to remove organic residues from Cd separates obtained by extraction
412 chromatography, *J. Anal. At. Spectrom.*, doi:10.1039/C5JA00115C.

413 Nelson, F., T. Murase, and K. A. Kraus (1964), Ion exchange procedures : I. Cation exchange
414 in concentration HCl and HClO₄ solutions, *J. Chromatogr. A*, **13**(0), 503–535,
415 doi:10.1016/S0021-9673(01)95146-5.

416 Pin, C., and J. S. Zalduegui (1997), Sequential separation of light rare-earth elements,
417 thorium and uranium by miniaturized extraction chromatography: Application to isotopic
418 analyses of silicate rocks, *Anal. Chim. Acta*, **339**(1–2), 79–89, doi:10.1016/S0003-
419 2670(96)00499-0.

420 Robinson, L. F., J. F. Adkins, L. D. Keigwin, J. Southon, D. P. Fernandez, S.-L. Wang, and
421 D. S. Scheirer (2005), Radiocarbon Variability in the Western North Atlantic During the
422 Last Deglaciation, *Science*, **310**(5753), 1469–1473, doi:10.1126/science.1114832.

423 Robinson, L. F., J. F. Adkins, N. Frank, A. C. Gagnon, N. G. Prouty, E. Brendan Roark, and
424 T. van de Flierdt (2014), The geochemistry of deep-sea coral skeletons: A review of vital
425 effects and applications for palaeoceanography, *Deep-Sea Res. Pt. II*, **99**(0), 184–198,
426 doi:10.1016/j.dsr2.2013.06.005.

427 SCOR Working Group (2007), GEOTRACES – An international study of the global marine
428 biogeochemical cycles of trace elements and their isotopes, *Chem. Erde – Geochem.*,
429 **67**(2), 85–131, doi:10.1016/j.chemer.2007.02.001.

430 Strelow, F. W. E. (1960), An Ion Exchange Selectivity Scale of Cations Based on
431 Equilibrium Distribution Coefficients, *Anal. Chem.*, **32**(9), 1185–1188,
432 doi:10.1021/ac60165a042.

433 Strelow, F. W. E., R. Rethemeyer, and C. J. C. Bothma (1965), Ion Exchange Selectivity
434 Scales for Cations in Nitric Acid and Sulfuric Acid Media with a Sulfonated Polystyrene
435 Resin., *Anal. Chem.*, **37**(1), 106–111, doi:10.1021/ac60220a027.

436 Tanaka, T. et al. (2000), JNdi-1: a neodymium isotopic reference in consistency with LaJolla
437 neodymium, *Chem. Geol.*, **168**(3–4), 279–281, doi:10.1016/S0009-2541(00)00198-4.

438 van de Flierdt, T., L. F. Robinson, J. F. Adkins, S. R. Hemming, und S. L. Goldstein (2006),
439 Temporal stability of the neodymium isotope signature of the Holocene to glacial North
440 Atlantic, *Paleoceanography*, **21**(4), PA4102, doi:10.1029/2006PA001294.

441 van de Flierdt, T., L. F. Robinson, and J. F. Adkins (2010), Deep-sea coral aragonite as a
442 recorder for the neodymium isotopic composition of seawater, *Geochim. Cosmochim.*
443 *Acta*, **74**(21), 6014–6032, doi:10.1016/j.gca.2010.08.001.

444 van de Flierdt, T. et al. (2012), GEOTRACES intercalibration of neodymium isotopes and
445 rare earth element concentrations in seawater and suspended particles. Part 1:

- 446 reproducibility of results for the international intercomparison, *Limnol. Oceanogr. Meth.*,
447 **10**(4), 234–251, doi:10.4319/lom.2012.10.234.
- 448 Weis, D. et al. (2006), High-precision isotopic characterization of USGS reference materials
449 by TIMS and MC-ICP-MS, *Geochem. Geophys. Geosyst.*, **7**(8), Q08006,
450 doi:10.1029/2006GC001283.
- 451 Wilson, D. J., K. C. Crocket, T. van de Flierdt, L. F. Robinson, and J. F. Adkins (2014),
452 Dynamic intermediate ocean circulation in the North Atlantic during Heinrich Stadial 1: A
453 radiocarbon and neodymium isotope perspective, *Paleoceanography*, **29**(11),
454 2014PA002674, doi:10.1002/2014PA002674.

Table 1: Neodymium isotope results for BATS seawater and a deep-sea coral reference material grouped by chemical procedure applied.

Sample	$^{143}\text{Nd}/^{144}\text{Nd}$	2SE	ϵ_{Nd}	2SE	2SD	Nd in wash fraction (ng)	Pre-chemistry Nd (ng)
Seawater samples (this study)							
KNR193-6-Th-720 (BATS 15 m)	0.512167	0.000006	-9.20	0.13	0.21	7.5	20.7
KNR193-6-Th-648 (BATS 2000 m)	0.511965	0.000007	-13.12	0.13	0.21	8.0	25.9
KNR193-6-Th-649 (BATS 2000 m)	0.511965	0.000010	-13.14	0.20	0.21	9.2	25.9
KNR193-6-Th-650 (BATS 2000 m)	0.511968	0.000008	-13.08	0.16	0.21	7.3	25.9
Seawater samples of published consensus values from 14 laboratories [van de Flierdt et al., 2012]							
GEOTRACES BATS 15 m	0.512167	0.000029	-9.19		0.57		
GEOTRACES BATS 2000 m	0.511964	0.000029	-13.14		0.57		
In-house deep-sea coral reference material (this study)							
Coral Ref 1 (U-Th fraction)	0.512337	0.000004	-5.87	0.08	0.18	26.68	29.72
Coral Ref 2 (U-Th fraction)	0.512332	0.000004	-5.97	0.07	0.18	26.64	29.81
Coral Ref 3 (U-Th fraction)	0.512336	0.000004	-5.89	0.08	0.18	26.23	29.77
Coral Ref RE spec® (n = 11)	0.512337	0.000009	-5.89		0.19		
Coral Ref AG50W-X8 (n = 9)	0.512335	0.000009	-5.90		0.18		
In-house deep-sea coral reference material [Crocket et al., 2014]							
Coral Ref (n = 13)	0.512338	0.000008	-5.86		0.16		

456 **Table 1: Neodymium isotope results for BATS seawater and a deep-sea coral reference**
457 **material grouped by chemical procedure applied.** Neodymium isotope results for Pa-Th
458 anion exchange chemistry wash fractions are based on BATS GEOTRACES Pa-Th
459 intercalibration samples (KNR193-6-Th). ‘Neodymium in wash fraction’ refers to the amount
460 of Nd in the respective anion exchange chemistry wash fractions, determined by ^{150}Nd doping
461 after collection. The pre-chemistry Nd content is estimated based on the $[\text{Nd}]_{\text{seawater}}$ at BATS
462 from *van de Flierdt et al.* [2012]. Neodymium results on our in-house coral reference
463 material, processed through combined U-Th-Nd chemistry, are listed individually (n = 3);
464 REE were isolated using cation exchange chemistry. Pre-chemistry Nd amounts were
465 determined by weighing of an aliquot of dissolved in-house coral reference material of
466 known Nd concentration. Results for in-house coral reference material are grouped according
467 to chemical procedures applied, i.e. RE spec® chemistry (n = 11) and cation exchange
468 chemistry with Biorad® AG50W-X8 resin (n = 9). All in-house coral reference material
469 aliquots were taken from the original solution prepared from homogenized deep-sea coral
470 powder by *Crocket et al.* [2014]. Literature GEOTRACES and coral reference material data
471 taken from *van de Flierdt et al.* [2012] and *Crocket et al.* [2014]. 2SE is the analytical 2σ
472 standard error. 2SE for Nd concentrations is ≤ 0.005 . 2SD is the external long term 2σ
473 standard deviation. Seawater results from this study are shown with the 2SD obtained from
474 repeated analyses of BCR-2 rock reference material (see section 2.5). In the case of the

475 GEOTRACES BATS results, 2SD represents the 2σ standard deviation of the 14 laboratories
476 involved in the respective measurements [*van de Flierdt et al.*, 2012].

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Figure 1: Working scheme of combined Pa-Th-Nd and U-Th-Nd chemical procedures towards Nd isotope analyses.

480 **Figure 1: Working scheme of combined Pa-Th-Nd and U-Th-Nd chemical procedures**
481 **towards Nd isotope analyses.** Purified U, Pa and Th fractions were analyzed by MC-ICP-
482 MS [*Anderson et al.*, 2012; *Auro et al.*, 2012; *Hines et al.*, 2015]. Note that some laboratories
483 apply a second Th purification step during U-Th separation [cf. *Burke and Robinson*, 2012].
484 It is also noted that isotopic spiking is not yet tested for the combined method in seawater and
485 corals. It has however successfully been achieved for combined Pa-Th-Nd chemistry of
486 marine particulate samples (Kretschmer, Lambelet et al., pers. comm.). Finally, our preferred
487 method for REE separation after Fe co-precipitation and actinide extraction is the traditional
488 cation exchange chemistry, as the application of strong oxidizing agents to combat leaking
489 organics from such resins can be avoided [e.g., *Lambelet et al.*, submitted].

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Figure 2: Neodymium isotope results obtained for wash fractions from anion exchange chemistry further processed for Nd separation on GEOTRACES BATS seawater Pa-Th intercalibration samples.

492 **Figure 2: Neodymium isotope results obtained for wash fractions from anion exchange**
493 **chemistry further processed for Nd separation on GEOTRACES BATS seawater Pa-Th**
494 **intercalibration samples.** Data are presented as $\Delta\epsilon_{Nd}$ deviation from GEOTRACES Nd
495 intercalibration results from 14 laboratories (dashed line) [*van de Flierdt et al.*, 2012].
496 Numbers represent consensus values and the grey shading indicates the 2SD.

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Figure 3: In-house coral reference material Nd isotope analyses of sample loads containing 10 and 30 ng Nd, measured over a period of 26 months.

500 **Figure 3: In-house coral reference material Nd isotope analyses of sample loads**
501 **containing 10 and 30 ng Nd, measured over a period of 26 months.** Error bars of
502 individual measurements are given as internal 2SE. Sample loads containing 10 ng of Nd are
503 indicated by white symbols with black outline. The first 20 results (diamonds and squares)
504 were obtained for samples processed through Nd isotope chemistry only, using Eichrom RE
505 spec[®] resin (with and without addition of ascorbic acid) and cation exchange chemistry,
506 respectively, to isolate REE from the sample matrix. Black circles mark results obtained by
507 processing the same coral reference material through Fe co-precipitation and U-Th anion
508 exchange chemistry followed by Nd isotope separation (i.e. the combined method). The long
509 term average of all results is $^{143}\text{Nd}/^{144}\text{Nd} = 0.512336 \pm 0.000009$ (n = 23) and the grey
510 shading marks the 2SD. The grey triangle marks the results previously published by *Crocket*
511 *et al.* [2014] on the same in-house coral reference material.