Measurement of fossil deep-sea coral Nd isotopic compositions and concentrations by TIMS as NdO+, with evaluation of cleaning protocols
Crocket, Kirsty C.; Lambelet, Myriam; de Flierdt, Tina van; Rehkaemper, Mark; Robinson, Laura F.

Published in:
Chemical Geology
Publication date:
2014

The re-use license for this item is:
Other

The Document Version you have downloaded here is:
Publisher's PDF, also known as Version of record

The final published version is available direct from the publisher website at:
10.1016/j.chemgeo.2014.03.011

Link to author version on UHI Research Database

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the UHI Research Database are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights:

1) Users may download and print one copy of any publication from the UHI Research Database for the purpose of private study or research.
2) You may not further distribute the material or use it for any profit-making activity or commercial gain
3) You may freely distribute the URL identifying the publication in the UHI Research Database

Take down policy
If you believe that this document breaches copyright please contact us at RO@uhi.ac.uk providing details; we will remove access to the work immediately and investigate your claim.

Download date: 14. Jun. 2020
This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier’s archiving and manuscript policies are encouraged to visit:

http://www.elsevier.com/authorsrights
Measurement of fossil deep-sea coral Nd isotopic compositions and concentrations by TIMS as NdO+, with evaluation of cleaning protocols

Kirsty C. Crocket a,⁎, Myriam Lambeleta a, Tina van de Flierdta, a, Mark Rehkämper a, Laura F. Robinson b

a Department of Earth Science and Engineering, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom
b School of Earth Sciences, University of Bristol, Wills Memorial Building, Queen’s Road, Bristol BS8 1JQ, United Kingdom

ARTICLE INFO

Article history:
Received 7 November 2013
Received in revised form 11 March 2014
Accepted 12 March 2014
Available online 22 March 2014

Keywords:
TIMS
NdD
Nd isotopes
Deep-sea corals
Scleractinian corals

Densmophyllum dianthus

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 NdJdi-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 = 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 ≤ 0.68). 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.

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; Arsouze 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 isotope compositions. The latter are commonly expressed as $\delta_{\text{Eu}}$ 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 $\delta_{\text{Eu}}$ 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 ≤0.3 $\delta_{\text{Eu}}$ 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 Nd 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 100 s 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 $^{150}$Nd/$^{146}$Nd and $^{152}$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 ≤30 ng Nd with sub-10 ppm internal precision (2RSE: 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 Nd isotopic measurement, we have performed the NdO$^+$ measurements on a mix of ~100 s ng of Nd measured as Nd$^+$ (Thirlwall, 1991). In practice, the aliquots represented between 5 and 100 ng Nd. After equilibration, the coral sample aliquots were processed for Nd isotopic composition.

2. Samples

Coral samples were collected from the New England Seamounts (30°) and the Mid-Atlantic Ridge (8°) in the North Atlantic, at water depths of 1125 to 2820 m, sub-sampled from a collection held at California Institute of Technology. Most samples were of the species Desmophyllum dianthus, with a few Solenosmilia variabilis, Caryophyllia ambrosia, and Flabellum apertum. 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 (transsects). 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). Savillex Teflon vials and purified water from a Millipore Milli-Q Element system (resistance ~18.2 MΩ; henceforth 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 oxhydroxides 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 flushing 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 $^{150}$Nd to spike $^{150}$Nd (97.8% purity) in a targeted ~1.65:1 ratio of sample 150Nd to spike 150Nd 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$_3$. 

Author’s personal copy
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).

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 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 mass. Capacity testing of the RE columns determined a maximum mass. Capacity testing of the RE columns determined a maximum of 100%.

The same column cleaning procedure was followed for the subsequent Ln columns. Before use, the Ln resin was cleaned in the same way as the RE resin. After loading the resin, 1 ml each of 6 M HCl and MQ was passed sequentially to further clean the resin, and 1 ml 0.142 M HCl to condition the resin. After loading the sample fraction, the LREE was eluted in a total of 8.35 ml 0.142 M HCl followed by sample Nd collection in 3.5 ml 0.142 M HCl. Prior to drying at 120 °C, 10 μl 0.001 M H₃PO₄ was added to the Nd sample fraction to help draw the sample together during drying. Total procedural blanks measured by isotope dilution, which include coral digestion, the combined RE and Ln column chemistry, and the activator loading blank, are < 5 pg (average 2.8 pg ± 1.8 ISD, n = 14).

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 (see Section 3.2.4, Table 2). The calibration of the Ln chemistry is therefore crucial for obtaining a Nd fraction that is entirely free of Sm with minimal Pr and Ce. Whilst the Ln resin provides good separation of Sm from Nd, overlap exists between the elution peaks of Pr and Nd and to a lesser extent between Ce and Nd when eluted with molarities of 0.20 to 0.25 M HCl (e.g. see elution curve using 0.25 M HCl in Huang et al., 2012). We improved the Pr/Nd separation typically obtained with Ln resin from 15% Pr in the Nd fraction (e.g. Pin and Zalduegui, 1997) to 5% by using a smaller resin bead size and lower molarity HCl (Fig. 1). This prolonged the duration of the Ln column chemistry 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). 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 (see Section 3.2.4, Table 2). The calibration of the Ln chemistry is therefore crucial for obtaining a Nd fraction that is entirely free of Sm with minimal Pr and Ce. Whilst the Ln resin provides good separation of Sm from Nd, overlap exists between the elution peaks of Pr and Nd and to a lesser extent between Ce and Nd when eluted with molarities of 0.20 to 0.25 M HCl (e.g. see elution curve using 0.25 M HCl in Huang et al., 2012). We improved the Pr/Nd separation typically obtained with Ln resin from 15% Pr in the Nd fraction (e.g. Pin and Zalduegui, 1997) to 5% by using a smaller resin bead size and lower molarity HCl (Fig. 1). This prolonged the duration of the Ln column chemistry 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%.

3.2.1. 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 (Thirlwall, 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, ¹⁴⁸Nd¹⁷O was monitored to calculate the interference of ¹⁴⁸Nd¹⁸O 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 3000 mA) and filament glows.

Table 1

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

3.2.2. 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 ~0.1 Pa (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 on mass 160 (centre cup), but lower for column processed aliquots, e.g. ~0.12 to 0.40 V per ng (see Fig. 2, Section 4.1.3), not taking into account the yield from the Ln column.

We tested and discarded the idea of bleeding high purity bottled O$_2$ into the source chamber to provide an oxygen source. When using bottled oxygen, the liquid N$_2$ trap is required to maintain the ion source vacuum below 1.2 × 10$^{-7}$ mbar and we observed destabilisation of beam intensities under such conditions, possibly because of a condensing effect of oxygen on the liquid N$_2$-cooled filament.

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 $^{140}$CeO$^+$, 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 ($^{140}$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, 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/$^{144}$Nd (derived iteratively based on the sample + spike mixture) was chosen for mass bias correction and an error magnification factor was calculated.

![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.](image1)

![Fig. 2. The internal precision (2RSE ppm) for the corrected $^{144}$Nd/$^{146}$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).](image2)

<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>
</tr>
</thead>
<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>140Ce16O</td>
<td>141Pr16O</td>
<td>142Nd16O</td>
<td>143Nd16O</td>
<td>144Nd16O</td>
<td>146Nd16O</td>
<td>147Sm16O</td>
<td>148Nd16O</td>
<td>150Nd16O</td>
</tr>
<tr>
<td>Interferences</td>
<td>138La17O</td>
<td>140Ce17O</td>
<td>141Pr17O</td>
<td>142Nd17O</td>
<td>143Nd17O</td>
<td>144Nd17O</td>
<td>145Sm17O</td>
<td>146Nd17O</td>
<td>148Nd17O</td>
</tr>
</tbody>
</table>
| Data reduction was carried out of 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/$^{144}$Nd (derived iteratively based on the sample + spike mixture) was chosen for mass bias correction and an error magnification factor was calculated.

![Fig. 2. The internal precision (2RSE ppm) for the corrected $^{144}$Nd/$^{146}$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).](image2)
based on the relative isotopic abundances of the spike and the sample (VanHeuven et al., 1989).

Per turret, 5 filaments of 15 ng or 5 ng JNdi-1 were measured, the internal (within-run) precision of which varied between 6 and 20 ppm 2RSE on 143Nd/144Nd (Fig. 2, Table A.3). The precision was directly dependent on the ion beam intensity of the Nd signal, whereby older activator appeared to provide less efficient ionisation and hence generated less precise results. Repeated measurements of JNdi-1 during the course of this study yielded a mean 143Nd/144Nd ratio of 0.512106 ± 6 (2SD), with a long term reproducibility of 12 ppm (n = 44: Fig. 3, Table A.3). The within-turret precision for multiple JNdi-1 runs varied by 8 ppm (2RSD: Table 3). To account for the different turret averages, sample data were normalised to a JNdi-1 reference value of 0.512115 (Tanaka et al., 2000), based on the offset of the within-turret JNdi-1 average from the reference data. This resulted in corrections of 10 to 19 ppm to the sample data per turret, with one instance of 24 ppm ( ageing of the activator), generating small shifts in the normalised relative to unnormalised sample data. The effect on data precision is best gauged by the reduction in the 2SD of the normalised BCR-2 data (Section 4.1.3), which decreases by 6e-8 in absolute terms as a result of normalisation.

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.

Digested samples were diluted to a sample/solution ratio (m/m) of ~100 ppm in 2% HNO3 (v/v) to avoid matrix interference effects. The results are presented in Table A.4. Coral Nd concentrations obtained by analysis on the element (n = 37) were also compared to 150Nd 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 150Nd 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, replac- ing 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; 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 isotopic 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 150Nd spike on the basis that Griselin et al. (2001) found differences between the ratios obtained by 141Pr compared to 150Nd, 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 18O or 150Nd 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 18O compared to 150Nd (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. A1, Table A2), this should not influence standard and sample filaments, which were run ~1480 to 1570 °C. The corrected 143Nd/144Nd ratios on JNdi-1 filaments of
varying Nd mass (5 to 15 ng) and intensities (1 to 9 V on uncorrected 144Nd/16O) show good precision (12 ppm, 2RSD; Table A3), suggesting effects resulting from variation in 18O/16O with temperature and/or intensity are not appreciable.

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 reduced data (Thirlwall, 1991). Low measured intensities on masses 156 and 157 also become less effective after two to three months, and required either production of a new batch or "rejuvenation" by addition of small aliquots of concentrated HF and H3PO4 (see Fig. 3). When discussing the internal consistency of our in-house coral standard, we found that the TaF5 activator had a tendency to produce less precise (±16 ppm 2RSD) results with raw 157/160 ratios ranging from 0.01 to 0.54 (Fig. 6, Table 4, Section 4.1.3).

Fig. 4. Published oxygen isotope ratios, grouped according to method of measurement. Data from Amelin et al. (1997), Chavagnac et al. (1998), Chu et al. (2009), Griselin et al. (2001), Harvey and Baxter (2000), Li et al. (2007), Monterro-Serrano et al. (2013), Nier (1950), Reisberg and Zindler (1986), Thirlwall (1991), and Wasserburg et al. (1981). See Table A.6 for compiled list.

Table 3
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 143Nd/144Nd 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 A3), and not the averages per turret.

<table>
<thead>
<tr>
<th>143Nd/144Nd</th>
<th>2SD</th>
<th>148Nd/144Nd</th>
<th>2SD</th>
<th>150Nd/144Nd</th>
<th>2SD</th>
<th>Turret 2RSD (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref value</td>
<td>1.141876</td>
<td>0.512115</td>
<td>0.000007</td>
<td>0.241578</td>
<td>0.236466</td>
<td></td>
</tr>
<tr>
<td>Mean + 2SD</td>
<td>1.141849</td>
<td>0.000022</td>
<td>0.512106</td>
<td>0.000006</td>
<td>0.241574</td>
<td>0.236448</td>
</tr>
<tr>
<td>JNdi-1 loads</td>
<td>19</td>
<td>12</td>
<td>24</td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 ng</td>
<td>1.141849</td>
<td>0.000010</td>
<td>0.512106</td>
<td>0.000005</td>
<td>0.241570</td>
<td>0.236450</td>
</tr>
<tr>
<td>5 ng</td>
<td>1.141851</td>
<td>0.000013</td>
<td>0.512105</td>
<td>0.000008</td>
<td>0.241576</td>
<td>0.236449</td>
</tr>
</tbody>
</table>

Fig. 5. Block by block averages of a 5 ng JNdi-1 filament purposely doped with 2.5 ng Ce. The left y-axis shows the progression of the average raw 156/160 (143Nd/144Nd) ratios, other studies report accurate data despite 157/160 ratios of up to 0.5 (Amelin et al., 1997; Li et al., 2007; Chu et al., 2009). The results from 10 ng and 30 ng aliquots of BCR-2 processed through full chemistry yielded accurate (11 ppm deviation to the reference value of Weis et al., 2006) and precise (±16 ppm 2RSD) results with raw 157/160 ratios ranging from 0.01 to 0.54 (Fig. 6, Table 4, Section 4.1.3).

Repeat analyses of our in-house coral standard yielded a wider range of raw 157/160 ratios from 0.02 to 0.68 (Fig. 6, Table 5), but no effect on the precision of the corrected 143Nd/144Nd 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 TaF5 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 H3PO4 (see Fig. 3). When discussing the internal chemistry, whilst Thirlwall (1991) recommended a threshold value of 0.020 for raw 157/160 (143Nd/144Nd) ratios, other studies report accurate data despite 157/160 ratios of up to 0.5 (Amelin et al., 1997; Li et al., 2007; Chu et al., 2009). The results from 10 ng and 30 ng aliquots of BCR-2 processed through full chemistry yielded accurate (11 ppm deviation to the reference value of Weis et al., 2006) and precise (±16 ppm 2RSD) results with raw 157/160 ratios ranging from 0.01 to 0.54 (Fig. 6, Table 4, Section 4.1.3).
(within-run) and external (between-run) precision of the \( \frac{^{143}\text{Nd}}{^{144}\text{Nd}} \) data, it is important to note that Nd ion beam intensities are highly dependent on 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 (2RSE ppm) is plotted against the uncorrected \( \frac{^{157}\text{Nd}}{^{160}\text{O}} \) 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 \( \frac{^{143}\text{Nd}}{^{144}\text{Nd}} \) ratio of 0.512106 ± 6 (2SD; n = 44) is identical within uncertainty to the reference value 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 (Tables 4 and 5). As mentioned above, the external reproducibility on 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 loaded 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; Copard et al., 2010, 2011; this study) to those measured in fossil corals (~7 to 310 ppb Nd; Copard et al., 2010; Colijn et al., 2010; Copard et al., 2010, 2011; this study). It is important to note that this 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>
<thead>
<tr>
<th>Table 4</th>
<th>Results for individual USGS BCR-2 aliquots processed through column chemistry, both spiked and unspiked.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>εNd (2SE)</strong>, <strong>Nd (ng)</strong>, <strong>Nd (ppm)</strong></td>
<td><strong>Uncorrected 156/160</strong></td>
</tr>
<tr>
<td><strong>Table 4</strong></td>
<td><strong>Results for individual USGS BCR-2 aliquots processed through column chemistry, both spiked and unspiked.</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Table 5</strong></th>
<th>Results for individual in-house coral standard aliquots processed through column chemistry, both spiked and unspiked.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>εNd (2SE)</strong>, <strong>Nd (ng)</strong>, <strong>Nd (ppm)</strong></td>
<td><strong>Uncorrected 156/160</strong></td>
</tr>
</tbody>
</table>
The samples in this study are mostly not necessarily collected alive). The samples in this study are mostly and corals were museum specimens with close-to modern ages (i.e. Flierdt et al. (2010) were not derived from exactly the same location, nation. To note, corals and seawater in the study conducted by van de other processes and/or environmental parameters may be involved in introduction of a sampling bias due to preferential partitioning between concentration of Ti, Mn, Fe and Th, appear to be more rigorous indicators of 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, Fe and Th, 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 in the clean corals and the minimum FeMn coating concentrations. For 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).

4.2.1. Major and trace metals Ferromanganese coats 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* = CeN / ( √(LaN × PrN)), 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, Fe and Th, 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).

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 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.
4.2.2. 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 $\varepsilon_{\text{Nd}}$ 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 $\text{[M]}$ contribution from coating to coral:

$$[\text{M}]_{\text{contribution}} = \frac{[\text{Fe}]_{\text{coral}} \times ([\text{M}]/[\text{Fe}])_{\text{coating}}}{100}.$$  

**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) gives 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 δ143Nd units (Fig. 10), i.e. within the external uncertainty in most cases, and by a maximum of 0.65 δ143Nd units (sample #80).

The estimated Nd contribution from FeMn coatings to corals has a relatively small effect on the mass-balance corrected (“true”) coral 143Nd, 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 143Nd in some of the FeMn coatings, mostly within 1.3 143Nd of the coral 143Nd value. Where coral 143Nd and coating 143Nd differ by ≤3.3 units, the effect on “true” coral 143Nd 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 (~23%) combined with a large difference in 143Nd between the coatings and coral sample (>2 143Nd) results in a large shift in the “true” coral 143Nd of +0.65 143Nd. 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 143Nd for each of these corals is not significant (i.e. <1 ppm for #14, <20 ppm for #32, and <7 ppm for #58) because the 143Nd of the FeMn coating is similar to coral 143Nd.

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) 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 143Nd values. Ultimately, these observations demonstrate that contamination from FeMn coatings had negligible impact on the measured 143Nd 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 (2RSD) 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/144NdNd 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 from FeMn coatings based on the measured coral Fe contents are a useful approach to assess the effects of contamination on sample 143Nd/144NdNd. In this study, they demonstrated that corrected 143Nd/144NdNd ratios generally deviate by less than 12 ppm from the measured 143Nd/144NdNd data. This small difference is similar to the uncertainty of the isotopic analyses and thus substantiates the applied cleaning protocol.

In order to explain the elevated Nd concentrations of fossil corals a better understanding of Nd concentrations and distributions in pristine corals would be useful as well as studies that examine how Nd uptake responds to different environmental conditions.

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 150Nd spike for the purposes of this study from Derek Vance. This research was supported 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.

References
