



# A triple tandem columns extraction chromatography method for isolation of highly purified neodymium prior to $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{142}\text{Nd}/^{144}\text{Nd}$ isotope ratios determinations

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**A triple tandem columns extraction chromatography method  
for isolation of highly purified Neodymium  
prior to  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{142}\text{Nd}/^{144}\text{Nd}$  isotope ratios determinations**

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**Abstract**

A new separation scheme is presented for the isolation of Nd fractions highly purified from adjacent lanthanides, especially Ce and Pr, in preparation to demanding isotope ratios applications, e.g. determination of  $^{142}\text{Nd}/^{144}\text{Nd}$ , or measurement of  $^{143}\text{Nd}/^{144}\text{Nd}$  on very small samples by using  $\text{NdO}^+$  ion beams. Following sample dissolution with hydrofluoric and nitric acids, the method avoids lengthy evaporations, and does not require an oxidation stage to get rid of most of Ce as Ce(IV). The scheme is based on the concatenation of several small extraction chromatographic (EXC) columns filled with three different, commercially available resins, and used in successive tandem configurations, without intervening evaporation step. In the first column, filled with 0.25 ml of the well established TRU-resin, the LREE are separated from matrix elements, and directly stripped onto a second 1 ml column filled with an HEH[HEP]-based EXC material (LN2-resin), which performs an early separation of Nd from most of Ce and Pr, and from all Sm and heavier lanthanides. The Nd fraction separated in this way is eluted on-line onto a third column filled with 1 ml of resin based on a diglycolamide extracting agent (DGA-resin), for further removal of Ce and Pr impurities.

Finally, the Nd fraction is stripped from the DGA column onto the previously used LN2 column for a second pass achieving an additional “skimming” of residual Ce and Pr. The LN2-DGA tandem column cycle can be repeated as many times as desired, thereby providing Nd in an extremely pure form.

## 1. Introduction

Since its inception in the 1970's for cosmochemical and geochemical applications, the long-lived ( $T_{1/2}=106 \times 10^9$  years)  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  radioactive decay system, based on two closely related lanthanides, has become a major tracing and dating tool in the earth and planetary sciences<sup>1</sup>. This great interest necessitated the development of various methods for the chemical isolation of these two elements prior to mass spectrometric isotope ratio measurements. In general, these procedures involve two main stages: a first group separation of the REE or LREE from matrix elements, and the subsequent isolation of Nd and Sm from the adjacent lanthanides and from each other, although a single-step procedure suitable for micro-samples (1-3 mg) has been described<sup>2</sup>. Following the early cosmochemical work of Eugster et al. (1970)<sup>3</sup>, the first separation of the REE from major elements is usually made by cation-exchange chromatography (CEC) in HCl medium [or in HCl and then HNO<sub>3</sub> to improve the separation from barium<sup>4</sup>] by using relatively large columns and volumes of 2-6 M acids. An alternative, more selective approach based on combined anion-exchange solvent extraction in acetic acid-nitric acid has also been used<sup>5</sup>. Later, combined cation-exchange and extraction chromatography<sup>6</sup> or EXC alone<sup>7-9</sup> have been used, allowing to down-scale the procedure an order of magnitude at least.

The second step, aiming to recover a Nd fraction suitable for mass spectrometric analyses, has been realized by using one of the following methods, developed in the late 1950's or early 1960's: (i) cation exchange chromatography by using a solution of ammonium  $\alpha$ -hydroxy isobutyrate (HIBA, synonym: 2-methyl lactic acid, MLA) as the eluant, first described by Choppin and Silva<sup>10</sup>, and subsequently applied by many cosmo- and geochemists<sup>3</sup>; (ii) anion-exchange chromatography in mixed methanol-nitric acid or methanol-acetic acid-nitric acid medium<sup>11</sup>, based on the work of Faris and Warton<sup>12</sup>; (iii) extraction chromatography with the organophosphorus ligand Di-(2-ethyl hexyl)phosphoric acid<sup>13</sup> (HDEHP, or DEHPA)

following its introduction by Peppard et al. (1957)<sup>14</sup> and its early application to the chromatographic separation of the REE<sup>15</sup>. This third method has largely superseded the others for routine work by virtue of its ease of operation, commercial availability of a ready-to-use extraction chromatography (EXC) material (Ln resin, Eichrom), and its ability to achieve an excellent separation of Nd from Sm, an important aspect due the isobaric overlap at mass 144, the isotope used as the reference to report Nd isotope ratios.

Following the first identifications of a positive anomaly in  $^{142}\text{Nd}$  in a meteorite<sup>16,17</sup>, there has been a great interest in the extinct radioactive decay of  $^{146}\text{Sm}$  into  $^{142}\text{Nd}$  (estimates for  $T_{1/2}$  ranging from  $103 \times 10^6$  to  $68 \times 10^6$  years<sup>18</sup>) for constraining the chronology of solar system formation<sup>19</sup> and early silicate differentiation processes of planetary bodies<sup>20</sup>. Whether isotope anomalies observed in much younger terrestrial rocks<sup>21</sup> are real or analytical artifacts is a controversial issue<sup>22-25</sup>.

Using the  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  system puts more stringent constraints on the chemical separation procedures, because any excess or deficit of radiogenic  $^{142}\text{Nd}$  is exceedingly tiny and potentially blurred by even small amounts of  $^{142}\text{Ce}$  remaining after the usual separation protocols. In order to cope with these requirements, different methods have been used, mainly based on either the MLA- or the HDEHP-based approach, or a combination thereof. Albeit able to achieve valuable results, most of the corresponding protocols suffer from being rather cumbersome, because they involve a great number of handlings, and each of them has specific drawbacks. Specifically, the MLA method requires recalibrating the columns for each batch of MLA, a precise adjustment of the pH of the eluting solution, may depend on the purity of the specific batch of reagent used, and involves long columns with a narrow bore necessitating the application of an overpressure of nitrogen to the top of the resin. Further, Nd is eluted as a lactate, and it is necessary to get rid of residual organic matter before mass spectrometry. The HDEHP method suffers from its inherently rather weak separation factor between Nd and Ce, and even more, Pr. Accordingly, several column passes and intervening evaporation steps are required to achieve a satisfactory separation<sup>26</sup>.

For this reason, most people have implemented an oxidation step of Ce(III) to the Ce(IV) species to achieve a better decoupling of Nd from Ce, following the early work of Rehkämper et al.<sup>27</sup>. The separation subsequent to the oxidation procedure is made either by solvent extraction with HDEHP as the organic phase<sup>8,28</sup>, or by extraction chromatography derivatives<sup>29,30</sup> following adaptations of a scheme initially designed for Ce isotope work<sup>31</sup>. However, this separation strategy involves a strong inorganic oxidizing agent ( $\text{KBrO}_3$  or  $\text{NaBrO}_3$ ) which may cause blank problems, and fairly concentrated (10 M) nitric acid which is

not so pleasant to handle. A variant using 0.05M HNO<sub>3</sub> 0.025M in HBrO<sub>3</sub> (prepared from a KBrO<sub>3</sub> solution by removing K by cation exchange) has been described<sup>32</sup>, but HBrO<sub>3</sub> is unstable at room temperature.

In one of these methods<sup>32</sup>, the final separation stage involves a large, extremely long column (85 cm x 2.4 cm) filled with very fine grained (20-50 µm) Ln resin and operated by an automated low-pressure chromatography system using a syringe pump. In this way, quantitative separations of Nd with removal of *ca.* 95% of Pr are achieved, but the method requires an expensive piece of equipment, which performs the separation sample per sample in some 24 hours.

Recently, a comparative assessment of these two major approaches has been published<sup>33</sup>. The authors concluded that, besides its inherent constraints, the MLA method is able to provide a good separation with low blanks (< 55 pg) for basaltic matrices, but suffers from non reproducible yields (60-100%), and from the sporadic presence of residual Ce for non-basaltic samples. The oxidative approach (“NaBrO<sub>3</sub> method”) was described as easier to set up, and able to give better recoveries (80-100%) and purification of Nd from Ce and Sm, but 10-20% of Pr of the samples was found in the purified Nd fraction, and the blank was significantly higher (125 pg). Both methods were broadly similar (*viz.*, 4 days for MLA, *vs.* 3.5 days for NaBrO<sub>3</sub>) in terms of overall duration.

In this work, we describe a new integrated procedure entirely based on EXC, taking benefit from organic extracting agents offering improved characteristics compared with those of classical compounds coined sixty years ago such as α-HIBA or HDEHP. The lanthanides are processed as their standard trivalent species throughout the procedure, with limited volumes of dilute acids flowing under gravity through concatenated, small sized columns, without intervening evaporation step. This protocol has the flexibility to achieve as many on-line purification stages as desired with limited effort of the analyst, and is able to achieve a satisfactory separation of Nd from Ce and Pr in a relatively short time span.

## **2. Experimental**

### **2.1. Chemicals**

Water was first deionized with conventional ion-exchange resins and then further purified to a resistivity of 18.20 MOhm cm with an Aqua System Distribution (Bondoufle, France) device.

Reagent grade hydrofluoric, nitric, and hydrochloric acids (Fluka, Seelze, Germany) were purified by subboiling distillation in PFA DST-100 systems (Savillex, Eden Prairie, MN, USA). Orthoboric acid (Merck, Suprapur) and ascorbic acid (Aldrich, Analytical grade) were used without further purification.

## 2.2 Extraction chromatographic materials

Three extraction chromatography materials obtained from Triskem International (Bruz, France) were used in this study, specifically, TRU resin (based on octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) dissolved in tributyl phosphate (TBP)<sup>34</sup>, DGA resin (based on tetra(n-octyl)diglycolamide)<sup>35</sup>, and LN2 resin, based on 2-ethylhexyl 2-ethylhexylphosphonic acid (EHEHPA), also known as 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, (HEH[EHP])<sup>36</sup>. In every case, the ligands were sorbed onto Amberchrom CG-71 acrylic ester beads of 50-100  $\mu\text{m}$  particle size, but finer grained (20-50  $\mu\text{m}$ ) LN2 resin was also tested during the development of the method.

## 2.3. Instrumentation

All chemical handlings were made under Class 10 vertical laminar flow hoods in a laboratory supplied with an overpressure of filtered air, at a temperature of 20.5  $\pm$  1°C. PFA vessels (Savillex, Eden Prairie, MN, USA) were used for sample dissolution. Nd fractions were collected in 5 ml screw cap PFA vials with a conical bottom (Savillex) and evaporated to dryness. Small columns were used throughout. The first column (4 mm i.d., *ca.* 2 cm height), used to get rid of matrix elements, is made of silica glass, fitted with a polyethylene frit at the bottom, and filled with 83 mg of TRU resin, corresponding to a *ca.* 250  $\mu\text{l}$  bed. The next columns, used to separate and then further purify the Nd fraction, are made from disposable polyethylene pipettes (Bio-Rad DPTP Style E) *ca.* 4 mm i.d. and *ca.* 80 mm length, with polyethylene frits at the bottom. They are filled with 350 mg of LN2 and DGA resins, respectively, corresponding to *ca.* 950  $\mu\text{l}$  beds, and a polyethylene frit is placed on top of the resin bed. In order to overcome any unwanted effect which might occur due to the adsorption on the DGA column of trace amounts of HEH[EHP] leached from the LN2 column, a small quantity (5 to 10 mg) of UTEVA resin was placed on top of the upper frit of the DGA column as a neutralizing agent<sup>37</sup>.

A quadrupole ICP-MS (Agilent 7500, Agilent Technologies, Massy, France) was used in the semi-quantitative mode for setting up the method. Isotope ratio measurements were made with a 13-year old Triton TI thermal ionization mass spectrometer operated in the static multi-collection mode following methods described elsewhere<sup>38</sup>. Briefly, the sample was loaded in a 0.5  $\mu\text{L}$  droplet of 1 M  $\text{H}_3\text{PO}_4$  on the evaporation Re ribbon of a double filament assembly. Although zone refined (>99.995%) metal would be preferable, regular grade (99.98%) Re (H. Cross Co, Moonachie, N.J., USA) was used in this work. Twenty-seven blocks of data, each consisting of 20 cycles of 8 seconds, were collected, with baseline measurements before each block during 30 integrations of 1 second, after deflection of the ion beam in the ion source. Between each block, the “amplifier rotation” function was used to interchange, by means of a relay matrix, the connections between the 9 collectors and the 9 amplifiers in order to cancel relative differences of amplifier gains<sup>39</sup>. After correction for any residual isobaric interference of  $^{142}\text{Ce}$  on  $^{142}\text{Nd}$  and  $^{144}\text{Sm}$  on  $^{144}\text{Nd}$ , the raw isotope ratios were corrected for mass fractionation by using the empirical exponential “law” and  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$  as the reference ratio.

Besides, a Neptune Plus (Thermo Finnigan, Bremen, Germany) multi-collector ICP-MS was used for blank measurements on the one hand, and determination of Ce/Nd in the Nd cut on the other, because - at variance with TIMS - both elements are ionized to the same extent in the ICP, thereby providing a reliable estimate. The  $^{140}\text{Ce}$  signal was monitored by ion counting with the SEM and then the  $^{142}\text{Nd}$  peak measured with a Faraday cup.

## 2.4. Chemical Procedure

*2.4.1. Sample digestion:* 100 mg to 200 mg of sample powder is weighted, wetted with 1 ml of 7M  $\text{HNO}_3$ , then dissolved with 1 to 2 ml of 29M HF at 110°C. The solution is evaporated to dryness, then treated several times with a mixture of 6M HCl and conc.  $\text{HNO}_3$ . After evaporation the residue is treated again with conc.  $\text{HNO}_3$ . Then, the solid residue is taken up with 2 ml of 1M  $\text{HNO}_3$ , and centrifuged, in order to check for the presence of solid residues, especially sparingly soluble fluorides. Any whitish residue observed at that stage is treated with a few hundred  $\mu\text{L}$  of a 1M  $\text{HNO}_3$  solution saturated in boric acid. This generally ensures a nearly complete dissolution, and the resulting solution is combined with the bulk sample solution. Finally, 50 to 100 mg (depending on the concentration of iron in the sample) of ascorbic is added as a reducing agent to decrease the amount of Fe(III). After *ca.* 5-10 minutes for the dissolution and reducing action of ascorbic acid, the sample solution is ready

for the next, column step. In case of samples containing refractory minerals such as zircon or garnet, an appropriate treatment involving high-pressure dissolution of the solid residue left after dissolution under mild conditions would be required<sup>6</sup>.

#### *2.4.2. Tandem column separation scheme:*

The separation protocol relies on four successive EXC stages linked through three tandem columns steps allowing for the on-line transfer of the target element from one separation step to the next one, without any collection or intervening evaporation.

First, the bulk sample solution is loaded portion wise onto the TRU column (Fig. 1, step 1), previously conditioned with 0.25 ml of 1M HNO<sub>3</sub> containing 25 mg ml<sup>-1</sup> of ascorbic acid. Then, the column is rinsed with 0.25 ml of the same solution. Following this step of extraction of LREE by the TRU resin, the column is washed with 4 x 0.5 ml of 1M HNO<sub>3</sub> to remove unwanted major and trace elements. At this stage, only the L- and M-REE (+ Th and U) are still held on the column. In preparation to the next step, 0.25 ml of HNO<sub>3</sub> 0.05M, followed by 100 µl HNO<sub>3</sub> 0.025M, are passed through the TRU column. This takes about 1.5 h.

##### First, TRU/LN2 tandem columns stage:

The LN2 column is placed beneath the tip of the TRU column (Fig. 1, step 2), and 100 µl H<sub>2</sub>O are dispensed into its reservoir to ensure that the top of the column is soaked with very dilute nitric acid during the subsequent on-line elution. Then, the LREE are stripped and transferred directly to the LN2 column with 4 x 0.5 ml of 0.025 M HNO<sub>3</sub> medium which achieves the back-extraction of the LREE from the TRU resin, while permitting their sorption onto the LN2 resin. Following this on-line elution (*ca.* 1.5 hour, due to the slower flow rate of the LN2 column), the columns are decoupled, the reservoir of the LN2 column is rinsed with 100 µl 0.025 M HNO<sub>3</sub> and the LREE are eluted sequentially from the lighter to the heavier elements by using 0.08 M HNO<sub>3</sub>. La, Ce, and Pr are stripped with 2.9 ml and discarded (Fig. 1, step 3). At this stage, 7.5 hours have elapsed since the separation chemistry was started.

##### Second, LN2/DGA tandem columns stage:

Before stripping of Nd from the LN2 column, the third, DGA column is preconditioned with 2 x 100 µl HNO<sub>3</sub> 0.10 M, and placed below the tip of the LN2 column, and Nd is eluted on-line from



the LN2 to the DGA column with 3 ml of 0.10 M HNO<sub>3</sub> (Fig. 1, step 4). This can be made overnight. Then, the columns are decoupled, and treated as follows:

LN2 column: If required, Sm can be recovered from the LN2 column with a further 1.2 ml of 0.30M HNO<sub>3</sub>. The subsequent column washing sequence includes 1 ml 0.50 M HNO<sub>3</sub> and 0.5 ml 3M HNO<sub>3</sub>. Then the column is reconditioned in view of the next step with 0.2 ml of 0.5 M HNO<sub>3</sub>, 0.1 ml 0.030M HNO<sub>3</sub> and finally 0.2 ml 0.01M HCl.

DGA column: First, the column reservoir is rinsed with 0.5 ml of 0.050 M HNO<sub>3</sub>; then, the residual LREE impurities left as tails of their respective elution peaks during the previous step are stripped with 2 × 2.5 ml of 0.0275 M HNO<sub>3</sub> followed by 0.25 ml of HCl 0.01M which are discarded (Fig. 1, step 5). These steps take about 4 hours.

#### Third, DGA/LN2 tandem columns stage:

The DGA column is placed on top of the reconditioned LN2 column, and 2 ml of 0.01M HCl are passed through the two superposed columns to transfer Nd from the DGA resin to the LN2 resin (Fig. 1, step 6). This is made within less than 2 hours.

After decoupling the columns, the LN2 column reservoir is rinsed with 0.1 ml 0.05M HNO<sub>3</sub> and 2.5 ml 0.08M HNO<sub>3</sub> followed by 0.1 ml 0.10 M HNO<sub>3</sub> are passed through the resin to get rid of the last traces of Ce and Pr (Fig. 1, step 7). Finally, a purified Nd cut is recovered with 3 ml 0.15M HNO<sub>3</sub> (Fig. 1, step 8). This second LN2 step takes approximately 4 hours. The Nd fraction is evaporated to dryness in view of TIMS analyses, or could be diluted for direct measurements by MC-ICP-MS. A detailed flow chart of the separation protocol is given in the supplementary information.

### **3. Results**

#### *3.1. <sup>142</sup>Nd/<sup>144</sup>Nd and <sup>143</sup>Nd/<sup>144</sup>Nd isotope ratios measurements*

The aim of this study was to set up a separation scheme able to provide Nd in a sufficiently pure form to allow <sup>142</sup>Nd/<sup>144</sup>Nd ratios to be measured in silicate rocks. Therefore, the method was tested by processing, at least in triplicate starting from a single dissolution, 3 international basalts (BHVO-2, BCR-2, and BE-N), since these rocks contain higher contents of Fe and Ti, the most challenging major elements for the first step of the protocol, and measuring isotope

ratios by TIMS. Our study being strongly focused on chemical separation, these measurements were not intended to provide the most precise and accurate data, but simply to demonstrate that the Ce interference was reduced to a sufficiently low level. This is why we did not use the best state of the art data acquisition and reduction protocols<sup>40,41, 33</sup> based on dynamic multi-collection, in which transmission and Faraday cup efficiencies cancel out, or are included in the normalization process used to correct for mass dependent fractionation<sup>42</sup>. Instead, and since the graphite liners (“inserts”) of the Faraday cups of the mass spectrometer used had been changed two months earlier, the measurements were made in static multi-collection mode, which has been shown to provide reasonably accurate data when the Faraday cups are fresh<sup>41</sup>. The results are listed in Table 1. It can be seen that the <sup>142</sup>Ce contribution to the m/z 142 signal (average <sup>142</sup>Ce/<sup>142</sup>Nd =  $1.5 \times 10^{-6}$  SD = 1.1, n = 10) was reduced within a factor of 2 to the background level, as estimated by 12 measurements of the chemically pure JNdi-1 isotopic standard (m =  $0.7 \times 10^{-6}$ , SD = 0.7). Further, the Sm interference was practically eliminated. After correction of the residual contribution of <sup>142</sup>Ce, the <sup>142</sup>Nd/<sup>144</sup>Nd ratios of the three basalts do not depart significantly from the value measured for the JNdi-1 standard, as shown (Fig. 2) by the overlap of their  $\mu$  values ( $\mu$  = deviation from JNdi-1 measured under the same conditions and expressed in parts in  $10^6$ ). The <sup>143</sup>Nd/<sup>144</sup>Nd ratios have good within-run precisions and external reproducibility (2 SD =  $3 \times 10^{-6}$ ) and agree well with literature values<sup>43</sup>. Besides, the ratios involving isotopes free of radiogenic components (<sup>145</sup>Nd/<sup>144</sup>Nd, <sup>148</sup>Nd/<sup>144</sup>Nd, and <sup>150</sup>Nd/<sup>144</sup>Nd) measured in the three basalts are indistinguishable from those measured in the JNd-1 isotopic standard (Tab. 1).

### 3.2 Decontamination from Ce and chemical yield

Ce/Nd and Pr/Nd elemental ratios measured by ICP-MS during the method development on the rock standard BHVO-2 (containing 37.5 ppm Ce, 5.3 ppm Pr, and 24.3 ppm Nd<sup>43</sup>) were in the low  $10^{-5}$  and  $10^{-4}$  ranges, respectively, starting from Ce/Nd = 1.54 and Pr/Nd = 0.22. This corresponds to decontamination factors higher than  $10^5$  for Ce and  $2 \times 10^3$  for Pr.

Chemical recoveries between 80% and 90% were achieved during the separation of Nd from BHVO-2, BCR-2 and BE-N. It is emphasized that these data were obtained on a set of LN2 and DGA columns which were *not* calibrated one by one. Keeping in mind that making perfectly reproducible EXC columns is not a trivial task, it is suggested that Nd yields close to the upper value of that range might consistently be achieved by using columns calibrated on

an individual basis. Also, there is a trade-off between the resolution between adjacent chromatographic peaks, *i.e.*, the purity of the target element, and the chemical recovery. In other words, an improved separation of Nd from Ce is achievable if the initial part of the Nd peak of the first LN2 column is discarded, at the expense of the final Nd yield.

The LN2 column used in this study is appropriate for handling typical LREE cuts containing 0.5 to 1 µg Nd, but the quality (chemical yield and degree of purification) of the first separation with this column is not independent on the amount of ΣREE of the feed solution. Indeed, all the REE stripped from the TRU column are extracted by the LN2 resin and may therefore have an impact on the column capacity. In case of column overloading peak broadening or even an “upstream” shift of the elution profile are anticipated. Accordingly, if larger REE quantities are to be handled, using columns of the same length but with a larger internal diameter would be preferable.

### 3.3 *Blanks*

Six total procedural blanks (including the dissolution steps) measured with the SEM ion counting system of the Neptune ICP-MS range from 11 to 45 pg with a mean of 30 pg (SD = 13; Tab. 2). These values correspond to blank contributions amounting to less than  $5 \cdot 10^{-5}$  of the typical Nd amount processed of 1 µg, and can be neglected. This demonstrates that the columns can be re-used. This is convenient for the LN2 and DGA columns, the preparation of which is relatively long. However, taking into account that the TRU columns can be prepared quickly, use a small amount (83 mg) of resin, and do not require a detailed calibration, it is advisable to use new resin for these first columns, because their washing procedure is tedious.

### 3.3 *Separation duration*

The slower flow rates inherent to a finer grained resin should in principle provide a better resolution. However, based on preliminary experiments with 20-50 µm LN2 resin, it was found that the improvement was not sufficient to justify a much more lengthy separation. Although a more thorough comparative assessment would be useful, the 50-100 µm LN2 resin has been preferred for the analyses of geostandards, permitting to achieve the separation in two working days, including the intervening night, although the column elution itself takes less than 20 hours. It might be possible to improve the time usage and hopefully achieve a better separation by using longer columns such as the longest elution step, made overnight, would take about 12 hours, but such optimization was beyond the scope of this study.

#### 4. Discussion

The first step of the separation uses a well-established procedure<sup>7-9</sup> based on the CMPO-based TRU resin<sup>33</sup>. Although initially designed for separating transuranic elements from nuclear wastes [including Am(III) which is chemically analogous to Nd], this EXC resin offers outstanding properties in geochemistry as it allows the isolation of a bulk LREE fraction from virtually all matrix elements in 1M nitric acid, as predicted from distribution ratios measured by Huff & Huff<sup>44</sup>. Specifically, Ce, Pr, Nd, and Sm are well extracted ( $D \approx 170$ ) by the CMPO ligand, along with the actinides Th and U ( $D > 400$ ). In marked contrast, the rest of the elements, including the troublesome Ba, are not extracted ( $D$ 's  $< 5$ ). Only Fe(III) and Ti, with  $D$ 's of 5 and 7, respectively<sup>44</sup>, can be extracted appreciably from 1M HNO<sub>3</sub> solutions. However, it appears that Ti is essentially not extracted, most likely as a result of its earlier complexation by fluorine during sample dissolution. Besides, Fe(III) can be reduced to the non extractable Fe(II) by using ascorbic acid, in so far as the strong oxidizing perchloric acid was not used previously. Further, the LREE can be stripped from the TRU resin with very dilute (0.02 M) nitric acid, while Th and U are still retained by the resin in this medium.

The key-feature of the subsequent steps of the method is the use of several stages of EXC columns in tandem, namely, a TRU/LN2/DGA/LN2 sequence, inspired from a LN2-DGA combination used by Horwitz et al.<sup>37</sup> to separate <sup>177</sup>Lu from irradiated <sup>176</sup>Yb targets. On general grounds, the necessary prerequisite for using chromatographic columns in tandem is that the medium used to strip an element from the first column should enable its on-line extraction by the next column. The three different resins used in our protocol fulfill this requirement, firstly from TRU to LN2, then from LN2 to DGA, and reciprocally, from DGA to LN2.

Specifically, the elution of the LREE from the TRU resin with very dilute HNO<sub>3</sub> or HCl can immediately be followed by their extraction by the next resin provided this behaves as a cation exchanger. This is indeed the case for the LN2 resin, an EXC material based on (2-ethyl-1-hexyl) phosphonic acid (HEH[EHP]). This compound is not new<sup>45</sup> but as yet it has been little used in geochemistry<sup>46,29</sup> compared to the classical HDEHP. Both ligands belong to the same class of acidic organophosphorus extractants, which have an increasing affinity for

lanthanide complexation from the light to the heavy elements, allowing individual lanthanides to be separated from adjacent species. Accordingly, the lanthanides can be eluted sequentially from the light to the heavy elements by using a LN2 EXC column, with separation factors between Nd and Ce of 4.8, some 20% higher than that obtained with HDEHP<sup>47</sup>. Just as for HDEHP, the distribution coefficients between HEH[EHP] and the aqueous phase decrease with decreasing pH. Moreover, HEH[EHP] is a weaker extractant than HDEHP, enabling to use even more dilute acid to extract the LREE. In this work, La-Ce-Pr were eluted with 0.08M HNO<sub>3</sub>, before Nd was stripped from the LN2 column with a limited volume of slightly stronger (0.10 M) HNO<sub>3</sub>. This medium allows the extraction of the LREE by the subsequent DGA resin, for a further separation stage of Ce and Pr left in the Nd cut. The diglycolamide ligands<sup>48,49</sup> form tridentate chelates with lanthanides, with the heavier Ln(III) complexes being more stable than the lighter Ln(III) ones<sup>50</sup>. This is reflected by an increasing extraction trend from La to Lu similar to that displayed by alkyl phosphorus acids, but through a different mechanism in which the extraction into the organic phase is favoured by high concentration of anion (NO<sub>3</sub><sup>-</sup> or Cl<sup>-</sup>). Therefore, at variance with the LN2 resin, it is not possible to strip the analytes with stronger acids. In this work, very dilute (0.0275 M) HNO<sub>3</sub> was used to get rid of residual Ce and Pr before Nd starts to elute from the column. Although D's for Nd decrease with decreasing nitric acid molarity, stripping Nd with 0.01M HNO<sub>3</sub> proved to be ineffective. Therefore, very dilute, 0.01M HCl was used instead, based on published distribution coefficients<sup>51</sup>. Neodymium is strongly extracted by the LN2 resin from this medium, thereby offering the opportunity for a further on-line separation step. Noticeably, the LN2-DGA-LN2, and so on... pattern might be repeated *ad libitum* in order to achieve even greater degrees of purification of the final Nd cut, at the cost of a protracted procedure and a limited loss of chemical yield. However, it was found that a single LN2-DGA-LN2 sequence was sufficient to reduce the Ce signal close to instrumental background levels, as shown by the data reported in Table 1.

The practical advantages of this protocol based on small sized columns and gravity driven flow are its overall simplicity, the use of very dilute acid solutions, and the relatively small amount of analyst time required to achieve the separation of a batch of samples.

The first separation of the LREE from matrix elements is both very rapid and effective compared to alternative schemes based on conventional cation-exchange, as a consequence of the intrinsically much better selectivity of extraction chromatography with the CMPO-based TRU resin. Only small volumes of dilute acids are needed, and the separation can be made in

less than two hours, which compares very favourably with cation-exchange methods which require one working day and much larger volumes of more concentrated acids. Also, the LREE fraction is very well purified from Ba, a troublesome element not easy to eliminate by cation exchange chromatography, at least in HCl medium.

The further isolation of a purified Nd fraction through multiple tandem chromatography spans about 18 hours. The combination in a single operation of the stripping step of a column and the loading step of the next one alleviates the need for intervening evaporation steps, thereby saving time and ensuring a short overall duration (2 days) of the whole process compared with other methods. Throughout the procedure, little operator time and effort are needed, simply to change the position of the columns relative to each other, and dispense the small volumes of eluting media. Our method does not resort to an oxidation step of Ce to achieve a good purification of Nd from this unwanted companion, and the tandem separation scheme achieves a good separation of Nd from Pr, a notoriously difficult task with conventional techniques. Finally, compared to existing methods, this procedure is environmentally friendly because only very dilute solutions of nitric and hydrochloric acids are used.

A drawback inherent to EXC is the great difficulty in achieving a fully quantitative recovery of the elements which were previously extracted, because residual quantities of the target element, typically amounting *ca.* 1 %, are not back-extracted by the regular stripping step, in so far as it is limited to reasonably small volumes of eluting solution. This may be interpreted to reflect the tortuous porosity of the inert support, the very narrow diameter of at least some of their pores that are accessible only by diffusional mass transfer, and the presence of “dead end” pores and stagnant microvolumes failing to equilibrate promptly with the stripping solution<sup>52</sup>. Although the memory effects of the columns can be reduced to a low level as shown by the data listed in Table 2, this requires long and thorough washing steps involving relatively large volumes of appropriate acids and water soluble complexing agents. Accordingly, our protocol should be amended in case a fully quantitative recovery would be aimed, *e.g.*, for stable isotope studies. Unless more effective stripping strategies are found, this would require collecting the first washing step following each Nd peak, combining these solutions, and evaporating them to dryness before reprocessing through the LN2-DGA cycle to recover and purify the Nd left behind on the columns.

In its present state, the method cannot handle the large sample sizes required for isotopic analyses by TIMS (by using Nd<sup>+</sup> ion beams) of highly depleted samples. For this purpose, the first step of the procedure should be modified to make the group separation of the LREE from

large volumes of sample solution possible. This is the aim of work presently in progress in our laboratory.

## 5. Conclusion

This triple tandem column separation protocol, entirely based on miniaturized extraction chromatography, may offer an alternative to existing methods aiming to isolate Nd in view of high precision isotope ratios measurements. Besides its overall rather short duration, the method is relatively simple to implement, does not require an oxidation step to get rid of most of the cerium nor any expensive piece of equipment, and does not generate much toxic wastes because small volumes of extremely dilute solutions of inorganic acids are used throughout.

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## Figure captions

**Fig. 1:** Scheme of the elution sequence depicting the successive steps of the separation procedure: (1) separation of the LREE from matrix elements by selective extraction on the TRU column; (2) first tandem step: back-extraction of the LREE from the TRU column and on-line extraction on the LN2 column; (3) elution of La, Ce, and Pr from the LN2 column; (4) second tandem step: on-line elution of Nd from the LN2 column to the next, DGA column; (5) elution of residual Ce and Pr; (6) third tandem step: stripping of the Nd from the DGA column and concomitant loading onto the re-conditioned LN2 column; (7) elution of residual Ce and Pr; (8) final stripping of the purified Nd fraction.

**Fig. 2:**  $^{142}\text{Nd}/^{144}\text{Nd}$  ratios in basaltic reference materials expressed as the deviations ( $\mu^{142}\text{Nd}$ , in ppm) relative to the mean of values measured for the JNdi-1 standard under the same analytical conditions.

**Table 1.** Nd isotope ratios measured by static multi-collection TIMS for the isotopic standard JNdi-1 and three or four aliquots of a single dissolution of the international basaltic standards BHVO-2, BCR-2, and BE-N processed through the separation scheme. The individual ratios are listed with their individual within-run precision (expressed as 2 standard error), while the average values (in bold) are quoted with their external reproducibility (expressed as 2 standard deviation).

	142Ce/142Nd (ppm)	144Sm/144Nd (ppm)	142Nd/144Nd	$\mu$ 142Nd (ppm)	143Nd/144Nd	145Nd/144Nd	148Nd/144Nd	150Nd/144Nd
JNdi-1 #1	1.3	0.2	1.141832 ± 0.000004	-3.0 ± 3.5	0.512101 ± 0.000002	0.348402 ± 0.000001	0.241582 ± 0.000001	0.236450 ± 0.000002
JNdi-1 #2	2.0	0.5	1.141837 ± 0.000003	1.0 ± 2.6	0.512099 ± 0.000004	0.348401 ± 0.000002	0.241582 ± 0.000003	0.236455 ± 0.000004
JNdi-1 #3	0.4	0.4	1.141839 ± 0.000006	2.8 ± 4.8	0.512103 ± 0.000002	0.348401 ± 0.000001	0.241582 ± 0.000001	0.236453 ± 0.000002
JNdi-1 #4	0.9	0.4	1.141841 ± 0.000003	5.0 ± 2.7	0.512103 ± 0.000001	0.348401 ± 0.000001	0.241580 ± 0.000001	0.236451 ± 0.000001
JNdi-1 #5	0.2	0.6	1.141840 ± 0.000003	4.2 ± 2.7	0.512102 ± 0.000001	0.348401 ± 0.000001	0.241583 ± 0.000001	0.236455 ± 0.000001
JNdi-1 #6	1.0	0.3	1.141832 ± 0.000003	-3.2 ± 2.7	0.512099 ± 0.000001	0.348401 ± 0.000001	0.241580 ± 0.000001	0.236450 ± 0.000001
JNdi-1 #7	1.7	0.5	1.141837 ± 0.000006	1.4 ± 5.6	0.512102 ± 0.000004	0.348404 ± 0.000002	0.241578 ± 0.000003	0.236448 ± 0.000004
JNdi-1 #8	0.1	0.5	1.141833 ± 0.000003	-1.9 ± 3.0	0.512101 ± 0.000001	0.348401 ± 0.000001	0.241582 ± 0.000001	0.236451 ± 0.000001
JNdi-1 #9	0.3	0.3	1.141830 ± 0.000004	-4.4 ± 3.2	0.512099 ± 0.000001	0.348401 ± 0.000001	0.241581 ± 0.000001	0.236450 ± 0.000001
JNdi-1 #10	0.1	0.6	1.141833 ± 0.000004	-2.0 ± 3.7	0.512100 ± 0.000002	0.348400 ± 0.000001	0.241578 ± 0.000001	0.236446 ± 0.000002
JNdi-1 #11	0.8	0.2	1.141835 ± 0.000003	-0.8 ± 3.0	0.512101 ± 0.000001	0.348401 ± 0.000001	0.241580 ± 0.000001	0.236449 ± 0.000001
JNdi-1 #12	0.1	0.4	1.141837 ± 0.000004	1.0 ± 3.2	0.512100 ± 0.000001	0.348401 ± 0.000001	0.241581 ± 0.000001	0.236450 ± 0.000001
<b>Average</b>	<b>0.7 ± 1.3</b>	<b>0.4 ± 0.3</b>	<b>1.141836 ± 0.000007</b>	<b>0.0 ± 6.0</b>	<b>0.512101 ± 0.000003</b>	<b>0.348401 ± 0.000002</b>	<b>0.241581 ± 0.000003</b>	<b>0.236451 ± 0.000005</b>
BCR-2 #1	1.9	0.3	1.141834 ± 0.000007	-1.1 ± 6.3	0.512621 ± 0.000004	0.348401 ± 0.000002	0.241579 ± 0.000003	0.236455 ± 0.000004
BCR-2 #2	0.9	0.3	1.141837 ± 0.000007	1.2 ± 6.2	0.512624 ± 0.000005	0.348402 ± 0.000003	0.241579 ± 0.000004	0.236445 ± 0.000005
BCR-2 #3	0.3	0.0	1.141836 ± 0.000004	0.6 ± 3.6	0.512624 ± 0.000002	0.348401 ± 0.000001	0.241581 ± 0.000001	0.236450 ± 0.000001
BCR-2 #4	0.8	0.1	1.141841 ± 0.000004	5.1 ± 3.8	0.512624 ± 0.000002	0.348400 ± 0.000001	0.241582 ± 0.000001	0.236450 ± 0.000002
<b>Average</b>	<b>1.0 ± 1.4</b>	<b>0.2 ± 0.3</b>	<b>1.141837 ± 0.000006</b>	<b>1.4 ± 5.3</b>	<b>0.512623 ± 0.000003</b>	<b>0.348401 ± 0.000002</b>	<b>0.241580 ± 0.000003</b>	<b>0.236450 ± 0.000008</b>
BHVO-2 #1	0.8	-0.1	1.141836 ± 0.000005	0.2 ± 4.4	0.512972 ± 0.000002	0.348403 ± 0.000001	0.241580 ± 0.000001	0.236449 ± 0.000002
BHVO-2 #2	1.1	0.2	1.141834 ± 0.000005	-1.4 ± 4.6	0.512973 ± 0.000005	0.348398 ± 0.000003	0.241579 ± 0.000004	0.236448 ± 0.000005
BHVO-2 #3	3.0	0.0	1.141829 ± 0.000007	-5.3 ± 6.5	0.512975 ± 0.000007	0.348405 ± 0.000004	0.241592 ± 0.000006	0.236455 ± 0.000006
<b>Average</b>	<b>1.6 ± 2.3</b>	<b>0.1 ± 0.3</b>	<b>1.141833 ± 0.000006</b>	<b>-2.2 ± 5.6</b>	<b>0.512973 ± 0.000003</b>	<b>0.348402 ± 0.000007</b>	<b>0.241584 ± 0.000014</b>	<b>0.236451 ± 0.000007</b>
BE-N #1	3.0	0.3	1.141835 ± 0.000005	-0.5 ± 4.4	0.512869 ± 0.000002	0.348400 ± 0.000002	0.241579 ± 0.000003	0.236447 ± 0.000003
BE-N #2	0.4	0.0	1.141839 ± 0.000005	3.3 ± 4.5	0.512871 ± 0.000002	0.348401 ± 0.000001	0.241582 ± 0.000001	0.236451 ± 0.000002
BE-N #3	1.4	0.1	1.141837 ± 0.000008	1.6 ± 6.7	0.512869 ± 0.000003	0.348402 ± 0.000002	0.241580 ± 0.000003	0.236452 ± 0.000003
BE-N #4	0.4	0.0	1.141834 ± 0.000007	-1.1 ± 5.8	0.512867 ± 0.000002	0.348400 ± 0.000002	0.241582 ± 0.000002	0.236452 ± 0.000002
BE-N #5	2.7	0.3	1.141842 ± 0.000006	5.3 ± 5.4	0.512870 ± 0.000003	0.348403 ± 0.000003	0.241578 ± 0.000004	0.236444 ± 0.000005
<b>Average</b>	<b>1.6 ± 2.2</b>	<b>0.1 ± 0.3</b>	<b>1.141838 ± 0.000006</b>	<b>1.7 ± 5.3</b>	<b>0.512869 ± 0.000003</b>	<b>0.348401 ± 0.000002</b>	<b>0.241580 ± 0.000003</b>	<b>0.236449 ± 0.000007</b>

**Table 2.** Results of six measurements (by using MC-ICP-MS operated in SEM ion-counting mode) of total procedural blanks (TPB)

Column set	1	2	3	4	5	6
TPB Nd (pg)	24	45	23	40	11	38
Blank effect on 1 µg of Nd	2E-05	4E-05	2E-05	4E-05	1E-05	4E-05

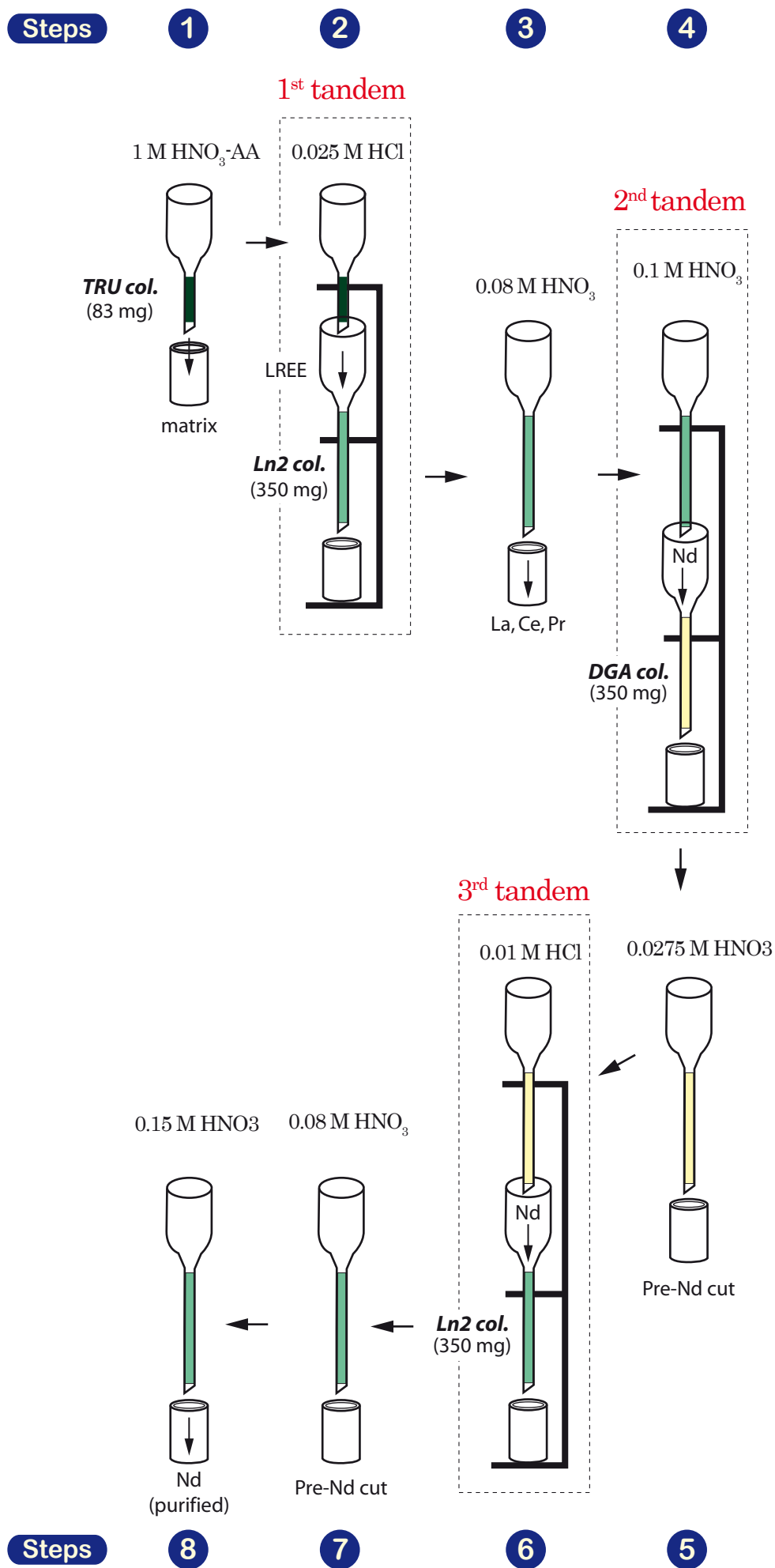


Figure 1

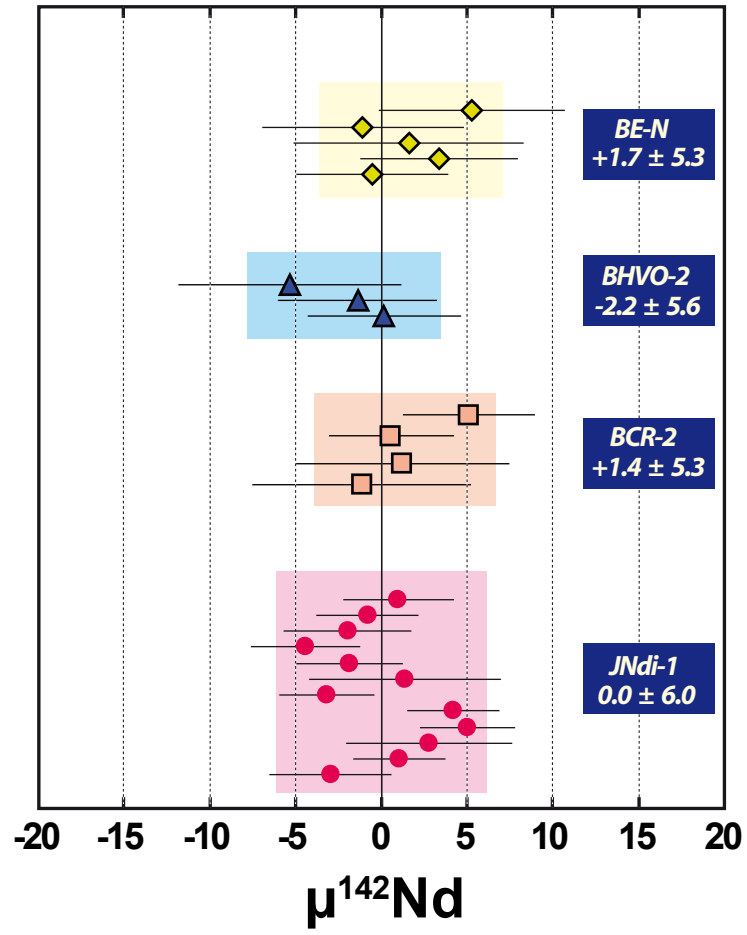
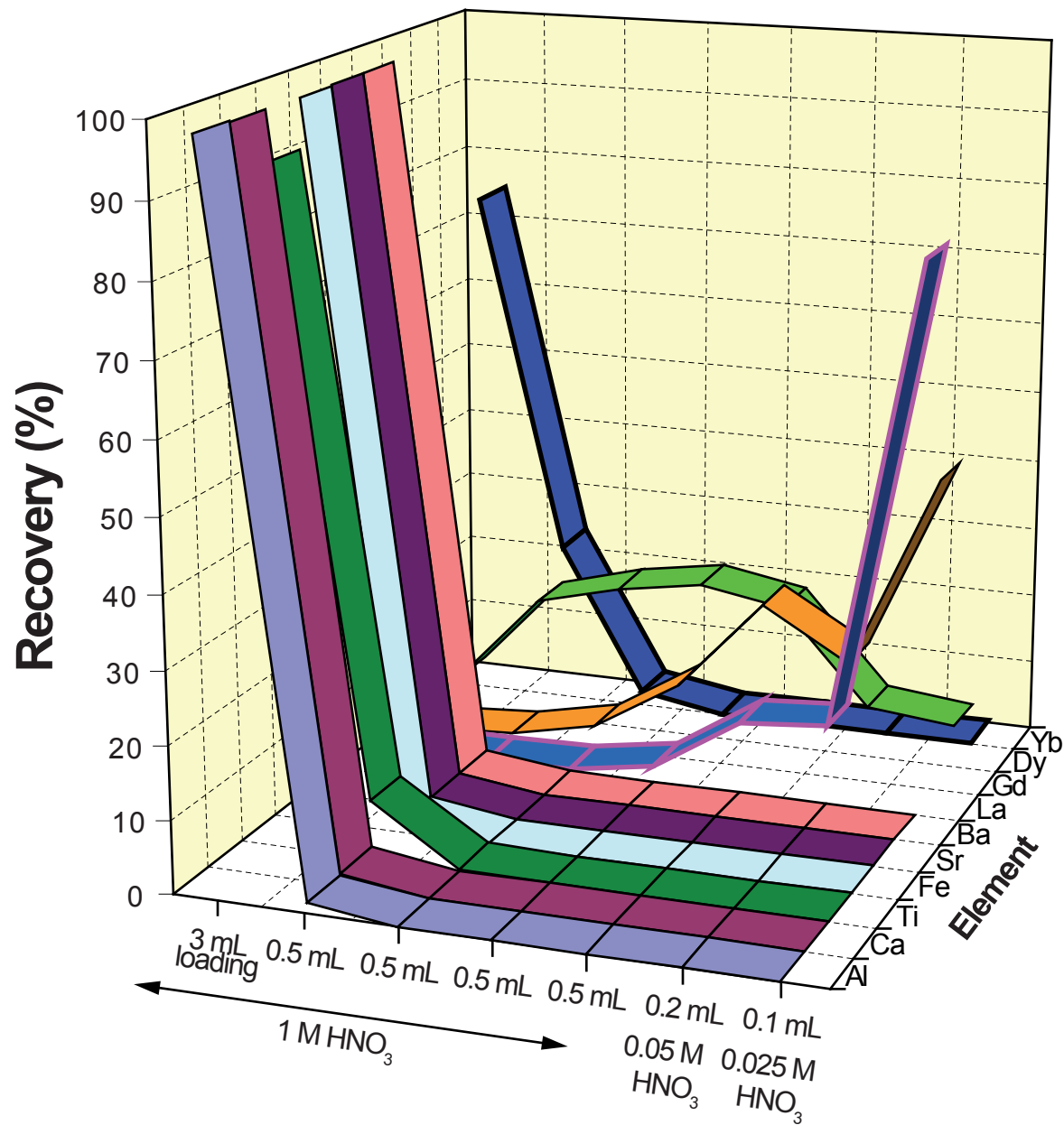


Figure 2

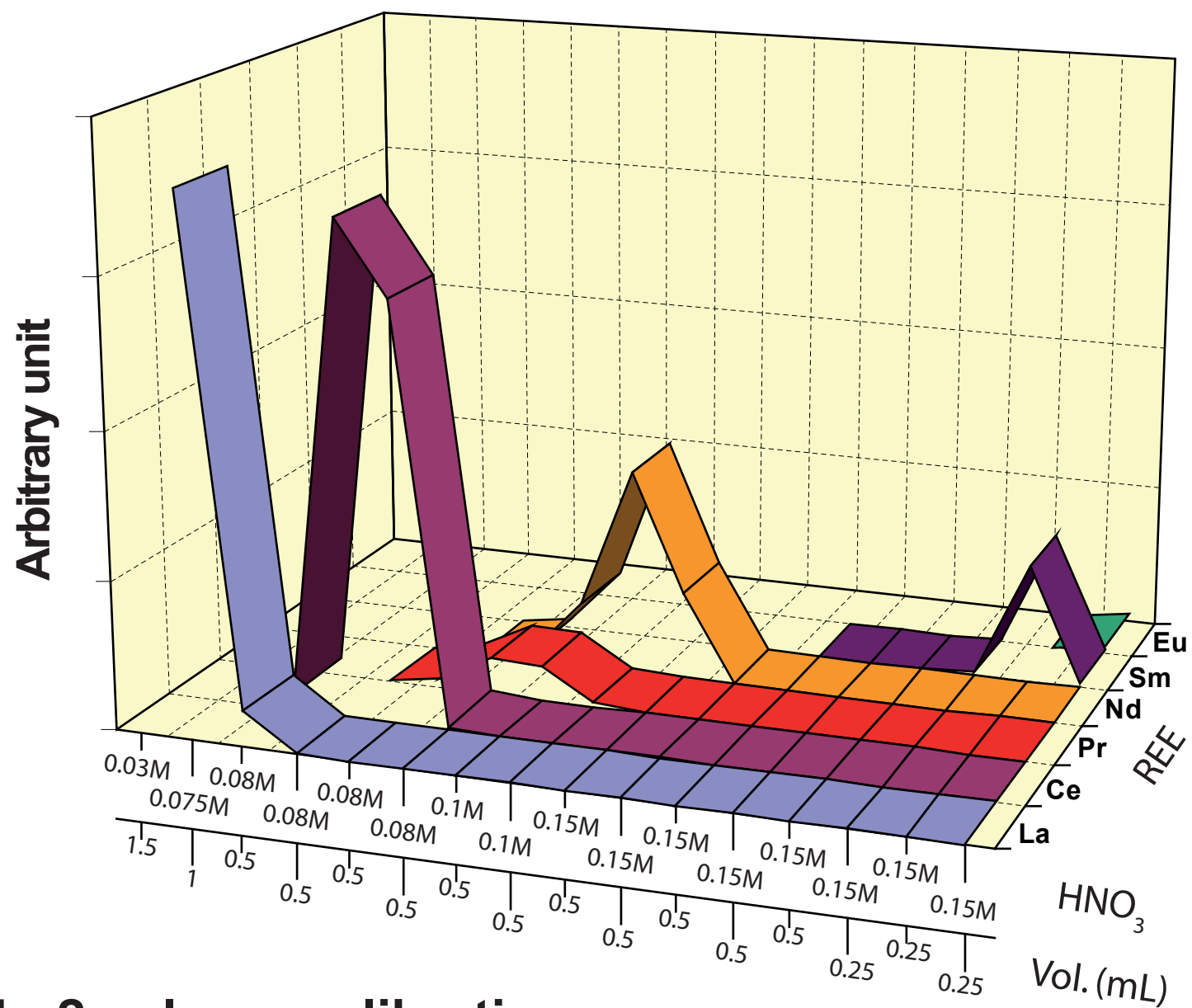
Supplementary information. Outline of the separation scheme enabling the isolation of highly purified Nd by extraction chromatography

	Reagents	Volume (mL)
<b>Column pre-cleaning and pre-conditioning</b>		
TRU Spec (83 mg)	1 M HNO <sub>3</sub>	2 × 0.2
	1 M HNO <sub>3</sub> -C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	0.25
Ln2 (350 mg)	0.025 M HNO <sub>3</sub>	2 × 0.1
	H <sub>2</sub> O	0.1
	(just before tandem setup)	
DGA (350 mg)	0.1 M HNO <sub>3</sub>	2 × 0.1
<b>TRU Spec alone</b>		
Sample loading	1 M HNO <sub>3</sub> -C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	4 × 0.5
Rinse	1 M HNO <sub>3</sub> -C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	0.25
Matrix elution	1 M HNO <sub>3</sub>	4 × 0.5
	0.05 M HNO <sub>3</sub>	0.25
	0.025 M HNO <sub>3</sub>	0.1
<b>TRU spec and Ln2 columns in tandem</b>		
Elution of LREE	0.025 M HNO <sub>3</sub>	4 × 0.5
<b>Columns decoupling and further elution</b>		
Ln2		
Elution of La, Ce, Pr	0.08 M HNO <sub>3</sub>	2.9
<b>Ln2 and DGA columns in tandem</b>		
Online elution of Nd	0.1 M HNO <sub>3</sub>	3
<b>Columns decoupling and further elution</b>		
DGA		
Rinse	0.05 M HNO <sub>3</sub>	0.5
Pre-Nd cut	0.0275 M HNO <sub>3</sub>	2 × 2.5
	0.01 M HCl	0.25
Ln2		
(Elution of Sm, optional)	0.3 M HNO <sub>3</sub>	1.2
	0.5 M HNO <sub>3</sub>	1
	3M HNO <sub>3</sub>	0.5
	0.5 M HNO <sub>3</sub>	0.2
	0.03 M HNO <sub>3</sub>	0.1
pre-conditioning	0.01 M HCl	0.2
<b>DGA and preconditioned Ln2 in tandem</b>		
Online elution of Nd	0.01 M HCl	2
<b>Columns decoupling and further elution</b>		
Ln2	0.05 M HNO <sub>3</sub>	0.1
	0.08 M HNO <sub>3</sub>	2.5
	0.1 M HNO <sub>3</sub>	0.1
Elution of Nd	<b>0.15 M HNO<sub>3</sub></b>	<b>3</b>
<b>Cleaning before storage</b>		
Ln2	3 M HNO <sub>3</sub>	1
	0.3 M HNO <sub>3</sub>	1
DGA	1 M HCl	1
	0.01 M HCl	2
TRU Spec		
	0.1 M HCl - 0.29 M HF	3
	0.05 M HNO <sub>3</sub>	3
	2 M HCl	2
	0.05 M HNO <sub>3</sub>	2





**TRU Spec column calibration**



**Ln2 column calibration**