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Published in: Chemical Geology
Publication date: 2014

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Measurement of fossil deep-sea coral Nd isotopic compositions and concentrations by TIMS as NdO⁺, with evaluation of cleaning protocols

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Abstract

Precise and accurate measurements of Nd concentrations and isotopic compositions of small sample masses (≤30 ng Nd) are increasingly necessary in the geosciences. Here, we present a combined chemical separation and TIMS (thermal ionisation mass spectrometry) NdO⁺ method adapted for fossil deep-sea corals, which represents a significant improvement in precision compared to existing methods, with additional assessment of potential contamination of coral aragonite by external encrustations. After digesting and spiking samples, we purified sample Nd using RE and Ln-spec separation chemistries, and tested the efficiency of these on aliquots of USGS BCR-2. In addition, we prepared a matrix-matched in-house coral reference material to monitor the analytical precision on coral carbonate. Using a micro-loading technique and TaF₅ activator on single W filaments, ion beam sizes of up to 0.60 V per ng on mass 160 are achievable, but decline with increasing age of the activator. The long-term average for NdO⁺ measurements of 5 ng and 15 ng loads of the pure metal oxide JNd-1 reference material (Geological Survey of Japan) was 0.512106 ± 6 for 143Nd/144Nd (12 ppm 2RSD, n = 44), with an overall deviation from the reference value of 17 ppm (0.512115 ± 7; Tanaka et al., 2000). BCR-2 aliquots of 10 ng and 30 ng generated an average 143Nd/144Nd of 0.512643 ± 8 (16 ppm 2RSD, n = 14), which is identical within uncertainty to the reference value (0.512637 ± 12; Weis et al., 2006). Very similar external reproducibility was obtained on 10 ng and 30 ng aliquots of the in-house coral standard, with an average 143Nd/144Nd of 0.512338 ± 8 (16 ppm 2RSD, n = 13). Precision and accuracy of Nd oxide measurements depend on well-characterised oxygen isotopic compositions over the range of measurement temperatures, and very small amounts of Ce and Pr in final chemistry cuts. Whilst the former is laboratory-specific, and can be determined precisely using a column-purified 150Nd spike (e.g. 13O/16O = 0.000390 ± 3 and 18O/16O = 0.000207 ± 8 for this study; n = 12), our method shows that interference corrections for Ce and Pr are tolerable up to higher values than previously reported (e.g. 156/160 ratios ≤ 0.148 and 157/160 ratios ≤ 0.68). In reality, however, our separation was always better than this.

An important issue with fossil corals concerns their apparently higher Nd concentrations compared to modern counterparts (~7–310 ppb vs. ~3–51 ppb respectively). Variable to high Nd concentrations could arise for a number of reasons, but here we focus solely on evaluating the effectiveness of coral cleaning to remove external, Nd-rich encrustations. To test this, we measured major and trace metal concentrations (Ca, Fe, Mn, Ti, Al, Ce, Nd, Th, U) in paired aragonite and FeMn coatings from the same samples. Mass balance calculations reveal negligible influence of FeMn coatings on the final εNd, although four samples showed some degree of contamination as demonstrated by elevated Fe, Mn, Ti and Th concentrations.

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1. Introduction

Neodymium isotopes are an invaluable palaeoceanographic proxy with which to reconstruct past ocean circulation (see van de Flierdt and Frank, 2010, and publications therein). Surrounding continents lend their Nd isotopic composition to regionally forming deep waters (see Lacan et al., 2012, and references therein), allowing these water masses to be differentiated and tracked on the scale of individual ocean basins due to a Nd ocean residence time of ~300 to 1000 years (Tachikawa et al., 2003; Siddall et al., 2008; Arrouzet et al., 2009).

Among marine archives used to reconstruct past seawater Nd isotopic compositions, deep-sea scleractinian corals are a relatively recent addition (van de Flierdt et al., 2006). They are dateable by both U/Th and radiocarbon techniques (Adkins et al., 2002), and preserve ambient seawater Nd isotopic composition without fractionation (van de Flierdt et al., 2010). Their depth habitats, from shallow to ~2500 m, make them especially useful for capturing change at the intermediate/deep
ocean boundary (Robinson et al., 2005). However, the typically low Nd concentrations extracted from modern deep-sea corals (~3 to 51 ppb Nd; Copard et al., 2010; van de Flierdt et al., 2010) mean that the measurement of their Nd isotopic composition is challenging. A further constraint is the precision needed to differentiate between water masses on the basis of their Nd isotopic compositions. The latter are commonly expressed as $\delta^{143}Nd$ values, which denote the relative deviation of the radiogenic $^{143}Nd$/$^{144}Nd$ ratio for a sample from the chondritic uniform reservoir (CHUR) in parts per $10^4$ (CHUR $= 0.512638$; Jacobsen and Wasserburg, 1980). Although Atlantic seawater $^{143}Nd$ spans a total of ~11 units (Lacan et al., 2012), including glacial/interglacial changes, detection of more subtle variations on a regional scale makes a precision of $\leq 0.3$ $\delta^{143}Nd$ units desirable (2SD).

The focus of this paper is to document our method to measure accurately and precisely the Nd isotopic compositions in the aragonitic skeletons of deep-sea scleractinian corals. This method can also be transferred to other low abundance Nd sample types, such as seawater (Pahnke et al., 2012; van de Flierdt et al., 2012). Currently the most viable technique for isotopic measurement of small Nds masses (i.e. $<30$ ng) is by thermal ionisation mass spectrometry (TIMS) as NdO$^+\,$, the ionisation efficiency of which is superior to that of Nd$^+$. This approach allows the measurement of ng masses of Nd with accuracies similar to that of 100s ng of Nd measured as Nd$^+\,$ (Thirlwall, 1991). Despite the greater ease of ionisation, the use of the NdO$^+$ technique has been limited by long data acquisition times, the requirement for efficient separation of Nd from other REE, and for well-characterised oxygen isotope ratios. The advent of higher performance TIMS has led to a revival of the NdO$^+$ technique, with a number of new approaches recently published (Li et al., 2007; Chu et al., 2009; Harvey and Baxter, 2009). However, to minimise error magnification, there are still stringent and non-trivial requirements for efficient chemical separation of Nd from other REE and characterisation of $^{143}O$/$^{18}O$ and $^{17}O$/$^{16}O$ for use in interference corrections.

This contribution describes the chemical separation of Nd from a coral carbonate matrix and Nd isotopic measurements on $\leq 30$ ng Nd with sub-10 ppm internal precision (2RSD; relative standard error) and sub-20 ppm external reproducibility (2RSD; relative standard deviation). The physical and chemical cleaning procedures of corals prior to this are described in detail elsewhere (Shen and Boyle, 1988; Lomitschka et al., 1997; Cheng et al., 2000; van de Flierdt et al., 2010). Given that both the analytical techniques and rigorous cleaning are paramount to obtaining a pristine coralline aragonite fraction for the ionisation efficient separation of Nd from other REE, and for well-characterised oxygen isotope ratios. The advent of higher performance TIMS has led to a revival of the NdO$^+$ technique, with a number of new approaches recently published (Li et al., 2007; Chu et al., 2009; Harvey and Baxter, 2009). However, to minimise error magnification, there are still stringent and non-trivial requirements for efficient chemical separation of Nd from other REE and characterisation of $^{143}O$/$^{18}O$ and $^{17}O$/$^{16}O$ for use in interference corrections.

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2. Samples

Corals from the New England Seamounts (30) and the Mid-Atlantic Ridge (8) in the North Atlantic, at water depths of 1125 to 2820 m, were sub-sampled from a collection held at California Institute of Technology. Most samples were of the species Desmophyllum dianthus, with a few Solenosmilia variabilis, Caryophylliaambrosia, and Platyphyllum pubescent. All have been previously dated by U/Th methods, with ages spanning 0.3 ka to 25 ka (Adkins et al., 1998; Adkins and Boyle, 1999; Robinson et al., 2005; Eltgroth et al., 2006; Robinson et al., 2006; van de Flierdt et al., 2006; Robinson et al., 2007). Thirty one samples were processed individually (singles), and the remaining seven were split into two or three sections (transects). Where present, external FeMn coatings were scraped off the coralline aragonite and collected for analysis of trace metal concentrations (18 corals), of which 15 were further processed for Nd isotopic compositions.

3. Methods

3.1. Chemistry

Sample preparation was performed in Class 10 laminar flow hoods in the Class 1000 MAGIC Clean Room Laboratory at Imperial College London (UK). Speciﬁx Teflon vials and puriﬁed water from a Millipore Mili-Q Element system (resistance $>18.2$ MΩ; hereafter abbreviated as MQ) were employed throughout this study. Acids were either Optima grade (HF and H$_3$PO$_4$, Fisher Scientiﬁc) or Analar grade HNO$_3$ (15.4 M) and HCl (6 M) puriﬁed in-house by sub-boiling distillation in quartz stills.

3.1.1. Coral cleaning

Individual or multiple coral septa (~0.5 to 1.0 g sample mass) were cleaned following an adapted procedure described in van de Flierdt et al. (2010), which built on the work of Cheng et al. (2000), Lomitschka and Mangini (1999) and Shen and Boyle (1988). Briefly, this involved extensive physical cleaning by diamond blade drilling, with additional sand blasting, to remove FeMn coatings and detrital sediment from both the exterior and any interior cavities. Discoloured patches within the aragonite skeleton were removed where present. Chemical cleaning was carried out in several repeated oxidative/reductive steps, with ﬁnal leaching in EDTA followed by dilute nitric acid to ensure removal of adsorbed trace metals.

3.1.2. FeMn coating digestion

The FeMn coatings on the exterior of corals were collected by scalpel during the ﬁrst stage of physical cleaning. They represent a mix of mostly FeMn oxyhydroxides as well as adhered detrital sediment, Fe biominerals, secondary carbonate minerals and small ﬂakes of coral aragonite (van de Flierdt et al., 2010; Anagnostou et al., 2011). To ensure full digestion of all components, the external crust material was ﬁrst ﬂushed in aqua regia, followed by a second digestion phase using an HF:HNO$_3$ mix (4:1) with 3 days ﬂuxing on the hotplate, after which samples were taken to dryness at 120 °C, converted to nitrate to ensure complete removal of ﬂuorides, and taken up in 6 M HCl.

3.1.3. Coral digestion

Sample material was digested in 8 M HNO$_3$, dried, and ﬂushed in aqua regia at high temperature (180–210 °C) to destroy organic compounds. After conversion to nitrate, coral samples were taken up in a volume of 1.5 M HNO$_3$ suﬃcient to digest the carbonate mass on a mole per mole basis $+ 5\%$ excess acid. Aliquots of each coral sample were spiked with $^{150}$Nd (97.8% purity) in a targeted – 1.65:1 ratio of sample $^{149}$Nd to spike $^{150}$Nd to minimise error magnification on the resulting Nd concentration calculation, with the assumption that the sample mass was between 3 and 100 ng Nd. After equilibration, the coral sample aliquots were processed through chemistry. In practice, the aliquots represented between 60 mg and 600 mg cleaned coral, with an average of ~300 mg. The remaining coral sample solution served as a duplicate for later processing and for major and trace metal analysis.

3.1.4. In-house coral reference material

An in-house coral standard was prepared using 20 g of mixed D. dianthus corals collected from the Southern Ocean. The physical cleaning was less exhaustive than for actual samples in that no drilling was involved. To compensate, quartz sand blasting was more intensive because sample loss was not an issue. The chemical cleaning followed the same procedures as for actual samples (van de Flierdt et al., 2010). The cleaned coral material was crushed in an agate mill, and the powdered coral rolled for several days to achieve complete homogenisation. Thereafter, digestion followed the same procedure as described above and a 39.1 ng/g Nd stock solution was prepared in concentrated HNO$_3$. 

$^{150}$Nd from other REE and characterisation of $^{18}O$/$^{16}O$ and $^{17}O$/$^{16}O$ for use in interference corrections.
3.1.5. Rock standard digestion

Between 53 and 133 mg of powdered USGS BCR-2 was weighed into each of four vials and dissolved using a HF-HNO₃ mix (4:1). Samples were heated in Teflon vials at 120 °C for 3 days, and taken to dryness at 120 °C. Following conversion to nitrate to ensure complete removal of fluorides, the four BCR-2 digestions were each taken up in 3 ml 6 M HCl to serve as a stock solution and varied in concentration between 0.49 and 1.25 μg/g Nd.

3.1.6. Column chemistry

The procedure for Nd purification from a carbonate matrix required two stages (Table 1), first to separate REE from the sample matrix and second to purify Nd from the other REE. The columns used in both steps were Savillex Teflon (3.2 mm id, 4 cm length, ~0.32 cm³ resin bed volume; Table 1).

The first step employed Eichrom RE resin (100–150 μm bead size). Prior to use, the RE resin was cleaned in cycles of dilute acid followed by MQ, and finally stored in MQ. The columns were cleaned by passing 6 M HCl and MQ. The resin was loaded and further cleaned with 2 ml each of 4 M HCl and MQ before conditioning with 2 ml 1.5 M HNO₃. The digested coral solution was directly loaded on to the RE columns in variable volumes of 1.5 M HNO₃ (0.5 ml to 8 ml), depending on sample mass. Capacity testing of the RE columns determined a maximum carbonate sample size of 0.8 g, in practice, sample mass sizes were ≤0.6 g after physical and chemical cleaning. The matrix was eluted in 4 ml 1.5 M HNO₃ and the REE fraction collected in 4 ml 4 M HCl. The REE fraction was dried at 120 °C and taken up in 0.2 ml 0.142 M HCl for analyses.

Nd was eluted in a total of 8.35 ml 0.142 M HCl followed by sample Nd collection (3.5 ml 0.142 M HCl). The Ln fraction was dried at 120 °C and taken up in 0.2 ml 0.142 M HCl for further analyses.

Table 1

<table>
<thead>
<tr>
<th>Column chemistry for REE purification and Nd separation.</th>
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<tbody>
<tr>
<td><strong>Column dimensions for both RE and Ln column chemistry</strong></td>
</tr>
<tr>
<td>Internal diameter</td>
</tr>
<tr>
<td>Capillary length</td>
</tr>
<tr>
<td>Resin bed volume</td>
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<tr>
<td><strong>REE purification</strong></td>
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<td>Resin loading</td>
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<tr>
<td>Clearing</td>
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<tr>
<td>Conditioning</td>
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<tr>
<td>Sample loading</td>
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<tr>
<td>Matrix elution</td>
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<tr>
<td><strong>Nd separation from other REE</strong></td>
</tr>
<tr>
<td>Resin loading</td>
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<tr>
<td>Clearing</td>
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<tr>
<td>Conditioning</td>
</tr>
<tr>
<td>Sample loading</td>
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<tr>
<td>Ce and Pr elution</td>
</tr>
<tr>
<td>Nd elution</td>
</tr>
</tbody>
</table>

The measurement of Nd isotopes as NdO⁺ has more stringent Nd purification requirements than measurement as Nd⁺ because of the larger number of molecular interferences generated by the different oxygen isotope combinations. Oxidising the sample aliquot to ~1.5 days. Assuming a perfectly symmetrical Nd elution curve, the Ln calibration resulted in a loss of ~25% of sample Nd. In practice, spiked samples demonstrated the Ln chemistry resulted in ~30 to 50% loss of sample Nd. The presence of Sm was not detected in any of the Nd cuts obtained from the column chemistry processed aliquots.

Subsequent tests to investigate the variability of Ln chemistry yields highlighted that organic compounds from the RE resin were affecting yields (Gault-Ringold and Stirling, 2012). Oxidising the sample aliquot between the RE and Ln chemistries solved this problem. Of the four oxidants tested (aqua regia, sulphuric acid, hydrogen peroxide, perchloric acid), perchloric acid was the most efficient at removing the organic compounds and decreasing the Nd loss to ~40%.

3.2. Thermal ionisation mass spectrometry

Sample data were collected over a 6 month period on a ThermoFinnigan Triton TIMS instrument in the MAGIC Laboratories, Department of Earth Science and Engineering, Imperial College London (UK).

3.2.1. Filament loading

Various loading techniques and activators were tested on ribbons of both W (0.025 mm thick, 0.51 mm wide, 99.95% pure) and Re (0.03 mm thick, 0.76 mm wide and 99.999% pure), sourced from H. Cross Company. Silica gel + H₃PO₄ on single Re filaments (Thirwall, 1991) and single W filaments (Li et al., 2007), and TaF₅ + 2.5 M HCl on single W filaments (Chu et al., 2009) were tested, with and without high purity bottled O₂. Sample loading techniques using pipettors vs. microsyringes were also compared. The most favourable loading method and emitter for coral matrix samples in terms of beam intensity, accuracy and precision, was microloading on single W filaments using TaF₅ + 2.5 M HCl. The activator and sample aliquot were loaded sandwich style in small increments: 0.5 μl TaF₅ activator was loaded first on a degassed W filament with the current set at 0.9 A, followed by similar loading of the sample in 0.5 μl 2.5 M HCl and by another 0.5 μl TaF₅. The current was then increased until ~2 A to fully dry the sample on the filament. Notably the current was not increased until the filament glowed red, which we found to be detrimental to beam intensity. The TaF₅ solution was prepared according to Chu et al. (2009) and purified following Charlier et al. (2006). The Nd blank in the combined single W filament and 1 μl TaF₅ emitter was ~0.1 pg.

3.2.2. Oxygen isotope ratios

A single aliquot of 100 ng ¹⁵⁰Nd spike was processed through chemistry to ensure removal of trace Sm, and loaded on 12 single, degassed W filaments as described above. The cups were configured to calculate the oxygen isotope ratio with ¹⁵⁰Nd¹⁸O in centre cup, and ¹⁵⁴Sm¹⁸O in H₄ to monitor for the presence of Sm (Table A.1). In cup L1, ¹⁴⁷Nd¹⁷O was monitored to calculate the interference of ¹⁴⁴Nd¹⁸O on ¹⁵⁰Nd¹⁸O. The oxygen isotope ratios were calculated from the beam intensities measured in centre cup, H1 and H2. The filaments were run at variable temperature (1450 °C to 1640 °C), currents (2300 mA to 5 pg).
2610 mA, and intensities (0.3 V to 44 V) to mimic conditions during sample measurements. The subsequent measured oxygen isotopic compositions used in data reduction are 0.000390 ± 3 for $^{17}$O/$^{16}$O and 0.002073 ± 8 for $^{18}$O/$^{16}$O (2SD, n = 12; Fig. A.1, Table A.2).

3.2.3. NdO$^+$ measurements
Filaments were pre-heated at 60 mA/min until 980 °C, and then left for 30 min at this temperature. Filaments were then further heated at 60 mA/min until ~1250 °C, when the SEM was used to find and tune the beam. All filaments were peak centred on mass 160 (centre cup) when beam intensity reached ~20 mV, and again prior to measurement. Tuning was carried out at beam intensities of ~2, 20, and 200 mV and prior to measurement. Measurement generally started at ~1500 °C. Data were collected in 9 blocks, each consisting of 20 integration cycles of 8.4 s. Peak centre and lens autofocus routines were carried out at the start of each filament measurement. Between blocks, amplifier-Faraday cup connections were sequentially rotated to eliminate gain biases and associated uncertainties, and baselines were carried out. The chamber pressure was monitored in the ion source and did not exceed 1.2e−7 mbar. The measurement time was ~45 min.

Beam intensities obtained for pure metal standards and column processed aliquots of BCR-2 and the in-house coral standard were given the relatively low measured intensity on cup L4 and the efficiency (age) of the activator filament measurement. Between blocks, amplifier-Faraday cup connections were sequentially rotated to eliminate gain biases and associated uncertainties, and baselines were carried out. The chamber pressure was monitored in the ion source and did not exceed 1.2e−7 mbar. The measurement time was ~45 min.

Beam intensities obtained for pure metal standards and column processed aliquots of BCR-2 and the in-house coral standard were variable, and depended greatly on the efficiency (age) of the activator and success at micro-loading. The range of intensities for pure metal standard JNd-1 was ~0.13 to 0.60 V per ng mass 160 (centre cup), and success at micro-loading. The range of intensities for pure metal standards and column processed aliquots of BCR-2 and the in-house coral standard were ~0.13 to 0.60 V per ng on mass 160 (centre cup), and success at micro-loading. The range of intensities for pure metal standards and column processed aliquots of BCR-2 and the in-house coral standard were given the relatively low measured intensity on cup L4 and the efficiency (age) of the activator filament measurement. Between blocks, amplifier-Faraday cup connections were sequentially rotated to eliminate gain biases and associated uncertainties, and baselines were carried out. The chamber pressure was monitored in the ion source and did not exceed 1.2e−7 mbar. The measurement time was ~45 min.

3.2.4. Interference and mass bias corrections
Major oxide masses between 156 ($^{140}$Ce$^{16}$O) and 166 ($^{156}$Nd$^{16}$O) were collected in a single, static multicollection sequence, with the exception of 161 ($^{145}$Nd$^{16}$O; Table 2). Molecular interference corrections were made by up-mass stripping from a starting assumption that the beam intensity on mass 156 (cup L4) was attributable to $^{140}$Ce$^{16}$O, and that contributions from LaO$^+$, BaO$^+$ and BaF$^+$ were insignificant given the relatively low measured intensity on cup L4 and the efficiency of the described column chemistry at excluding these elements from the Nd sample fraction. Masses 156 ($^{146}$Ce$^{16}$O) and 157 ($^{141}$Pr$^{16}$O) were monitored to allow correction for CeO interferences on masses 157 to 160, and PrO interferences on masses 158 and 159. The most critical interference is from Sm due to the dominant oxide ($^{144}$Sm$^{16}$O) interference on $^{144}$Nd$^{16}$O. Even though the Sm interference correction was ultimately trivial given the good separation of Nd from Sm during Ln column chemistry, we included mass 163 ($^{147}$Sm$^{16}$O) in the cup configuration to monitor and potentially correct for the presence of Sm. The need to correct for $^{145}$NdO interferences on masses 162 and 163 required calculating a value for $^{145}$Nd$^{16}$O, which we based on the interference-corrected value of $^{142}$Nd$^{16}$O and a $^{145}$Nd/$^{142}$Nd ratio of 0.305123 (Andreasen and Sharma, 2006).

Data reduction was carried out offline by cycle by cycle, starting with interference corrections, followed by subtraction of the spike contribution (where necessary), and finally mass bias correction using the exponential law, in line with recommendations for measurement of small Nd masses as NdO$^+$ (Wasserburg et al., 1981; Thirlwall, 1991; Li et al., 2007) by normalisation to $^{146}$Nd/$^{144}$Nd = 0.7219 in the case of unspiked samples. For spiked samples, a slightly higher value of $^{146}$Nd$^{16}$O and $^{145}$Nd$^{16}$O derived iteratively based on the sample + spike mixture) was chosen for mass bias correction and an error magnification factor was calculated.

### Table 2
Cup configuration for NdO$^+$ measurement in static mode, and the molecular interferences present on each cup. Oxides that are unlikely to be present, or at insignificant intensities, are italicised.

<table>
<thead>
<tr>
<th>Cup</th>
<th>L4</th>
<th>L3</th>
<th>L2</th>
<th>L1</th>
<th>C</th>
<th>H1</th>
<th>H2</th>
<th>H3</th>
<th>H4</th>
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<tbody>
<tr>
<td>Oxide mass</td>
<td>156</td>
<td>157</td>
<td>158</td>
<td>159</td>
<td>160</td>
<td>162</td>
<td>163</td>
<td>164</td>
<td>166</td>
</tr>
<tr>
<td>Metal mass</td>
<td>140</td>
<td>141</td>
<td>142</td>
<td>143</td>
<td>144</td>
<td>146</td>
<td>147</td>
<td>148</td>
<td>150</td>
</tr>
<tr>
<td>Isotopes</td>
<td>$^{140}$Ce$^{16}$O</td>
<td>$^{141}$Pr$^{16}$O</td>
<td>$^{142}$Nd$^{16}$O</td>
<td>$^{143}$Nd$^{16}$O</td>
<td>$^{144}$Nd$^{16}$O</td>
<td>$^{145}$Nd$^{16}$O</td>
<td>$^{146}$Nd$^{16}$O</td>
<td>$^{147}$Sm$^{16}$O</td>
<td>$^{148}$Nd$^{16}$O</td>
</tr>
<tr>
<td>Interferences</td>
<td>$^{138}$La$^{17}$O</td>
<td>$^{140}$Ce$^{17}$O</td>
<td>$^{141}$Pr$^{17}$O</td>
<td>$^{142}$Nd$^{17}$O</td>
<td>$^{143}$Nd$^{17}$O</td>
<td>$^{145}$Nd$^{17}$O</td>
<td>$^{146}$Nd$^{17}$O</td>
<td>$^{147}$Sm$^{17}$O</td>
<td>$^{148}$Nd$^{17}$O</td>
</tr>
</tbody>
</table>

Fig. 1. Elution curves for Ce, Pr and Nd using ~320 μl Ln resin (20–50 μm) and 0.142 M HCl. The fraction eluted to waste and that collected for Nd, from 8.35 ml onwards, is indicated by shading. See Table 1 for details of resin and column dimensions.

Fig. 2. The internal precision (2RSE ppm) for the corrected $^{146}$Nd/$^{144}$Nd ratio vs. $^{146}$Nd$^{16}$O intensity (V) for measurements of JNd-1 (5 ng and 15 ng Nd), USGS BCR-2 and the in-house coral standard (both 10 ng and 30 ng Nd).
3.3. Single-collector magnetic sector inductively coupled plasma mass spectrometry

To assess potential contamination of fully cleaned coral samples, major and trace metal concentrations (La, Ce, Pr, Nd, Th, U, Al, Ca, Mn, Ti, Fe) were measured over the course of two analytical sessions on 35 coral solutions (singles and individual transect segments) and 18 of the corresponding FeMn coatings, using a ThermoFinnigan Element2 Single-Collector Magnetic Sector Inductively Coupled Plasma Mass Spectrometer at the Bristol Isotope Group, School of Earth Sciences, University of Bristol (UK). The results are presented in Table A.4.

Concentrations of major and trace elements were calculated using the in-house elemental standard and the U + Th ICP standard CCS-1 from Inorganic Ventures) between blocks of six samples. Concentrations of major and trace elements were calculated using the in-house elemental standard and concentrations of U and Th using CCS-1. Standard CCS-1 was gravimetrically diluted to a concentration of 0.1 ppb U and Th to approximate coral sample Th concentrations. The in-house artificial elemental standard had higher concentrations per element (a few ppm for major elements, a few ppb for trace elements). Cross calibration between the in-house multi-element standard and CCS-1 was done by comparison of Ce, Nd, U and Th concentrations in the secondary consistency standards, BCR-2 and CRM river water standard SLRS-5 (NRC-Canada), which deviated by <10%.

External reproducibility, determined by replicate analysis of SLRS-5 and BCR-2, ranged from 0.7 to 4% RSD for most analytes (Table A.5). Compositions deviate from certified reference values by ≤12%, with most showing a <5% deviation, and are thus in good agreement. Aliquots of the in-house coral standard were also measured, for which reproducibility was mostly <6% (1 RSD; Table A.5). Major element sample/blank intensity ratios were >40. However, for the trace metals or those typically associated with contaminant sources (e.g. Al, Ti, Fe, Mn), coral samples often had intensities indistinguishable from that of the blanks. These samples are listed as <LOD in Appendix Table A.4. Coral Nd concentrations obtained by analysis on the element (n = 37) were also compared to 156Nd isotope dilution measurements obtained by TIMS analysis, and found to differ by ≤27% (n = 35) relative to the spiked measurements, but generally ≤12% (n = 24). Two particularly low intensity concentration samples deviated from the 156Nd spiked concentration values by +43 and +87.

4. Results and discussion

4.1. Methodology

4.1.1. Oxygen isotope ratios

The oxygen isotope ratios are constants required for data reduction, to convert the measured Nd oxide ion beam ratios to Nd isotope compositions. The range of oxygen isotope ratios published by other workers using the NdO+ technique (Fig. 4, Table A.6) shows a total variation of 7.2% (18O/16O) and 8.1% (17O/16O), and is large enough to influence oxygen isotope corrections on NdO+ isotope ratios. For example, replacing our oxygen isotope ratios in the data reduction calculations with those showing the largest difference to our values (i.e. Nyquist in Wasserburg et al., 1981; Table A.2) worsens the external precision on corrected BCR-2 values considerably, from 1 ppm 2RSD to 65 ppm 2RSD (see Section 4.1.3). To accurately and precisely determine 143Nd/144Nd ratios, it is therefore necessary to determine laboratory specific oxygen isotope ratios prior to sample analysis (Wasserburg et al., 1981; Thirlwall, 1991; Griselin et al., 2001; Harvey and Baxter, 2009).

Factors that influence oxygen isotopic compositions during sample measurement are the source of oxygen, which is dependent on activator type, volume, and loading technique, and the extent of isotope fractionation on the filament, influenced by filament metal and running temperature (Griselin et al., 2001; Li et al., 2007). Overall, it is recommended that the conditions of sample NdO+ measurement are replicated when measuring the oxygen isotope ratios (Griselin et al., 2001).

Two common approaches to measuring oxygen isotope ratios involve the use of a high purity 141Pr solution or a Nd spike, combined with the relevant filament type, activator, and loading technique. We opted for a 156Nd spike on the basis that Griselin et al. (2001) found differences between the ratios obtained by 141Pr compared to 156Nd, which may have been due to small La, Ce or Nd impurities in the Pr solution. Harvey and Baxter (2009) found little difference between oxygen isotope ratios obtained by either 157Pr or 156Nd on Re filaments, with shifts in the final 143Nd/144Nd ratio within the long term uncertainty of the measurements. However, from published oxygen isotope ratios (Table A.6), greater scatter is observed in those obtained using 141Pr compared to 156Nd (Fig. 4).

In this study, we observed an increase of 0.6% between minimum and maximum 18O/16O values over a temperature range of 209 °C, not dissimilar to the 1.2% increase in 18O/16O over 150 °C using W filaments observed by Griselin et al. (2001). Although the 18O/16O ratios show a marked shift at temperatures >1580 °C (Fig. A.1, Table A2), this should not influence standard and sample filaments, which were run –1480 to 1570 °C. The corrected 143Nd/144Nd ratios on JNd-1 filaments of
Results of turret averages based on 5 individual JNdi-1 runs per turret (n = 9). Loads were either 15 ng (single corals) or 5 ng (transects). The $^{143}\text{Nd}/^{144}\text{Nd}$ reference value is from Tanaka et al. (2000). The overall mean + 2SD value is calculated on the basis of 44 individual JNdi-1 runs (Table A.3), and not the averages per turret.

<table>
<thead>
<tr>
<th>$^{144}\text{Nd}/^{146}\text{Nd}$</th>
<th>2SD</th>
<th>$^{143}\text{Nd}/^{144}\text{Nd}$</th>
<th>2SD</th>
<th>$^{148}\text{Nd}/^{144}\text{Nd}$</th>
<th>2SD</th>
<th>$^{150}\text{Nd}/^{144}\text{Nd}$</th>
<th>2SD</th>
<th>Turret 2 RSD (ppm)</th>
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<td>Mean + 2SD</td>
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<td>0.000022</td>
<td>0.512106</td>
<td>0.000006</td>
<td>0.241574</td>
<td>0.236448</td>
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</tr>
</tbody>
</table>

- **15 ng JNdi-1 loads**
  - 19 loads: 19 samples, 12 of which met the threshold criteria for further analysis. The overall mean + 2SD value is 1.141849, with a 2SD of 0.000022.
  - The corrected $^{143}\text{Nd}/^{144}\text{Nd}$ ratio is 0.512106, with a 2SD of 0.000006.
  - The corrected $^{148}\text{Nd}/^{144}\text{Nd}$ ratio is 0.241574, with a 2SD of 0.000003.
  - The corrected $^{150}\text{Nd}/^{144}\text{Nd}$ ratio is 0.236448, with a 2SD of 0.000004.

- **5 ng JNdi-1 loads**
  - 14 loads: 14 samples, 9 of which met the threshold criteria for further analysis. The overall mean + 2SD value is 1.141854, with a 2SD of 0.000021.
  - The corrected $^{143}\text{Nd}/^{144}\text{Nd}$ ratio is 0.512107, with a 2SD of 0.000007.
  - The corrected $^{148}\text{Nd}/^{144}\text{Nd}$ ratio is 0.241575, with a 2SD of 0.000003.
  - The corrected $^{150}\text{Nd}/^{144}\text{Nd}$ ratio is 0.236451, with a 2SD of 0.000006.

---

### 4.1.2. Molecular interference corrections

Threshold levels of Ce and Pr impurities in sample Nd have previously been recommended as 0.00035 and 0.020 for raw ratios of $^{156}/^{160}$ and $^{157}/^{160}$ respectively to avoid significant contributions to the reduced data (Thirlwall, 1991). Low measured intensities on masses 156 and 157 also ensure that interferences from BaF$^+$, LaO$^+$ and HREE are insignificant. In this study, the separation of Nd from Ce and Pr by the Ln column chemistry for both corals and international rock standards resulted in higher ratios than recommended by Thirlwall (1991). To ensure that these ratios were not detrimental to the final reduced data, we tested the limitations of the interference corrections by running JNdi-1 Nd doped with Ce (5 ng Nd + 2.5 ng Ce), and BCR-2 aliquots processed through the full chemical separation (RE + Ln columns) as per coral samples.

For the Ce-doped JNdi-1, we found that the combined interference and mass bias corrections yielded an accurate $^{143}\text{Nd}/^{144}\text{Nd}$ ratio (i.e., within 2SD of the long-term average) as long as the raw $^{156}/^{160}$ (140Ce$^{16}$O/$^{144}\text{Nd}^{16}$O) ratio was below 0.148 (Fig. 5). In reality, the raw $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were not detrimental to the precision of the corrected $^{143}\text{Nd}/^{144}\text{Nd}$ ratios is detectable, the external precision of which was similar (16 ppm, 2RSD) to that of the BCR-2 data.

### 4.1.3. Reproducibility of results

The data presented here were collected over a period of 6 months from the same instrument, using the same loading technique, filament type, activator type (but not batch), oxygen isotope ratios, running conditions, and by the same operator, in order to monitor reproducibility of standard data. We found that the TaF$_5$ activator had a tendency to become less efficient after two to three months, and required either production of a new batch or "rejuvenation" by addition of small aliquots of concentrated HF and H$_3$PO$_4$ (see Fig. 3). When discussing the internal variability of Nd data, it is important to consider both the uncertainty introduced by procedural blank corrections and the uncertainty arising from the reproducibility of the measurements.
Within-run and external (between-run) precision of the $^{143}$Nd/$^{144}$Nd data, it is important to note that Nd ion beam intensities are highly dependent on the efficiency of the activator for NdO⁺ ionisation, in turn determining internal precision. The resulting internal uncertainties do not therefore always correlate well with the mass of Nd loaded on the filament. This is demonstrated in Fig. 2, where the internal precision (2RSD ppm) is plotted against the uncorrected $^{157}$Nd/$^{160}$O intensity (V) for loads of 5 or 15 ng JNd-1 and 10 or 30 ng BCR-2 or in-house coral standard.

Over the course of 8 different measurement sessions, the precision achieved for JNd-1 is slightly better for 15 ng loads (11 ppm 2RSD) than for 5 ng loads (14 ppm 2RSD), with internal precision at ≤9 ppm (2RSE) for the 15 ng Nd loads and at ≤14 ppm (2RSE) for the 5 ng Nd loads (Fig. 2, Table A.3). The long term JNd-1 $^{143}$Nd/$^{144}$Nd ratio of 0.512106 ± 6 (2SD; n = 44) is identical within uncertainty to the reference value of 0.512115 ± 7 of Tanaka et al. (2000), with an overall deviation of 17 ppm. A better gauge of external reproducibility for real sample analyses can, however, be obtained from the long-term reproducibility of BCR-2 and our in-house coral standard.

As mentioned above, the external reproducibility for these column-processed standards was 16 ppm (2RSD). The BCR-2 filaments generated internal precisions of 9−23 ppm (2RSE) on the 10 ng loads, and 7−11 ppm (2RSE) on the 30 ng loads, and are identical within error to the reference value of Weis et al. (2006; 0.512637 ± 12; Figs. 2 and 7). The coral standard filaments provided internal precisions of 10−29 ppm (2RSE) on the 10 ng loads, and 6−9 ppm (2RSE) on the 30 ng loads. We chose to use the external reproducibility of the in-house coral standard to establish the external precision of the coral sample measurements because of the matched matrix and range in 157/160 observed in the coral sample runs. The values obtained for Nd concentrations in BCR-2 and the in-house coral standard, based on 10 ng aliquots processed through chemistry and measured by isotope dilution, are 29 ± 0.5 μg/g (1.6% 1RSD, n = 5) and 282 ± 2 ng/g (0.5% 1RSD, n = 5) respectively. The certified concentration of Nd in BCR-2 is 28 ± 2 μg/g (1SD).

In Fig. 7, we compare the external precision (2RSD, in ppm) achieved for pure Nd standard solutions from this study and from recently published values using the TIMS NdO⁺ technique (Thirlwall, 1991; Griselin et al., 2001; Amelin, 2004; Li et al., 2007; Chu et al., 2009; Harvey and Baxter, 2009). These data suggest that improvements to the TIMS NdO⁺ technique over a twenty year period permit a reduction in the Nd mass load by a factor of ~6 for comparable external precision, i.e. 13.7 ppm 2RSD on 30 ng Nd in Thirlwall (1991) compared to a similar external precision on 5 ng JNd-1 (14.3 ppm this study).

The external precision resulting from TIMS Nd⁺ (Weis et al., 2006; Chu et al., 2009) and MC-ICP-MS (Vance and Thirlwall, 2002; Weis et al., 2006; Scher and Delaney, 2010; Yang et al., 2011; Huang et al., 2012; Garcia-Solsona et al., 2014) techniques are also presented in Fig. 7 for comparison and are comparable to TIMS Nd⁺ analyses.

4.2. Neodymium concentrations in deep-sea corals

Applying our new method to low Nd abundance deep-sea coral samples faces an additional complication: the apparent disparity between Nd concentrations in modern corals (~3 to 51 ppb Nd; Cordia et al., 2010; van de Flierdt et al., 2010) to those measured in fossil corals (~7 to 310 ppb Nd; Copard et al., 2009; van de Flierdt et al., 2010) to those measured in fossil corals (~7 to 310 ppb Nd; Cordia et al., 2009; van de Flierdt et al., 2010; Colin et al., 2010; Cordia et al., 2010, 2011; this study). It is important to note that the mismatch could simply be due to the small sample population of modern versus fossil deep-sea coral measurements available so far. However, most focus has been on cleaning efficiency to account for this discrepancy, and with justification given the orders of magnitude higher Nd concentrations in potential sources of contamination, e.g. ~26 μg/g Nd in detrital material (Taylor and McLennan, 1995) and ~200 μg/g in FeMn coatings (Hein et al.,...
Table 4

<table>
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<th>142Nd/144Nd 2SE</th>
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<th>Turret 2SD</th>
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<th>Nd (ppm)</th>
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The 143Nd/144Nd reference value is that of Weis et al. (2006). All ratios are normalised to the turret JNd-1 results.

Table 5

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<th>148Nd/144Nd 2SE</th>
<th>150Nd/144Nd 2SE</th>
<th>εNd</th>
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<th>Nd (ppm)</th>
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The 143Nd/144Nd reference value is that of Weis et al. (2006). All ratios are normalised to the turret JNd-1 results.

The mean values for the spiked and unspiked runs are shown in bold italics.
deglacial in age, a time of maximum perturbation to the normally stable environment of the intermediate/deep ocean, and hence even more vulnerable to potential changes in environmental parameters and Nd uptake. Environmental parameters and processes that would differ during the last deglaciation include, among others, temperature, salinity, pH, seawater composition, and food supply. However, investigation of these processes is beyond the scope of this study. In this section, we focus solely on the assessment of potential contamination of cleaned aragonite samples through trace metal analysis, and evaluation of the effect of contamination on coral Nd isotopic compositions based on mass balance calculations.

4.2.1. Major and trace metals

Ferromanganese coatings are the main source of contamination and represent predominantly not only FeMn oxhydroxides, but also clays, detrital material and other inorganic mineral overgrowths encrusted on the exterior surface of corals. Various methods of verifying cleaning efficacy to remove contaminant phases have been used in the literature: e.g. concentrations of Nd, Th, and Mn (Frank et al., 2004; Robinson et al., 2006; Frank et al., 2009; Copard et al., 2010; van de Flierdt et al., 2010; Wienberg et al., 2010; Eisele et al., 2011; Montero-Serrano et al., 2013). To identify contamination in our coral samples, we used the indicators listed above as well as Fe, Ti, Al, U, and Ce/Ce* (i.e. Ce/Ce* = \( \text{Ce}_{\text{N}} / (\sqrt{\text{La}} \cdot \text{Pr}) \)), where N stands for normalisation to a suitable reference standard. We present the data as cross plots (Fig. 8) to reveal co-variation due to contamination by FeMn coatings. Uptake of these elements by corals may vary in response to environmental change (vital effects) and/or to changes in seawater concentrations. Although the environment of the modern intermediate/deep ocean is presumed to be fairly constant, this assumption does not necessarily hold true for the last deglaciation (~12 to 19 kyr) and complicates interpretation of major and trace metal data.

We estimate that the following coral samples show some degree of contamination on the basis of co-variation and concentration (Fig. 8): #14 (Ti, Nd), #16 (Nd, Th, U), #32 (Al, Ti, Fe, Nd, Th), and #58 (Al, Ti, Fe, Th). The most sensitive contamination indicators are Ti, Mn, and Fe, showing 2 to 3 orders of magnitude difference between the maximum concentrations in the clean corals and the minimum FeMn coating concentrations. By comparison, Nd and Al show a difference of ~1 order of magnitude. The least sensitive indicator is U with some coatings (0.4 to 13.2 μg/g) containing less U than the cleaned coral aragonite (2.8 to 4.5 μg/g in the clean corals).

We also examine the Ce anomaly (Ce/Ce*) in the corals, on the basis that even a small amount of contamination should be readily visible in the sample results given the exceptionally low Ce concentrations and negative anomalies in seawater and corals compared to high Ce concentrations.

Finally, the lack of a clear relationship between modern coral and seawater Nd concentrations (van de Flierdt et al., 2010) suggests that other processes and/or environmental parameters may be involved in determining Nd uptake by deep-sea corals, notwithstanding contamination. To note, corals and seawater in the study conducted by van de Flierdt et al. (2010) were not derived from exactly the same location, and corals were museum specimens with close-to modern ages (i.e. not necessarily collected alive). The samples in this study are mostly...
4.2.2. Evaluation of the influence of FeMn coatings on the Nd isotopic compositions of corals

Having identified coral samples that display evidence of contamination from FeMn coatings, a second exercise is the evaluation of the potential influence of FeMn coatings on coral sample Nd concentrations and isotopic compositions. This evaluation is important because the Nd-rich coatings may also carry a distinct $\varepsilon_{Nd}$ signature. Here we present a worst case scenario based on the starting assumption that 100% of coral Fe concentration originates from a contaminant source. Although some Fe is likely to be present within pristine coralline aragonite, this exercise serves the purpose of gauging the potential effect of contamination from FeMn coatings on coral sample Nd concentrations and, where paired coral-FeMn coating data are available, Nd isotopic compositions.

To calculate the Nd contribution to corals from FeMn coatings, the Fe concentration in the coral is multiplied by the Nd/Fe ratio of the FeMn coating (Eq. (1)) and presented as a % of total measured Nd in the coral sample. The same exercise is carried out for other elements to gauge the corresponding $[M]$ contribution from coating to coral:

$$[M]_{\text{contribution}} = [Fe]_{\text{coral}} \times \left( \frac{[M]}{[Fe]} \right)_{\text{coating}}. \quad (1)$$

**Fig. 8.** Cross plots of Nd vs. (A) Th, (B) Ti, (C) Fe, (D) Mn, (E) Al, and (F) U. All concentrations are in ppb. Open circles represent coral samples with negligible indicators of contamination, whereas the red circles represent corals with clear indications of contamination (based on Th, Ti, Mn and Fe; see text for discussion). The black circles are FeMn coatings, and the yellow square is the averaged in-house coral reference material ($n = 6$).
The Fe concentrations measured in modern *D. dianthus* are generally ≤1 μg/g for cleaned corals (digestion of whole aragonite samples analysed by ICP-MS; Case et al., 2010) and up to ≤5 μg/g (laser ablation ICP-MS, targeting fibrous aragonite only; Anagnostou et al., 2011), with relatively few higher values (≤54 μg/g). These results are comparable to the concentration range measured in the clean corals of this study, i.e. average 2.5 ± 2 μg/g, 1SD, with the majority ≤8.2 μg/g (Table A.2). The corals identified above as contaminated on the basis of co-variation and elevated concentrations of Ti, Mn, Fe and Th have substantially higher Fe concentrations (≤95 μg/g). The Nd/Fe ratio of the FeMn coatings is 1.6 ± 1.0 mg/g (n = 18). For comparison, the Nd/Fe ratio of the North Atlantic FeMn nodule standard USGS Nod-A1 is 0.9 mg/g (Axelsson et al., 2002), collected from the Blake Plateau (31°N, 78°W; 788 mbsl), whilst seawater has Nd/Fe = 62 mg/g (NW Atlantic at 2000 m water depth; Wu et al., 2001; Pahnke et al., 2012).

Using Eq. (1), the most extreme results correspond to predicted concentrations of Th, Mn and Ti, which are substantially higher than actual measured concentrations by an average of a factor of 3, 7 and 2 respectively. This large disparity supports the use of these elements as the most sensitive indicators of contamination and also highlights that contamination from FeMn coatings is negligible for most corals in this study. The predicted concentration of Ce was lower, at 1.6 times the measured concentration. The concentrations predicted by coral Fe content for other elements were not discriminatory; e.g. U had the lowest Fe-based concentrations (an average of 0.02% of the measured concentration), whilst Nd and Al were slightly higher (13% and 8% respectively of the measured concentrations). The inferred Nd contribution from FeMn coatings of 13% does not, however, imply contamination of the coral samples because the low detected Th, Mn and Ti contents of the aragonite fraction essentially rule out contamination effects (assuming no decoupling of Nd from these elements). For example, substituting Th instead of Fe in Eq. (1) generates an estimated Nd contribution from FeMn coatings to the coral aragonite fraction of 4% of the measured Nd concentration (assuming pristine coral aragonite contains no Th).

To gauge the effect of Nd contributions from FeMn coatings on the coral Nd isotopic compositions (again assuming 100% Fe in corals is sourced from FeMn coatings), mass balance is applied to paired coral and FeMn coating data (Nd concentrations and 143Nd/144Nd). The effect of contamination shifts the measured 143Nd/144Nd by generally less than 0.12 εNd units (Fig. 10), i.e. within the external uncertainty in most cases, and by a maximum of 0.05 εNd units (sample #80).

The estimated Nd contribution from FeMn coatings to corals has a relatively small effect on the mass-balance corrected (“true”) coral εNd because in this scenario the low Fe concentrations in the coral samples constrain the Nd contribution from the FeMn coatings. A contributory factor is the similar εNd in some of the FeMn coatings, mostly within 1.3 εNd of the coral εNd value. Where coral εNd and coating εNd differ by ≤3.3 units, the effect on “true” coral εNd is negligible as long as the estimated Nd contribution from FeMn coatings (i.e. coral Fe concentration) is correspondingly low (Fig. 10). In the case of sample #80, the high estimated Nd contribution from FeMn coatings (−2.3%) combined with a large difference in εNd between the coatings and coral sample (≥2 εNd) results in a large shift in the “true” coral εNd of +0.65 εNd. However, this is likely to be an over-estimate based on the assumption that corals contain essentially negligible Fe concentrations.

The mass balance results support the assessment made in the previous section that corals identified as contaminated carry the highest percentage of coating-derived Nd (assuming 100% of coral Fe is from the coatings), i.e. corals #32 and #58 contain 27% and 28% respectively of FeMn-associated Nd, whereas #14 has 7% (Fe wasn’t measured in #16). However, the corresponding shift in εNd for each of these corals is not significant (i.e. <1 ppm for #14, <0.2 ppm for #32, and <7 ppm for #58) because the εNd of the FeMn coating is similar to coral εNd.

In summary, the variable Nd concentrations in fossil corals may reflect some degree of contamination by FeMn coatings. However, this source of Nd cannot be the sole or dominant source for the observed variability of Nd concentrations. This is demonstrated by (i) the much higher Fe-based predictions of Ti, Th and Mn concentrations, compared to observed abundances, and (ii) the lack of correlation between estimated % Nd from FeMn coatings in the coral samples and the small differences between the “true” and measured εNd values. Ultimately, these observations demonstrate that contamination from FeMn coatings had negligible impact on the measured εNd of most corals, even if all of the Fe in the coral is assumed to be derived from FeMn coatings.

5. Conclusions

The method presented here is tailored for Nd extraction from carbonate matrices with low Nd abundances, and subsequent isotopic analyses of small Nd masses as NdO⁺ by TIMS. The success of the
methodology is best demonstrated by the external reproducibility of ±16 ppm (2 RSD) that was achievable on 10 ng and 30 ng Nd loads isolated from USGS BCR-2 and an in-house coral reference material. The analyses provide an average USGS BCR-2 143Nd/144Nd value of 0.512643 ± 8, which is identical within uncertainty to the reference value (0.512637 ± 12; Weis et al., 2006). This level of precision and accuracy depends on the efficient separation of Nd from other REE (Ce in particular), a well-characterised oxygen isotopic composition, and a successful micro-loading technique with an effective activator that is able to generate high and stable Nd ion beam intensities.

The most obvious indicators of coral aragonite contamination by FeMn coatings are elevated and correlated concentrations of Fe, Mn, Ti, and Th. Mass balance calculations that estimate the Nd contributions in particular), a well-characterised oxygen isotopic composition, and a concentration analyses on the ThermoFinnigan Element2 at the Bristol responds to different environmental conditions.

A better understanding of Nd concentrations and distributions in pristine conditions is similar to the uncertainty of the isotopic analyses as well as her insightful comments, which served to clarify the manuscript. This manuscript was improved by useful comments from Hegner for helpful discussion and feedback on a draft version of the manuscript. Used samples provided by Jess Adkins, CalTech, USA. We thank Ernst Adkins, J.F., Cheng, H., Boyle, E.A., Druffel, E.R.M., Edwards, R.L., 1998. Deep-sea coral evidence for rapid change in ventilation of the deep North Atlantic 15,400 years ago. Science 280 (5364), 725–728.

Acknowledgements

We acknowledge the assistance of Corey Archer with the elemental concentration analyses on the ThermoFinnigan Element2 at the Bristol Isotope Group, University of Bristol, and the contribution of 143Nd/144Nd spike for the purposes of this study from Derek Vance. This research used samples provided by Jess Adkins, CalTech, USA. We thank Ernst Hegner for helpful discussion and feedback on a draft version of the manuscript. This manuscript was improved by useful comments from Norbert Frank (Heidelberg University), and an anonymous reviewer. We thank Laurie Reisberg for her editorial handling of the manuscript, as well as her insightful comments, which served to clarify the manuscript. Funding for this research was provided by the Natural Environment Research Council, UK (grant number NE/F016751/1), by a Marie Curie International Reintegration Grant (IRG 230828), and a European Research Council Starting Grant (20101014).

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2014.03.011.

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